Microgels – Intramolecularly Crosslinked Macromolecules with a Globular Structure

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List of Symbols and Abbreviations

a	exponent of Mark-Houwink equation
AIBN	2,2'-azobis(isobutyronitrile)
BD	butanediol-1,4
BuLi	butyl lithium
c/t	degree of isomerization maleic /fumaric acid units
d	polymer density
$\overline{d}_v$	volume average hydrodynamic diameter

$\overline{d}_z$	z-average hydrodynamic diameter
DHM	dodecyl hydrogen maleate
DIPB	1,4-diisopropenylbenzene
DMF	N,N'-dimethylformamide
DVB	divinylbenzene (unspecified)
1,4-DVB	1,4-divinylbenzene
1,3-DVB	1,3-divinylbenzene
t-DVB	technical DVB
DVM	divinyl monomer
E	emulsifier concentration
EP	emulsion polymerization
ECP	emulsion copolymerization
micro-EP	microemulsion polymerisation
micro-ECP	microemulsion copolymerization
EDMA	ethylene glycol dimethacrylate
EUP	self-emulsifying unsaturated polyester
GTP	group transfer polymerization
HD	hexane diol-1,6
MA	maleic anhydride
$\overline{M}_n$	number average molar mass
$\overline{M}_w$	weight-average molar mass
$\overline{M}_{w,0}$	the value $\overline{M}_w$ at zero monomer conversion
MMA	methyl methacrylate
N	number of particles
PA	phthalic anhydride
PBS	poly(*tert*-butylstyrene)
PPS	potassium persulfate
PVS	poly(4-vinylstyrene)
$Q_{v(x)}$, Q_v	equilibrium volume swelling ratio at conversion x resp. at complete conversion
$Q^0_{v(x)}$, Q^{00}_v	degree of dilution of the polymer gel in the reaction mixture at conversion x resp. at complete conversion
RCC	radical crosslinking copolymerization
R_g	radius of gyration
R_h	hydrodynamic radius
RU	residual unsaturation
S	styrene
SDS	sodium dodecylsulfate
THF	tetrahydrofuran
V_e	elution volume
W/M	water/monomer ratio (serum ratio)
x	monomer conversion
x_3	pendant vinyl group conversion
$[\eta]$	intrinsic viscosity

1 History

In polymer science and technology, linear, branched and crosslinked structures are usually distinguished. For crosslinked polymers, insolubility and lack of fusibility are considered as characteristic properties. However, insoluble polymers are not necessarily covalently crosslinked because insolubility and infusibility may be also caused by extremely high molecular masses, strong intermolecular interaction via secondary valency forces or by the lack of suitable solvents. For a long time, insolubility was the major obstacle for characterization of crosslinked polymers because it excluded analytical methods applicable to linear and branched macromolecules. In particular, the most important structural characteristic of crosslinked polymers, the crosslink density, could mostly be determined by indirect methods only [1], or was expressed relatively by the fraction of crosslinking monomers used in the synthesis.

For a crosslinking polyreaction the functionality of the monomers is the basic parameter. However, it was found long ago that, after their reaction, not all functional groups are involved in intermolecular crosslinks but also in intramolecular and cyclic links.

In the early days of polymer science, when polystyrene became a commercial product, insolubility was sometimes observed which was not expected from the functionality of this monomer. Staudinger and Heuer [2] could show that this insolubility was due to small amounts of tetrafunctional divinylbenzene present in styrene as an impurity from its synthesis. As little as 0.02 mass % is sufficient to make polystyrene of a molecular mass of 200|000 insoluble [3]. This knowledge and the limitations of the technical processing of insoluble and non-fusible polymers as compared with linear or branched polymers explains why, over many years, research on the polymerization of crosslinking monomers alone or the copolymerization of bifunctional monomers with large fractions of crosslinking monomers was scarcely studied.

Despite this situation, it was before 1935 when Staudinger and Husemann expected to obtain a soluble product by the polymerization of divinyl benzene (DVB) in presence of a solvent and expected that this product should be a colloidal molecule of a globular shape which, despite a high molecular mass, should be soluble to obtain solutions of relatively low viscosity [4]. After heating a very dilute solution of DVB for several days to 100 °C they really isolated a soluble polymer of a low viscosity in solution. The osmotically determined molecular mass was between 20|000 and 40|000. As the specific viscosity of solutions of a 'hemicolloidal' polystyrene was much lower than that of their poly-DVB, they concluded that *this polymer is a product consisting of strongly branched, 3-dimensional molecules*. As the weight-average molecular mass presumably was much higher than the number-average values obtained by osmometry, it must be concluded that Staudinger and Husemann actually obtained the colloidal macromolecules of globular shape, i.e. microgels, which they wished to prepare. But due to the inadequate methods available at this time for polymer characterization, their conclusions were not correct.

As early as 1930 microgels were considered as constituents of synthetic rubber and as the primary reaction gel in the synthesis of polybutadiene [5]. Baker [6] reviewed the early literature on microgels with emphasis on synthetic rubber. He was the first who designated microgel particles as 'new molecules' and suggested emulsion copolymerization (ECP) for localizing gelation to small dimensions.

Schulze and Crouch [7] observed that the viscosity of the soluble fraction of copolymers from butadiene and styrene decreased sharply with the conversion after an initial increase up to the point of gelation. This decrease could not be solely attributed to a selective incorporation of higher molecular mass fractions in the gel, thus leaving fractions of low molecular mass in solution. Cragg and Manson [8] reported a similar relationship between the intrinsic viscosity and the fraction of the crosslinking DVB in the ECP with styrene. Within the concentration range up to 0.1 mass % of DVB no gel was formed. Therefore, a selective removal of species with a high molecular mass could not have taken place to explain the decrease in the intrinsic viscosity observed after its increase at lower concentrations of DVB.

Shashoua and Beaman [9] prepared microgels by ECP of styrene resp. acrylonitrile with small fractions of technical DVB (t-DVB) and also other crosslinking monomers. They stated that *"each microgel particle is a single macromolecule and that the swelling forces of solvation give rise to dispersion to molecular size"*. Medalia [10] postulated that solvent dispersed microgels are thermodynamically true solutions which, according to Shashoua and Van Holde [11], may be called *microsols*.

The intrinsic viscosity of microgels described in [9] decreased with increasing fractions of the crosslinking monomer to about 8 ml/g which was still above the theoretical value for hard spheres of about 2.36 ml/g according to the Einstein equation and assuming a density of 1.1 g/ml. Obviously, due to the relatively low fraction of the crosslinking monomer, these microgels did not behave like hard spheres and were still swellable to some extent.

Sieglaff [12] prepared slightly crosslinked microgels by ECP of DVB and styrene and studied the viscosity and swelling behavior. Nicolas [13] reported on microgels in high-pressure polyethene and Heyn [14] studied microgels in polyacrylonitrile and mentioned other early works on microgels.

The history of microgels is closely related to inhomogeneous polymer networks. The first crosslinked polymer, whose structure and properties has been extensively studied, was rubber. The classical kinetic theory of rubber elasticity assumed an ideal, homogeneous network with a statistical distribution of crosslinks and network chains long enough to be treated by Gaussian statistics [15, 16]. However, in the early microgel literature the presence of microgels in synthetic rubber [e.g. 5–7] had already been mentioned as a reason for inhomogenous network structures, even in case of low crosslink densities. Later on strong experimental evidence indicated that network structures of other crosslinking polymers, such as unsaturated polyester resins, phenolic and melamine formaldehyde resins and even epoxide and isocyanate resins after curing are inhomogeneous (reviews and original literature, e.g.[17–31]).

Probably most network structures obtained by copolymerization of bifunctional monomers and larger fractions of monomers with a higher functionality

are inhomogeneous, consisting of more densely crosslinked domains embedded in a less densely crosslinked matrix, often with fluent transitions.

Besides the inhomogeneity due to a non-uniform distribution of crosslinks, other inhomogeneities due to pre-existing orders, network defects (unreacted groups, intramolecular loops and chain entanglements) or inhomogeneities due to phase separation during crosslinking may contribute to network structures [24]. It may be concluded therefore that network inhomogeneity is a widespread structural phenomenon of crosslinked polymers.

Storey [32] observed some anomalies in the dependence of the gel point at higher concentrations of DVB which suggested some inhomogeneity and a tendency to microgel formation which explained the shift of the gel point towards higher conversions.

Malinsky et al. [33] studied the copolymerization of DVB and styrene in bulk and provided further evidence of the formation of inhomogeneous structures consisting of domains of different crosslink density.

Funke et al. [34] found that on thermal curing of unsaturated polyesters (UP) and styrene the conversion of fumaric acid units decreased with an increase in temperature. A following treatment of all samples at the highest curing temperature used before, had no effect on the conversion of the fumaric acid units. By a temperature increase at an early stage of the copolymerization reaction only the reaction rate could be increased, but the final conversion was the same as that obtained after a longer time at a lower temperature.

From these results it was concluded [18] that the final crosslink density was already fixed very shortly after the beginning of the copolymerization and that a primary network was formed which determined the final network structure. Therefore, the network of cured UP-resins was considered to be inhomogeneous, consisting of domains of a higher crosslink density in a matrix of a lower crosslink density. This conclusion was supported by the fact that, unlike vulcanized rubber, samples of cured UP-resins, on swelling in thermodynamically good solvents such as benzene or chlorinated hydrocarbons, disintegrated strongly and could be easily powdered by rubbing between the fingers. Another direct support for the inhomogeneous structure of cured UP-resins came from Gallacher and Bettelheim [35] who followed the copolymerization by light scattering experiments.

These findings encouraged the synthesis of polymer networks with a well-defined inhomogeneous structure [36], using reactive microgels as multifunctional crosslinking species. Experiments of Rempp [37], who grafted living polystyrene with divinylbenzene to obtain star polymers with crosslinked centers, represented another step to preparation of inhomogeneous networks with a defined structure.

As known from Loshaek and Fox [38], substantial amounts of pendant vinyl groups remain unreacted at the end of the polymerization, especially when a larger fraction of the crosslinking monomer is used in bulk. It was close at hand, therefore, to consider the polymerization of crosslinking monomers alone in order to obtain reactive microgels. For this purpose the crosslinking reaction had to be limited to reaction volumes small enough to obtain polymer particles with a size corresponding to the stronger crosslinked domains found in

cured UP-resins. Accordingly, the method of first choice was emulsion polymerization.

For the formation of microgels the presence of a crosslinking monomer is not always necessary. Thus, microgels have also been detected in polymers prepared with bifunctional monomers, e.g. poly(acrylonitrile-co-vinylacetate) [39], polyethylene [40], poly(vinylchloride) [41] and poly(vinylidene fluoride) [42]. Obviously, the reason for the intramolecular crosslinking with the formation of microgels are side reactions.

2 Definitions

A microgel is an *intramolecularly crosslinked macromolecule* which is dispersed in normal or colloidal solutions, in which, depending on the degree of crosslinking and on the nature of the solvent, it is more or less swollen. Besides linear and branched macromolecules and crosslinked polymers, intramolecularly crosslinked macromolecules may be considered as a fourth class of macromolecules.

Though the term *microgel* has long been used and is well established, it is not quite satisfactory because it is only appropriate for the swollen state, i.e. if crosslinked macromolecules are dissolved. Moreover, *micro* refers to dimensions of more than one micrometer whereas the dimensions of microgels are usually in the range of nanometers. However, in colloquial language 'micro' is also used for something very small. Another term which has been proposed for microgels is *nanoparticles* [43]. But this name generally designates particles with dimensions in the nanometer range, irrespectively of their chemical or structural nature. Other names which have been used are *microglobules* [25], *microspheres* [44], *microparticles* [45], *microlatex* [46], *colloidal particles* and even *polymer network colloids*.

The IUPAC Commission on Macromolecular Nomenclature recommended *micronetwork* as a term for microgel [47] and defined it as *a highly ramified macromolecule of colloidal dimensions*. However, it should be noted that a *micronetwork* implies a structure and not a macromolecule or a particle, that a high ramification is not typical for these molecular particles and that the same wrong dimension is used as with *microgel*.

Because the term *microgel* has the longest tradition and is most commonly used in polymer science and technology it is reasonable to accept it as the generic term for intramolecularly crosslinked macromolecules in solution, a state in which these species of macromolecules are usually handled and characterized.

Microgels are molecular species on the border between normal molecules and particles. Contrary to linear and branched macromolecules, the surface of microgels is rather fixed, thus approaching the characteristics of solid particles. As to their size, it is somewhat difficult to define a limit because the transition from a microgel to a larger polymer particle, e.g. in coarser polymer dispersions, is gradual. Nonetheless, optical criteria related to solubility may be applied to distinguish microgels from larger polymer particles as, contrary to normal polymer dispersions, microgels form colloidal, opalescent or even clear solutions.

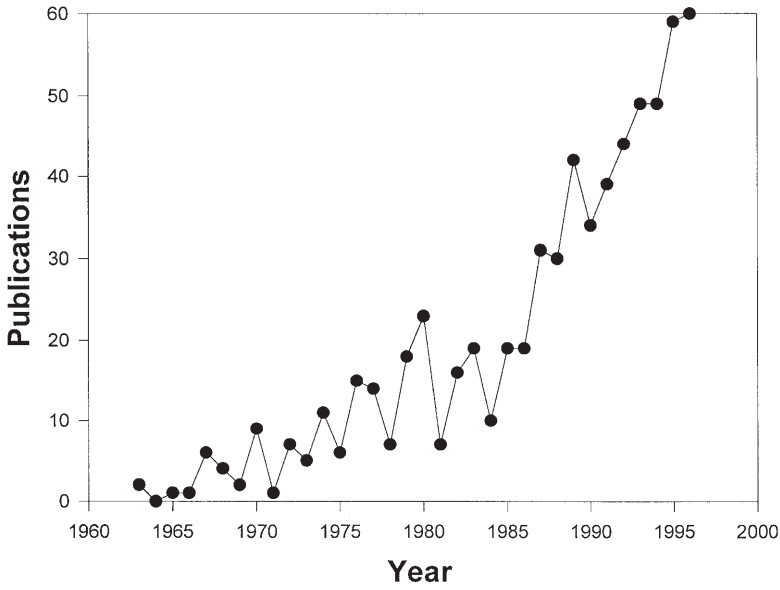


Fig. 1. Publications on microgels from 1966 until 1996 cited in Chemical Abstracts.

For a long time, microgels were rather a nuisance to the science and technology of polymers because they interfered with the characterization of macromolecules by light scattering, blocked pipes and valves in the equipment of polymer production and influenced polymer properties in an unpredictable way. Since the beginning of the 1970s, however, literature on microgels increased steadily and significantly (Fig. 1) parallel with their growing industrial and commercial importance.

Microemulsions are a convenient medium for preparing microgels in high yields and rather uniform size distribution. The name for these special emulsions was introduced by Schulman et al. [48] for transparent systems containing oil, water and surfactants, although no precise and commonly accepted definitions exist. In general a microemulsion may be considered as a thermodynamically stable colloidal solution in which the disperse phase has diameters between about 5 to 100 nm.

3
General Aspects of Microgel Synthesis

Carothers was the first who pointed out that gelation is the result of a linking process of polymer molecules into a three-dimensional network of infinitely large size [49]. The term "infinitely large size", according to Flory, refers to a molecule having dimensions of an order of magnitude approaching that of the containing vessel [50]. Thus, *such molecules are finite in size, but by comparison with ordi-*

nary molecules they may be considered infinitely large [50]. However, by decreasing the dimensions of the containing vessel, the size of the macrogel formed can be reduced. For example, crosslinking polymerization in a micelle produces a gel with a diameter of 50 nm and a molar mass of about 40×10^6 g/mol [51].

Since microgels are intramolecularly crosslinked macromolecules of colloidal dimensions, it is necessary for their synthesis to control the size of the growing crosslinked molecules. This can be achieved by carrying out polymerization and crosslinking in a restricted volume, i.e. that of a micelle or of a polymer coil. Thus, two general methods of microgel synthesis are available : (1) emulsion polymerization, and (2) solution polymerization.

According to the first method, each micelle in an emulsion behaves like a separate micro-continuous reactor which contains all the components, i.e. monomers and radicals from the aqueous phase. Thus, analogous to the latex particles in emulsion polymerization, microgels formed by emulsion polymerization are distributed in the whole available volume.

A different type of microgels can be obtained by solution polymerization. Since an increase of dilution during crosslinking increases the probability of intramolecular crosslinking, the growing polymer chains in a highly dilute solution become intramolecularly crosslinked and their structure approaches that of the microgels formed within the micelles.

Microgels prepared by these two methods exhibit different properties. Microgels, formed in an emulsion with a sufficient amount of crosslinker, behave like a macroscopic globular gel and have a similar internal structure. Unlike microgels formed in an emulsion, microgels formed in solution may have various shapes depending on the relative contributions of intra- and intermolecular crosslinking. It may be assumed, therefore, that microgels are an intermediate state of the macrogelation in solution. Figure 2 shows schematically how the polymer structure varies with the degree of dilution and the content of the crosslinker in the polymerization mixture.

In the following discussion radical crosslinking copolymerization (RCC) of mono- and bis-unsaturated monomers is considered. If a small amount of the crosslinking agent is used and equal reactivities of the vinyl groups as well as absence of cyclization are assumed, RCC would lead to a homogeneous network structure with a constant crosslink density throughout its space. However, the reactivities of vinyl groups in RCC may be different and may depend on conversion. Moreover, cyclization is possible, at least at zero monomer conversion. Therefore, inhomogeneous gel structures are always obtained, as illustrated by the Gel A, shown in Fig. 2.

If an inert good solvent is used in solution polymerization, the gel thus obtained will have a supercoiled (expanded) structure (Gel B). Gel B swells in good solvents much more than Gel A which is synthesized in bulk. If the amount of the crosslinking divinyl monomer in the reaction mixture is increased while the amount of solvent remains constant, highly crosslinked networks are formed that cannot absorb all solvent molecules present in the reaction mixture and a heterogeneous structure results (Gel C). A part of the solvent separates from the gel phase during polymerization and the formed Gel C consists of two continuous phases, a gel and a solvent phase. If the amount of solvent is further increased, a

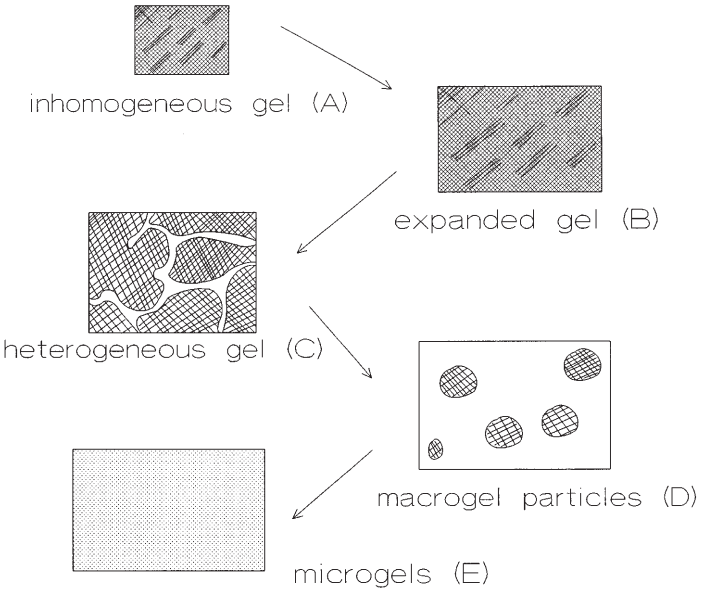


Fig. 2. Formation of various structures in radical crosslinking copolymerization of monovinyl – divinyl monomers with or without using a solvent (diluent).

critical point is passed, at which the system becomes discontinuous, because the amount of the monomer is not sufficient and the growing chains cannot occupy the whole available volume. Consequently, a dispersion of macrogel particles in the solvent results (Gel D). Increasing the amount of solvent decreases the size of the gel particles, and finally they are as small as ordinary macromolecules. These gel particles are microgels, which are dissolved as a colloidal solution (Gel E). It may be expected that at infinite dilution the macromolecules consist of intramolecularly crosslinked primary chains only which may be considered as primary particles. According to this picture of the gel formation, three main transitions can be distinguished: 1) the transition from inhomogeneous to heterogeneous gels (macrophase separation) Gel B $\rightarrow$ Gel C; 2) the "solid-liquid" transition Gel C $\rightarrow$ Gel D; and 3) the macrogel-microgel transition Gel D $\rightarrow$ Gel E. Therefore, the preparation of microgels in RCC requires a careful choice of the experimental parameters.

It is well known that, contrary to linear or branched polymers, the structural characterization of crosslinked polymers is distinctly more difficult due to their insolubility. Since microgels prepared in emulsion behave similar to a macrogel but are soluble, they may serve as a model for the macrogels in order to study the relationships between their synthesis, structure and properties. For example, the intrinsic viscosity $[\eta]$ of the microgels can be substituted in Flory's swelling equation to estimate the crosslinking density. Phase transition phenomena which are observed in macrogels on changing external parameters can also be studied by a discontinuous change of the volume of corresponding microgels [52, 53].

Although microgels formed in a dilute solution have various structures and therefore are not as well-defined as those formed in emulsion, their characterization improved the understanding of the mechanism of gel formation in radical crosslinking copolymerization. Millar et al. showed that, in copolymerization of 1,4-DVB and styrene (S) in the presence of solvents, structures with highly crosslinked regions, so-called "nuclei", are formed which are rich in polymerized 1,4-DVB. From the surface of these nuclei a number of chain radicals grow outwardly [54]. Kast and Funke [55] and Dusek et al. [56] pointed out that the mechanism of gel formation in radical copolymerization differs significantly from the classical gelation theory [50], which assumes an initial formation of essentially linear primary molecules, followed by their linking together. According to Kast and Funke and to Dusek, intramolecularly crosslinked primary particles, i.e. microgels, may form at moderate to high concentrations of crosslinker or solvent. As the polymerization proceeds, new particles are continuously generated. However, reactions between microgels are responsible for the aggregation which leads to the formation of the macrogel [55, 56]. Macrogel formation via microgels may be described by Smoluchowski's equation [57, 58]:

$$\frac{dc_k}{dt} = \frac{1}{2}\sum_{i+j=k} k_{ij} c_i c_j - c_k \sum_{j=1}^{\infty} k_{jk} c_j \tag{1}$$

$$k_{ij} = i^{\alpha} j^{\alpha} \tag{1a}$$

where c_i is the concentration of i-mer and k_{ij} is the rate constant of the interparticle crosslinking to form i+j-mers from i-mers and j-mers [59–63]. If all microgels are mutually penetrable, all functional groups are able to react, α becomes unity and, according to the Flory-Stockmayer model, gelation occurs [50, 64–66]. If only a certain fraction of the functional groups can react, e.g. those at the surface of the particles, α is less than unity.

Therefore, in a crosslinking process which is governed by the intramolecular crosslinking, the structure of the microgels is important. Currently, gel formation is qualitatively quite well understood by using the knowledge about the properties of microgels. However, a satisfactory quantitative treatment is still desirable.

4
Microgel Formation in Emulsion

4.1
Macroemulsion Polymerization

Normal emulsion polymerization is sometimes referred to as "macroemulsion" polymerization because of the large size of monomer droplets (hundreds of microns) compared to those of a "microemulsion" (tens of nanometer).

At first, the mechanism of macroemulsion polymerization of vinyl monomers [67] is shortly considered. Emulsion polymerization usually takes place in three

periods. In Period I initiation occurs where particles are nucleated. This nucleation period ends with the disappearance of the micelles. In Period II the particles grow by diffusion of monomers from droplets through the aqueous phase to and into the particles. When the monomers in the droplets have been consumed, Period III starts, in which the residual monomer in the particles and any monomer dissolved in the aqueous phase is polymerized. The end of Period III corresponds to the complete conversion of monomer to polymer. Thus, in macroemulsion polymerization the monomer is found at four locations: (i) in monomer droplets, (ii) in not yet initiated micelles, (iii) in growing polymer particles, and (iv) dissolved in the aqueous phase. As the concentration of the emulsifier increases, the amount of monomer in the droplets decreases. If the emulsifier concentration exceeds a critical value, all the monomer molecules are solubilized in the aqueous phase and the polymerization system becomes transparent which is typical for a microemulsion or a micellar solution.

Shashoua and Beaman were the first who pointed out that the emulsion polymerization of crosslinking systems is different from systems of linear polymerization [9]. They reported that there is "a tendency for the emulsion polymerization systems to coagulate during the course of polymerization. This is particularly great when high concentrations of crosslinking agent are employed" [9]. In their experiments the mol fraction of DVB isomers in the monomer mixture was less than 0.05. Kühnle and Funke synthesized reactive microgels by emulsion polymerization of 1,4-DVB and of t-DVB and determined the pendant, reactive vinyl groups by addition of mercury acetate and of BuLi [68,69]. Later on, Hoffmann prepared a series of microgels by emulsion copolymerization of t-DVB and S with amounts of DVB varying up to 17 % [70]. In these experiments, an excess amount of emulsifier was used, so that monomer droplets were absent. In the following years many studies were carried out to synthesize crosslinked polymer particles, i.e. microgels, by emulsion copolymerization of vinyl/divinyl monomers [71–76].

During the past 25 years, Funke and co-workers have extensively studied the emulsion polymerization of divinyl monomers alone including 1,4-DVB and ethylene glycol dimethacrylate (EDMA) under various reaction conditions. They found that the intraparticle crosslinking changes drastically the classical picture of emulsion polymerization.

1,4-DVB (purity > 98 %) was polymerized using sodium dodecyl sulfate (SDS) as emulsifier in the presence of various initiators, such as potassium persulfate (PPS) [51, 77–82], 2,2'-azobisisobutyronitrile (AIBN) [83] and also by thermal initiation [84].

Table 1. Comparison of polymer latexes obtained by emulsion polymerization of 1,4-DVB and S [79]. Experimental conditions: temperature = 50 °C; volume ratio water to monomer = 6.25, SDS concentration = 0.02 M, PPS concentration = 0.01 M. Particle diameters were measured by soap titration and by electron microscopy.

MONOMER :	$\bar{d}_z$ [nm]	10^{-15} [N / mL^{-1}]	mass % coagulum
1,4-DVB	26	13	21.7
S	57	1.5	0

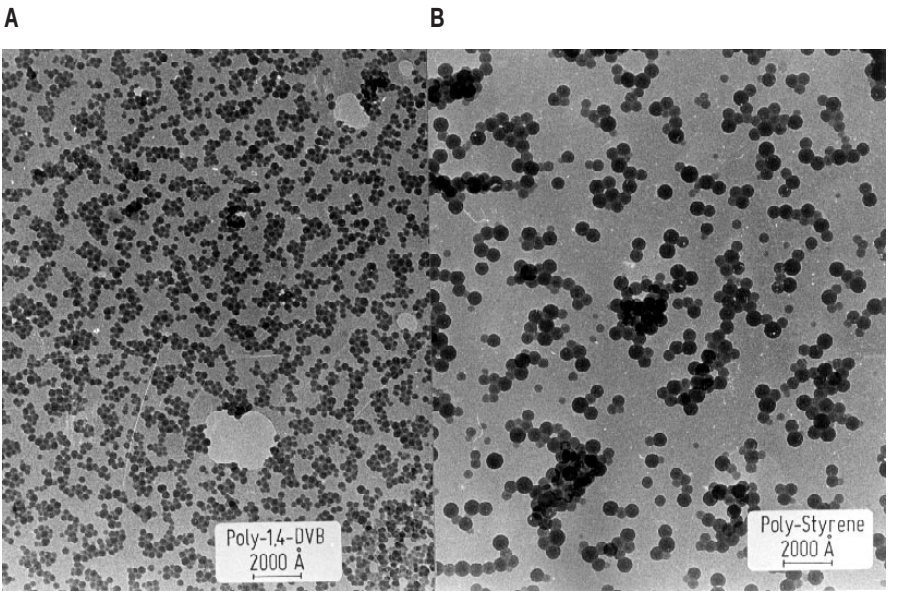


Fig. 3. Electron micrographs of polymer particles formed by emulsion polymerization of 1,4-DVB and S [79]. SDS concentration = 0.02 M, Initiator concentration = 0.01 M, temperature = 50 °C, water/monomer ratio = 6.25. [Reproduced from Ref. 79 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

The polymer particles obtained by emulsion polymerization of 1,4-DVB were microgels and therefore much smaller than normal polystyrene latex particles prepared under the same experimental conditions (Table 1, Fig. 3). Table 1 shows that the average diameter of these microgels was about half of that of latex particles consisting of polystyrene. The maximum diameters of these microgels were about 50 nm. Their small particle size can be considered as a consequence of the intraparticle crosslinking which strongly restricts the swelling by monomers.

According to the classical Smith-Ewart mechanism [85], the number of particles, N, is related to the emulsifier concentration, E, by

$$N \infty E^{\nu} \tag{2}$$

where the exponent ν is predicted to be 0.6, which has been confirmed in the EP of S. However, in all experiments with 1,4-DVB at least five to ten times more particles were formed than with S [79]. The exponent ν was found to be 1.6 [80] and 1.85 [86] in the emulsion polymerization of 1,4-DVB and t-DVB respectively. When saturated polyesters instead of SDS were used as emulsifiers for the polymerization of t-DVB, the exponent ν was 1.65 [87]. Bolle showed that the exponent ν increased gradually as the fraction of 1,4-DVB in the 1,4-DVB/S mixture increased [83]. Moreover, the size distribution of microgels from 1,4-DVB is narrower than that of polystyrene latexes (Fig. 4). Another interesting property of the 1,4-DVB microgels, prepared by persulfate as initiator, is their solubility. If

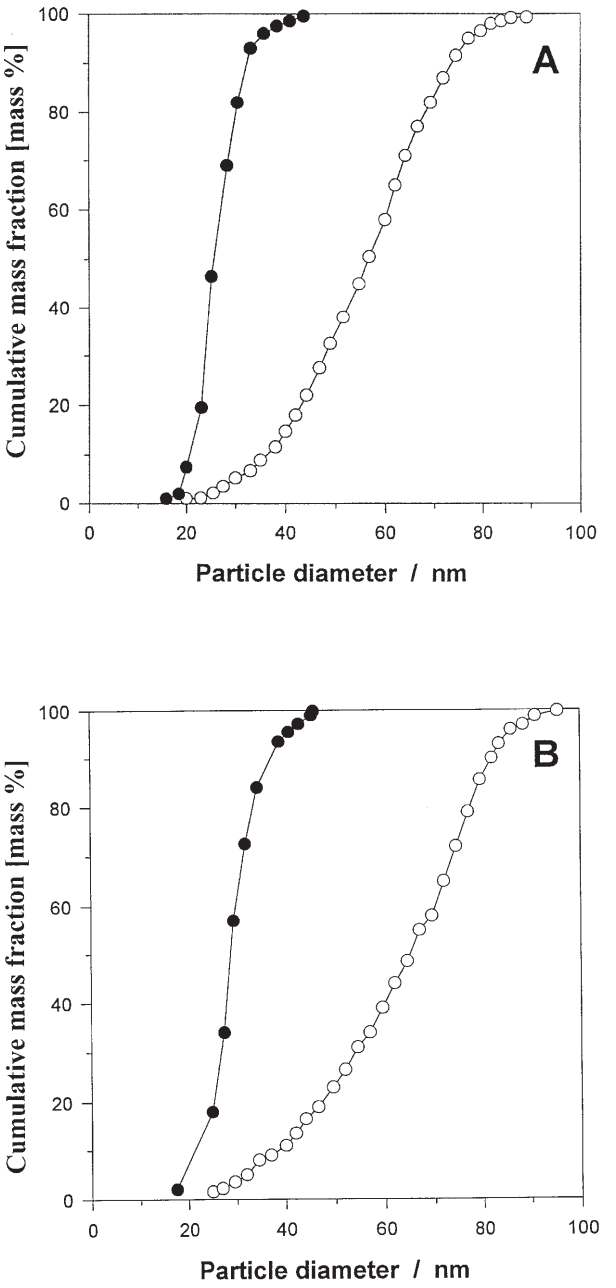


Fig. 4. Size distribution of polymer particles obtained by emulsion polymerization of 1,4-DVB (●) and S (○). SDS concentration = 0.04 M **(A)** and 0.02 M **(B)**. [Reproduced from Ref. 79 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

the reaction time is sufficiently long or if a high amount of the initiator is used, the microgels become soluble in methanol [81]. Whereas latex particles and microgels prepared from styrene or DVB are completely insoluble in methanol, the addition of sulfate anion radicals to pendant vinyl groups at the surface of the microgels makes them hydrophilic and soluble in methanol.

Depending on the reaction conditions of the EP of 1,4-DVB, variable amounts of large polymer particles are formed as by-products which can easily be removed by filtration. By electron microscopy, these particles were identified as polymerized monomer droplets and as aggregates of microgels [77]. Aggregation is not surprising, because microgels may collide with each other and residual pendant vinyl groups of particles may react with radical centers of neighboring particles thus bonding them covalently together. This reaction is called interparticle crosslinking.

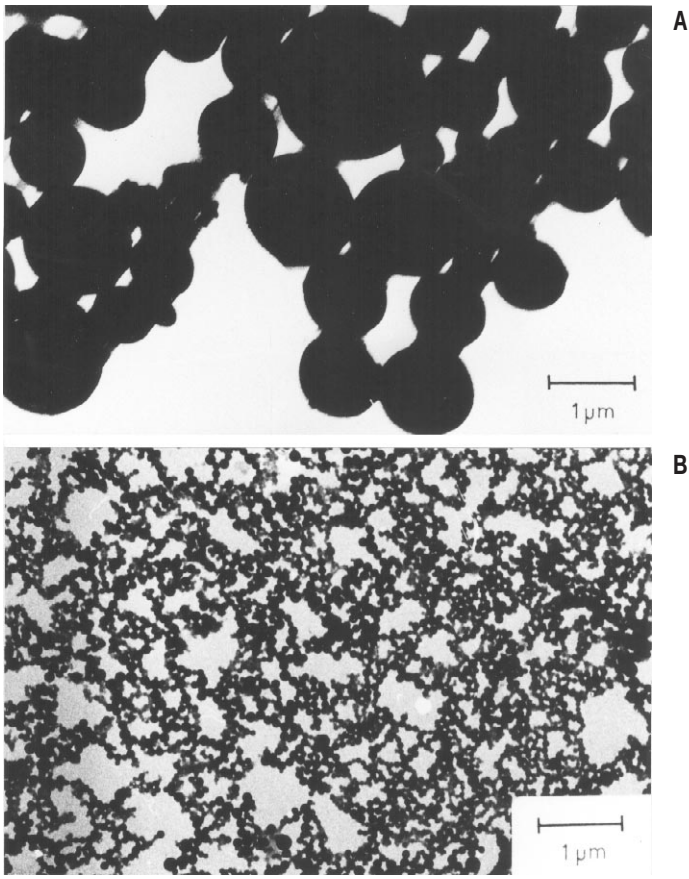


Fig. 5. Electron micrograph of the polymers formed by thermal emulsion polymerization of 1,4-DVB (A) and S (B). SDS concentration = 0.1 M, water/monomer volume ratio = 12.5, polymerization temperature = 90 °C. [Reproduced from Ref. 84 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

The appearance of polymerized monomer droplets indicates that polymerization is initiated both in the monomer droplets and in monomer-containing micelles. This result is completely different from that obtained in the EP of styrene under identical conditions, where no monomer droplets polymerize. Similar experiments with 1,3,5-trivinylbenzene also yielded polymerized monomer droplets as by-products [77]. The amount of polymerized 1,4-DVB droplets further increased when PPS was replaced by an oil soluble initiator, such as, AIBN [83] or, when the EP was thermally initiated [84]. Figure 5 compares electron micrographs of the polymers formed by thermally (90 °C) initiated EP of 1,4-DVB and S.

In linear EP of bifunctional monomers, such as S, with water soluble initiators, the monomer droplets do not compete with micelles in capturing radicals from the aqueous phase because the total surface area of the droplets is much smaller than that of micelles and growing particles. Nevertheless, if some radicals enter monomer droplets, rapid termination takes place. Therefore, polymerization in monomer droplets is negligible [88]. However, if in the crosslinking EP of 1,4-DVB a few radicals are captured by monomer droplets, they can polymerize completely because the recombination of radicals is suppressed by the gel effect. Moreover, in thermal initiation or in initiation by hydrophobic initiators, such as AIBN, radicals are formed predominantly in the hydrophobic phase, i.e. in monomer droplets and in micelles, and crosslinking EP is initiated in the organic phase.

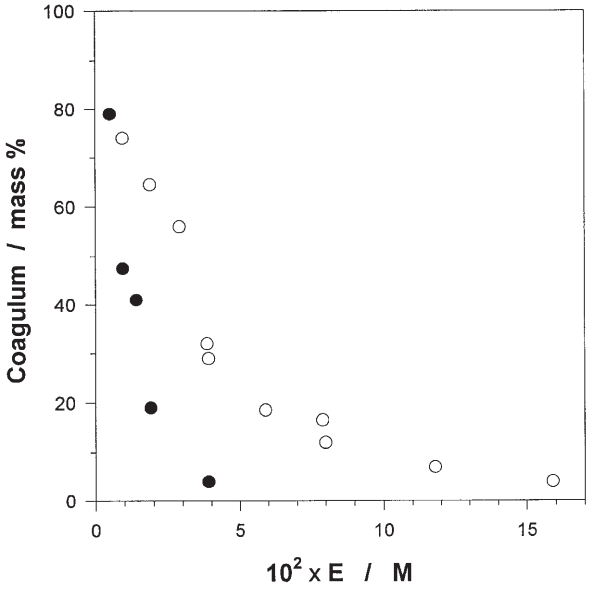


Fig. 6. Amount of coagulum as a function of the emulsifier concentration in 1,4-DVB polymerization. Polymerization temperature = 50 °C, water/monomer volume ratio = 6.25 (○), and 12.5 (●). [Reproduced from Ref. 79 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

As shown in Fig. 6, the amount of polymerized monomer droplets strongly depends on the emulsifier concentration. With increasing emulsifier concentration, the amount of monomer initially present in the monomer droplets decreases in favor of monomer solubilized in micelles. Concurrently the fraction of polymerized monomer droplets decreases and more microgels are formed. Above a certain emulsifier concentration which is about 0.8 mol/l in thermal initiation, the monomer is completely solubilized prior to polymerization and no polymerized monomer droplets are formed.

Contrary to all results known for emulsion polymerization the rate of polymerization decreases with increasing emulsifier content [83, 84] (Fig. 7). Time-conversion curves show an initial period of high polymerization rate and a subsequent period of a significantly lower rate. It seems that two parallel reactions are involved in the emulsion polymerization of 1,4-DVB: a fast polymerization in the monomer droplets and a slower polymerization in the growing microgel particles. If all monomer molecules are solubilized in the aqueous phase, i.e. at high emulsifier concentrations, the slope of the time-conversion curve changes gradually (Curve III in Fig. 7).

Spang studied the EP of EDMA under various reaction conditions and obtained similar results [89]. The differences between the crosslinking EP and EP of comonomers with similar chemical and physical properties, but different functionalities, e.g. 1,4-DVB and S or EDMA and MMA, can be explained by the

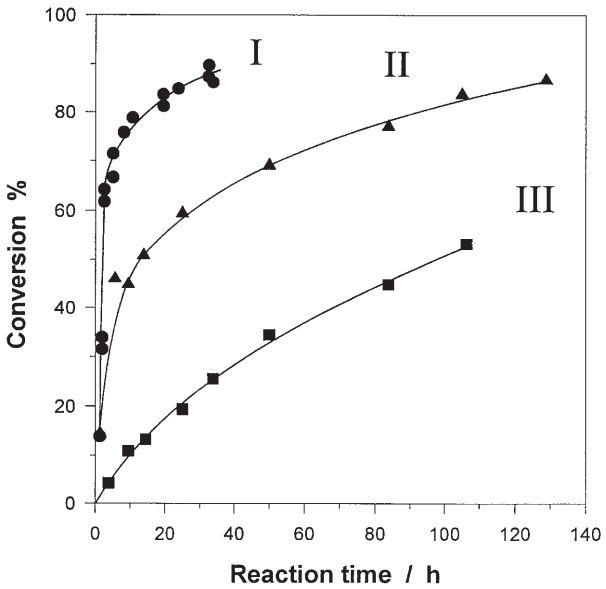


Fig. 7. Time-conversion curves of thermally initiated emulsion polymerization of 1,4-DVB at 0.1 (I); 0.65 (II); and 0.85 (III) M SDS concentrations. Polymerization temperature = 90 °C; water/monomer volume ratio = 12.5. [Reproduced from Ref. 84 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

characteristics of radical crosslinking emulsion polymerization. These characteristics which are due to the network formation, are:

- formation of significantly more and smaller monodisperse polymer particles;
- polymerization of monomers in the monomer droplets as well as in the polymer particles;
- decrease in the polymerization rate with increasing emulsifier concentration.

In the following a possible mechanism of microgel formation in crosslinking EP, using water soluble initiators, is given [79, 84, 90, 91].

Radicals or oligomer radicals are generated in the aqueous phase and enter monomer-swollen micelles and initiate polymerization and crosslinking to form microgels. Polymer particles formed from vinyl monomers consist of 50–70% monomers and, until the end of Period II, i.e. as long as monomer droplets are present, the monomer concentration in the polymer particles remains almost constant. However, in crosslinking EP the network formation of microgels limits the amount of absorbable monomer, thus also limiting their growth. It must be noted that in EP the molar mass of the growing polymer chains is much higher than in bulk polymerization because of the compartmentalization in the particles. Because the primary polymer molecules are long and since the reactions within the polymer particles occur under bulk conditions, one may expect a very early onset of macrogelation within the particles, i.e. already during Period I. Recent calculations also show that in crosslinking EP of tetrafunctional monomers the crosslink density is very high from the very beginning of the reaction, so that the absorption of monomer by the polymer particles is restricted even in Period I [92]. Beyond the gel point, the decrease of the monomer concentration in the polymer particles will enhance the probability of multiple crosslinking, so that the crosslinking density of the particles will increase very rapidly and a tighter network structure results. This also reduces the growth rate of the polymer particles and the size of the particles.

During the period of particle nucleation in the EP of vinyl monomers, usually one of every 100–1000 micelles captures a radical and becomes a polymer particle. All other micelles give their monomers and emulsifier molecules to neighboring micelles which have captured a radical. However, since the growth rate of polymer particles decreases by crosslinking, monomer-containing micelles exist for a longer time and therefore have a better chance to capture radicals for polymerization. As a result, more polymer particles are produced in crosslinking than in linear EP.

Due to the reduced absorption of monomers and the low rate of polymerization in the micelles, the diffusion of monomer molecules from droplets to the growing particles is limited. Correspondingly, the probability of polymerization in the droplets increases.

In EP of bifunctional vinyl monomers, the reaction rate increases with the emulsifier concentration because the number of particles increases. However, in the crosslinking EP of divinyl monomers, the reaction rate is inversely proportional to the emulsifier concentration. This unusual behavior is due to nucleation taking place in both micelles and monomer droplets. In monomer droplets, the kinetics resembles that of bulk polymerization and therefore the reaction rates

are higher than in micelles. As the amount of monomers available for the polymerization in the monomer droplets is determined by the emulsifier concentration, an increase of the emulsifier concentration decreases the amount of the monomer in the droplets and accordingly the rate of polymerization also decreases.

4.2 Microemulsion Polymerization

A more efficient way to synthesize microgels is microemulsion polymerization (micro-EP). Three characteristics distinguish micro-EP from EP [93, 94]: (1) no monomer droplets exist but only micelles or microemulsion droplets which are probably identical; (2) the initiator stays in the microemulsion droplets only and polymerization occurs only there, provided oil-soluble initiators are used; and (3) the reaction mixture is optically transparent and in an equilibrium state. Compared to EP, polymerization in a microemulsion is a very simple method for the controlled synthesis of microgels because monomer droplets are absent. Using micro-EP, Antonietti et al. prepared spherical microgels with diameters of 60–170 nm by copolymerization of 1,3-disopropenylbenzene and S, using a combination of a derivative of a polyethylene oxide as a polymeric emulsifier and sodium dodecyl sulfate (SDS) [95]. Bolle studied the micro-ECP of 1,4-DVB and S using only SDS and synthesized a series of microgels with different diameters and degrees of swelling [83].

4.3 Characteristic Properties of Microgels

Since a microgel is a solvent-containing three-dimensional macromolecule, its mass in the dry state may be compared with the mass of a polymer particle formed in EP. Accordingly, each factor that influences the size of monomer-containing species also influence the molar mass of a microgel. Figure 8 shows how the weight-average molar mass $\overline{M}_w$ of 1,4-DVB microgels and their hydrodynamic diameter $\overline{d}_z$ in toluene vary with the emulsifier (SDS) concentration [83]. Both $\overline{M}_w$ and $\overline{d}_z$ decrease with an increase of the emulsifier concentration because the size of the micelles is decreased. This decrease is first rapid but then slower at a SDS concentration of about 0.6 mol/l, where all 1,4-DVB molecules are solubilized in micelles [83].

Due to the compact structure of microgels, their intrinsic viscosities, $[\eta]$, are much smaller than those of corresponding linear or branched polymers. In Fig. 9, $[\eta]$ of DVB-microgels is plotted against their crosslink density in terms of the mol % of crosslinking monomer in the initial monomer mixture. The experimental data points were taken from different sources [9, 12, 70, 83, 95]. Though both the conditions of synthesis and measurement and the kind of monomers differed, the results can be represented by a single curve. $[\eta]$ first decreases strongly up to about 3% of crosslinking monomers, and finally attains a limiting value of 4 ml/g which is somewhat higher than the value for rigid spheres 2.3 ml/g of the Einstein equation for viscosity. For EDMA microgels formed by EP, $[\eta]$ in

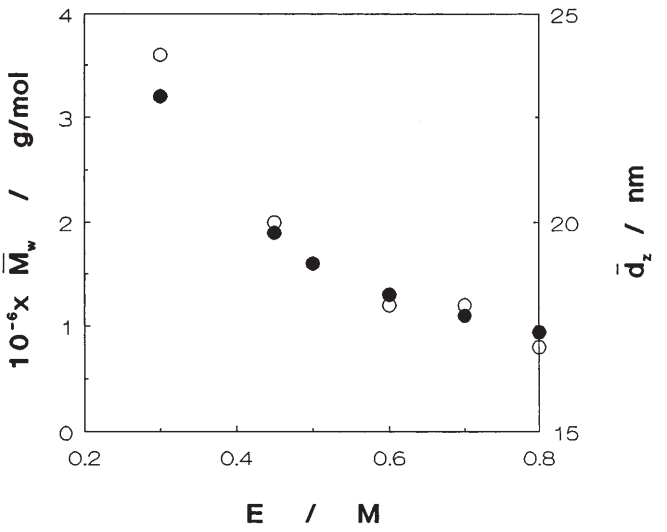


Fig. 8. Variation of the weight-average molar mass $\overline{M}_w$ (●) and z-average hydrodynamic diameter in toluene $\overline{d}_z$ (○) with the emulsifier concentration in the emulsion polymerization of 1,4-DVB [83]. Polymerization temperature = 70 °C , initiator = AIBN, water/monomer ratio = 12.5.

n-butyl acetate or in dioxane was also 4 ± 1 ml/g [89]. It seems that this is a limiting value of [η] for microgels which corresponds to a volume swelling ratio of 1.8.

Accordingly, microgels swell a little in good solvents, of course, depending on their crosslink densities. Shashoua and Beaman [9], Hoffmann [70], and Antonietti et al. [95] showed that the swelling ratios of microgels, calculated from their [η], agree with the swelling ratios of macrogels. This would mean that microgels qualitatively obey the theory of rubber elasticity. By applying Flory's swelling equation, the calculated crosslink density of microgels is lower than that expected from their composition due to an inefficient crosslinking [95]. It was also shown that, like with macroscopic gels, the dependence of the degree of swelling on the solubility parameter of the swelling agent can be used to estimate the solubility parameter of the microgels [12].

Figure 10 shows the variation of the exponent a of the Mark-Houwink equation with the 1,4-DVB content of microgels. The measurements were carried out at 25 °C in salt-containing *N,N'*-dimethylformamide (DMF) (<10 mass % of 1,4-DVB) or in toluene (>10 mass % of 1,4-DVB) [70, 83]. The exponent a is close to zero for 1,4-DVB contents higher than 0.3 mass % and becomes zero above 10 mass % of 1,4-DVB. At low crosslinker contents one may expect that the network chain ends, emerging from the microgel surface, may lead to the observed slight molar mass dependence [η]. However, for 1,4-DVB contents higher than 10 mass %, microgels in solution behave like homogeneous gel spheres with a constant density.

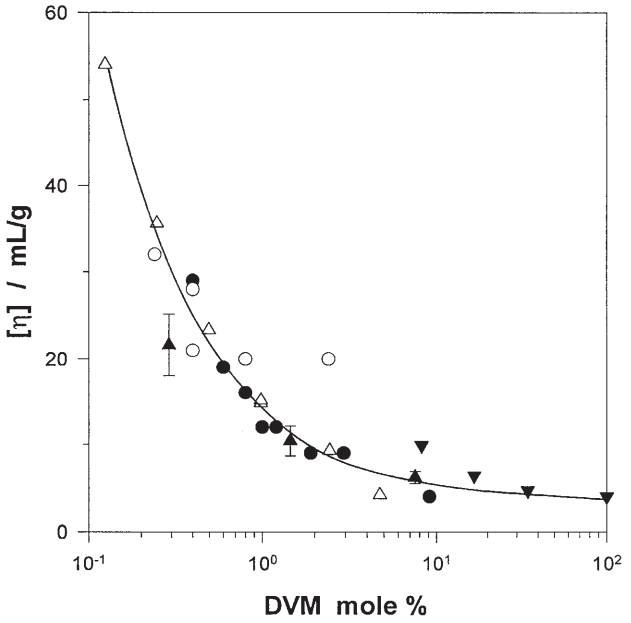


Fig. 9. Variation of the [η] of microgels formed by emulsion polymerization with the amount of divinyl monomer (DVM) in the monomer mixture. The experimental data points were taken from following sources:
(●): Shashoua and Beaman [9]; t-DVB/S microgels; initiator = PPS; measurements in benzene at 30 °C.
(○): Sieglaff [12]; t-DVB/S microgels; initiator = PPS ; measurements in toluene at 25 °C.
(▲): Hoffmann [70]; t-DVB/S microgels; initiator = PPS; measurements in salt-containing DMF at 25 °C. Average values of microgel fractions were taken. The error bars indicate the standard deviations.
(△): Antonietti et al [95]; 1,3-diisopropenylbenzene/S microgels; initiator = AIBN; measurements in toluene at 20 °C.
(▼): Bolle [83]; 1,4-DVB/S microgels; initiator = AIBN; measurements in toluene at 25 °C.

Since the radius of gyration, R_G, is sensitive to refractive index distribution (mass distribution) within the polymer coil, while the hydrodynamic radius, R_H, is sensitive to the flow properties, the ratio R_G/R_H also informs us about the inner structure of microgels. For a random coil in a Θ-solvent this ratio is 1.73 while for a hard sphere of uniform density it is 0.775 [96, 97]. For various microgels prepared in emulsion, the R_G/R_H ratio was found to be smaller than that for a rigid sphere and approaches its ratio with increasing crosslinker content [73, 95–98]. These measurements also indicate that the microgels with low crosslink densities have a non-uniform polymer segment density, whereas those with a high crosslink density behave like homogeneous spheres.

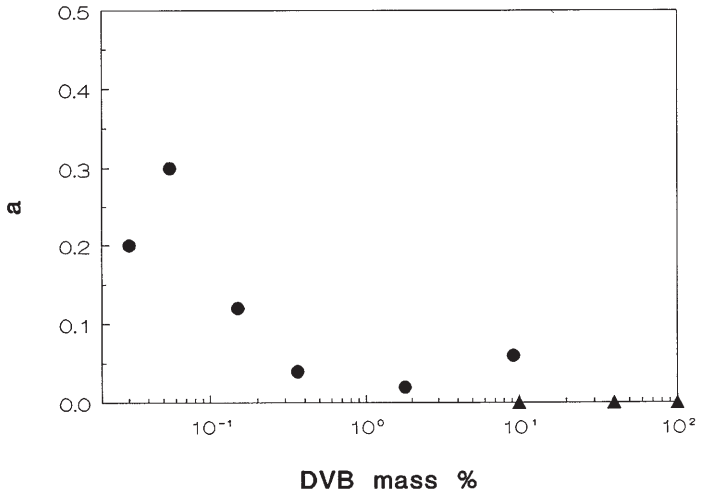


Fig. 10. Dependence of the exponent a of Mark-Houwink equation on the 1,4-DVB content of the microgels formed in emulsion. The data points were calculated from the $[\eta]$ and $\overline{M}_w$ values reported by Hoffmann (●) [70] and by Bolle (▲) [83].

4.4 Expanded (Preswollen) and Heterogeneous (Porous) Microgels

Heterogeneous (porous) macrogels are widely used as starting materials for ion exchangers and as specific sorbents. Therefore, the mechanism, with which these structures are formed by copolymerization of divinyl/vinyl monomer mixtures has been the subject of many studies [e.g. 54, 99–106]. It is interesting to compare these results with those obtained using microgels, though only a few experiments with microgels have been reported [70, 95].

Depending on the conditions of synthesis, copolymerization of divinyl/vinyl-monomers in the presence of an inert solvent leads to the formation of expanded (preswollen) or heterogeneous (porous) structures [54, 99, 100]. If the solvent remains in the network (gel) phase throughout the copolymerization, expanded networks are formed. If the solvent separates from the network phase the network becomes heterogeneous. According to Dusek et al., heterogeneities may appear in poor solvents due to the polymer-solvent incompatibility (χ-induced syneresis), while in good solvents due to an increase in crosslink density (ν-induced syneresis) [99].

Now the post-gelation period of the copolymerization of divinyl/vinyl monomers in the presence of a good solvent as a diluent will be considered. Let $Q_{v(x)}$ be the equilibrium volume swelling ratio of the gel formed at conversion x, and $Q^0_{v(x)}$ its degree of dilution in the reaction system, i.e.,

$$Q^0_{v(x)} = \frac{\text{volume of swollen gel in (monomer + solvent) mixture}}{\text{volume of dry gel at conversion x}} \qquad (3)$$

Both $Q_{v(x)}$ and $Q^0_{v(x)}$ decrease as the polymerization proceeds and, after a definite conversion $Q_{v(x)}$ may reach the value of $Q^0_{v(x)}$. Since the dilution of a gel cannot be greater than its equilibrium degree of swelling, the excess of solvent should separate from the gel phase resulting in the syneresis, i.e. in phase separation. The condition for incipient phase separation during copolymerization of divinyl/vinyl monomers is given by [107]

$$\frac{Q_{v(x)}}{Q^0_{v(x)}} \leq 1 \tag{4}$$

Assuming a homogeneous distribution of crosslinks, the equality, given by Eq. (4), becomes independent of conversion. Thus on complete conversion (x = 1), $Q^0_{v(x)}$ reduces to Q_v^{00} (initial degree of dilution of the monomers) and $Q_{v(x)}$ can be replaced by the experimentally determined equilibrium swelling ratio Q_v. Accordingly, the condition of phase separation becomes

$$\frac{Q_v}{Q_v^{00}} \leq 1 \tag{5}$$

The experimental data obtained with macrogels formed in the presence of solvents, agreed well with Eq. (5) [99, 105, 108]. In order to check the applicability of this equation to microgels, the experimental data reported by Hoffmann [70] are used. He prepared a series of microgels with different crosslink densities, using toluene as a solvent, at $Q_v^{00} = 5$. Q_v was calculated from the reported data using the equation $Q_v = \frac{[\eta]d_p}{2.5}$ and assuming the density of the polymer as $d_p = 1.1$ g/ml [83]. The normalized swelling ratio of the Hoffmann's microgels is given by $[\eta]/[\eta]_0$ where $[\eta]$ and $[\eta]_0$ are the intrinsic viscosities of the microgels prepared with and without using a solvent respectively.

Figure 11 illustrates the Q_v/Q_v^{00} ratio and the normalized swelling ratio $[\eta]/[\eta]_0$ plotted as a function of the 1,4-DVB content of the monomer mixture. For Q_v/Q_v^{00} values greater than unity, the microgels prepared in the presence of toluene swell twice as much as those prepared without a solvent . Thus, these microgels have an expanded (supercoiled) structure. Like in macrogels, the swelling ratios do not depend on the crosslinker content. However, if the ratio Q_v/Q_v^{00} of microgels drops below unity, the swelling ratio decreases simultaneously, which indicates the onset of phase separation within the microgels during polymerization and the appearance of heterogeneities. Since toluene separates from the gel phase, the swelling ratio approaches that of microgels formed without a solvent. As seen in Fig. 11, the incipient phase separation within the microgel particles occurs at about 6 mass % of 1,4-DVB. This value of a critical DVB concentration is reasonable considering reported values for t-DVB/S macrogels formed in toluene. Millar et al. reported critical DVB concentrations of 30 and 15 mass % t-DVB for $Q_v^{00} = 1.5$ and 4.0 respectively [54]. Although the experi-

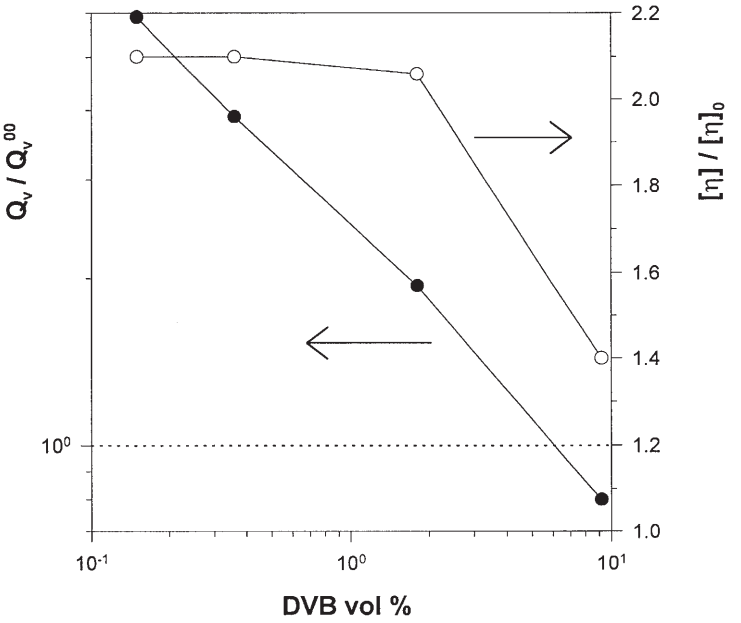


Fig. 11. Variation of Q_v/Q_v^{00} ratio (●) and the reduced intrinsic viscosity of microgels $[\eta]/[\eta]_0$ (○) with the DVB content in the monomer mixture. Experimental data points were taken from Hoffmann [70]. The dotted horizontal line represents the critical Q_v/Q_v^{00} value for the onset of a phase separation.

ments, carried out in the presence of solvents are incomplete and more experimental evidence is necessary, these experiments and calculations demonstrate the formation of preswollen and heterogeneous microgels.

5 Microgels by Emulsion Copolymerization of Self-Emulsifying Unsaturated Polyesters and Comonomers

By emulsion copolymerization (ECP) of self-emulsifying unsaturated polyesters (EUP) and bifunctional monomers, such as styrene (S), microgels may be prepared which have a rather uniform diameter [109]. This uniformity of size is due to a special mechanism of particle formation involved in using EUP as comonomers.

Unsaturated polyesters that are terminated by carboxylic acid groups at both ends of the chain after neutralization are efficient emulsifiers for lipophilic monomers [110] and thus act as self-emulsifying crosslinking agents in the ECP of these systems. Normal emulsions of EUP and comonomers have a white, milky appearance. With an appropriate structure and molar mass of the EUP and within a certain range of EUP/comonomer ratios, however, microemulsions are

obtained [111] which are opaque or almost clear. If EUP/comonomer mixtures are copolymerized in such microemulsions, high yields of microgels result without formation of insoluble coagulates or agglomerates.

For preparing microemulsions, normally larger amounts of an external emulsifier, if not other additives, are needed. Both have to be removed after the reaction. Self-emulsifying copolymerization of EUP and comonomers in a microemulsion (micro-ECP) avoids these disadvantages. Moreover, besides the emulsifying and crosslinking function, the EUP provides carboxylic acid groups at the surface of the microgels that may be used for further chemical modifications or for crosslinking with other reactive compounds or macromolecules.

By using lipophilic initiators, such as 2,2'-azobis(isobutyronitrile) (AIBN), in the micro-ECP, diffusion of monomers is too slow compared with the reaction rate. Therefore, copolymerization is confined to the incoherent, lipophilic phase [112, 113] and very small microgel particles with a rather uniform size result.

5.1
Unsaturated Polyesters as Self-Emulsifying Components of Copolymerization

Unsaturated polyesters with neutralized terminal carboxyl acid groups (EUP) are efficient emulsifiers which, at a sufficient concentration, may form aqueous microemulsions. Microemulsions are liquid dispersions of translucent (opalescent or transparent) appearance. Their disperse phase contains particles of diameters between 20 and 80 nm which closely approaches the diameters (5–15 nm) of micelles [114].

In aqueous dispersions of EUP the diameters were found to be about 5–25 nm and the corresponding dispersions of these EUP and comonomers up to about 50–60 nm [115]. Accordingly, these dispersions may be classified as microemulsions.

For the self-emulsifying function of EUP, its molar mass should be within certain limits which depend on the molecular structure of EUP. With higher molar masses normal emulsions are formed and, depending on the solubilization procedure of the lipophilic monomers, normal or multiple emulsions may be obtained [111]. Moreover, the degree of isomerization, *cis/trans* (c/t) is important for the solubilizing property and the reactivity of the EUP. For acting as emulsifiers the terminal acid groups of the EUP must be neutralized by inorganic or organic bases, such as NaOH or tertiary amines.

Because the conditions of solubilization and copolymerization of EUP/comonomer systems as well as the characteristics and properties of the microgels depend on a variety of parameters, these data are included in the following figures and their captions.

5.1.1
Solubilization of the Monomer Mixture

The sequence of dispersing the EUP and the lipophilic comonomer in water profoundly influences the structure of the emulsion obtained. If the EUP is first dissolved in the comonomer and then this mixture dispersed in water containing

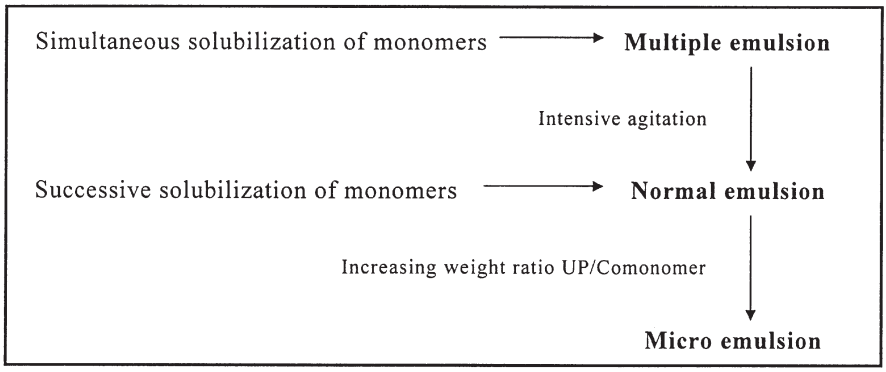


Fig. 12. Preparation of different emulsions of self-emulsifying unsaturated polyesters (EUP) and comonomers.

the base needed for neutralizing the carboxylic acid groups of the EUP, multiple emulsions are obtained. Only by very efficient agitation, such as ultrasonic treatment, do multiple emulsions gradually change to normal emulsions (Fig. 12). This indicates that diffusion processes in mixing of a colloidal systems may be much slower than in mixing components of normal solutions.

By first dispersing the EUP in water containing the base for neutralization of the carboxyl acid groups of the EUP and then adding the comonomer with intensive stirring, normal emulsions are obtained. They are favorable because, with multiple emulsions, insoluble polymers are formed, which decrease the yield of microgels.

For self-emulsification the molar mass of the EUP must be within a certain range. If the molar mass is too high, the solubility of the EUP is too low. If the molar mass is too low, the solubilizing efficiency is insufficient. With an EUP from maleic anhydride (MA) and hexanediol-1,6 (HD) and acid terminal groups, the optimal molar mass for the solubilization of a hydrophobic comonomer, such as styrene (S), was found to be between about 1700 and 2200 [116].

For studying the emulsifying properties, saturated polyesters can be used to avoid complications by the reactivity of unsaturated units of the EUP [117]

5.1.2
Critical Micelle Concentration of Unsaturated Polyesters

Like other emulsifiers, an EUP forms micelles at a critical micelle concentration (CMC). For comonomer-free EUP-emulsions of the (MA+HD)- type the CMC is about 5×10^{-4} g/ml [115, 118]. The CMC depends on the composition and chain length of the polyester, the presence of an electrolyte [118] and the temperature.

An increase in the molar mass of EUP decreases the CMC (Fig. 13), but this effect almost disappears at higher molar masses. With higher molar masses, less EUP molecules are needed for micelle formation, but this tendency is limited by the required solubility of the EUP in water.

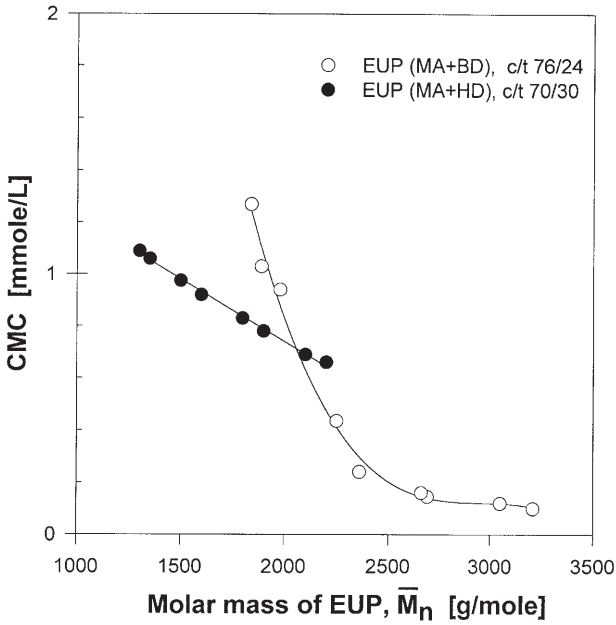


Fig. 13. Relation between the critical micelle concentration (CMC) of self-emulsifying unsaturated polyesters (EUP) and their $\overline{M}_n$ [119, 120].

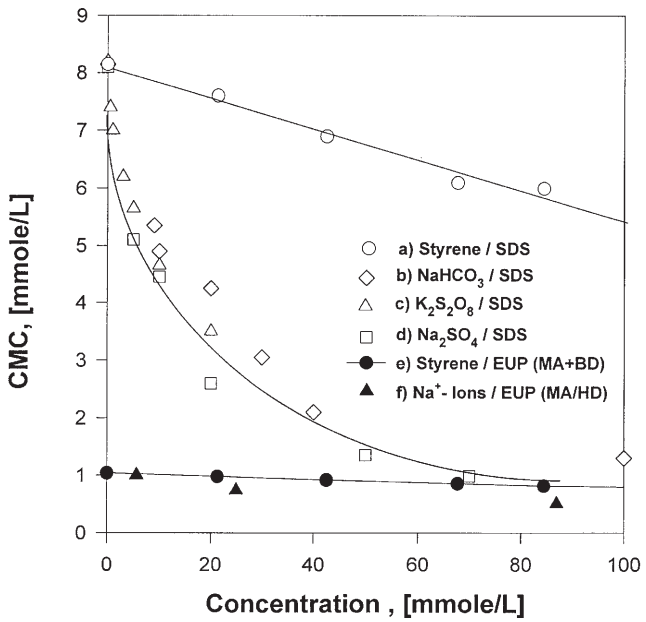


Fig. 14. Relation between the CMC of SDS and EUP. a) – e): [119], f): [118].

Electrolytes strongly decrease the CMC of usual emulsifiers, such as sodium dodecyl sulfate (SDS) (Fig. 14). The source of electrolytes in an emulsion polymerization may be carboxylate groups terminating the EUP molecules, radical initiators (e.g. $K_2S_2O_8$), inorganic bases (e.g. $NaHCO_3$) for neutralizing acid degradation products of persulfate initiators or other external electrolytes. With an EUP, the effect of electrolytes, such as Na^+-ions, on the CMC is much less pronounced than in case of SDS. The presence of hydrophobic comonomers, such as S, decreases the CMC. This decrease is smaller with EUP- than with SDS-micelles. The nature of the cation also plays a role for CMC.

With increasing temperature the CMC passes through a minimum (Fig. 15). The initial small decrease at low temperatures is due to a positive enthalpy of the micelle formation whereas the stronger increase of CMC towards higher temperatures is caused by a thermal perturbation of the emulsifier molecules in the micelles. The smaller influence of the temperature on the CMC in case of EUP indicates that these micelles are thermally more stable than SDS-micelles.

5.1.3
Micelles and Microemulsion Droplets

The incorporation of comonomers increases the mean hydrodynamic diameter of EUP-micelles, $\bar{d}_z$ (Fig. 16). Contrary to CMC, the $\bar{d}_z$ of micelles resp. microemulsion droplets increases with the concentration of an external electrolyte.

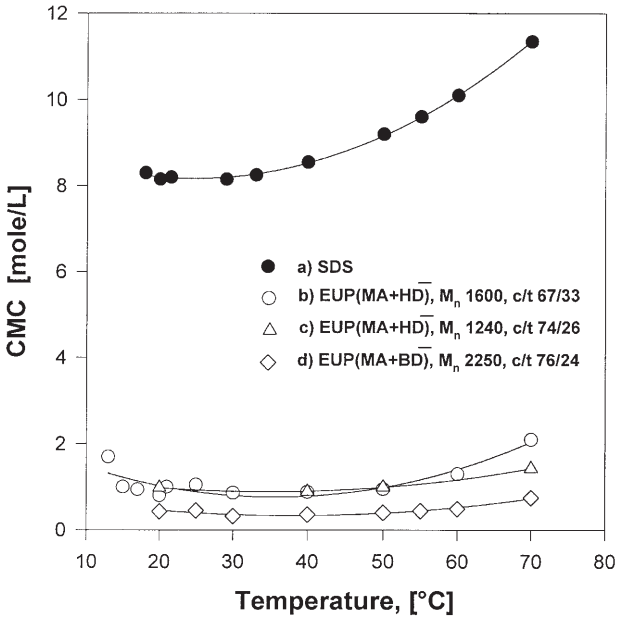


Fig. 15. Dependency of CMC of SDS and various EUP on temperature a) + d): [119], b): [120], c): [118].

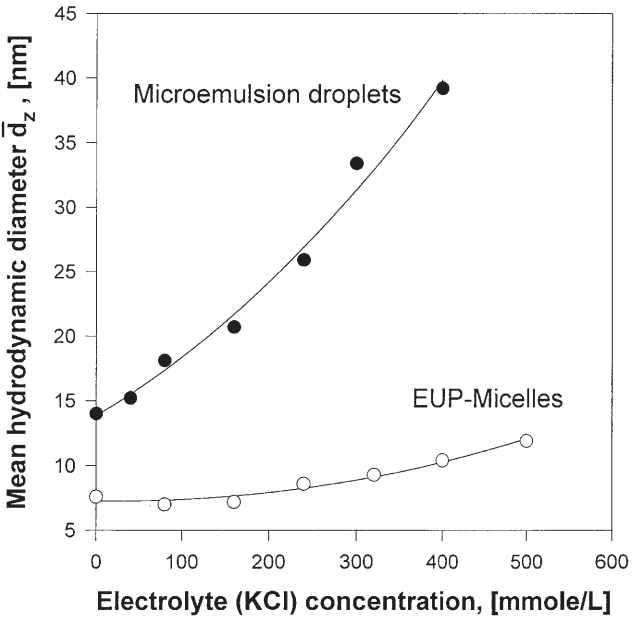


Fig. 16. Influence of electrolyte (KCl) on $\bar{d}_z$ of EUP-micelles and EUP/S-microemulsion droplets [122]. EUP(MA+HD), $\overline{M}_n$ 1290, c/t 80/20, EUP/S 4, pH 7.5,W/M 25.

However, this increase is much more significant in case of the microemulsion droplets than of EUP-micelles. The volume of a EUP-micelle increases by a factor of 6 when S is added in the mass ratio EUP/S of 80/20 and the volume of such a microemulsion droplet increases once more by a factor of 2 when 100 mmol of KCl are added.

Towards high concentrations of the electrolyte, the microemulsion changes to an emulsion containing normal monomer droplets. With a further increase in the electrolyte concentration, the emulsion becomes unstable and breaks down ("salting out").

Considering the diameters of both disperse species, the transition from micelles, containing comonomers, to microemulsion droplets seems to be rather continuous. It is therefore questionable whether a distinction between both species is justified.

By choosing a suitable structure of the EUP, not using a large excess of the base for neutralizing the carboxyl acid end groups and by applying a low temperature, a significant hydrolytic degradation of the polyester during solubilization and copolymerization can be avoided.

Hydrophobic solubilizates such as styrene (S) decrease the saponification rate of the EUP. Accordingly, the EUP-molecules in micelles containing S are more resistant against hydrolytic degradation than molecularly dissolved EUP-molecules. Obviously, the access of the base to the hydrophobic interior of these micelles and microemulsion droplets is more difficult.

5.2 Emulsion Copolymerization of Self-Emulsifying Unsaturated Polyesters and Comonomers

In normal emulsion polymerization the diffusion of monomers from droplets allows particles to grow. The polymerization is usually initiated in the aqueous phase and the oligomeric radicals either enter micelles or merge with other growing species. In the crosslinking ECP of EUP the ratio EUP/comonomer and the solubility or insolubility of both components and the initiator in the aqueous and non-aqueous phases respectively are parameters which decide whether diffusion of the reactants in the aqueous phase plays a role and where the initiation takes place.

Emulsion copolymerization of EUP and comonomers may be initiated in the aqueous (persulfate) or in the non-aqueous phase (AIBN). On the decomposition of persulfates, sulfate and hydroxyl groups are introduced into macromolecules and microgels, thus influencing their surface properties [118, 123–125]. By using AIBN as initiator a change of the chemical character of the surface and of the properties of the microgels is avoided.

Apart from the kind of components used in preparing microgels from EUP and comonomers, the yield essentially depends on the composition of the reactive components, on the water/monomer ratio, the W/M (serum ratio), the degree of neutralization of the EUP [91] and on the concentration of electrolytes.

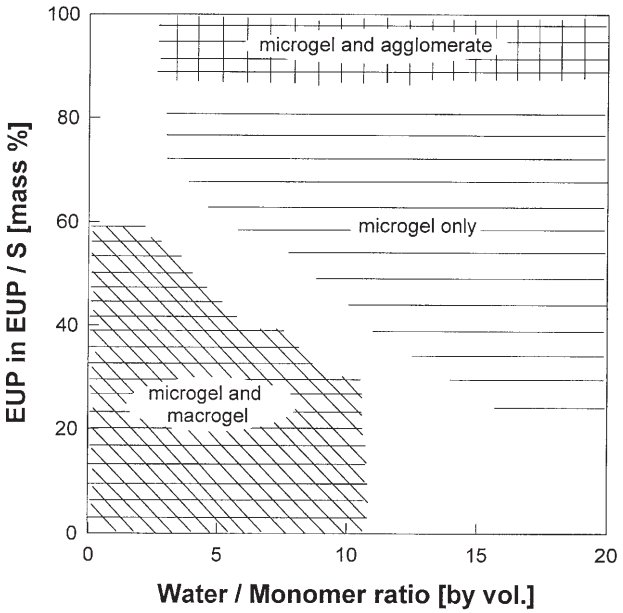


Fig. 17. Product profile of ECP of EUP(MA+PA+HD) and S [110].

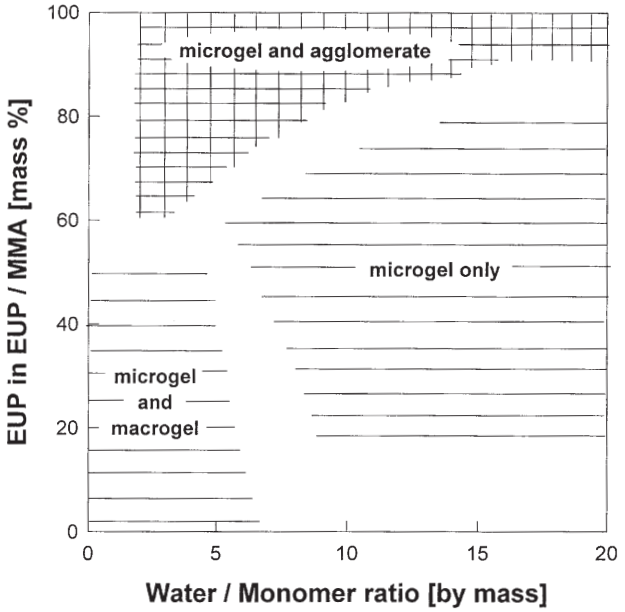


Fig. 18. Product profile of ECP of EUP(MA+PA+HD) and MMA [126].

Yields of microgels may be impaired by the polymerization of monomer droplets with formation of insoluble, coarse coagulates or by reactions of growing microgels with terminated or with other growing microgels and formation of insoluble agglomerates or aggregates.

As a consequence of the self-emulsifying property of EUP, the ratio EUP/comonomer in the reaction mixture not only determines the composition of the microgels but is also an important factor for their yield. The product profiles of microgels, prepared by ECP of EUP/styrene (S) (Fig. 17) and of EUP/methylmethacrylate (MMA) (Fig. 18) using a water-soluble initiator, show that an exclusive formation of microgels is limited by the EUP/comonomer ratio and the W/M-ratio. Above a certain EUP/comonomer ratio, microemulsions are formed, and if the W/M-ratio is sufficiently high, microgels are the only reaction product. With high EUP/comonomer ratios, besides microgels insoluble copolymers are obtained. Their formation may be explained by reactions between microgel particles after longer reaction times. With low EUP/comonomer ratios, normal emulsion are formed containing both micelles and monomer droplets. In this case, besides microgels the formation of a macrogel is observed. Its formation may be explained by the reaction between polymerized monomer droplets.

In non-crosslinking ECP, monomers are supplied to the growing polymer species by diffusion of monomer from droplets. In crosslinking ECP, however, the gel effect increases the copolymerization rate in the droplets as well as in the growing microgel particles. As the diffusion rate of lipophilic monomers in the aqueous phase is lower than the copolymerization rate, monomer droplets may

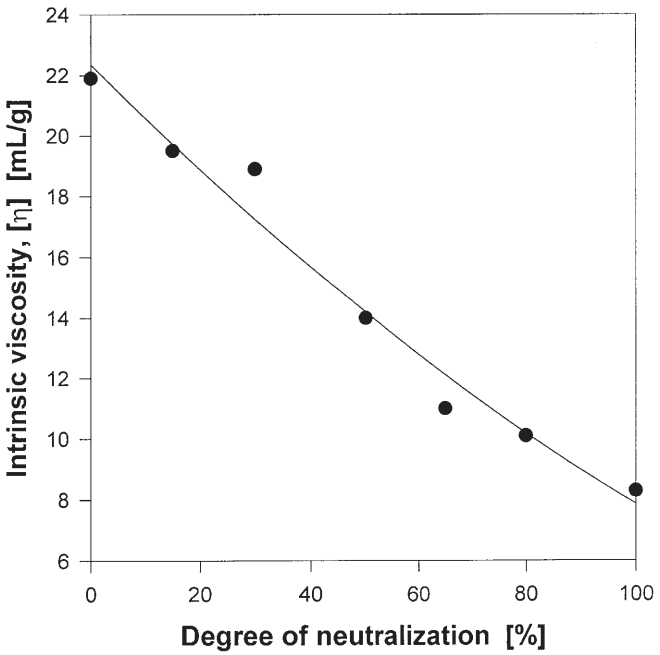


Fig. 19. Influence of the degree of neutralization of the ECP on [η] of microgels [116]. EUP(MA+HD), $\overline{M}_n$ 2100, c/t 77/23, EUP/S 2/3, W/M 5, external emulsifier poly(oxymethylene octylphenyl ether).

be polymerized, despite their much smaller surface area available for entering of radicals from the aqueous phase.

The window in the product profile of the ECP, where microgels are exclusively formed, also comprises the compositions of the reaction mixture in which microemulsions are formed.

The [η] of microgel solutions decreases with increasing degree of neutralization of the carboxyl acid groups of the EUP (Fig. 19) because the emulsifier concentration increases and, accordingly, the micelles or microemulsion droplets become smaller. In this case an external emulsifier poly(oxymethylene) octylphenyl ether was added to insure complete solubilization over the whole range of neutralization.

In order to prevent the formation of macrogels due to the polymerization of monomer droplets and to the reaction between them, the degree of neutralization should be close to 100 %, i.e. the pH of the emulsion should be in the range of complete neutralization which is about pH 8, (Fig. 20). Then a droplet-free microemulsion exists and a sufficiently high EUP fraction protects the growing microgels by electrostatic repulsion from reacting with each other. At a high pH the yield of microgels decreases probably due to agglomeration and degradation of the EUP but the composition of the microgels remains constant.

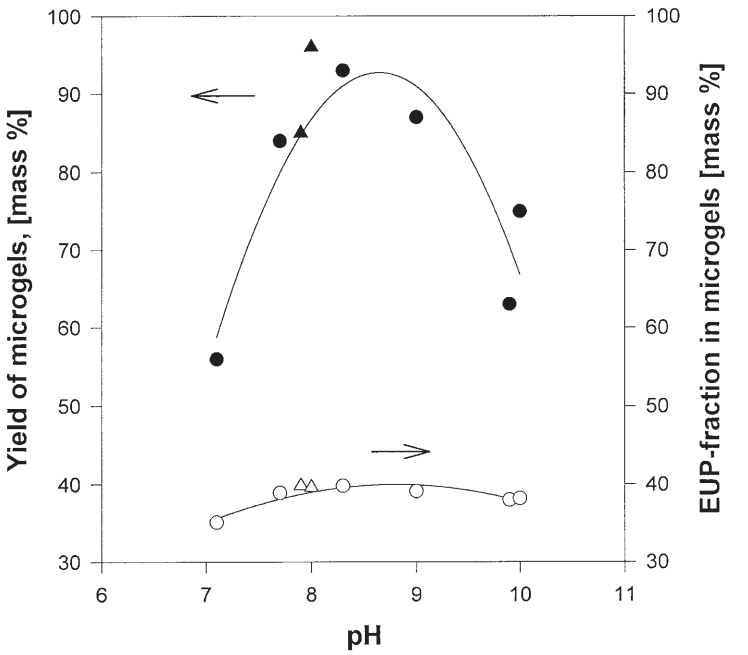


Fig. 20. Dependence of the yield and composition of microgels on pH of the emulsified reaction mixture [116]. (EUP/S: black and white circles 0.33, black and white triangles 1.5; other data see Figure 19).

5.2.1
Molar Mass and Diameter of Microgels

As the EUP is an emulsifier, an increase of the EUP/comonomer ratio not only causes an increase of the number of micelles and microemulsion droplets respectively but also of the number of microgels and, correspondingly, a decrease of their molar mass [110, 126] and their diameter [127]

Because the presence of an electrolyte increases the dimensions of micelles and microemulsion droplets [115], it may be expected that in presence of ions the size of microgels is also increased. This expectation could be confirmed: external electrolyte increases $\overline{M}_w$ (Fig. 21) as well as $\bar{d}_z$ and $[\eta]$ (Fig. 22) up to the limit of the emulsion stability. Therefore, the addition of an external electrolyte to the reaction mixture for the ECP of EUP and comonomers is a means to vary the molar mass, the diameter and the intrinsic viscosity of microgels from EUP and comonomers deliberately.

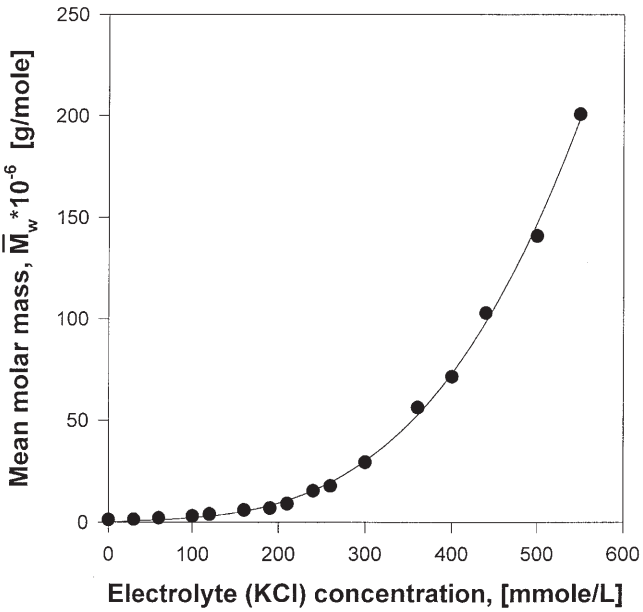


Fig. 21. Influence of an external electrolyte (KCl) on $\overline{M}_w$ (dioxane) [122]. EUP(MA+HD), $\overline{M}_n$ 1290. c/t 77/23, EUP/S 4, W/M 25, pH 7.5.

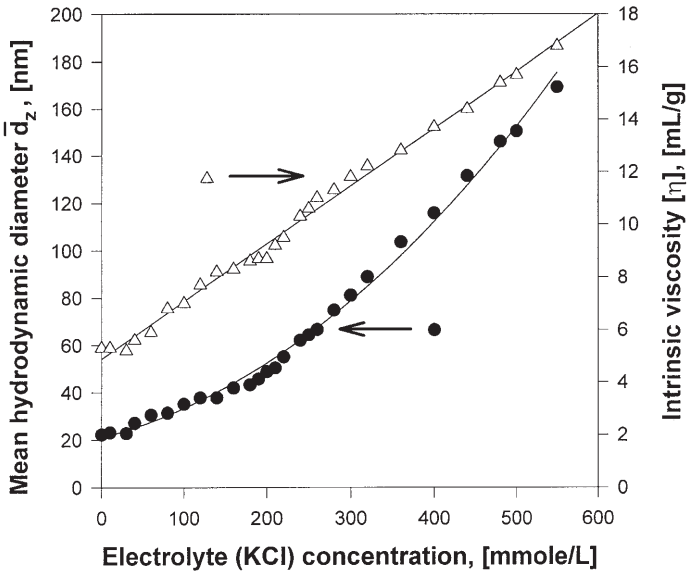


Fig. 22. Influence of the electrolyte concentration (KCl) on $\overline{d}_z$ and [η] (dioxane) [122], (reaction parameters as in Figure 21).

5.2.2
Viscosity

The [η] of microgels increases slightly with the concentration of an external electrolyte (Fig. 23). Probably a slope of $[\eta]/\overline{M}_w > 0$ is caused by the presence of the electrolyte which decreases the density of these microgels.

If persulfate is used as an initiator, its decomposition and the reactions of the radicals formed are rather complex [118]. Sulfate radicals and hydroxyl radicals are formed and may add to the unsaturated acid units of the EUP or are introduced into the surface of microgels, thus making them more hydrophilic and influencing their surface properties [81]. Moreover, persulfate radicals also react with the carboylic acid groups of the EUP, as had been shown by the accelerated decomposition of this initiator in presence of EUP [128]. Contrary to these disadvantages, the radical fragments of AIBN do not change essentially the chemical character of the growing chains and of the microgel surface and therefore are more suitable for the initiation of ECP.

Compared with persulfates, the solubility of AIBN in water is very low (Fig. 24). At the usual reaction temperature of the ECP (70 °C) only about 2 mg of this initiator dissolves in 1 l of water. This means that, irrespective of the distribution ratio in both phases, most of the AIBN in the usually applied concentration range (about 1–6 g/l) is dissolved in the non-aqueous phase. Conse-

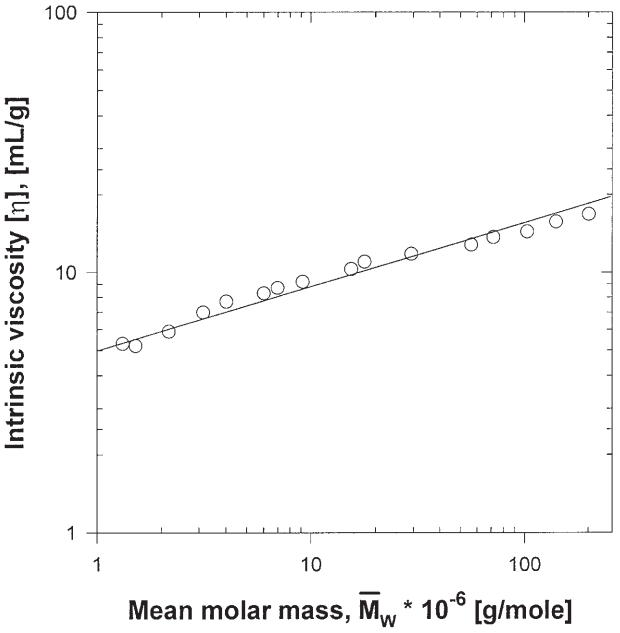


Fig. 23. Relation between [η] and $\overline{M}_w$ (dioxane) [122](reaction parameters as in Fig. 21).

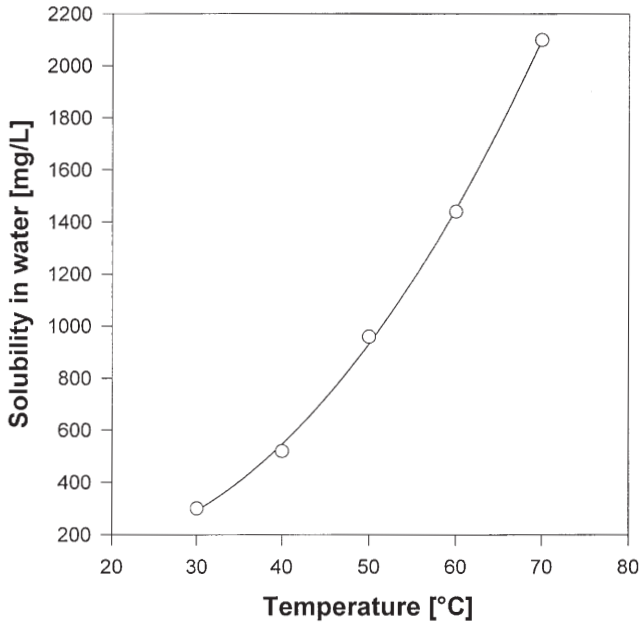


Fig. 24. Dependency of the solubility of AIBN in water on the temperature [128].

quently, contrary to earlier conclusions [129], AIBN, due to its low solubility in water and its higher decay rate in presence of EUP [128], decomposes predominantly in the lipophilic phase of an aqueous emulsion. Therefore, ECP is initiated in the micelles or in microemulsion droplets and not in the aqueous phase.

Because the copolymerization of the components of micelles is very rapid, the microgel particles scarcely grow by intermicellar diffusion of the comonomers or by diffusion from the microemulsion droplets. This has been confirmed by the microgel composition [112] which remains constant over the whole reaction time (Fig. 25), even when using different ratios of EUP/comonomer [113, 116].

A small increase of the molar mass during the copolymerization [115] is explained by an incorporation of not yet initiated micelles or droplets of the microemulsion in the growing microgels or by their aggregation to larger particles.

5.3 Characterization and Properties of Microgels from Self-Emulsifying Unsaturated Polyesters and Comonomers

The molar mass of microgels obtained by ECP of EUP and comonomers ranges from below 10^6 to more than 10^7. Similar to the decrease of the particle size with increasing concentration of other emulsifiers, an increase of the EUP-fraction in the monomer mixture decreases the $\overline{M}_w$ of the microgels (Fig. 26).

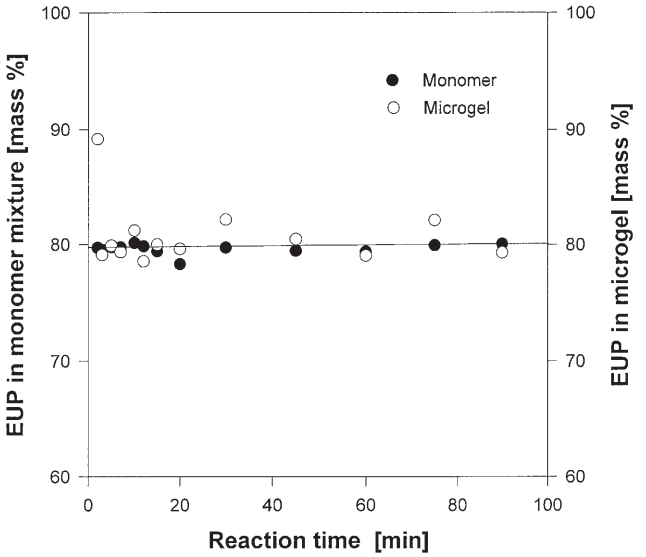


Fig. 25. Composition of microgels and of the reaction mixture (EUP/S) in the course of the micro-ECP [112]. EUP(MA+HD), $\overline{M}_n$ 1290, c/t 77/23, W/M 25, KCl 200 mmole/L, AIBN.

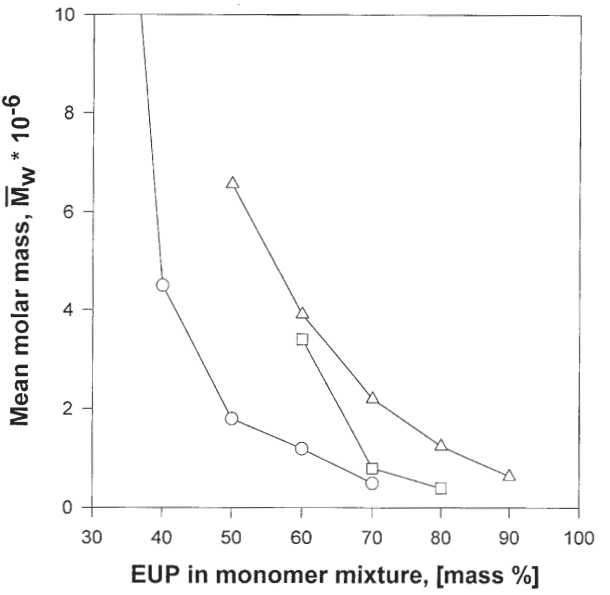


Fig. 26. Relation between the EUP-content in the reaction mixture and $\overline{M}_w$ of microgels. EUP(MA+HD), M_n 1300, c/t 75/25, AIBN [115]. EUP(MA+PA+HD), $\overline{M}_n$ 1330, c/t 71/29, EUP/DVB, W/M 20 [130]. EUP(MA+PD+HD), $\overline{M}_n$ 1330, c/t 71/29, EUP/EDMA, W/M 30 [130].

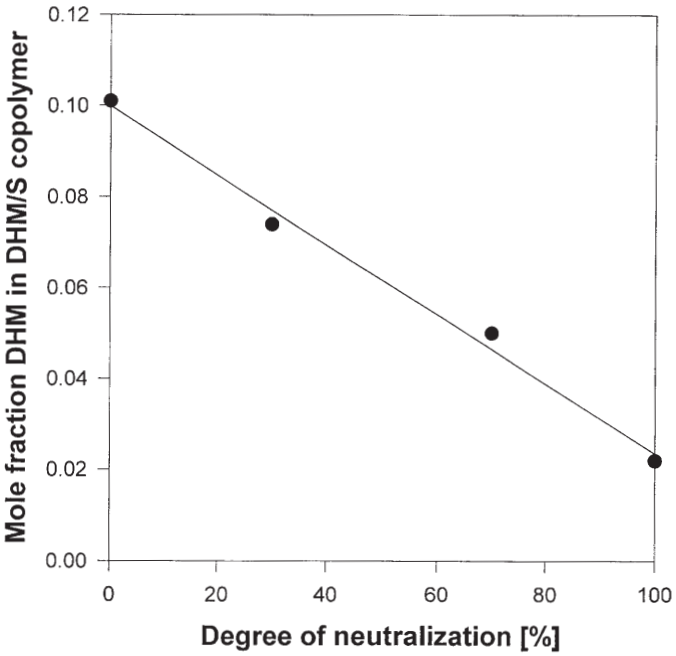


Fig. 27. Relation between the degree of neutralization and the mole fraction of dodecyl hydrogen maleate (DHM) in the copolymerization with S [131]. (DHM/S in reaction mixture 0.133).

Viscosity, dispersion stability and reactivity of microgels from EUP and comonomers are influenced by the location, concentration and dissociation of terminal carboxyl acid groups. In the dissociated state, terminal acid groups deactivate the double bonds of the neighboring unsaturated terminal units [116]. This deactivation is very obvious in the copolymerization of half-esters of maleic (Fig. 27) and fumaric acids with styrene. As Fig. 27 shows, the incorporation of dodecyl hydrogen maleate (DHM) in the copolymerization with S is rather low and strongly decreases further with increasing neutralization of the acid groups. As a consequence, short chains of terminal units of EUP-molecules remain unreacted at the surface of the microgel particles. The presence of these unsaturated terminal units of the EUP could also be confirmed by the formation of pyrazolin dicarbonic acid units with CH_2N_2 [132]. However, due to hydrolysis, even on complete neutralization still enough reactive terminal ester units are available at the surface of microgels for copolymerization. It may be assumed, therefore, that the compactness of the microgel particles is not essentially decreased by the deactivation of terminal unsaturation.

5.3.1
Viscosity and Hydrodynamic Diameter

An interesting feature of microgels is that, unlike crosslinked polymers, they are soluble in suitable solvents and can therefore be characterized by the viscosity of their solution. As compared with linear macromolecules of the same molar mass and composition, microgels have a rather compact structure. If microgels behave like rigid solid spheres, according to the Einstein law the intrinsic viscosity, [η] should only depend on the density of the particles and not on their molar mass. However, even with a uniform density of the microgel particle throughout its volume, [η] may depend on the thermodynamic quality of the solvent and on the crosslink density. Provided the same solvent is used and the composition of the microgels is the same, their crosslink density may be related to their [η]. In this case viscosity measurements can be used for determining the crosslink density of a microgel network.

As may be seen in Figs. 28 and 29, values for [η] of various microgels from UP and S resp. 1,4-DVB and EDMA are only as low as about 4–8 ml/g and depend little on the molar mass over a range of about 0.5×10^6 to 40×10^6 g/mol. As compared with these values, the [η] of linear polystyrene for the same range of molar

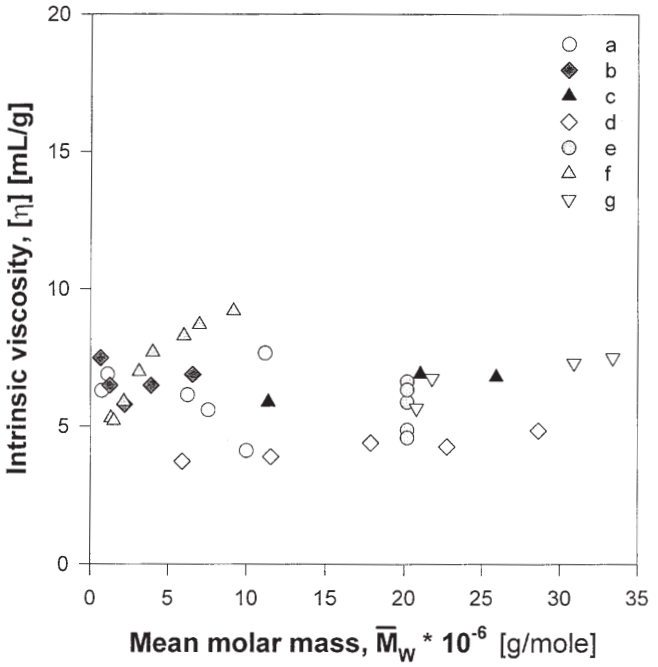


Fig. 28. Relation between [η] (dioxane) and $\overline{M}_w$ of microgels from various EUP and bifunctional comonomers.a): [136], b): [115], c),d),e): [116], f): [122], g): [132])

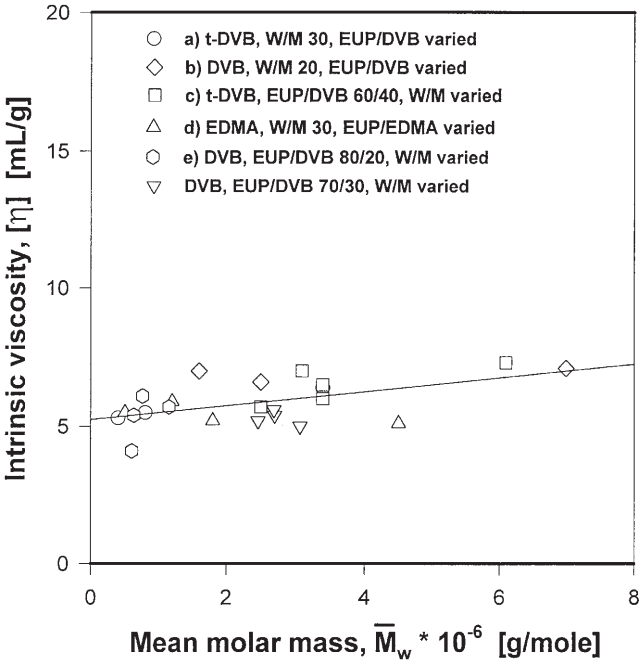


Fig. 29. Relation between [η] (dioxane) and $\overline{M}_w$ of microgels from various EUP and tetrafunctional comonomers a) EUP(MA+PA+HD), $\overline{M}_n$ 1330, c/t 71/29, W/M 30, $K_2S_2O_8$ [130]. b) EUP(Ma+HD), $\overline{M}_n$ 1300, c/t 75/25 , W/M 20, AIBN [115]. c) EUP(MA+PA+HD), see a), $K_2S_2O_8$ [130]. d) EUP(MA+PA+HD), W/M 30, see c) [130]. e) and f) EUP(MA+PA+HD), $\overline{M}_n$ 1270, c/t 84/16, W/M varied, $K_2S_2O_8$ [121].

mass would extend from about 160 to 3900 ml/g, calculated by $[\eta] = K \times \overline{M}^a$ with $K = 11 \times 10^{-3}$ and $a = 0.73$. The scattering of the points in Fig. 28 is due to experimental variations, such as UP/S ratio, molar mass of the UP, serum ratio and concentration of the initiator.

In agreement with the decrease of $\overline{M}_w$ of microgels on increasing the amount of EUP in the monomer mixture (Fig. 26), their mean particle diameter likewise decreases (Fig. 30). With the molar mass of microgels also their diameter increases (Fig. 31). However, a 20-fold increase of the $\overline{M}_w$ corresponds to only less than a 3-fold increase of d_z. These results illustrate results that microgels from EUP are rather compact globular particles with intrinsic viscosities closely approaching that of hard spheres.

As to the homogeneity of microgels, their composition and their structure has to be considered. In an aqueous alkaline solution a stepwise degradation of microgels by hydrolysis is possible [133], by which especially the unreacted terminal EUP-units are removed [115]. The degradation rate increases with the EUP-fraction incorporated in the microgel.

Because the composition of microgels prepared by micro-ECP of EUP and styrene with AIBN as initiator remains constant and irrespective of the reaction

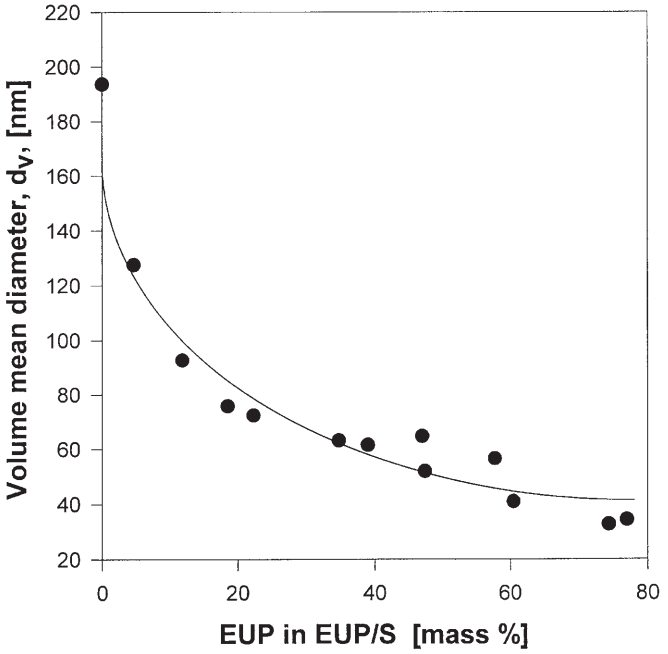


Fig. 30. Dependency of $\bar{d}_v$ of microgels on the EUP-content of the monomer mixture [127]. EUP(MA+HD), $\overline{M}_n$ 2700, c/t 80/20, W/M 15, $K_2S_2O_8$, external emulsifier poly(oxymethylene octylphenyl ether).

time, it is practically the same as that of the monomer mixture [112, 113, 116], it follows that these microgels have a homogeneous composition. This means that during the reaction diffusion of monomers from not yet initiated micelles to growing particles is negligible. Otherwise, a change of the composition would be expected because the rates of diffusion of EUP and styrene certainly are very different. However, because the reactivity ratios of the copolymerizing components differ significantly, a structural inhomogeneity is possible, especially with high amounts of the bifunctional comonomer or with crosslinking comonomers such as DVB.

The parameters which influence the particle size of microgels have been studied during self-emulsifying, seeded emulsion copolymerization of an unsaturated polyester and butyl acrylate [134].

5.3.2 *Reactive Groups*

The reactivity of microgels resides in terminal carboxyl acid groups and in residual unsaturated dicarboxylic acid groups of the EUP-component. Due to sterical hindrance, presence of less reactive maleic acid units and deactivation of termi-

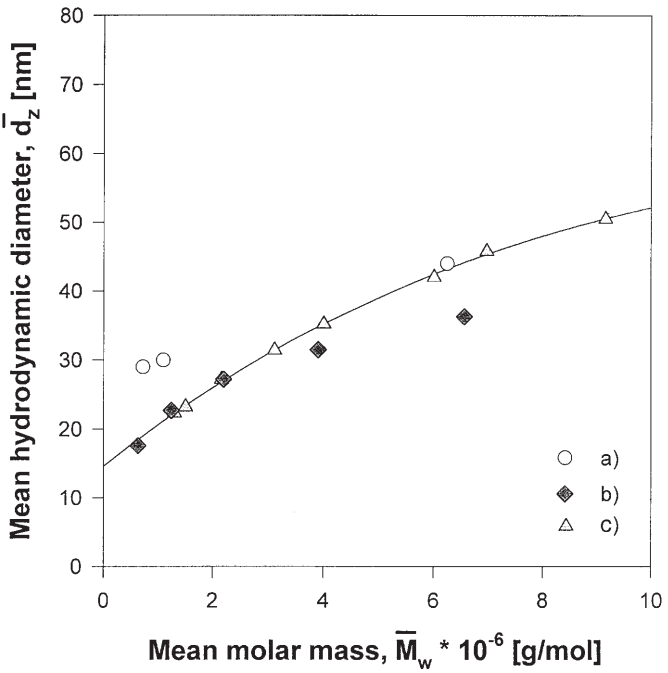


Fig. 31. Relation between $\bar{d}_z$ of microgels and their $\overline{M}_w$. a): [136], b): [115], c): [122].

nal carboxylate groups, a relative large fraction of unsaturated units remains unreacted within and at the surface of microgels (Fig. 32). This residual unsaturation increases with the EUP-fraction in the microgels because the crosslink density increases and therefore the mobility of reactive chain segments decreases.

Independently of the microgel composition, the fraction of terminal acid groups of the EUP-component determined by conductivity titration is only about 75 mol % of the total amount of acid groups incorporated in the microgels by polymerization (Fig. 32). This means that the residual 25 mol % acid groups are located within the microgel particles and are not easily accessible by ions. It may be assumed that these interior acid groups have been in the free acid state during the copolymerization due to hydrolysis of carboxylate groups.

A possible reason for the inaccessibility of a part of the acid groups could be the crosslink density which depends on the composition of the microgels. However, because the number of titratable acid groups does not depend on the composition and, therefore, on the crosslink density of the microgels, it must be concluded that electrostatic forces prevent ions from entering the microgel particles.

Solutions of microgels from EUP and bifunctional comonomers are rather stable over weeks and months. However, on exposing freeze-dried samples of microgels from ECP of EUP and S to O_2 or N_2, insoluble fractions are formed which increase with exposure time and temperature. As insolubilization is prevented in

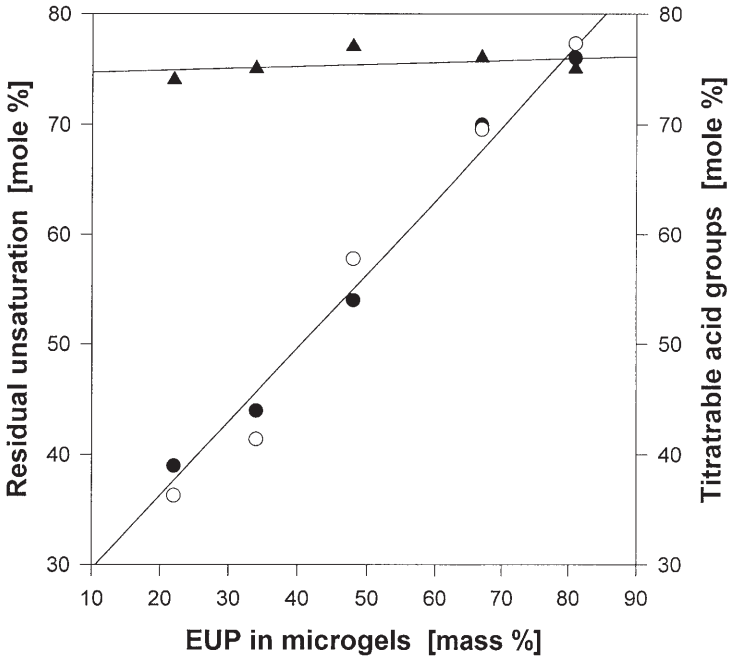


Fig. 32. Relation between the residual unsaturation (●) IR-spectroscopy, (○) hydrolytic degradation resp. the titratable acid groups of microgels (▲) and their EUP-content [132]. EUP(MA+HD), $\overline{M}_n$ 1640, c/t 67/33, EUP/S varied, W/M 20.

presence of radical inhibitors, it is probably caused by reactions between these particles in their non-swollen state via pendent unreacted groups of the EUP [116].

On repeated freeze-drying of microgels with EUP-components an irreversible formation of an insoluble aggregate was observed [135]. It was supposed that this aggregation is due to radical reactions between adjacent microgel particles. The radicals are possibly formed by a mechanical rupture of chains due to stresses within the particles caused by freezing.

5.3.3
Rheological Properties of EUP/Comonomer-Microgels

Rheological properties of microgels composed of EUP (MA and HD) and S, EDMA, resp. DVB have been measured in 2-ethoxyethylacetate [136]. Below concentrations of 40 mass %, very low viscosities and an almost Newtonian flow have been observed (Fig. 33). At higher concentrations, shear thickening is observed. Accordingly, these microgels are rather compact particles that intereact very little with each other and are not deformed by shearing up to high concentrations, where the close packing causes rheopexy. The compactness of EUP/S-microgels has been also confirmed by 2H-NMR spectroscopy using selectively deuterated components [137].

		Polymer Concentration [mass %]						
Monomer	UP/M	40	35	30	25	20	15	
Styrene	1.5	1	9					
Styrene	0.67	2						
Styrene	1	3	8	13+18				
Styrene	1		6	12+17	15+20	21	22	
Diacrylate Polystyrene	0.67		7	11+16	14+19 4	5	10	
Ethylglycol acetate	Solvent							23

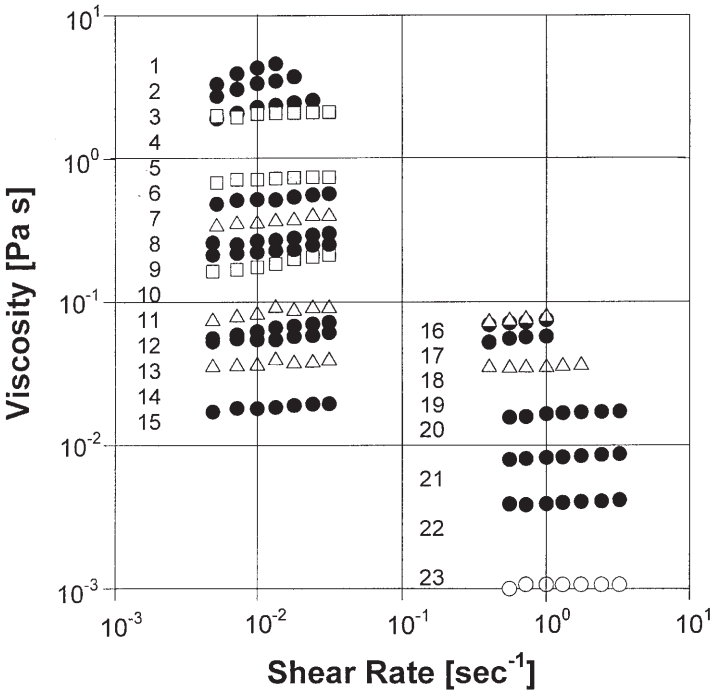


Fig. 33. Dependence of viscosity on the shear rate of microgel solutions in $C_2H_5OC_2H_4OCOCCH_3$. EUP(MA+HD), c/t 70/30, EUP/S and EUP/EDMA(D), AIBN, P.-S. polystyrene [136].

6 Microgel Formation in Solution by Free-Radical Crosslinking Copolymerization

6.1 Theoretical Considerations

Several theories of network formation have been developed in the past half century, including statistic [50, 64–66, 138–144] and kinetic ones [100, 145–153], and

simulation of network formation in a n-dimensional space, such as the percolation theory [154–156]. However, up to now, no exact theory of network formation for radical crosslinking copolymerization (RCC) exists that takes into account heterogeneities and microgel formation due to an extensive cyclization and multiple crosslinking. This deficiency is explained by the complicated mechanism of these reactions. If long-range correlations such as cyclization and multiple crosslinking with resulting heterogeneities are neglected, kinetic approaches may successfully solve the complex mechanism of RCC. Deviations observed in real systems are then useful for understanding the reasons for the non-ideal behavior.

Radical polymerizations have three important reaction steps in common: chain initiation, chain propagation, and chain termination. For the termination of chain radicals several mechanisms are possible. Since the lifetime of a radical is usually less than 1 s, radicals are continuously generated and terminated. Each propagating radical can add a finite number of monomers between its initiation and termination. If a divinyl monomer is in the monomer mixture, the reaction kinetics changes drastically. In this case, a dead polymer chain may grow again as a macroradical, when its pendant vinyl groups react with radicals, and the size of the macromolecule increases until it extends over the whole available volume.

RCC involves at least two types of vinyl groups which have different reactivities [100], those of the monomers and those of pendant vinyl groups. Accordingly, the homopolymerization of divinyl monomers can be considered as a special case of copolymerization, in which the second vinyl group of the divinyl monomer changes its reactivity after the first vinyl group has polymerized. During RCC the pendant vinyl groups thus formed can still react or remain pendant. Understanding the behavior of pendant vinyl groups is a key for explaining the formation of microgels.

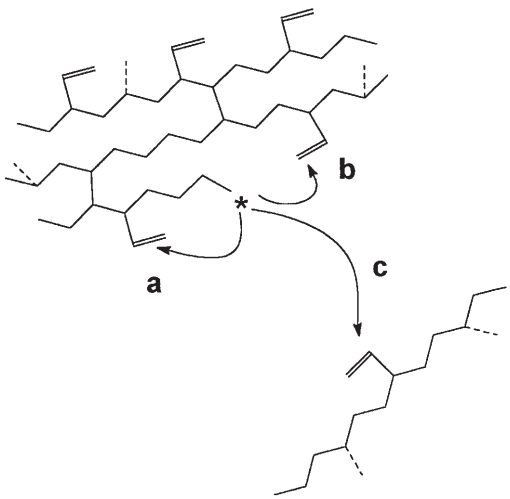


Fig. 34. Schematic picture of cyclization (a), multiple crosslinking (b), and crosslinking (c) in radical crosslinking copolymerization.

Two possible reactions of a pendant vinyl group may be distinguished, shown schematically in Fig. 34:

– intramolecular crosslinking (a and b),
– intermolecular crosslinking (c).

Intramolecular crosslinking occurs between pendant vinyls and radical centers located on the same macromolecule and results in the formation of cyclic chains and multiple crosslinks [157]. A cyclic chain is formed if both, the pendant vinyl group and the radical center are located on the same kinetic chain (a); otherwise a multiple crosslink (b) is formed. Cyclic chains can be of a short-range type, e.g. loops within a monomer, or of a long-range type, i.e. between radical centers and pendant vinyl groups located at different distances in the same kinetic chain [100]. Chain cycles and multiple crosslinks do not contribute to the growth of the macromolecule and have no influence on the onset of macrogelation but cause the macromolecules to contract and thus reduce their size. The contraction of the macromolecules by intramolecular crosslinking also reduces the reactivity of pendant vinyl groups by steric hindrance. It should be mentioned that cyclization and multiple crosslinking were recently re-defined as primary and secondary cyclization [147], or as intramolecular cyclization and intramolecular crosslinking, respectively [30]. In the present review, the classical definitions will be used.

Intermolecular crosslinking between pendant vinyl groups and radical centers located on different macromolecules produce crosslinks that are responsible for the aggregation of macromolecules, which leads to the formation of a macrogel. It must be remembered that both normal and multiple crosslinks may contribute to the rubber elasticity of a network, whereas small cycles are wasted links.

The divinyl monomers can thus be found in macromolecules as units which bear pendant vinyl groups or which are involved in cycles, crosslinks or multiple crosslinks. Since the number of crosslinks necessary for the onset of macrogelation is very low [64], pendant vinyl groups in RCC are mainly consumed in cycles and multiple crosslinks. Therefore, the reaction rate of pendant vinyl groups is a very sensitive indicator for the formation of cycles and multiple crosslinks in finite species [100, 147, 157–160].

The conversion of pendant vinyl groups, x_3, may be defined as the fraction of divinyl monomer units with both vinyl groups reacted

$$x_3 = \frac{\text{number of divinyl monomer units in the polymer with both vinyl groups reacted}}{\text{total number of divinyl monomer units in the polymer}} \quad (6)$$

x_3 is zero for linear chains bearing pendant vinyl groups only, and unity for chains carrying only divinyl monomer units with both vinyl groups reacted. Assuming no cyclization, every divinyl monomer unit in the polymer should initially bear a pendant vinyl group, i.e., $\lim_{x \to 0} x_3 = 0$, where x is the monomer conversion. Since crosslinking and multiple crosslinking are second order reactions,

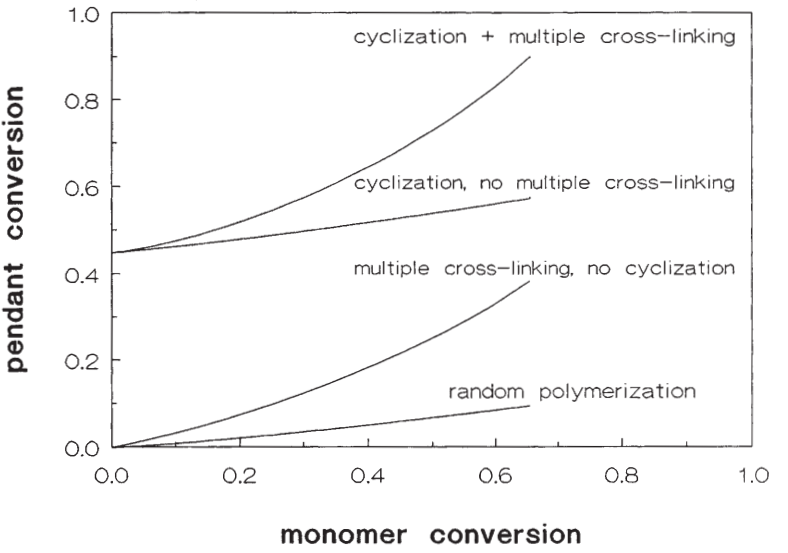


Fig. 35. Graphical representation of variation of the conversion of pendant vinyl groups x_3 with the monomer conversion x for various types of intramolecular reactions [157].

deviation from zero indicates the cyclization. Thus, the initial rate of cyclization can be calculated by plotting the experimentally determined conversion x_3 of pendant groups vs the monomer conversion x and extrapolation to zero monomer conversion. Moreover, the conversion rate of pendant vinyl groups is a measure of the extent of multiple crosslinking [157]. The greater the slope of the curve x_3 vs x curve, the larger is the number of multiple crosslinks formed per crosslink. Therefore, multiple crosslinking is reflected in a greater decrease of polymer unsaturation than without it. Figure 35 shows schematically the variation of the conversion of pendant vinyl x_3 with monomer conversion x for various types of intramolecular reactions.

6.2 Experimental Evidences of Intramolecular Crosslinking

Investigations of intramolecular crosslinking in RCC are found in the literature from as early as 1935. Staudinger and Husemann could isolate a soluble polymer by polymerizing DVB alone in very dilute solutions [4]. Walling observed that the actual gel point in the bulk polymerization of EDMA exceeds that predicted by the classical theory of gelation by more than two orders of magnitude (2.9 % vs 0.022 % in terms of critical conversion) [161]. This author stated that "the growing chain undergoes so many crosslinking reactions within itself that its ability to swell is reduced" [161]. Zimm et al. observed that [η] of branched DVB/S copolymers depends only a little on the molar mass [162]. They found an exponent a = 0.25 of the Mark-Houwink equation which is between the value for

rigid spheres (a = 0) and that of an unperturbed Gaussian chain (a = 0.50). Storey observed that in 1,4-DVB/S copolymerization the critical conversion passes through a minimum at the gel point when the content of 1,4-DVB is increased [32]. He explained this unusual gelation behavior with macrogelation by an accumulation of microgels that have a high crosslinker content. Malinsky et al. observed that in 1,4-DVB/S copolymerization the fraction of pendant vinyl groups is lower at low conversions than calculated, whereas at high conversions the copolymers contain a large excess of these groups [33]. These authors explained their results by cyclization and reduced mobility of chain segments. Immobilization dominates at high conversions and reduces the reactivity of pendant vinyl groups. In studying the polymerization of pure divinyl monomers, Kast and Funke found that at no time during the polymerization in solution could linear or branched polymers be isolated, but only intramolecularly crosslinked polymers of high crosslink density [55]. They concluded that at high crosslinker contents a macroscopic gel forms via reaction between the functional groups of the microgel particles after enough microgel particles have been formed to fill the reaction volume. Galina and Rupicz found that in copolymerization of EDMA/S in benzene only a small fraction of EDMA units are involved in intermolecular crosslinks [163]. They concluded that cyclization and multiple crosslinking are the most important features of this polymerization. Dusek et al. emphasized the importance of cyclization and reduced reactivity of pendant vinyl groups in RCC and proposed a mechanism of macrogelation via microgels [56]. Cyclization and the reduced reactivity of pendant vinyl groups in RCC during the gel formation were also pointed out by many other researchers [28, 38, 164–186]. A consequence of cyclization and multiple crosslinking is the appearance of multiple glass transitions [187, 188], the existence of trapped radicals [189–192] and residual unsaturation in the final networks [193].

It was also shown that in RCC intra- and intermolecular crosslinking enhance the Trommsdorf [194] or gel effect significantly. The autoacceleration of the polymerization rate begins shortly after the start of the polymerization [160, 195–197]. The termination reactions are controlled by the rate of translational diffusion of chain segments and the radical chains. However, after the aggregation of the primary particles via multiple crosslinks, free radicals bound to aggregates should have extremely small diffusion coefficients. For such species, it is easy to imagine that they are immobile (trapped) in the time-scale of the kinetic events. Under these conditions, bimolecular termination in the particles can occur only by diffusion of two free-radical chain ends toward each other as a result of their propagational growth ("reaction diffusion" or "residual termination" mechanism) [198–200]. Indeed, in case of bulk polymerizations of divinyl monomers, the ratio of rate constants termination/propagation was found to be constant [201, 202]. On the other hand, it was also reported that the primary chain length, i.e. the chain length of polymers close to zero conversion or when connections between unsaturated groups in bisunsaturated monomer units are severed, increases with increasing crosslinker content in the monomer mixture [197, 203–206]. This unusual behavior was explained by cyclization, which decreases the mobility of segments and suppresses the diffusion-controlled termination due to steric reasons [204].

Tobita and Hamielec used the dependency between pendant vinyl conversion x_3 on the monomer conversion x of several systems to calculate the fraction of divinyl monomer units involved in formation of cycles [158, 207]. They showed that in copolymerization of *N,N'*-methylene bisacrylamide and acrylamide in water (56.6 g comonomers/l) at least 80 % of the pendant acryl groups are consumed by cyclization reactions. For the same system they also showed that the consumption of pendant acryl groups by multiple crosslinking is much greater than that by normal crosslinking. Assuming constant rates for intramolecular crosslinking, they calculated that, on average, 10^3 multiple crosslinks form per intermolecular crosslink [158]. Landin and Macosko [147], and more recently Dotson et al. [205] attempted to measure conversions of the pendant double bond in EDMA/MMA copolymers by NMR. They showed that both ^{1}H and ^{13}C NMR techniques result in negative values for the conversion of pendant methacrylic groups due to the decreased mobility of protons in intramolecularly crosslinked molecules. By using an analytical titration method, Okay et al. found that in dilute solutions almost half of the pendant double bonds of EDMA units are consumed by cyclization [197]. More recently, Dusek and coworkers studied the RCC of styrene with bismaleimide, *p*-maleimide, *p*-maleimidobenzoic anhydride, or with mixtures of *p*-maleimidobenzoic anhydride and methyl *p*-maleimidobezoate [208]. Their results also demonstrate the important role of cyclization in the early stage of crosslinking copolymerization and steric hindrance of pendant unsaturated groups at higher conversions.

Due to the sensitive dependence of the gel point on the reactivity of pendant vinyl groups for intermolecular links, it is possible to estimate the reactivity ratio of pendant to monomeric vinyl groups from experimental data. In 1,4-DVB polymerization in toluene the average pendant reactivity was found to be 2–3 orders of magnitude lower than the monomeric vinyl reactivity [209]. Lower pendant vinyl group reactivities were also calculated in EDMA/MMA and *N,N'*-methylene bisacrylamide/acrylamide copolymerization in dilute solutions [206, 210]. The decrease in pendant reactivity indicates a thermodynamic or steric excluded volume effect [30, 31]. It should be noted that both, the number of cycles and multiple crosslinks as well as the reactivity of pendant vinyl groups are functions of monomer conversion. It may be expected that no multiple crosslinks exist at zero monomer conversion and that their number increases as the reaction proceeds because multiple crosslinking becomes more probable if the macromolecules are larger. The opposite behavior can be expected for the cycle formation. On the other hand, increasing the number of multiple crosslinks during the reaction would cause a decrease of reactivity of the pendant groups because they are increasingly shielded [211].

It is obvious that intramolecular crosslinking is always observed in radical polymerization of divinyl monomers or divinyl/vinyl comonomers. Thus the experimental results clearly show that the prediction of ring-free theories fail . At the beginning of the reaction, the polymer radicals in a monomer/solvent mixture are rather isolated from each other. Hence the local concentration of pendant vinyl groups inside a macroradical coil is much higher than their overall concentration in the reaction mixture. Consequently, the probability of the radical chain end attacking a pendant vinyl group of its own chain is strongly

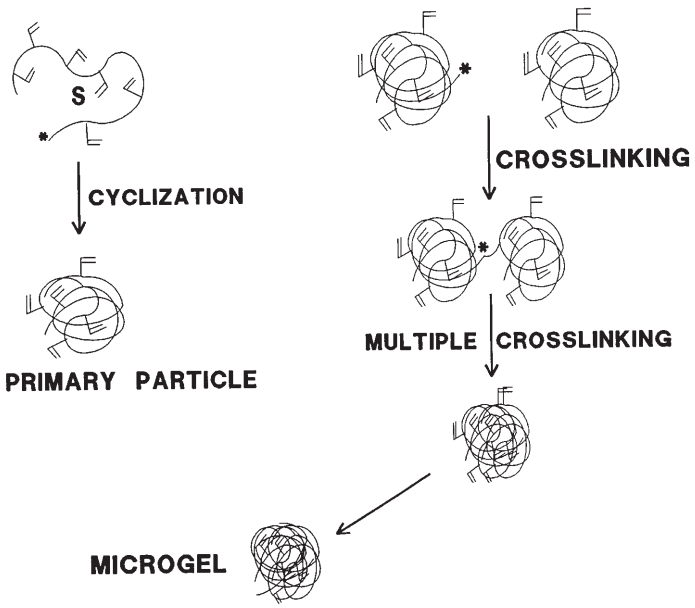


Fig. 36. Schematic representation of microgel formation in RCC.

favored, and in the early stage of RCC chain cycles are predominantly formed leading a to decreased size of coils of the same molar mass. Since every cycle reduces the coil dimensions as well as the monomer content inside the coil, the structure of the polymers is rather compact. Such crosslinked polymer coils may be considered as primary particles, analogous to the primary molecules as intermediates in the classical theories of gel formation [64] (Fig. 36). With increasing conversion the concentration of these primary particles increases and so does the opportunity to be added to a pendant vinyl group at the surface of some other particles. This intermolecular crosslinking leads to polymer aggregates. Since the concentration of pendant vinyl groups in a particle increases rapidly after the formation of each crosslink (Fig. 36), a number of multiple crosslinks is expected to occur after each single crosslink which results in a further reduction of the size of these aggregates. Accordingly, microgels isolated in solution polymerization may be considered as aggregates of intramolecularly crosslinked primary particles formed by multiple crosslinking.

6.3 Microgel Synthesis by Radical Copolymerization

Funke and coworkers extensively studied the conditions for the synthesis of 1,4-DVB microgels in dilute solutions of toluene, using AIBN as initiator [209, 212]. They prepared homologous series of 1,4-DVB microgels by a systematic variation of the polymerization temperature, the monomer and the initiator concen-

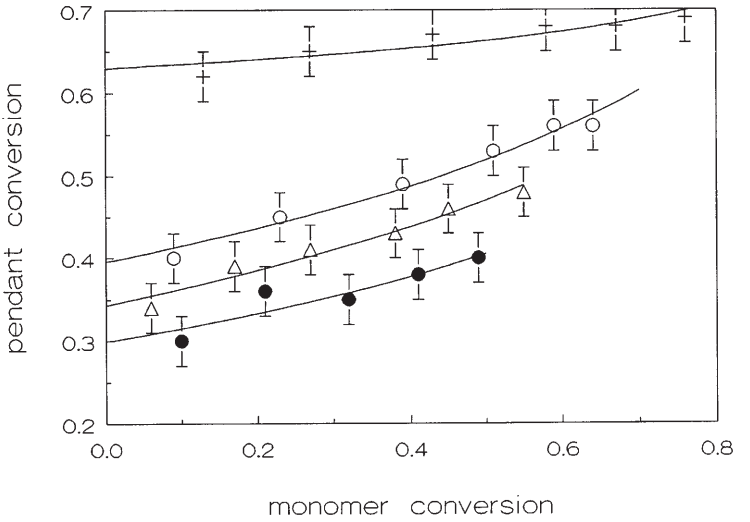


Fig. 37. Conversion of pendant vinyl groups x_3 versus monomer conversion x for different degrees of initial dilution in RCC of 1,4-DVB. Monomer concentration in toluene are 5 (●), 2 (△), 1 (○), and 0.5 g/100 mL (+). Initiator (AIBN) concentration = 8×10^{-3} M; temperature = 70 °C. [Reprinted with permission from Ref. 209, Copyright 1995, American Chemical Society].

tration. Figure 37 shows representative plots of the conversion of pendant vinyl groups x_3 vs the monomer conversion x for different initial monomer concentrations. Extrapolated values of the conversion of pendant vinyl group to zero monomer conversion indicate that, as the initial monomer concentration decreases from 5 to 0.5 g/100 ml the fraction of microgel units in cycles increases from 0.30 to 0.63 (Fig. 37). An increase of the initiator concentration also increased the fraction of units in cycles. This result may be explained by a more efficient consumption of pendant vinyl groups by cyclization in small particles than in large particles for sterical reasons [212]. It was also shown that in 1,4-DVB/S copolymerization the fraction of units in the chain cycles is a function of the 1,4-DVB content at low amounts of this crosslinker, but not at crosslinker contents as high as 40 mass %. The experimental results indicated that 30–60% of monomer units in 1,4-DVB microgels are engaged in cycles and that on average 100–800 multiple crosslinks exist per intermolecular crosslink [209]. According to these results, a large number of multiple crosslinks are formed between two primary particles after they are linked together by a single crosslink. This also means that in the final macrogels highly crosslinked regions exist which are stable against degradation to primary particles.

In order to check these results, Lutz et al. degraded polymer samples which had been isolated shortly before macrogelation, by ultrasonic waves [213]. Figure 38A shows the decrease of $\overline{M}_w$ and of the hydrodynamic diameter $\overline{d}_z$, measured by static and dynamic light scattering respectively, on ultrasonic treatment of a polymer of $\overline{M}_w = 2.2\times10^6$. Both $\overline{M}_w$ and $\overline{d}_z$ decrease first abruptly but then

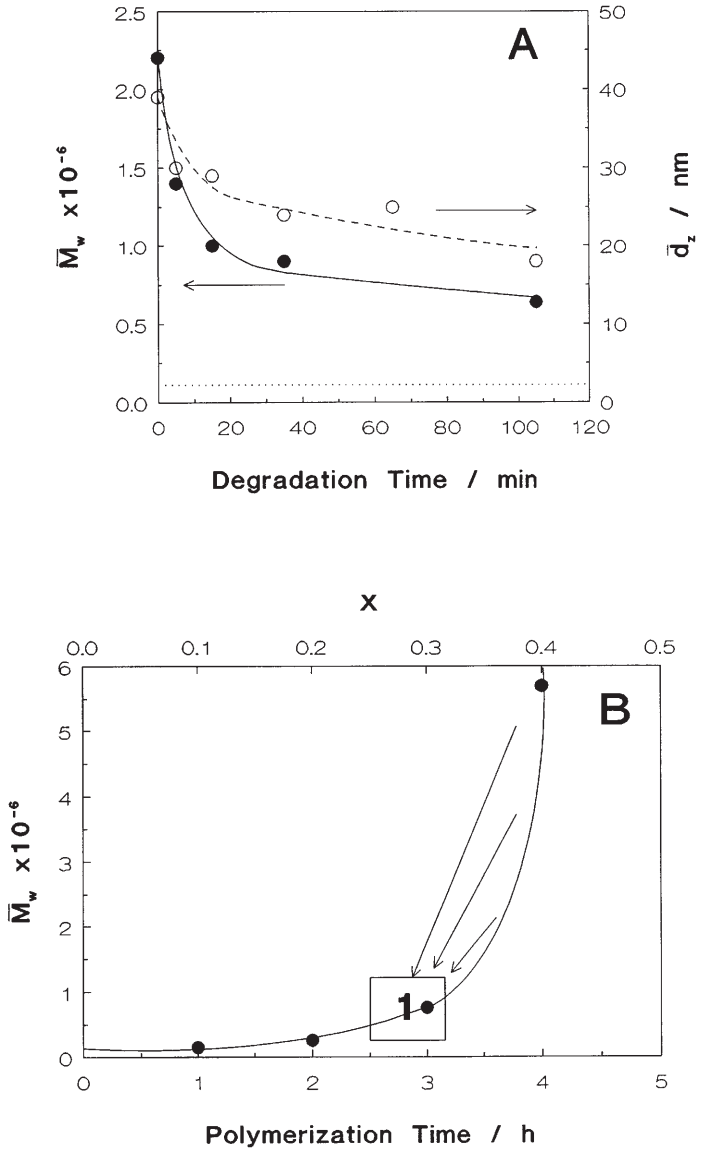


Fig. 38. **A:** Degradation experiments with pregel polymers isolated prior to the onset of macrogelation in 1,4-DVB polymerization [209]: Variation of $\overline{M}_w$ (●) and d_z (○) with the time of ultrasonic degradation. The polymer sample was prepared at 5 g/100 mL monomer concentration and its initial $\overline{M}_w$ was 2.2×10^6 g/mol. The dotted horizontal line shows $\overline{M}_w$ of zero conversion polymers ("individual microgels"). **B:** Variation of $\overline{M}_w$ with the polymerization time t and monomer conversion x in 1,4-DVB polymerization at 5 g/100 mL monomer concentration. The region 1 in the box represents the limiting $\overline{M}_w$ reached by degradation experiments. [Reprinted with permission from Ref. 209, Copyright 1995, American Chemical Society].

slowly and finally reach a limiting value. This final $\overline{M}_w$ was about 0.64×10^6 g/mol, compared with the molar mass of the primary particles of 0.11×10^6 g/mol (shown as a dotted line in Fig. 38 A) [209]. Under the same experimental conditions, poly(4-methylstyrene) chains could be degraded to a molar mass of 0.08×10^6 [213]. In several experiments with polymers of different molar mass the molar mass decreased down to the region 1 shown in Fig. 38B. These experiments confirm the existence of highly crosslinked regions in microgels due to an extensive multiple crosslinking. Only the large microgel aggregates formed shortly before macrogelation can be degraded.

Chen et al. synthesized microgels by copolymerization of 1,4-DVB and MMA in the presence of a chain transfer agent (CBr_4) [214]. They showed that when the concentration of the chain transfer agent becomes high, the intermolecular crosslinking is depressed and microgels are formed. During the polymerization the structure of the microgels gradually became tight [215] which demonstrates the important role of multiple crosslinks in the formation of microgels.

In order to obtain hydrophilic microgels with sulfo groups, Huang et al. studied the copolymerization of 2-acrylamido-2-methylpropane sulfonic acid and *N,N'*-methylene bisacrylamide in dilute aqueous solutions with potassium persulfate (PPS) as the initiator [216]. By varying the monomer concentration and the crosslinker content of the monomer mixture they obtained reactive microgels with $\overline{M}_w$ up to 25×10^6 g/mol. From the reduced reactivity of sulfo groups in the interior of the microgels, a core-shell structure was assumed with a densely crosslinked core surrounded by a shell of polymerized sulfonic acid monomer. The dimension of this shell varied with its amount in the initial monomer mixture [216].

Microgels can also be synthesized by intramolecular crosslinking of preformed polymers bearing functional groups. Batzilla and Funke prepared linear poly(4-vinylstyrene) (PVS) by anionic polymerization of 1,4-DVB (see next section) and subsequently crosslinked this polymer dissolved in toluene, using AIBN as initiator [217, 218]. They followed the intra- and intermolecular crosslinking reactions by viscosimetry, dynamic and static light scattering and by spectroscopic methods. If only cyclization takes place, the initial [η] should decrease during the reaction without any change of the molar mass. An increase in $\overline{M}_w$ is then a sensitive measure for intermolecular crosslinking.

Figure 39A shows, how [η] and $\overline{M}_w$ change during crosslinking of PVS of initial molar mass of $\overline{M}_{w,0}$, ranging from 0.3×10^6 to $2{,}4\times10^6$ g/mol. With increasing molar mass, [η] decreases first but then increases. This decrease can be explained by a prevailing intramolecular crosslinking, the following increase being determined by intermolecular crosslinks. The minimum of [η] indicates the transition from prevailing intramolecular crosslinking to prevailing intermolecular crosslinking. As $\overline{M}_{w,0}$ increases, the minimum of [η] becomes more pronounced.

It is well-known that the coil density of macromolecules decreases with increasing molar mass. Due to cyclization this decrease in density becomes less or even disappears because the macromolecules of higher molar mass are more strongly contracted than those of lower molar mass. After a certain conversion of pendant vinyl groups, the influence of the intermolecular reaction on [η]

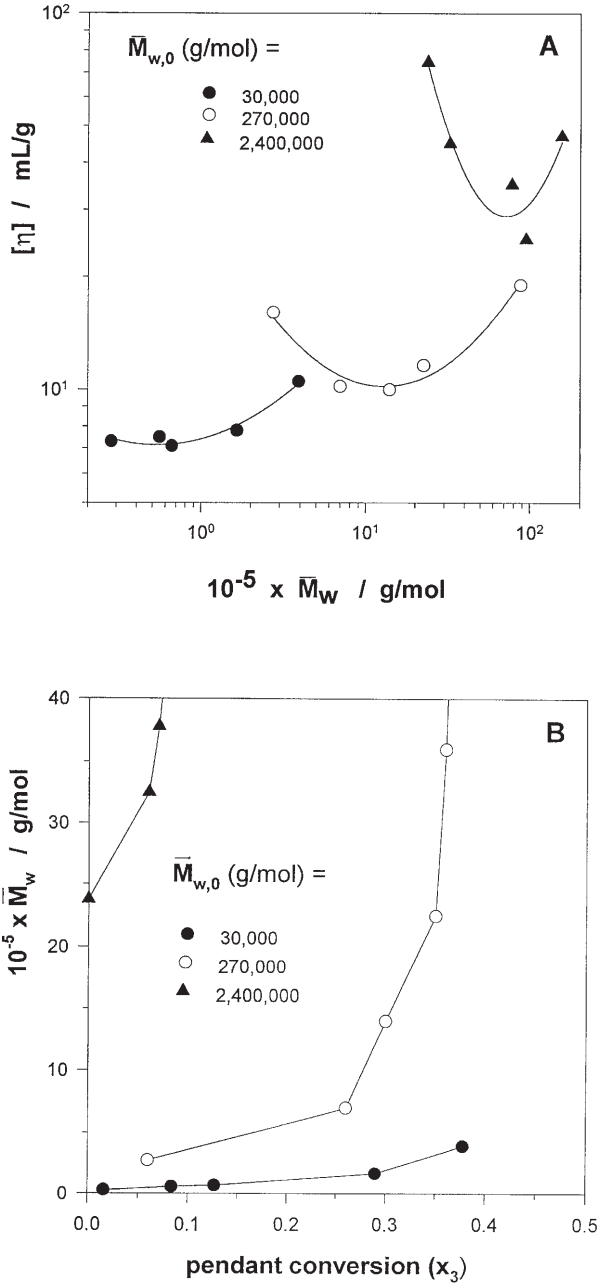


Fig. 39. Relation between [η] and $\overline{M}_w$ in the course of crosslinking of PVS. **B:** Increase of $\overline{M}_w$ with the conversion of pendant vinyl groups during crosslinking of PVS. PVS concentration = 0.35 mass %. Temperature = 70 °C. Molar masses of the starting PVS, $\overline{M}_{w,0}$ are shown in the figures. [Reproduced from Ref. 218 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

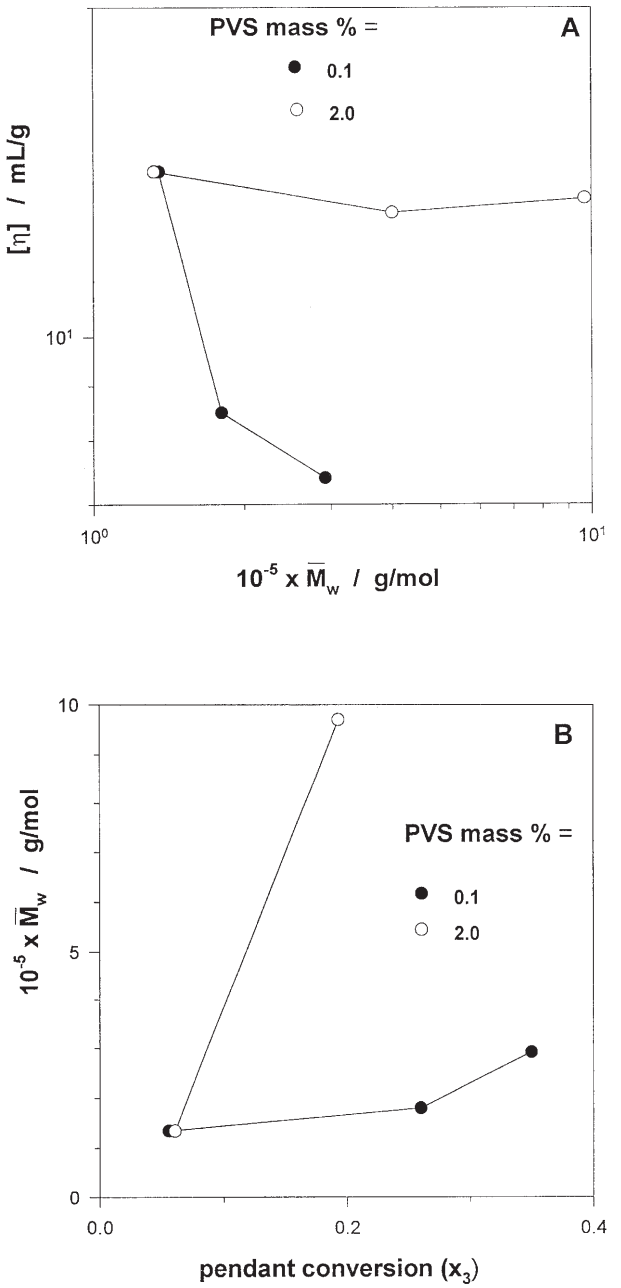


Fig. 40. **A:** Relation between [η] and $\overline{M}_w$ during crosslinking of PVS. **B:** Increase of $\overline{M}_w$ with the conversion of pendant vinyl groups during crosslinking of PVS. Molar mass of starting PVS, $\overline{M}_{w,0}$ = 135000 g/mol. Temperature = 70 °C. The PVS concentrations are shown in the figures [217].

dominates and aggregates are formed. The transition from microgels to a macrogel is indicated by an abrupt increase of $\overline{M}_w$ with the increase of the conversion of pendant vinyl groups x_3 (Fig. 39B).

The degree of initial dilution strongly influences the extent of cyclization during the formation of microgels [217]. As seen in Fig. 40A, the slope at the beginning of the $[\eta]/M_w$ curves becomes steeper when the concentration of PVS is decreased from 2.0 to 0.1 mass % which means that cyclization is much more favored. As a result, the onset of the fast increase of the molar mass and the gel point are shifted to higher conversions of pendant vinyl groups (Fig. 40B). It was also shown that the extent of cyclization increases and the point of the macrogel formation is shifted towards higher conversions of pendant vinyl groups when the chain transfer constant of the solvent used in polymerization increases [217]. This result confirms the observations of Chen et al. in 1,4-DVB/MMA copolymerization [214].

The solvating power of the solvent used in polymerization also strongly influences the rate of cyclization. Batzilla crosslinked PVS in a series of toluene/methanol mixtures of increasing content of the non-solvent methanol and measured the initial conversion rate of pendant vinyl groups, which corresponds to the rate of cyclization [217]. As seen in Fig. 41, this rate increases very rapidly

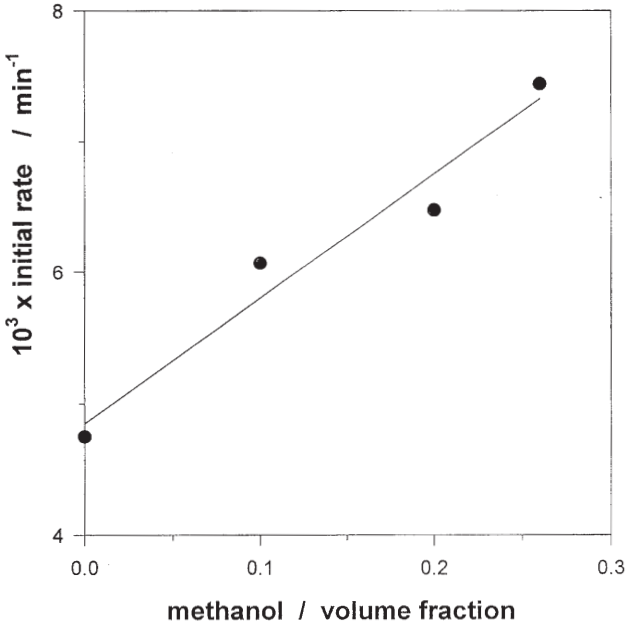


Fig. 41. Initial rate of the conversion of pendant vinyl groups during crosslinking of PVS shown as a function of the volume fraction of methanol in the toluene/methanol mixture [217]. PVS concentration = 0.30 – 0.35 mass %, initial molar mass of PVS = 170000 g/mol, temperature = 70 °C.

with the volume fraction of the non-solvent. In poor solvent mixtures the polymer coils are contracted which necessarily increases the local concentration of pendant vinyl groups within the polymer coils. Therefore, the probability of cyclization increases. Under identical conditions, however, macrogelation occurs earlier in poor than in good solvents [217]. The delayed gelation in good solvents was also observed by Matsumoto in several polymerization systems [30]. He explained this observation by the influence of a thermodynamically excluded volume effect on intermolecular crosslinking. Accordingly, the reactivity of pendant vinyl groups in large molecules is probably much lower in good than in poor solvents due to the excluded volume of the molecule. This excluded volume effect seems to dominate when macrogelation occurs at low conversions, i.e. when the concentration of PDS in the transition region to the macrogel is rather low. Similar results were reported with 1,4-DVB/MMA microgels dissolved in benzene-methanol mixtures [214, 215, 219, 220]. By varying the solvent composition of these solvent mixtures, Ishizu et al. measured the rate of cyclization and intermolecular crosslinking in the copolymerization of 1,4-DVB and MMA [219]. The rate of cyclization increased with the content of methanol in the solvent mixture. However, with a methanol fraction of 50 %, the rate of cyclization became extremely small. On the other hand, the dependence of the rate of intermolecular crosslinking on the solvent quality was maximal at a methanol fraction of 0.1.

With regard to these results, experiments were designed to prepare intramolecularly crosslinked macromolecules by starting from linear polymers with a negligible number of intermolecular links [217]. In Table 2 the reaction conditions as well as the properties of PVS before and after the reaction are collected. After a reaction time of 25 min, [η] decreased to half of the initial value whereas only a slight change of $\overline{M}_w$ could be detected by light scattering. It was calculated that the ratio of cycles to intermolecular links in the product was 500:1. Therefore, the reaction product can be considered as a primary particle, i.e. an intramolecularly crosslinked macromolecule. It is obvious that such intramolecularly crosslinked macromolecules may be formed during RCC of vinyl/divinyl monomer mixtures at zero monomer conversion. The intermolecular crosslinking between these molecules and the subsequent multiple crosslinking lead to the formation of microgels.

Table 2. Intramolecular crosslinking of PVS [217]. Reaction conditions: PVS concentration = 0.975 mass %; AIBN concentration = 1.65×10^{-3} M; temperature = 70 °C; n-butylmercaptan (chain transfer agent) concentration = 20 mL/L; reaction time = 25 min. The $\overline{M}_w$ and $\overline{M}_n$ were measured by light scattering and membrane osmometry respectively.

POLYMER :		PVS	→	PRODUCT
x_3		0	→	0.27
$\overline{M}_w$	[g.mol^{-1}]	120,000	→	160,000
$\overline{M}_n$	[g.mol^{-1}]	32,000	→	32,000
[η]	[mL/g^{-1}]	16	→	8

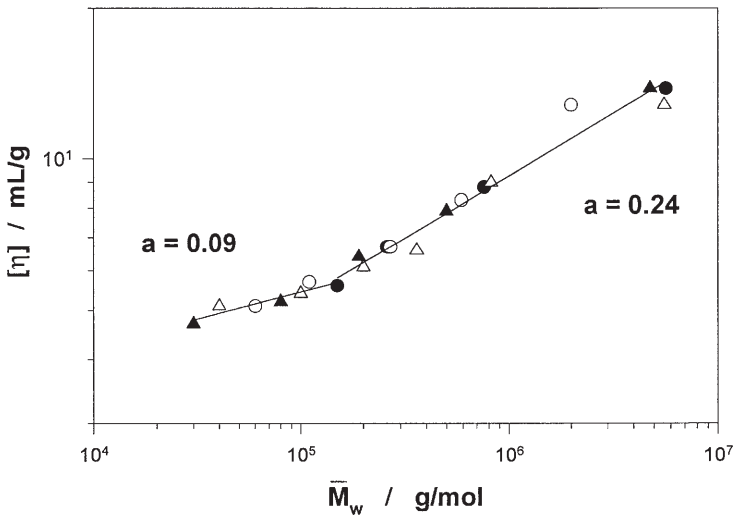


Fig. 42. Relation between $[\eta]$ and $\overline{M}_w$ of 1,4-DVB microgels synthesized at initial monomer concentration 5 (●), 2 (○), 1 (▲), and 0.5 g/100 mL (△). AIBN concentration = 8×10^{-3} M, temperature = 70 °C. [Reprinted with permission from Ref. 209, Copyright 1995, American Chemical Society].

6.4 Characteristics of Microgels

The compact structure of microgels which is due to extensive cyclization and multiple crosslinking, manifested itself in the $[\eta]/\overline{M}_w$ plots. Figure 42 shows the relation between $[\eta]$ and $\overline{M}_w$ for the microgels obtained by RCC of 1,4-DVB with different monomer concentrations [209, 212]. The exponent a of the Mark-Houwink equation, calculated for each monomer concentration, decreases gradually from 0.25 to 0.20 as the dilution increases. Moreover, the average value of the exponent a is close to zero for $\overline{M}_w < 10^5$ due to the predominant cyclization and multiple crosslinking, and becomes 0.24 above this molar mass, compared with the value a = 0.7 for linear polystyrene in benzene. Thus, the exponent a agrees well with previous results about the extent of cyclization. Figure 43 shows the same plot with a slope of 0.21 ± 0.01 for different initiator concentrations and 1,4-DVB/S ratios. This value of the exponent is close to the value of 0.25 reported by Zimm et al. for 1,4-DVB/S copolymers [162]. For the same system, Antonietti and Rosenauer found an exponent 0.38, which deviates distinctly from the first two values [221]. Their microgels were prepared by polymerization of t-DVB/S mixtures in dilute benzene solutions over a time of 20 days at 70 °C with repeated additions of AIBN. Obviously, these authors obtained a rather heterogeneous mixture of branched polystyrene and microgels which explains the high value for the exponent a.

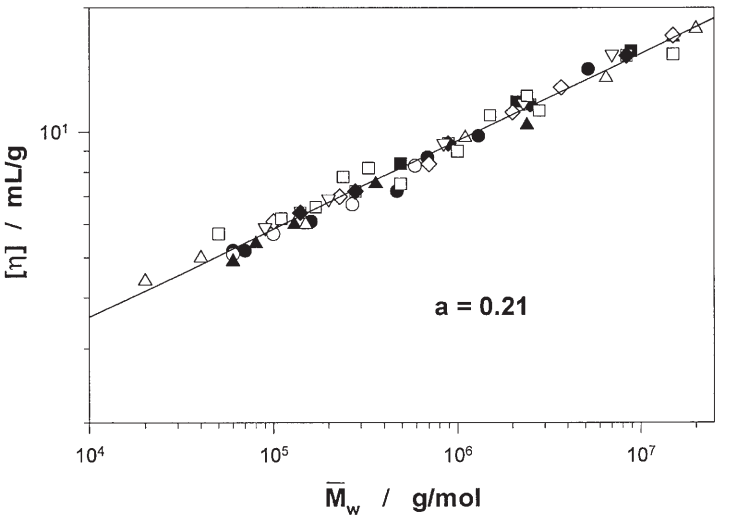


Fig. 43. [η] versus $\overline{M}_w$ of 1,4-DVB microgels obtained under various reaction conditions: 1) Pure 1,4-DVB microgels: Initial monomer concentration = 2 g/100 mL, temperature = 70 °C, AIBN concentration = 2.6 (●), 8(○), 16 (▲), and 32mM (△). 2) 1,4-DVB/S microgels: Initial monomer concentration = 5 g/100 mL, temperature = 70 °C, AIBN concentration = 2.6 mM, 1,4-DVB mass % = 100 (■), 80 (□), 70 (◆), 60 (◇), 40 (▽), and 20 (▼). [Reprinted with permission from Ref. 209, Copyright 1995, American Chemical Society].

In Figure 44, $[\eta]/\overline{M}_w$ plots for various microgels formed in an emulsion and in solution are schematically illustrated. Emulsion polymerization yields polymer gel spheres with a constant density, if the amount of crosslinker in the monomer mixture is higher than 10 %. If the crosslinking density of the microgels increases or if the quality of the swelling solvent decreases, [η] decreases but never attains the value of rigid spheres. Thus these microgels swell to some extent. However, because microgels formed in solution, compared to coils of linear macromolecules, are also contracted, the dependence of [η] on their molar mass indicates a density fluctuation within particles. Probably dangling chains on the microgels or loosely crosslinked regions between the primary particles within a microgel aggregate may cause the observed deviations. Only in the region of $\overline{M}_w < 10^5$, where the intermolecular reactions are insignificant, is the exponent a close to zero for microgels formed in solution and they behave like those formed in emulsion.

In t-DVB/S copolymerization, Antonietti and Rosenauer isolated microgels slightly below the macrogelation point [221]. Using small angle neutron scattering measurements they demonstrated that these microgels exhibit fractal behavior, i.e. they are self-similar like the critically branched structures formed close to the sol-gel transition.

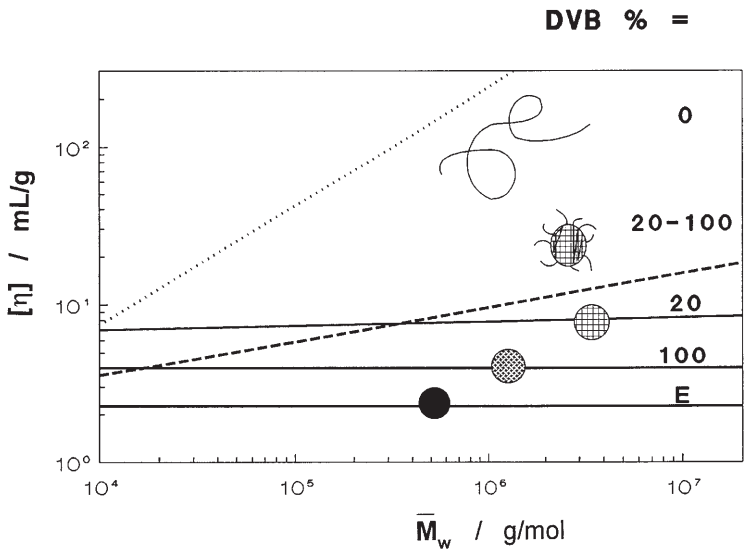


Fig. 44. Schematic representation of $[\eta]/\overline{M}_w$ plots for microgels formed in emulsion (solid lines) and in solution (dashed line). Solvent = toluene. Temperature = 25°C. The dotted line represents the plot of linear polystyrene. The 1,4-DVB contents are given in the figure. E = Einstein equation.

7
Microgel Formation by Anionic Polymerization

Anionic polymerization is a powerful method for the synthesis of polymers with a well defined structure [222]. By careful exclusion of oxygen, water and other impurities, Szwarc and coworkers were able to demonstrate the "living" nature of anionic polymerization [223, 224]. This discovery has found a wide range of applications in the synthesis of model macromolecules over the last 40 years [225–227]. Anionic polymerization is known to be limited to monomers with electron-withdrawing substituents, such as nitrile, carboxyl, phenyl, vinyl etc. These substituents facilitate the attack of anionic species by decreasing the electron density at the double bond and stabilizing the propagating anionic chains by resonance.

For the synthesis of reactive microgels, anionic polymerization has received less attention compared to the other methods. This is due to the experimental difficulties involved in this synthesis. For instance, the isolation of the polymers in the microgel stage is difficult because anionic polymerization proceeds at very high rates. However, anionic polymerization is advantageous for preparing predetermined and well-defined network structures. Moreover, the simple kinetics allows a better insight into the complex mechanism of microgel formation.

Among the divinyl monomers, 1,4-DVB and EDMA are the most extensively studied monomers for microgel formation by anionic polymerization. Com-

pared to EDMA, 1,4-DVB is less reactive because of its relatively weak electron-withdrawing substituent. Thus, strong nucleophiles such as alkyl carbanions are required to polymerize 1,4-DVB. EDMA can easily be polymerized anionically by using weaker nucleophiles such as alkoxide ions, although various side reactions are possible between anions and the ester groups of the monomer or of the growing polymer [228]. A variety of initiators have been used to initiate the anionic polymerization of divinyl monomers. Depending on the solvent used, the reactions may proceed in homogeneous or heterogeneous solutions. Various factors are known to influence the structure of the resulting polymers and their properties. The following discussion summarizes the experimental results of synthesizing reactive microgels by anionic methods and the conditions of their formation. The initiator concentrations will be expressed as mol % of the initial content of monomers. The content of pendant unsaturated groups of the polymers is expressed as the fraction of the tetrafunctional monomer units in the polymer that bear a pendant unsaturated group.

7.1
1,4-Divinylbenzene (1,4-DVB)

Both vinyl groups of 1,4-DVB have equal reactivities but after one of them has reacted, the remaining vinyl group (pendant group) has a lower reactivity. Worsfold showed that in anionic polymerization the reactivity of pendant vinyl groups is ten times smaller than the reactivity of vinyl groups of the 1,4-DVB monomer [229]. This suggests that at the beginning of the polymerization in dilute solutions almost linear poly(4-vinylstyrene) (PVS) chains must be formed, which then branch and, as polymerization proceeds, are finally connected to an infinite network.

On copolymerization of DVB containing 45 % ethylstyrene and on terpolymerization of this mixture with 75 % styrene, using a Ziegler-Natta catalyst and aliphatic or aromatic solvents, D'Alelio and Brüschweiler [384] obtained soluble polymers with an average intrinsic viscosity of 0.1 – 0.11. By using the K and a values of polystyrene they calculated a molar mass of 5000 – 6000, corresponding to an average degree of polymerization of 40–50. As the titration with bromine indicated that only one double bond of each polymerized DVB unit reacted, it was concluded that the polymers had a linear structure. However, considering the low $[\eta]$ values, it cannot be excluded that these co- and terpolymers were very weakly crosslinked microgels.

Dusek [385] found that on crosslinking of these soluble polyunsaturated polymers, the crosslink densities were much lower than those of corresponding polymers obtained by direct polymerization of the monomer mixtures. This result indicates a strong sterical hindrance of pendant vinyl groups.

Hiller and Funke obtained easily dissolvable linear macromolecules of PVS by anionic polymerization of 1,4-DVB up to conversions of 80 – 90 % [230, 231]. In these experiments very low concentrations of *n*-butyl lithium (*n*-BuLi) were used and tetrahydrofuran (THF) as solvent. The reactions were carried out at –78 °C and for 7 min. The contents of pendant vinyl groups in the polymer were determined by infrared spectroscopy, mercury-II-acetate addition and catalytic

hydrogenation with tris(triphenylphosphin)-rhodium-I-chloride as catalyst. These investigations indicated that each 1,4-DVB unit in the polymer had approximately one pendant vinyl group. The $\overline{M}_w$ of PVS thus prepared, varied, between 6×10^4 and 40×10^4 g/mol, depending on the initiator concentration [230–232]. The [η] of the polymers in toluene at 20 °C varied between 23.5 and 165 ml/g. As seen in the previous section, PVS macromolecules thus obtained are excellent multifunctional macromonomers for studying cyclization and multiple crosslinking in radical polymerization. According to Tsuruta et al., almost linear PVS can be also prepared in THF if the polymerization is initiated with lithium diisopropylamide in the presence of an excess diisopropylamine [233–235]. The molar mass of these polymers, however, is relatively low ($\overline{M}_w < 10^5$ g/mol) due to the chain transfer reactions of the free amine in the reaction medium.

Hiller and Funke extensively investigated the change of the polymer structure as a function of the monomer and the initiator concentration in various solvents [231]. The content of pendant vinyl groups in the polymer was about 100% for *n*-BuLi concentrations below 2 mol % and for the whole range of the monomer concentration studied (20–100 g/l). The content of pendant groups decreased when the *n*-BuLi concentration increased and approached 80 % in the transition region of a soluble polymer to a macrogel. As seen in Fig. 45, the decrease of pen-

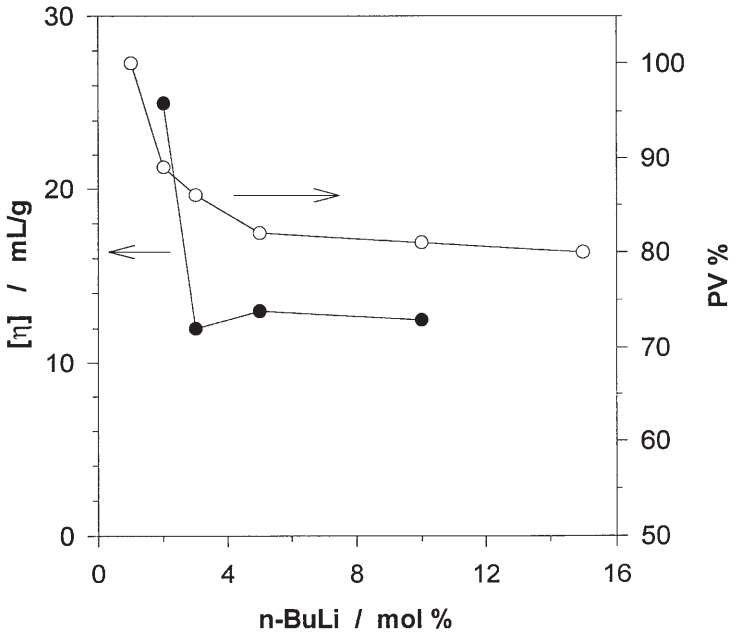


Fig. 45. [η] and content of pendant vinyl groups of polymers shown as a function of the initial n-BuLi concentration in the anionic polymerization of 1,4-DVB in THF. Initial 1,4-DVB concentration = 20 g/L. Reaction temperature = –78 °C. Reaction time = 7 min. [Reproduced from Ref. 231 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

dant vinyl groups and of [η] is rapid up to 3 mol % *n*-BuLi, indicating an increasing tendency of the polymer chains to cyclization. Later on the content of pendant groups decreases further, but [η] increases only slightly because of an increasing extent of intermolecular crosslinking. For *n*-BuLi contents above 15 mol %, insoluble aggregates were obtained. Thus, a gradual change from a linear to a crosslinked structure of the polymer can be achieved by with increasing the concentration of *n*-BuLi. Intramolecular crosslinking, leading to the formation of microgels, play an important role at medium *n*-BuLi concentrations . The [η] of the microgels were in the range of 12–14 ml/g and were almost independent of the molar mass (Fig. 46).

The pendant vinyl groups of the microgels react with mercury-II-acetate at different rates, depending on their location (Fig. 47). At the beginning vinyl groups located at the surface of microgels react fast. Then a low, diffusion-controlled reaction of the vinyl groups within the microgels takes place.

Electron micrographs of microgels at a magnification of ×152|000 show that their shape is spherical or sometimes irregular with diameters of 3–30 nm [230]. Because microgels are reactive crosslinked macromolecules, the particle growth during the polymerization may also proceed by aggregation of these primarily formed, reactive microgels, and larger, irregularly shaped aggregates of microgels are produced. Electron micrographs of macrogels showed that they are com-

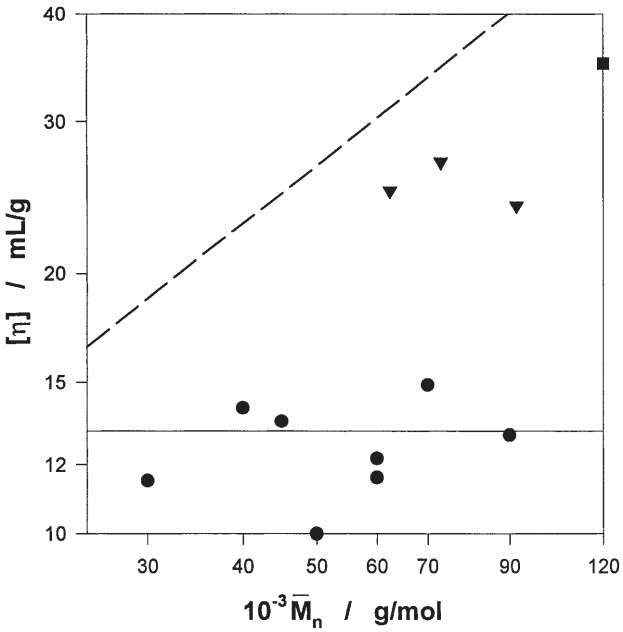


Fig. 46. Dependence of [η] on the $\overline{M}_n$ of polymers prepared by anionic polymerization of 1,4-DVB in THF. The symbols represent linear (■); branched (▼) and microgel (●) structures. The dashed line represents the [η]/$\overline{M}_n$ relationship of anionically prepared polystyrene. [Reproduced from Ref. 231 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

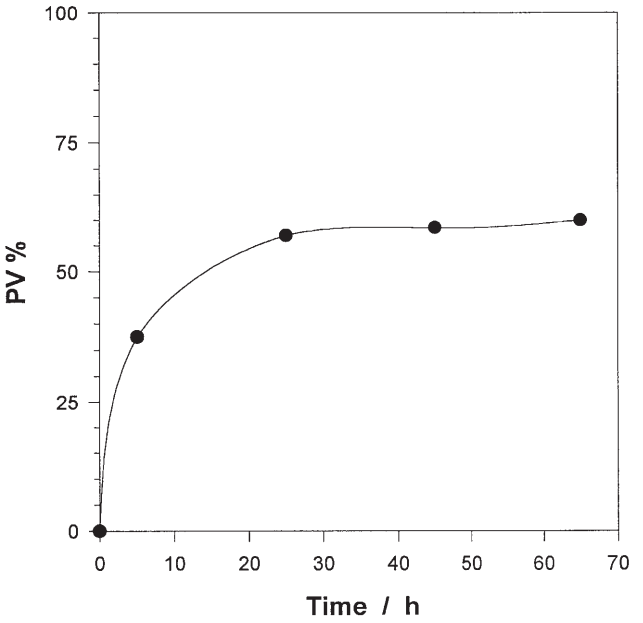


Fig. 47. Conversion of pendant vinyl groups (PV) in 1,4-DVB microgels shown as a function of the reaction time with mercury-II-acetate [230]. Initial monomer and initiator concentrations used for the synthesis of the microgels are 30 g/L and 4 mol % respectively.

posed of small particles with the same size and shape as those of microgels. This directly confirms that microgels are intermediates in the formation of highly crosslinked, macroscopic networks.

In Fig. 48, the regions of the formation of linear or branched polymers, microgels and macrogels are shown as a function of the concentration of 1,4-DVB and of *n*-BuLi. Reactive microgels can be obtained at a monomer concentration below 50 g/l and between 3 and 16 mol % of *n*-BuLi. The polymer structure approaches that of a macrogel when the concentration of 1,4-DVB or *n*-BuLi is increased.

Anionic polymerization of 1,4-DVB by *n*-BuLi leading to the microgels was also reported by Eschwey et al. [236, 237]. In their experiments, *n*-BuLi was used at very high concentrations of 17 and 200 mol % of the monomer. Contrary to the results of Hiller and Funke [231], they observed a transition from microgel to macrogel with decreasing *n*-BuLi concentration. Similar results were also reported by Lutz and Rempp [238]. They used potassium naphthalene as the initiator of the 1,4-DVB polymerization and THF as the solvent. Soluble polymers could only be obtained above 33 mol % initiator, whereas below this value macrogels were obtained as by-products.

The opposite effects of the initiator on the structure of 1,4-DVB polymers in a range of low (1–16 mol %) and a high (17–200 mol %) concentration of 1,4-DVB were explained by a kinetic model of anionic polymerization of 1,4-DVB [239]. Calculations indicated that, at low concentrations of the initiator, the poly-

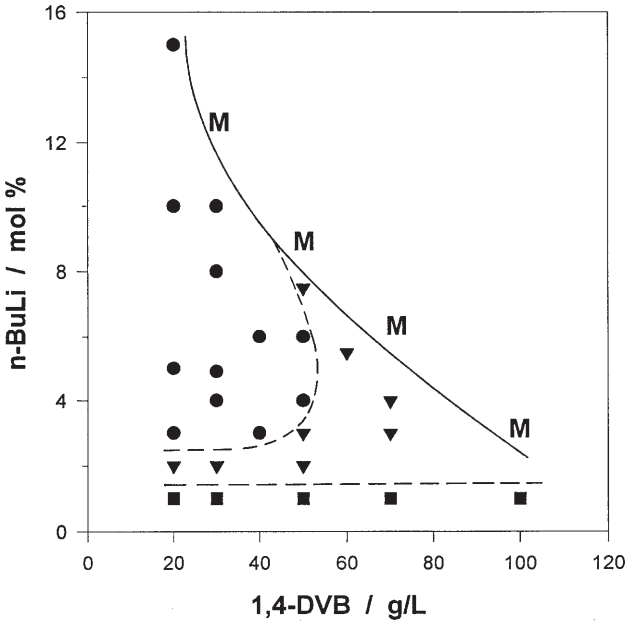


Fig. 48. Dependence of the polymer structure on the initial concentrations of n-BuLi and 1,4-DVB in the anionic 1,4-DVB polymerization in THF. The symbols represent linear (■); branched (▼); microgel (●) and macrogel (M) structures. [Reproduced from Ref. 231 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

merization is slow, and an increase of the concentration of *n*-BuLi leads to the formation of a macrogel because polymerization and crosslinking are accelerated. At high concentrations of the initiator, the polymerization and crosslinking are very fast, but the length of the primary chains limits the crosslinking density. Therefore, within this range macrogels are formed earlier with decreasing *n*-BuLi concentration because the length of the primary chains increases. The calculated dependence of the polymer structure on the initial concentration of monomer and initiator is shown in Fig. 49. The solid curve which represents the transition from microgels to a macrogel, resembles the experimental curve for the range of 1 to 16 mol % *n*-BuLi (Fig. 48).

The solvent used in the anionic polymerization of 1,4-DVB by *n*-BuLi also has an important effect on the polymer structure. If polymerization reactions are carried out in benzene/THF mixtures, the onset of macrogelation can be retarded by increasing the THF fraction in the solvent mixture [230]. Hexane, that is a solvent for the monomer but a precipitant for the resulting polymer, was not suitable because an insoluble aggregate was formed within a few minutes [230]. For hexane /THF mixtures with equal volumes, the conditions for the synthesis of a soluble polymer depends on the concentrations of 1,4-DVB and *n*-BuLi (Fig. 50). The course of the curve in the transition region from a soluble polymer to a macrogel is similar to that shown in Fig. 48 for *n*-BuLi/THF.

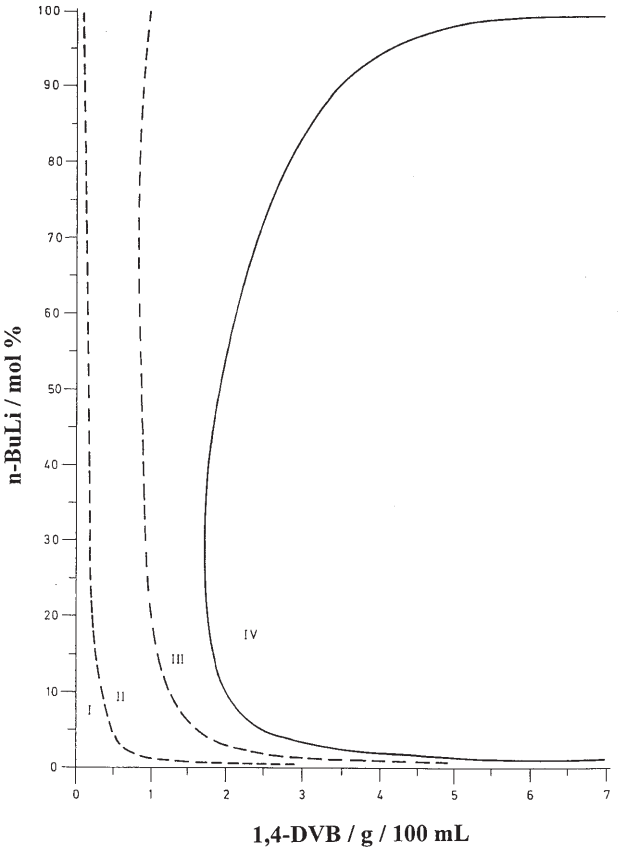


Fig. 49. Calculated dependence of the polymer structure on the initial 1,4-DVB and n-BuLi concentrations in the anionic 1,4-DVB polymerization. The numbers I to IV represent the region for the formation of linear, branched, microgel and macrogel structures, respectively. The solid and dashed curves represent the transition regions between these structures. [Reproduced from Ref. 239 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

The use of living polymers for initiating the anionic polymerization of 1,4-DVB may also lead to the formation of reactive microgels, which have a shell of linear polymers. This method is known to be applied in the synthesis of star-shaped polymers, where only a small amount of 1,4-DVB is used as crosslinking agent for the living chains [240–243]. In this polymerization of 1,4-DVB the nucleus of a star-shaped polymer is formed with linear polymer chains bound to its as branches. The mass of the nucleus of star-shaped polymers is usually negligible (1–5 mass %). Therefore these polymers may be considered as a limiting case of reactive microgels which are enveloped by linear polymer chains. Taromi and Rempp reported that the size of the nuclei in star-shaped polymers can be enlarged when more 1,4-DVB is used [244]. They applied the same

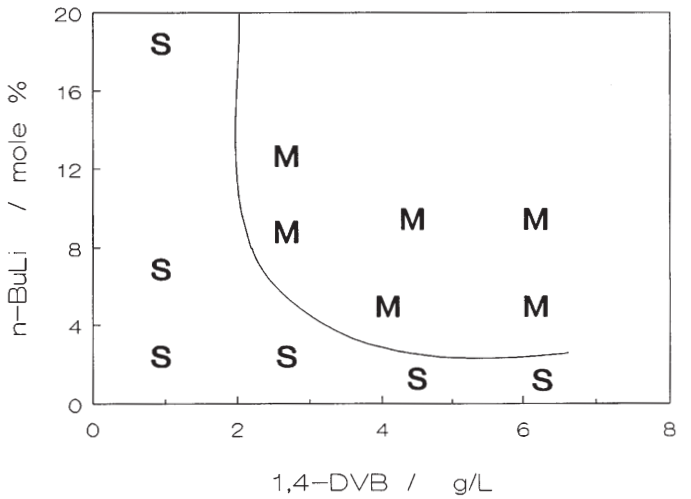


Fig. 50. Dependence of the polymer structure on the initial concentrations of n-BuLi and 1,4-DVB in the anionic polymerization of 1,4-DVB in a hexane / THF (1/1) mixture [230]. S = soluble polymer; M = macrogel. The solid curve represents the soluble polymer – macrogel transition region.

method as that for the synthesis of real star polymers: addition of 1,4-DVB to a solution of polystyryl lithium in benzene or in THF. The reaction proceeded in a homogeneous solution and reactive microgels ("porcupine polymers") were obtained which consisted of about 30–34 mass % of nuclei. The residual mass consisted of polystyrene chains attached to the surfaces of the nuclei (10–90 chains per nucleus). No gelation of the reaction mixture was observed even at very high concentrations of 1,4-DVB. This indicates that the polystyrene chains prevent the reaction between the pendant vinyl groups at the surface of the nuclei.

Another approach to the synthesis of reactive microgels with living polymer chains is anionic dispersion polymerization. This method, which was thoroughly reviewed by Barret [245], is a modified precipitation polymerization [246]. For applying this method to the synthesis of microgels the divinyl monomer and the living polymer must be soluble in the dispersion medium, while its block copolymer must be insoluble. Okay and Funke initiated the polymerization of 1,4-DVB by using living poly(4-*tert*-butylstyrene) (PBS) at 50 °C in *n*-heptane [247, 248]. Heptane is known to be a good solvent for PBS, but a non-solvent for polystyrene or PVS. The polymerization was thus initially homogeneous, but the growing block copolymer chains, consisting of PBS and PVS blocks, precipitated from the solution after attaining a critical size (Fig. 51). Further polymerization and crosslinking proceeded in the separated phase of the block copolymer, and reactive 1,4-DVB microgels were obtained which were enveloped by PBS chains. The chains of the living polymer act as the initiator for the polymerization of 1,4-

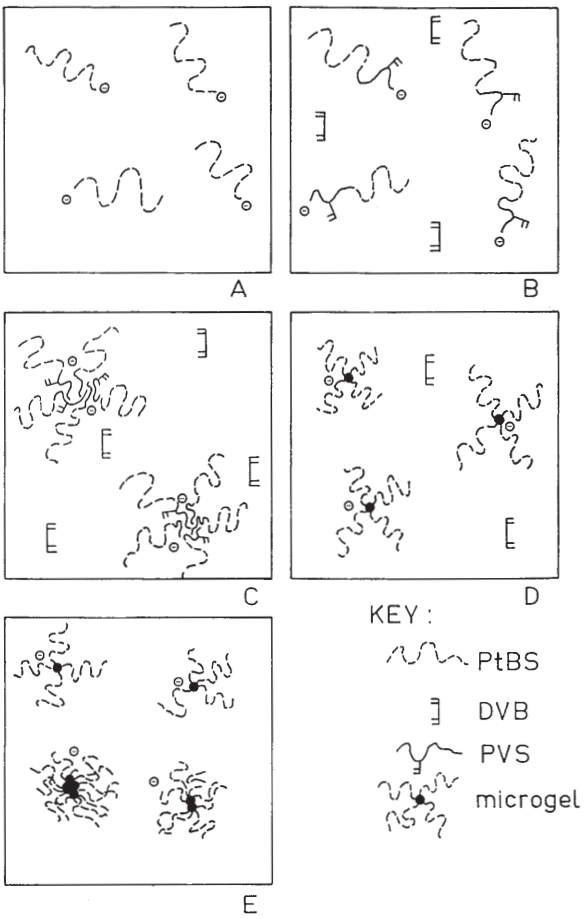


Fig. 51. Schematic illustration of the mechanism of microgel formation in the anionic dispersion polymerization of 1,4-DVB initiated by living PBS chains in heptane. [Reprinted with permission from Ref. 247, Copyright 1995, American Chemical Society].

DVB and also as steric stabilizers for the separated particle phase. By this method reactive microgels with nuclei fractions up to 30–35 mol % (25–30 mass %) could be prepared without macrogel formation [247]. The microgels had $\overline{M}_w$ up to 30×10^6 g/mol and possessed 10–5000 PBS chains per nucleus, which were packed closely together at the surface. In Fig. 52, the [η] of these microgels are plotted against their mol fractions of 1,4-DVB, (n_{DVB}). Though the $\overline{M}_w$ of the microgels is 20–6000 times higher than that of linear, soluble macromolecules ($n_{DVB} = 0$), their [η] does not differ much. The [η] of these microgels was only 1.5–3 times higher than those of linear macromolecules . The higher the [η] of the soluble macromolecules, the higher was also the [η] of the resulting microgels. Thus, the length of PBS chains attached to the surface of the nuclei controls

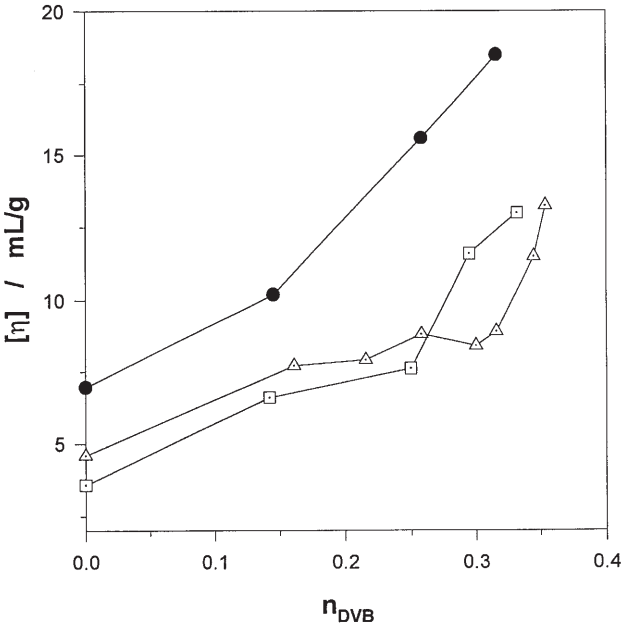


Fig. 52. [η] of the microgels shown as a function of mole fraction of nuclei in the microgels n_{DVB} in the anionic dispersion polymerization of 1,4-DVB. $\overline{M}_n$ of living PBS = 2700 – 3400 (□); 4000 – 5000 (△); 13000–16500 (●). [Reprinted with permission from Ref. 247, Copyright 1995, American Chemical Society].

the [η] of the microgels. The hydrodynamic volume of these microgels could be regulated by the length of living PBS used for their synthesis.

Pille and Solomon investigated the formation of the above mentioned microgels using gel-permeation chromatography with an on-line light scattering detector [249]. They showed that the primary particles appear very early in the reaction and microgels are formed by interparticular reactions of the primary particles.

7.2
1,3-Divinylbenzene (1,3-DVB)

Kast and Funke studied the anionic polymerization of 1,3-DVB and compared the results with those obtained using 1,4-DVB [250]. The polymerization was carried out under constant conditions (solvent = THF; initiator = *n*-BuLi; temperature = –78 °C). Significant differences between the behavior of both isomers were observed.

1) Polymerization of 1,3-DVB is much faster than 1,4-DVB. Conversion of 1,3-DVB was complete within seconds, whereas in the case of 1,4-DVB the conversion of the monomer was 80–90 % after 7 min.

2) The content of pendant vinyl groups of 1,3-DVB microgels was found to be 50–70% and almost independent of the monomer conversion. Linear or slightly branched 1,3-DVB polymers could not be isolated. In the case of 1,4-DVB, the content of pendant vinyl groups was about 100% at low conversions and decreased to 80% with increasing conversion. This comparison clearly shows that in the polymerization of 1,3-DVB cyclization dominates and that the reactivity of the pendant vinyl groups of 1,3-DVB units is much higher than of 1,4-DVB units.
3) Under the same reaction conditions macrogelation occurs later in the polymerization of 1,3-DVB. Moreover, the [η] of the microgels from 1,3-DVB is much smaller than that from 1,4-DVB. The exponent a of Mark-Houwink equation for the 1,3-DVB polymers in toluene was found to be only 0.25 [250] and 0.29 [251] compared with 0.48 for 1,4-DVB polymers obtained under similar reaction conditions [230]. The delay of the gel point and the small hydrodynamic volumes of 1,3-DVB microgels, compared with 1,4-DVB microgels also illustrate that the extent of cyclization is much higher in 1,3-DVB polymerization.

7.3 Ethylene Glycol Dimethacrylate (EDMA)

The methacrylate groups in EDMA do not interact electronically. Therefore, the reactivity of pendant methacrylate groups at the polymer backbone should be the same as that of the monomers [100]. Moreover, the crosslinks formed with EDMA are less bulky and more flexible than those with 1,4-DVB. Therefore, the pendant methacrylate groups should react more efficiently in polymerization and both polymerization and crosslinking may occur simultaneously at the beginning of the reaction. However, an equal reactivity of methacrylate groups in polymerization of EDMA is only valid in systems without steric hindrance. With increasing density of intra- and/or intermolecular crosslinking and with decreasing mobility of the polymer chains, the reactivity of pendant methacrylate groups may gradually decrease during the formation of microgels or within microgels with increasing distance of pendant groups from surface to the center of microgels.

Beer used sodium methylate/methanol as initiator system for the anionic polymerization of EDMA [252]. Since this initiator system yields oligomers in the polymerization of methyl methacrylate [253], it was aimed to synthesize EDMA oligomers and finally obtain EDMA microgels by their aggregation. However, insoluble macrogels were obtained due to the high reaction rate. With potassium *tert*-butylate and dibenzo-18-crown ether-6, insoluble products were also formed within a few seconds [252]. Initiation of the EDMA polymerization by *n*-BuLi in THF resulted in various side-reactions between *n*-BuLi and the ester groups of EDMA [254–256] as was observed in the anionic polymerization of methyl methacrylate [257–259]. When *n*-hexane was used as solvent, insoluble macrogels were obtained immediately after the addition of the monomer to the initiator solution. The best results were obtained in toluene, a good non-polar solvent for EDMA and also for the resulting polymer [256]. The polymerization

in toluene was carried out at 20 °C and with an initial monomer concentration of 78 g/l. The fraction of pendant methacrylate groups was between 51 and 59% and almost independent of conversion and molar mass. This interesting feature of anionic EDMA polymerization was also observed by Galina et al. in radical polymerization of EDMA [173].

These results suggest that reactive microgels are already formed at the very beginning of polymerization as a consequence of dominating cyclization. Thus, contrary to the anionic polymerization of 1,4-DVB, linear polymers bearing methacrylate groups do not appear in the EDMA polymerization. The higher extent of cyclization in EDMA microgels is also reflected by their "molecular" swelling ratios. Antonietti et al. showed that the swelling ratio of EDMA/S microgels formed in a microemulsion was much higher than expected from the chemical crosslink density [95].

Straehle observed two distinct reaction stages in the anionic polymerization of EDMA (Figs. 53 and 54) [254]. In the first stage, the rate of polymerization was rapid and after 3 min the polymer yield increased up to 25.8 %. During the same period $\overline{M}_w$ increased only slightly. This indicates a low rate of intermolecular crosslinking. Moreover, the relatively low content of pendant methacrylate groups (59 %) indicates strong cyclization. The exponent of the $\langle s^2 \rangle_z / \overline{M}_w$ relation was between 0.66 and 0.71 which indicates a spherical shape of the polymers. It must be concluded, therefore, that during the first stage of the reaction, spherical, intramolecularly crosslinked macromolecules, i. e. reactive microgels, are formed. In the second stage of the reaction (after 3 min) the yield of the polymer increases slowly and after 7 min reaches 36.5 %, but $\overline{M}_w$ increases rapidly as the reaction proceeds and after 8 min the first macrogel particles appear [254]. Thus, during this stage of the reaction the rate of monomer consumption decreases and mainly intermolecular crosslinking occurs. The transition from the first to

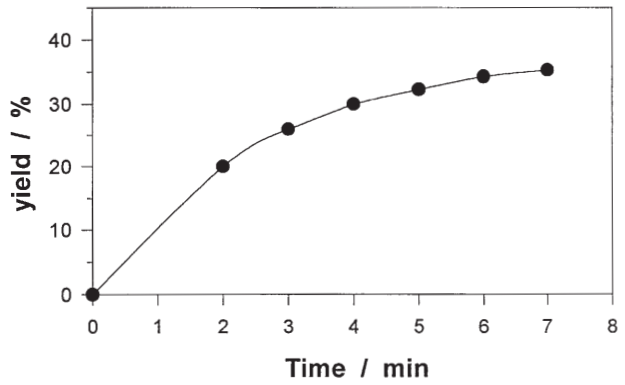


Fig. 53. Dependence of the polymer yield on the reaction time in the anionic polymerization of EDMA in toluene by n-BuLi [254]. Initial monomer and initiator concentrations are 78 g/L and 5.78 mol %, respectively. Reaction temperature = 20 °C.

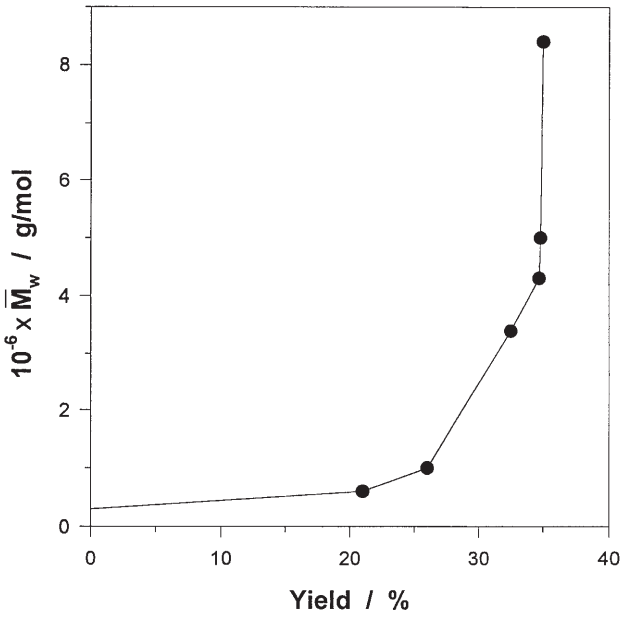


Fig. 54. Dependence of $\overline{M}_w$ of the microgels on the polymer yield in the anionic polymerization of EDMA in toluene by n-BuLi [254] (see Figure 53 caption for the reaction conditions).

the second reaction stage can also be induced by increasing the *n*-BuLi concentration at a constant reaction time. The gel-permeation chromatogram (GPC) of a polymer sample after a reaction time of 7 min shows a broad polymodal molar mass distribution that indicates various interparticle reactions (Fig. 55). Primary particles, which are formed during the first reaction stage, appear after an elution volume V_e = 28–33 ml and the aggregate up to 28 ml. The maximum at V_e = 23 ml, corresponds to a $\overline{M}_w$ of 10×10^6 g/mol for EDMA microgels but to only 0.8×10^6 g/mol for linear polystyrene. Thus, the structure of EDMA microgels is about 12 times more compact then that of a linear polymers with the same hydrodynamic volume [254].

From the experimental data, Straehle concluded that polymerization and crosslinking proceed at first within individual macromolecules which are separated by solvent molecules. Reactive EDMA microgels are formed by these reactions. From the content of pendant methacrylate groups of the microgels, it can be calculated that about half of the structural units of the microgels are involved in cycles. As the reactions proceeds, the microgel particles come into contact with each other and the free volume of the reaction mixture decreases, thus allowing interparticle reactions. It can be calculated that the free volume disappears after a reaction time of 4 min at a conversion of 32 %, which corresponds to the experimentally determined transition point from the first to the second reaction stage (Fig. 53).

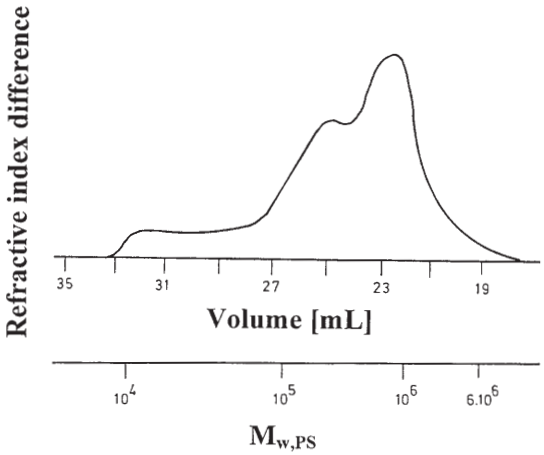


Fig. 55. Gel-permeation chromatogram(GPC) of a microgel sample of $\overline{M}_w = 10\times10^6$ g/mol obtained in the anionic polymerization of EDMA in toluene. Microgel concentration = 1 g/L; solvent = butyl acetate; elution temperature = 70 °C; is the weight-average molar mass of linear polystyrene used for comparison. [Reproduced from Ref. 256 with permission, Hüthig & Wepf Publ., Zug, Switzerland].

Pille et al. used living PBS chains to initiate the anionic polymerization of EGDM and 1,4-butanediol dimethacrylate. They obtained highly crosslinked microgels together with slightly branched oligomers of PBS of a low molar mass [260].

A comparison of the experimental data obtained in the anionic polymerization of EDMA, 1,4-DVB and 1,3-DVB shows the following characteristic features:

1) Almost linear polymers with pendant vinyl groups are formed as intermediates in the anionic polymerization of 1,4-DVB due to the different reactivities of monomers and pendant vinyl groups. 1,4-DVB microgels are formed towards the end of monomer conversion. In the anionic polymerization of EGDM or 1,3-DVB, reactive microgels are formed already at the beginning of the polymerization.
2) The content of pendant vinyl groups is 80–90 % in case of 1,4-DVB microgels but only 50–70 % and 50–60 % in cases of 1,3-DVB and EDMA microgels respectively. The extent of cyclization increases in the order 1,4-DVB < 1,3-DVB < EDMA.

7.4 Microgels from Other Divinyl Monomers

Only a few publications have appeared in which for the synthesis of reactive microgels other monomers were used than 1,4-DVB or EDMA. Hiller and Funke studied the anionic polymerization of 1,4-diisopropenylbenzene (1,4-DIPB) by *n*-BuLi in 1,2-dimethoxyethane and by sodium naphthalene in THF [231].

Although the initial monomer concentration was very high (25–200 g/l), soluble polymers were obtained even after complete conversion of DIPB. The measurements of the content of pendant isopropenyl groups indicated that poly(4-isopropenyl-α-methyl) styrene was formed.

Okamoto and Mita studied the anionic polymerization of 1,4-DIPB in THF [261]. They found the reactivity of the pendant vinyl groups by about three to four orders of magnitude lower than that of the vinyl groups of the monomers. Popov et al. compared the reactivities of 1,4-DVB and 1,4-DIPB in the reaction with polystyryl dianions in THF/benzene mixtures [262]. While addition of 1,4-DVB to the dianion solution caused an immediate macrogelation, no gel formation was observed on the addition of 1,4-DIPB. Anionic polymerization of 1,3-DIPB was also studied by several research groups [263–265]. They reported formation of low molar mass species.

8 Other Techniques for Microgel Synthesis

The instability of the growing end in the anionic polymerization of methacrylates requires very low polymerization temperatures which limits the practical applicability of this method. As an alternative, group transfer polymerization (GTP) was developed by Webster and co-workers [266]. This method is called GTP because it involves the repeated transfer of a trialkylsilyl group from the growing end to the arriving radical [266–269]. Lang et al. initiated the polymerization of EGDM by using poly(MMA) chains with active end groups, synthesized via GTP, and prepared EDMA microgels enveloped by poly(MMA) chains [270]. Schoettner studied GTP of methacrylates carrying various photostabilizers, e.g. 2,2,6,6-tetramethyl piperidine derivatives [271]. The active copolymer chains formed in this way were then used to initiate the polymerization of EDMA. The microgels thus obtained exhibited efficient photostabilizer properties.

Another method of microgel synthesis is crosslinking of an AB diblock copolymer with incompatible chain sections in a so-called selective solvent that is a good solvent for one part of the block and a non-solvent for the other. Since the diblock copolymers form polymer micelles in selective solvents, crosslinking of the core yields microgels with crosslinked core and a soluble shell. Ishizu and co-workers prepared polyisoprene and poly(4-vinyl pyridine) microgels by crosslinking diblock copolymers poly(styrene-β-isoprene) and poly(styrene-β-4-vinyl pyridine) respectively [44, 272–274]. Another route of microgel synthesis was reported by Antonietti et al. [275]. They terminated polystyrene chains bearing two reactive end groups with a tetrafunctional crosslinking agent in dilute THF solutions. The polymers obtained in this way had a more compact structure than linear polystyrene chains.

Microgels may also be produced by dispersion polymerization of multifunctional monomers [276, 277]. Kim et al. synthesized microgels by copolymerization of acrylamide with acryloyl terminated polyethylene glycol macromonomers in ethanol or in selective solvents [276]. The macromonomer acted

both as crosslinking agent and steric stabilizer for phase separated particles. Kiminta et al. synthesized microgels by emulsifier-free dispersion polymerization of *N*-isopropyl acrylamide and *N,N'*-methylene bisacrylamide in water [53]. Capek and Funke studied the dispersion polymerization of this bisacrylamide and its copolymerization with unsaturated polyesters [278–281]. It was shown that the formation of microgel particles proceeds via aggregation in the separated particle phase. The presence of internal or external emulsifiers increased the stability of particles.

9
Surface Modification of Microgels

Reactive microgels are suitable substrates for topochemical reactions, such as grafting, copolymerization with other monomers or other chemical modifications. The reactivity of microgels may be introduced by pendant vinyl or other reactive groups which have remained unreacted during the synthesis or by choosing comonomers with chemically different reactive groups from which one kind does not participate in the formation of microgels, e. g. acrylic acid or carboxyl-terminated unsaturated polyesters.

For special purposes the reactive groups may also be modified after the synthesis of microgels. In this case the reactive groups should be readily accessible to the reagent and the conversion should be as high as possible, to avoid nonmodified groups and by-products that cannot be removed afterwards through being bound to the microgel. Sometimes several reaction steps are necessary for surface modification., e. g. aldehyde groups after their introduction to the microgel surface for binding proteins must be chemically blocked for protection and freed again before the coupling reaction.

A very important requirement for the chemical modification of microgels is the accessibility of the reactive group to the reagent [282] and the limitation of the modifying reaction to the surface. Therefore, besides the high specific surface area, microgels should be densely crosslinked in order to restrict the modification to their surface. Such microgels may be prepared from 1,4-DVB. The pendant vinyl groups located at the surface of these microgels react as rapidly as corresponding reagents of low molar masses, whereas the reaction of vinyl groups in the interior is controlled by diffusion and therefore much slower (Fig. 47). From these reaction rates may be calculated that about 60% of the pendant vinyl groups have been used for crosslinking, 5% are in the interior are not accessible and 35%may be used for modification.

With slightly crosslinked microgels it becomes increasingly difficult to distinguish between vinyl groups located at the surface and those in the interior because the reaction at the surface overlaps that in the interior. In addition to the influence of crosslink density and swellability of microgels, the dimension of the reagent is also a determining factor for the location of modifying reactions. The modifying reaction can only then be unequivocally assigned to the microgel surface if the reagent is larger than the meshes of the microgel network.

9.1 Reactions for Modifying and Characterizing Surfaces of Microgels

Topochemical reactions may serve both the modification and the characterization of the microgel surface. Moreover, the determination of the reactive groups of microgels is a prerequisite for judging the success of the modifying reaction. These modifying reactions may be needed for various purposes, e.g. increasing the resistance against chemical aging or introduction of functional groups for technical applications.

9.1.1 *Characterization of Divinylbenzene Microgels*

Because of their insolubility, the restricted access of chemical reagents and the influence of the neighborhood on the mobility of chain segments and functional groups of crosslinked polymers, the determination of residual reactive or functional groups in crosslinked polymers is much more difficult than in linear or branched polymers. This is especially true for densely crosslinked polymers prepared from tetrafunctional monomers, such as DVB.

Non-reacted vinyl groups of these crosslinked polymers may be expressed by the residual unsaturation (RU). The RU is a measure for both the reactivity of the monomer and the structure of the crosslinked polymer. The RU may be determined by spectroscopic or chemical methods. For the spectroscopic determination a model compound of low molar mass is required as a reference for the standardization [217, 231, 254]. For the chemical determination a reagent of low molar mass is added to the pendant vinyl groups. Then the RU is obtained either by elemental analysis or by back-titration of the non-reacted reagent [231, 283–285].

The RU may be measured by following methods:
- quantitative ^{1}H-NMR-spectroscopy [231];
- quantitative infrared spectroscopy [54, 217];
- catalytic hydration and volumetric measurement of the consumption of hydrogen [231];
- reacting with mercury(II) acetate [283];
- ionic addition of hydrogen bromide and analytical determination of the bromine content [284];
- radical addition of butyl mercaptan and elemental analysis of the sulfur content [285].

Comparing the results of different methods, it turned out that RU strongly depended on the respective method [284, 286].

Values for RU differed by up to 100% with 1,4-DVB-microgels [286]. The reliability of methods for determining the RU of 1,4-DVB-microgels was checked [287] with poly(4-vinylstyrene) which was prepared by anionic polymerization of 1,4-DVB (Table 3). From these results, it can be concluded that only quantitative IR-spectroscopy is a reliable method for determining the RU of 1,4-DVB-

Table 3. RU of Poly(4-vinylstyrene) determined with different methods

Poly(4-vinylstyrene) No.[1)]	RU [%] determined by		
	IR-Spectroscopy	ICl-Addition	HBr-Addition
1	100.7	92.1	85.2
2	100.3	92.8	87.0
3	98.8	92.0	88.0
4	99.8	92.5	81.6
5	102.3	93.0	86.3

1) Samples 1-5 have been prepared with different inititator concentrations (0.26 - 0.78 mol % based on the monomer)

microgels. The RUs of 1,4-DVB-microgels obtained with IR-spectroscopy [287] were significantly higher than those of the other methods which are obviously too low (Table 4).

9.2 Aging of Divinylbenzene Microgels

The pendant vinyl groups of DVB-microgels, like the monomers, are still reactive and susceptible to unintentional reactions leading to irreversible agglomeration or aggregation. Such aggregates may already be formed during isolation and purification of microgels. During exposure of reactive DVB-microgels in solid state to air, insolubility often develops after 1–2 days. The reason for this insolubility is radical reactions between pendant vinyl groups of neighbored microgel particles.

Table 4. The RU of 1,4-DVB-Microgels determined with different methods

Poly(4-vinylstyrene) No.	RU [%] determined by		
	IR-Spectroscopy	ICl-Addition	HBr-Addition
1	72	60	45.1
2	62	62.5	48.3
3	49	53	45.6
4	70	58	55.0
5	62	56	52.8
6	60	58	48.6
7	62	57	52.2
8	62	57	48.0
9	59	56.5	53.3
10	60.3	58.2	50.2

These interparticle reactions can be avoided by a sterical blockade of the reactive groups with the help of suitable comonomers [135] or by formation of a core-shell structure of microgels, by which the reactive groups are covered with a shell [244, 248]. It is also possible to add silanes to the vinyl groups [221]. By adding *n*-butyl mercaptan and small amount of initiator the pendant vinyl groups of previously isolated microgels may be completely saturated without changing the molar mass and viscosity of the microgels [285]. Thus, modified microgels are chemically stable and may be stored and handled without a change of their molar mass.

9.3 Introduction of Other Functional Groups in Microgels

The pendant vinyl groups at the surface of microgels can be modified in various ways according to the purpose of their application.

9.3.1 *Surface Modification by Hydroxy Groups*

By hydroboration [288, 289], pendant vinyl groups of microgels are almost quantitatively converted to hydroxyethyl groups [290]. Because the reagent has a small size it may also react with vinyl groups in the interior. Hydroboration of vinyl groups is faster than the reaction with mercury(II) acetate. Whereas the latter reaction is still not complete after 120 h, hydroboration is already quantitative after 24 h. After hydroboration, the surface properties of the microgels had changed and the microgels were insoluble in solvents in which they could be dissolved before. It was assumed that larger aggregates were formed, although not necessarily by covalent bonds because a redispersion to a colloidal solution was possible after an ultrasonic treatment [291].

9.3.2 *Surface Modification by Epoxide Groups*

For introducing epoxide groups, 1,4-DVB microgels were reacted with *m*-chloroperbenzoic acid. Unlike the conversion of vinyl groups to hydroxyl groups, only about 70 % of the vinyl groups could be converted to epoxy groups. The modified microgels were isolated from a non-aqueous solution to avoid agglomeration [291].

9.3.3 *Surface Modification by Ozone*

Vinyl groups of 1,4-DVB microgels have been converted to carboxylic acid groups by ozone [291]. After modification the microgels could be dissolved in methanol. About 83 % of the vinyl groups could be converted. A simpler way to prepare microgels with carboxyl acid groups at their surface is the copolymerization of DVB with methacrylic acid in an aqueous emulsion [292].

9.3.4
Surface Modification by Dye Molecules

For binding dye molecules to the surface of 1,4-DVB microgels, at first hydrogen bromide was added to the pendant vinyl groups and then a basic dye was reacted with the bromide group by a nucleophilic substitution [284, 293]. Table 5 shows the relationship between bromine content of microgels, conversion and amount of dye bound to the surface. The smaller the content of bromide groups, the larger was the fraction substituted by dye molecules. The decrease of the conversion has been explained by the hindrance of vinyl groups in the interior to react. Experiments with different nucleophilic dyes showed that the substitution depended on the basicity and on the dimensions of the molecules (Table 6). Whereas the brominated microgels could still be dissolved in benzene, dioxane or dichloromethane, for dye-modified microgels more polar solvents such as nitrobenzene were needed.

9.3.5
Modification by Polymer Analogous Esterification

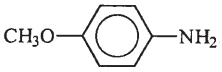
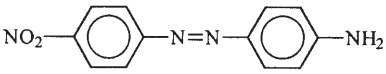
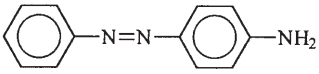
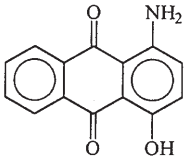
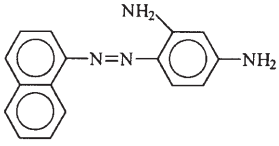
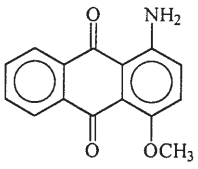
In self-emulsifying copolymerization of unsaturated polyesters and comonomers the terminal unsaturated groups of EUP are deactivated by the adjoining dissociated carboxyl acid group. By esterification of these acid groups the terminal unsaturated polyester units become active again. Moreover, an agglomeration of the microgels by hydrogen bonding between the particles may thus be prevented.

Ester formation by dimethylsulfate or diazomethane is not satisfactory because the microgels become insoluble when the reaction proceeds to higher conversions. With diazomethane part of the unsaturated groups is involved in a side reaction of a 1,3-dipolar cycloaddition [132]. A more efficient method for ester formation of microgels is the reaction with *O*-alkyl-*N,N*'-bisisopropyl isoureas of the alcohols. The alkyl ureas are easily separated from solutions in methanol [294–296]. The esterified microgels were isolated by precipitation and freeze-drying. Depending on the alcohol used for ester formation, the yields of

Table 5. Reaction of 4'-Nitro-1-aminoazobenzene with 1,4-DVB-Microgels of different bromide content.

Bromide content per unit [mol-%]	Conversion based on the bromide content [%]	Dye bound to the surface [mg /g polymer]
9.5	57	99
13.5	46	116
22.1	43	177
27.9	37	193

Table 6. Reaction of HBr-modified 1,4-DVB microgels with different dye molecules. (Br-content: 2.1 mmol/g, ∅ : 9 nm, specific surface: 630 m^2/g, reaction conditions: 40 h, 60 °C, solvent: ethanol)

Nucleophile	Conversion based on the bromide-content [%]	Bound nucleophile [mmol/g]
	45.0	0.94
	37.5	0.79
	36.0	0.76
	33.0	0.69
	26.0	0.55
	18.5	0.39

esterified microgels were between 60 and 80% [297]. Esterified microgels with short-chain alcohols are soluble in dioxane. Microgel esters with longer-chain alcohols may be dissolved in a mixture of dioxane and water. In all cases ester formation was quantitative, although molar masses and particle diameters indicated that some soluble agglomerates had been formed.

9.4 Synthesis and Modification of Microgels for Biochemical Purposes

As carriers for proteins and enzymes biocompatible reactive microgels must be synthesized which are soluble in the serum at 37 °C. Moreover they should be hydrophilic enough that no ionic monomers are needed but they should not be soluble in water. An inert comonomer should serve as a spacer as well as a reactive solvent that may dissolve solid comonomers. The coupling reaction should be possible under mild reaction conditions.

For using microgels as carriers of biological materials specific chemical groups (e.g. aldehyde groups) must be available at their surface which guarantee mild reaction conditions in aqueous media for coupling biomaterials. For this purpose, microgels must be soluble in water and their surface should be hydrophilic. Moreover, for diagnostic purposes DVB microgels are too small. The microgels have been prepared by copolymerization of functional comonomers in solution and in emulsion.

9.4.1 *Functional Comonomers*

Aldehyde groups are useful for binding proteins to polymers, e.g. via ϵ-lysine amino groups. However, the formation of semi-acetals and the oxidation of aldehyde groups during polymerization impose some problems. To avoid the formation of semi-acetals either copolymerization with an inert monomer as "spacer" or the use of a monomer with an aldehyde group at its "spacer arm" is indicated. Aldehyde groups can be protected by acetal formation [298, 299]. For aqueous ECP, monomers are needed which are insoluble in water such as di-*n*-pentylacetals [291]. These acetals are stable during ECP. A disadvantage of the acetal groups is the fact that they cannot be partially transformed into aldehyde groups necessary for binding proteins. Therefore, it is not possible to study how the bound molecules influence the residual bioactivity of bound enzymes. A possibility to vary the number of aldehyde groups in a polymer by choice is their copolymerization with acrylic- or methacrylic acid-2,3-epoxy propylesters [300–307]. However, most enzymes are denaturized because most functional groups of the proteins react with epoxide groups. Because glycidyl methacrylate causes some additional problems [291], N-substituted acryl- and methacrylamides have been synthesized with a 1,3-dioxolan group which is a protected diol group. These comonomers are not soluble in water, and after the ECP the dioxolane ring is easily opened to form the diol [308].

Microgels prepared in that way are hydrophilic, stable and do not tend to agglomerate. By oxidation of the diol group with sodium periodate a free alde-

hyde group is formed which is firmly bound to the microgel surface. As crosslinking comonomers, bisacryl- and bismethacrylamides are suitable [291].

9.4.2
Copolymerization in a Homogeneous-Aqueous Solution

For this reaction, soluble monomers are needed, e.g. a mixture of *N N*'-methylene bisacrylamide as crosslinker, methacrylamide as an inert comonomer, methacrylic acid as ionic comonomer for stabilization [309] and methacryl amido-*N*-acetaldehyde-dimethylacetal as functional comonomer. The coupling with proteins is only possible if the free aldehyde groups are accessible, i.e. if they are not located in the interior of the microgel. This condition can only be fulfilled by a careful choice of the comonomer composition in the reaction mixture [291].

Compared with rigid microgels, the intrinsic viscosity of microgels prepared from the comonomer mixture mentioned before is higher, but the slope of the curve in Fig. 56 is still low because the composition of these microgels was close to the limit of stability.

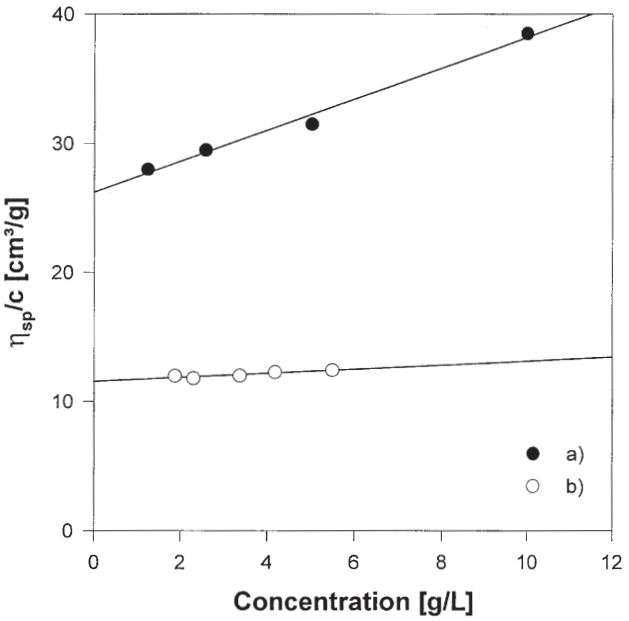


Fig. 56. Dependence of $\overline{M}_w$ of the microgels on the polymer yield in the anionic polymerization of EDMA in toluene by n-BuLi [254] (see Figure 53 caption for the reaction conditions). Reduced viscosity vs concentration of microgels a) Composition (mol %): N,N'-methylenebisacrylamide (55%), methacrylamide (33%), methacrylic acid (2%), methacrylamido acetaldehyd-dimethylacetal (10%), measured at 20 °C in water. b) Composition (mol %): 1,4-DVB (35%), propenic acid amide-2-methyl-N-(4-methyl-2-butyl-1,3-dioxolane prepared by emulsion copolymerization and measured in dimethylformamide.

9.4.3
Copolymerization in an Aqueous Emulsion

Microgels as carriers of biomaterials may also be prepared by copolymerization in an aqueous emulsion. For this purpose, besides the crosslinker a functional comonomer is used which, in addition to a polymerizable vinyl group, also contains a precursor for the aldehyde function. Microgels from ethylene dimethacrylate and methacrylic acid-2,3-epoxypropylester in a molar ratio of 2:3 had a mean diameter of around 50 nm and a specific surface area of 107 m^2/g [291]. After opening of the epoxide ring these microgels are rather stable. After purification, colloidal solutions in water or in mixtures of water and ethanol, dioxane or acetone are obtained. These microgels are sufficiently hydrophilic to allow coupling with various proteins under mild reaction conditions.

Microgels prepared by aqueous ECP of DVB and propene-acid amide-2-methyl-*N*-(4-methyl-2-butyl-1,3-dioxolane [308] had a molar mass of $\overline{M}_w = 1.4 \times 10^7$ g/mol and a mean particle diameter $d_z = 66$ nm. These microgels have a compact structure with a coil density in water of 0.16 g/cm^3 and an intrinsic viscosity $[\eta] = 11.8$ cm^3/g with a very low slope of the η_{sp}/c-curve (Fig. 56) [291]. After splitting off the protective acetal groups, very stable aqueous solutions of microgels are obtained. After proteins are coupled to such microgels, the -C=N-group has to be reduced to a -CH-NH-group.

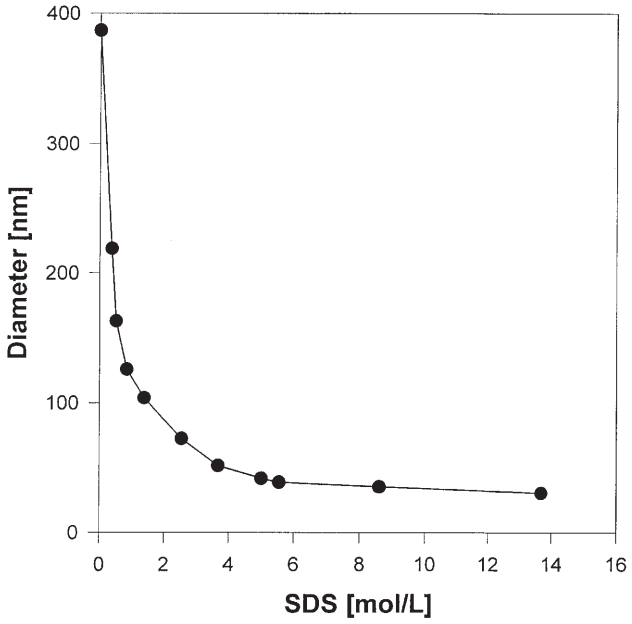


Fig. 57. Diameters of microgels prepared with different emulsifier concentrations (SDS). Composition (mol %): N,N'-tetramethylenebismethacrylamide (10 %), N-n-hexylmethacrylamide, propenic acid amide-N-(4-methyl-2-butyl-1,3 dioxolane (50 %)

A microgel of a $\bar{d}_z = 76$ nm which is suitable for coupling with proteins, can be prepared by emulsion terpolymerization of *N,N'*-tetramethylene bisacrylamide, *n*-hexylmethacrylamide and propene acid amide-*N*-(4-methyl-2-butyl-1,3-dioxolane) [291]. The diameter of these microgels may be varied by the concentration of the emulsifier (Fig. 57) and is rather uniform. As the CMC of this system is about 2.5×10^{-3} mol SDS/l, it may be assumed that below this value the copolymerization essentially takes place in the monomer droplets, whereas at higher concentrations of SDS preferentially the monomers in micelles are polymerized.

10 Applications of Microgels

Discussing applications of microgels for industrial purposes, it is interesting that microgels are formed unintentionally in the synthesis of elastomers and alkyd resins. Due to the presence of potentially crosslinking isoprene and butadiene units in elastomers some intramolecular crosslinking takes place, probably also involving radical transfer reactions [6]. The detection, isolation and characterization of these microgels in elastomers has been reported [310–312], as well as their influence on the mechanical properties of the elastomers [313, 314] and the conversion of microgels to macrogels [315].

Microgels have also been detected as a component of alkyd resins, an early but still important binder of organic coatings [316–321] and are accountable for their ability to fill pores, fissures and other irregularities of the substrate such as wood. This property may be explained by the size of the microgels which prevents the paint becoming soaked up by the substrate.

These examples show that microgels already played a role in the properties of important industrial polymers before they were intentionally added as a component. The more significant applications of microgels may be summarized as:

1) components of binders for organic coatings;
2) carriers of dyes, pharmaceuticals and biochemical compounds;
3) fillers and materials for reinforcing plastics.

10.1 Organic Coatings

The most important industrial application of microgels are organic coatings where they serve as a component of the binder. The advantage of microgels in the formulation of paints is their low viscosity. This property which allows formulations with high contents of solids have microgels in common with latex particles obtained by normal emulsion polymerization of bifunctional monomers. However, due to the much smaller size and compact structure of microgels, they can be dissolved in water or in organic solvents to form colloidal solutions whereas latex particles are only dispersible as emulsions or latices. Binder compositions containing microgels are often rather complex in order to comply with the requirement of application and performance.

Probably the first suggestion to use microgels, especially reactive ones, for organic coatings goes back to 1977 [322] when it was indicated that they might be suitable for preparing paints with high contents of solids and of low viscosities [323].

Crosslinked acrylic microgels in aqueous and non-aqueous media were patented as paint constituents in 1979 to improve the orientation of aluminum flake pigments, restrict the flow of the liquid coating on the substrate and restrict sagging [324]. As the patent speaks of emulsions, insolubility of the microgels and particle sizes up to 200 nm, it is questionable whether these polymers consisted of microgels only.

The industrial production and application of reactive and non-reactive microgels in organic coatings such as binders or components of binders, e.g. together with, e.g. acrylic and/or melamine/formaldehyde resins, especially for automotive coatings, was reported in a number of publications between 1980 and 1990 [325–333].

Special properties and advantages of using microgels as binder component for both aqueous and non-aqueous paints and coatings such as the decrease of sagging, the orientation of flake pigments, the increase of tensile strength, the low viscosity, the adjustment of the rheological behavior (Newtonian or pseudoplastic flow, depending on the microgel concentration), the increase of abrasion resistance, antiblocking properties, control of surface properties, the reduction of shrinkage, an increase of the permeability for water where needed, and an adjustment of the hiding power have been mentioned as the benefits of special paint formulations [334–338].

Acrylic microgels can be prepared as non-aqueous dispersions (NAD) and aqueous dispersions for the formulation of high solid paints for basecoats [339, 340]. The intramolecular crosslinking was achieved by the addition of triethylenediamine which reacts with linear acrylic terpolymers containing glycidyl methacrylate units or by incorporation of allyl methacrylate or hexamethoxymethylmelamine. Such microgels assist the rheological control during the application of thermosetting acrylic metallic finishes by improving the alignment of flake pigments which is needed to obtain the "flop effect" characteristic of metal effect coatings.

Other NAD microspheres are composed of styrene, MMA, hydroxyethyl acrylate, acrylic acid and acrylonitrile and are blended with acrylic copolymers and melamine/formaldehyde resins [341, 342]. Particles of this polymer are used as rheology modifiers to prevent sagging in automotive coatings and for controlling the orientation of metal flake pigments.

However, some doubt exists whether these dispersions really contain microgels only because their insolubility was emphasized and the range of particle size mentioned was up to 10 μm.

The question whether the intramolecularly crosslinked microparticles of non-aqueous polymer dispersions are really microgels is also justified, considering non-aqueous dispersions prepared from acrylic copolymers and melamine/formaldehyde crosslinker with particle sizes of about 300 nm. [45, 343]. In any case, these crosslinked polymeric microparticles are useful constituents of high-solids coatings, imparting a yield stress to those solutions which probably involves attractive forces between the microparticles.

Use of NAD microgels with a low glass transition temperature improved the mechanical performance, durability and resistance against blistering of coatings for household and industrial buildings [344, 345].

Crosslinked polymer particles with a rather complex structure, which have also been designated by the name microgels and recommended as components of metal effect paints, consist of carboxyl-terminated oligoesters of 12-hydroxy stearic acid which were reacted with glycidyl methacrylate, subsequently copolymerized with MMA and hydroxymethyl methacrylate and then crosslinked by hydroxy melamine [346].

Microgels with an acrylic core for waterborne base coats have been reported to resist the attack of subsequent clear coats, exhibit mechanical toughness and flexibility and have a good durability and chemical resistance [347].

Rheological properties of microgels used in automotive coatings have been reviewed and discussed in [348].

Following the knowledge of microgels as constituents of alkyd resins, microgels have been prepared from a maleinized alkyd resin which was copolymerized and crosslinked with 1,6-hexanediol diacrylate. [349]. Coatings from these microgels have increased, and are harder and more resistant to water. When blended with water-soluble resins air-drying coating materials are obtained which can be applied by airless spraying and give coatings with increased tensile strength.

Microgels can not only be synthesized by polymerization but also by polycondensation or polyaddition [350]. In an early work on crosslinking of single linear macromolecules, it could be shown that if a crosslinking agent, such as terephthal dialdehyde, was added to a very dilute solution of a linear polymer such as polyvinyl alcohol, almost exclusively a intramolecular crosslinking of the individual macromolecules took place [351].

Colloidal particles have been detected in thermosetting resins [352] and the production of particulate phenolic resins, albeit of larger sizes than microgels, has also been reported [353].

Microgels have been prepared from epoxy resins which were intramolecularly crosslinked by a polyalkylene polyamine/polycarboxylic acid for flexible, corrosion resistant coatings [354].

Microgels have been also synthesized using isocyanates or polyurethanes [355, 356] and by polycondensation of silanes [357–360]

10.2 Microgels as Carriers for Dyes

Due to their large surface area and the reactive groups located there, microgels may be used as carriers [362] and substrates for various purposes. The idea to bind dye molecules covalently to surfaces was realized first with reactive dye molecules [322]. Functionalized dye molecules were copolymerized by radicals with other monomers to obtain colored plastics, from which no dye molecules could migrate. Likewise it is possible to bind organic dye molecules covalently to the surface of microgels, thus obtaining colored organic pigments [284, 361–363].

Larger crosslinked polymer particles were prepared earlier for application as pigments [364].

For the synthesis of these pigments the dye molecules must possess a high light fastness. The colors are not very bright, and because of the thin dye layer these pigments are more susceptible to an oxidative photodegradation than normal pigments.

10.3 Microgels as Substrates for Biomedical and Diagnostic Purposes

Microgels may be used as substrates and carriers for enzymes and antibodies [291, 308, 365–371]. These agents may be covalently bound to the surface of suitable microgels and thus may easily be separated from the reaction mixture. As the amount of the reagent can be used in excess, the reaction equilibrium is shifted to the products and higher yields are obtained. For some diagnostic and therapeutic applications such as drug targeting, it is necessary that carriers have small, submicroscopic dimensions in the range of nanometers [372–374]. Therefore, microgel with sizes below 100 nm are specially suitable for these purposes. For such small particles the reticular endothelial system is penetratable.

Proteins may be bound to microgel surfaces by various reactions directly or via a spacer [375]. A suitable group, which can be introduced to the microgel surface, is the aldehyde group which reacts with the amino group of a protein. Then the resulting azomethine is reduced (see Sect 9.4). For modifying the microgel surface with aldehyde groups, they must be intermediately protected.

To avoid losses of the protein activity and to increase the stability of the microgel the protein may be coupled with a spacer, e.g. enzymatically cleavable oligopeptides. Like in the case of direct coupling, the oligopeptide is first bound to the microgel surface by the reaction between an aldehyde group of the microgel and an amino group of the oligopeptide. After the reduction, the protein is bound to the spacer by the reaction of its acid group with the amine group of the protein. For this reaction the carboxyl acid group is activated by carbodiimide [308]. The use of a spacer also prevents a direct contact of the protein with the microgel surface and thus denaturation. Moreover the active site of the protein is more easily accessible.

The amount of enzyme which can be bound to microgels depends on the structure of the enzyme. Enzymes with a higher isoelectric point are better bound to negatively charged microgels. It is also possible to bind sensitive enzymes such as lactate dehydrogenase or proteinase K to microgels with high yields and high residual activity [365, 366, 375].

An immuno assay for α-1-fetoprotein has been developed with microgels by binding antibodies to their surface [291, 375]. With corresponding antigenes in solution these microgels aggregate to form much larger particles which can be detected by photon correlation spectroscopy.

An essential prerequirement for the aggregation is the presence of different epitopes on the antigenes so that their functionality is greater than one. Reversible bridging flocculation of poly(lysine) with acrylic microgels has also been reported [376].

10.4 Microgels as Fillers

Reactive microgels may be incorporated into plastics by covalent bonds. It could be demonstrated that substantial amounts of polymer chains from bifunctional monomers can be attached at microgel surfaces and thus become insoluble [313, 377–380].

An interesting way to prepare shock-resistant coatings [381] follows the synthesis of the ABS-terpolymers, e.g. shock-resistant polystyrene, where a soft, elastomeric phase is incorporated in a hard polymer matrix via covalent bonds. Because organic coatings solidify in situ, elastomeric microgels have been synthesized and mixed to a binder which forms the hard matrix phase before the application of this mixture as a coating material.

Epoxy resins have been toughened by in situ copolymerization of microgels consisting of unsaturated polyesters and bifunctional comonomers [382, 383].

11 Concluding Remarks

For a long time crosslinking reaction steps in the polymerization of unsaturated monomers have been considered to lead inevitably to insoluble polymer materials, even with small amounts of the crosslinking component. Moreover, small crosslinked polymer particles were a nuisance in the production and characterization of polymers as unpredictable products of side reactions.

Experimental and analytical studies over the past 25–30 years revealed that microgels are intramolecularly crosslinked macromolecules, which represent a new class of polymers besides linear and branched macromolecules and crosslinked polymers of macroscopic dimensions. In some ways microgels may be considered as a transition from molecules to larger polymer particles or macroscopic polymer materials.

Microgels are distinguished from linear and branched macromolecules by their fixed shape which limits the number of conformations of their network chains like in crosslinked polymers of macroscopic dimensions. The feature of microgels common with linear and branched macromolecules is their ability to form colloidal solutions. This property opens up a number of methods to analyze microgels such as viscometry and determination of molar mass which are not applicable to the characterization of other crosslinked polymers.

Similar to macroscopic polymer networks, microgels have a more or less fixed surface. Due to the large value of their surface/mass ratio, microgels may be used as models for studying topochemical reactions at polymer surfaces.

The reactivity of microgels depends on the kind and composition of their monomer components and can be varied over a wide range. The reactive groups of microgels at their surface are useful for modifying reactions but also make them susceptible to interparticle crosslinking which leads to the formation of insoluble and irreversible agglomerates or aggregates. By careful choice of polymerization conditions, the formation of larger, insoluble polymer particles can be avoided.

The mechanism of crosslinking emulsion polymerization and copolymerization differs significantly from linear polymerization. Due to the gel effect and, in the case of oil-soluble initiators, monomer droplets polymerize preferentially thus reducing the yield of microgels. In microemulsion polymerization, no monomer droplets exist. Therefore this method is very suitable to form microgels with high yields and a narrow size distribution, especially if oil-soluble initiators are used.

Microgels which have been prepared in emulsions or microemulsion have a more compact structure than those obtained by polymerization in solution. For microemulsion copolymerization, preferentially self-emulsifying comonomers, such as unsaturated polyesters, are used as polymerizable surfactants, because no emulsifier must be removed after the reaction. By choosing suitable monomer combinations the composition, size and structure of microgels can be widely varied, thus adjusting these macromolecules to special applications.

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