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Formation and structural characteristics of loosely crosslinked styrene-divinylbenzene networks

Dedicated to Prof. *W. Funke* on the occasion of his 60th birthday

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SUMMARY:

The free-radical copolymerization of styrene with small quantities of a commercial DVB (conc.: 0,35 to 0,53 mol-% DVB) was carried out at 70 °C in bulk or in concentrated toluene solution. The extent of the crosslinking reactions beyond the gel point and the structural characteristics of the resulting networks were examined using equilibrium swelling in toluene and gel fraction measurements. The copolymerization reactions yield loosely crosslinked networks together with varying amounts of soluble polymer. The experimental results concerning the formation of the networks and their properties can be explained using the kinetic mechanism of the copolymerization reaction and neglecting cyclization. At a low degree of initial dilution, two opposing effects of the diluent, namely dilution and plasticizing effects, were found to determine the properties of the networks. Calculations using the theory of rubber elasticity indicate that considerable amounts of free chain ends are present in the networks. The crosslinking efficiency was found to decrease, but the size of the primary chains and that of the network chains increase with increasing degree of initial dilution.

Introduction

Since the pioneering work of network formation in the styrene-divinylbenzene (S-DVB) system by Staudinger[1)], the preparation of these copolymers and their properties have been the subject of a large number of studies[2–13)]. Properties of S-DVB copolymers are known to depend on their structure, and the latter is closely related to the network formation process. During the S-DVB copolymerization, the reaction of DVB molecules with the growing radicals results in the formation of pendant vinyl groups on the chains. The reaction of these vinyls with other chain radicals, namely the crosslinking reaction, is responsible for gelation and network formation. It is known that these copolymerization and crosslinking reactions occur simultaneously, and at any stage of the copolymerization, the DVB units are found to be incorporated into the polymer via one or both vinyl groups. Gelation occurs after a certain conversion, i.e., at the gel point, at which the average number of DVB units per "primary chain" with both vinyl groups reacted reaches the value 2. Beyond the gel point, a large number of soluble, branched polymer chains are still present in the

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system, and they become connected to an infinite network as the crosslinking reactions proceed. The network formation process ends at the total conversion of vinyl groups, or at the vitrification point, at which the reaction temperature becomes equal to the glass transition temperature of the polymerization system.

Previous studies have shown that the mechanism of network formation in S-DVB system and the properties of the resulting networks differ appreciably from ideal systems[8,9)]. For instance, the classical gelation theories of Flory and Stockmayer cannot be applied to S-DVB copolymerization due to the unequal vinyl group reactivities of the monomers[14)]. Cyclization reactions leading to the formation of intramolecular links and, at high DVB contents, to microgel-like particles with "frozen" vinyls also cause deviation from theory[7,15-17)]. The structure of S-DVB networks also differs from the ideal polymer networks because of network imperfections such as dangling chains (free chain ends), closed loops and permanent chain entanglements[8)]. Furthermore, the length of the network chain in S-DVB copolymers fluctuates around its mean value due to the unequal reactivities of the monomers[8)]. Consequently, the fraction of very short chains, which is likely to be non-Gaussian, does not afford an ideal system for testing the existing theories of rubber elasticity. In some cases, syneresis may occur during the crosslinking reaction, if the amount of diluent present in the gel exceeds the maximum swelling capacity of the gel, leading to the formation of heterogeneous structures[9,18)]. Such deviations from ideal network systems have been studied repeatedly[9)].

The present work deals with the synthesis of S-DVB copolymers with minimal network defects by free-radical copolymerization to allow application of the current theories of network formation of rubber elasticity. For this purpose, the free-radical S-DVB copolymerization was carried out in the bulk, or in concentrated toluene solution, with small quantities of a commercial DVB (a mixture of *m*- and *p*-DVB isomers and ethylvinylbenzene). The extent of crosslinking beyond the gel point and the structural characteristics of the resulting networks were examined using the equilibrium swelling in toluene and gel fraction measurements.

Toluene is a good solvent for polystyrene, and its thermodynamic properties are the same as for the monomers used in the copolymerization[19,20)]. Accordingly, the gels obtained in this study are expected to be homogeneous. For the DVB concentrations used, namely 0,35 to 0,53 mol-% DVB, cyclization reactions can be neglected, because there will be very few DVB units in the growing chains. Thus, the usual copolymerization rate equations can be applied to this system, with some major simplifications such as neglecting the concentration of radicals having a DVB terminal unit[21)]. A new kinetic model developed by Mikos et al. was employed for the prediction of the gel point, monomer conversions and number-average molecular weights[22-24)]. The average number of styrene units between successive junctions of the network, calculated from stochiometry as 100 to 150, indicates that the networks should be Gaussian. Consequently, the molecular theory of rubber elasticity can be applied to these networks to evaluate their equilibrium swelling data[25,26)]. The results of the calculations give the structural characteristics of S-DVB networks and their dependence on the degree of initial dilution and on the DVB concentration.

Experimental part

Chemicals: Styrene (PETKIM, Turkey) and commercial DVB (Merck) were shaken with 10% NaOH, washed with water, dried with anhydrous $CaCl_2$, and finally distilled under reduced pressure. Purity was checked by gas chromatography. Various batches of commercial DVB solution were used, each with a known content of DVB isomers. Batch analyses ranged between 55 and 60% DVB isomers (*m*-DVB: *p*-DVB ratio 3 – 3,2 : 1), the rest being ethylvinylbenzenes, and non-polymerizable compounds (<2%). Benzoyl peroxide (Merck) was recrystallized from acetone solution. The diluent, toluene (Merck), was used as received (>99% purity).

Copolymerization: The radical copolymerization of styrene and commercial DVB was performed at 70 °C in bulk or in toluene solution. Benzoyl peroxide as an initiator (2,83 wt.-% in relation to the monomers) was dissolved in the selected monomer-toluene mixture, and this was divided and transferred into a series of glass tubes. The glass tubes were degassed, sealed under vacuum and placed in a thermostat at 70 ± 0,5 °C for a predetermined polymerization time. Homologous series of S-DVB networks were prepared in this way allowing systematic variation of the DVB and toluene concentrations. The initial composition of the gels prepared are given in columns 1 and 2 of Tab. 1. The content of the DVB isomers is expressed in mol-% of total monomers, and the degree of initial dilution as the volume fraction of the monomers in the monomer-toluene mixture (v_2^{00}).

Extraction of the sol fraction: Toluene was chosen as the extraction solvent and employed at room temperature. The crude gels, 5 mm in diameter, were cut into samples of 10 to 25 mm length. In order to remove the sol fraction, each sample was placed in an excess of toluene, and the solvent was replaced every other day over a period of 3 weeks until no further extractable polymer could be detected. The networks after extraction were carefully deswollen in a series of toluene-methanol mixtures with increasing methanol contents. They were then washed several times with methanol and dried at room temperature under vacuum to constant weight. The amount of soluble polymer in toluene solution was determined gravimetrically after evaporation and precipitation in methanol. The weight fraction of polystyrene chains incorporated into the network, i.e., the weight fraction of the gel W_g, was calculated as

$$W_g = \frac{g}{g + s} \tag{1}$$

where *g* and *s* are the weights of extracted network and soluble polymer, respectively.

Swelling measurements: The swelling measurements were carried out in toluene at room temperature. In order to reach the equilibrium degree of swelling, the networks were immersed in toluene for at least 3 weeks; the swelling equilibrium was tested by weighing the samples. To achieve good precision, three measurements were carried out on samples of different weight taken from the same gel. The networks were then weighed in the swollen state and dried under vacuum to constant weight.

The extent of swelling was characterized by v_2, the volume fraction of polymer in the swollen gel, which was calculated as

$$v_2 = [1 + (q_w - 1)\rho/d_1]^{-1} \tag{2}$$

where q_w is the ratio of the *weights* of the gel in the swollen state and the dry state, ρ and d_1 are the *densities* of polymer and solvent, respectively. The values for ρ and d_1 used are 1,08 $g \cdot cm^{-3}$ and 0,867 $g \cdot cm^{-3}$ (at 20 °C), respectively.

Results and discussion

Network formation

The weight fraction of polystyrene chains incorporated into the network, W_g, is given in Fig. 1 (A) as a function of the polymerization time for copolymers prepared

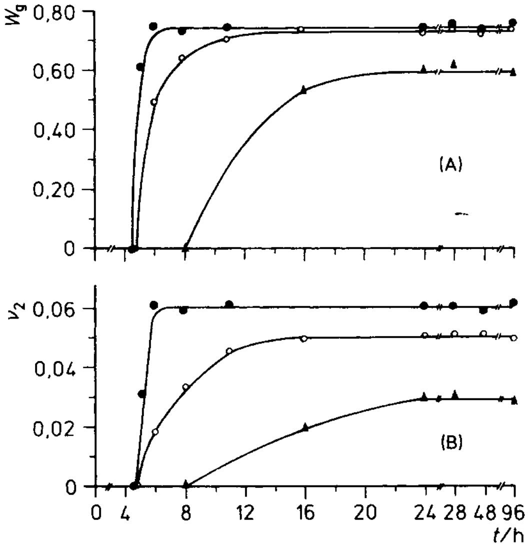

Fig. 1. Weight fraction of gel W_g (A) and equilibrium swelling values v_2 (B) shown as a function of the polymerization time t for 0,35 mol-% DVB. v_2^{00} = 1,000 (●); 0,833 (○); 0,714 (▲)

Tab. 1. Synthesis conditions, elastomeric properties and structural characteristics of S-DVB networks[a)]

DVB in mol-%	v_2^{00}	W_g	v_2	$\frac{[f^*]_{ph}}{N \cdot mm^{-2}}$	x_c	$\frac{10^5 \cdot (\mu/V_0)}{mol \cdot cm^{-3}}$
0,35	1,000	0,739	0,060	0,0161	97	3,50
0,39	1,000	0,745	0,064	0,0185	95	3,61
0,46	1,000	0,810	0,090	0,0384	81	4,30
0,53	1,000	0,847	0,105	0,0541	73	5,10
0,46	0,909	0,833	0,089	0,0375	53	6,52
0,53	0,893	0,874	0,109	0,0588	48	7,45
0,35	0,833	0,731	0,050	0,0111	91	3,65
0,39	0,833	0,728	0,056	0,0140	88	3,83
0,46	0,833	0,812	0,079	0,0289	77	4,59
0,53	0,833	0,859	0,098	0,0463	68	5,40
0,35	0,769	0,644	0,036	0,0058	115	2,85
0,39	0,769	0,690	0,046	0,0094	109	3,08
0,46	0,769	0,763	0,065	0,0191	97	3,61
0,53	0,769	0,833	0,083	0,0322	85	4,30
0,35	0,714	0,592	0,029	0,0038	138	2,36
0,39	0,714	0,624	0,034	0,0051	134	2,46
0,46	0,714	0,755	0,057	0,0145	116	3,01
0,53	0,714	0,797	0,071	0,0230	104	3,48
0,35	0,667	0,516	0,019	0,0017	—	—

[a)] DVB: mole percent of DVB isomers relative to total monomers, v_2^{00}: volume fraction of monomers in the initial monomer-toluene mixture, W_g : weight fraction of the gel, v_2 : volume fraction of polymer in the swollen gel at equilibrium in toluene, $[f^*]_{ph}$: phantom reduced force of the networks swollen in toluene, x_c : average number of segments between successive junctions of the networks, (μ/V_0): number density of junctions in the networks.

at 0,35 mol-% DVB and at different degrees of dilution. For the same copolymers, the plot of equilibrium v_2 values vs. the polymerization time is shown in Fig. 1(B).

In the absence of diluent, gelation occurs after 4,5 – 5,0 h. Beyond the gel point, both W_g and v_2 increase abruptly and reach constant values after similar times (6 h). The limiting value of the gel fraction corresponds to 0,739 indicating that 26% of the polymer chains are not incorporated into the network; they act as a polymeric diluent during the crosslinking reactions. Fig. 1 also shows that gel formation is retarded with rising dilution; thus, W_g and v_2 decrease as the dilution increases. Furthermore, the initial slopes of the curves indicate a decrease in the rate of the crosslinking reactions with increasing dilution.

The limiting values of W_g and v_2 of copolymers prepared at different degrees of initial dilution, and at various DVB concentrations, are collected in columns 3 and 4 of Tab. 1 and in Fig. 2. The networks prepared in more diluted solution, or at lower DVB concentration, clearly exhibit larger degrees of swelling and lesser gel fractions. Moreover, it is interesting to note that the values of W_g as well as those of v_2 do not change, or increase only slightly, with increasing dilution from $v_2^{00} = 1,00$ to 0,90 (v_2^{00} is the volume fraction of the monomers in the initial monomer-diluent mixture).

All the experimental data shown in Figs. 1 and 2 are collected in Fig. 3 as the dependence of W_g on the corresponding v_2 values. It can be seen that the plot of W_g

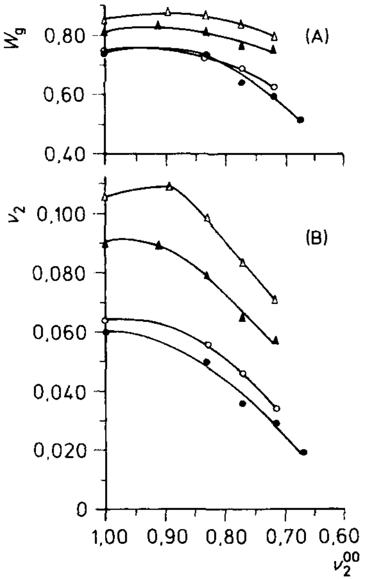

Fig. 2.

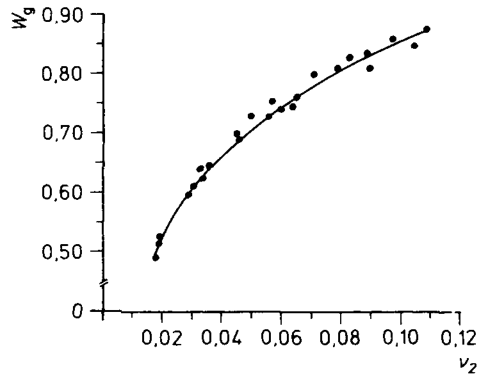

Fig. 3.

Fig. 2. Weight fraction of gel W_g (A) and equilibrium swelling values v_2 (B) shown as a function of the degree of initial dilution v_2^{00}. DVB content = 0,35 (●); 0,39 (○); 0,46 (▲); 0,53 mol-% (△)

Fig. 3. Dependence of the weight fraction of gel W_g on the equilibrium swelling values v_2 of copolymers shown in Figs. 1 and 2

vs. ν_2 fits to a single curve, regardless of conversion, initial dilution, and DVB and initiator concentrations.

Kinetic considerations

In the Appendix, the kinetic model of Mikos et al.[22)] has been applied to the copolymerization reaction of styrene with a small amount of a commercial DVB. Numerical solutions of Eqs. (A1) – (A20) predict the crosslinking densities, monomer conversions and number-average molecular weights as a function of the polymerization time, DVB concentration and initial dilution.

The calculated number of crosslinks per primary chain ν_e is given in Fig. 4 as a function of time of copolymerization reactions with 0,35 mol-% DVB and for different initial dilutions. The calculations were performed up to the gel point, i.e., up to $\nu_e = 2{,}0$. It appears that the number of crosslinks per primary chain shows a slower increase and the gelation occurs later as the dilution increases. The experimental results given in Fig. 1 are in accord with the predictions of theory. For a reaction time of 6 h, the gelation curve predicted by theory is shown in Fig. 5 as the dependence of ν_2^{00} on mol-% DVB. The coordinates of the curve correspond to the critical DVB concentration and the critical degree of initial dilution to achieve gelation in 6 h. No continuous network is formed left of the gelation curve. Gelation occurs only if the monomer concentration is above a critical value controlled by the DVB concentration.

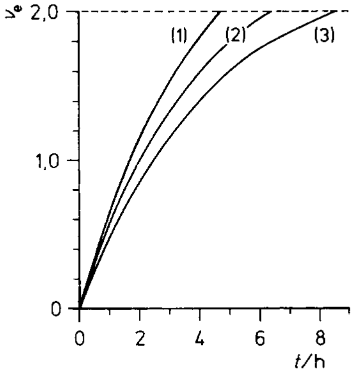

Fig. 4.

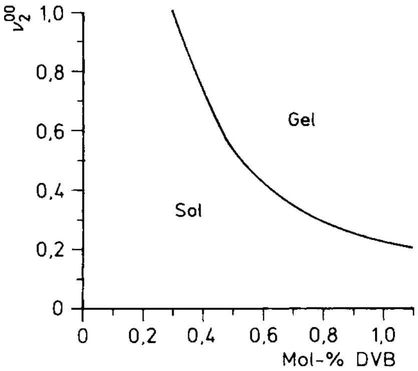

Fig. 5.

Fig. 4. Calculated dependence of the number of crosslinks per primary chain ν_e as a function of polymerization time t. DVB content = 0,35 mol-%, ν_2^{00} = 1,000 (1); 0,833 (2); 0,714 (3)

Fig. 5. Calculated dependence of the degree of initial dilution ν_2^{00} on the critical DVB concentration to achieve gelation in 6 h

Fig. 6 shows the fraction of DVB units with pendant vinyl groups, calculated as $\psi_{0,1,0}(\psi_{0,1,0} + \psi_{0,0,1})^{-1}$ (see Appendix), as a function of time, for a reaction period up to the gel point. The gelation times for 0,35 and 0,53 mol-% DVB and at various

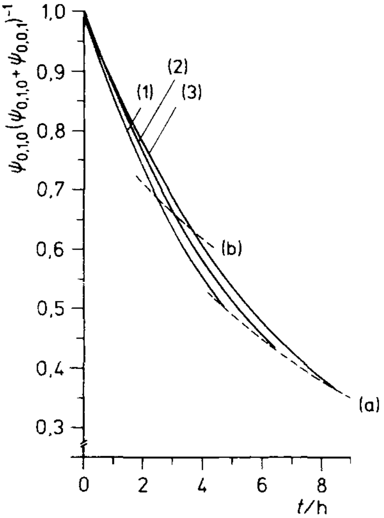

Fig. 6. Calculated dependence of the fraction of DVB units with pendant vinyl groups, $\psi_{0,1,0}(\psi_{0,1,0}+\psi_{0,0,1})^{-1}$, on the time t for the reaction period up to the gel point. The dashed curves show the calculated gelation times for 0,35 (a) and 0,53 mol-% DVB (b) and at various degree of initial dilution. ν_2^{00} = 1,000 (1); 0,833 (2); 0,714 (3)

degrees of dilution are shown by the dashed curves. It can be seen that the fraction of pendant vinyls at gelation decreases as the DVB concentration decreases or as dilution increases. For instance, at 0,53 mol-% DVB and ν_2^{00} = 1,00, 69% of the DVB units contain pendant vinyl groups at the gel point, whereas this value decreases to 37% at 0,35 mol-% DVB and ν_2^{00} = 0,714. Thus, it can be concluded that the probability to link all primary chains to the network decreases with increasing degree of dilution, or with decrasing DVB concentration, as it was found experimentally with the gel fraction measurements (Fig. 2).

The anomalous behaviour observed between ν_2^{00} = 1,00 and 0,90, namely the increase of the gel fraction with increasing dilution, can be explained as a result of vitrification of the polymerization system. The glass transition temperature of copolymer-monomer (+toluene) systems was calculated using the modified Couchman-Karasz equation, as described previously[27,28]. The calculations indicate that in the absence of diluent, the reaction temperature (70 °C) becomes equal to the glass transition temperature of the polymer system at 94% monomer conversion. This results in the cessation of the polymerization and crosslinking reactions at 94% conversion. With increasing dilution from ν_2^{00} = 1,00 up to 0,94, the critical degree of conversion for the onset of vitrification is shifted towards higher values, which results in a more efficient use of pendant vinyl groups and opposes the effect of dilution. At ν_2^{00} < 0,94, the polymer chains are in the rubbery state throughout the polymerization.

The calculated monomer conversion and the number-average molecular weight of the primary chains, $\bar{M}_n$, are given in Figs. 7(A) and 7(B) as a function of time for copolymerization reactions with 0,35 and 0,53 mol-% DVB, respectively. The calculations were performed for three different degrees of initial dilution. The monomer conversions and the molecular weight of the chains decrease with increasing dilution because the initial concentrations of monomers and initiator decrease simultaneously.

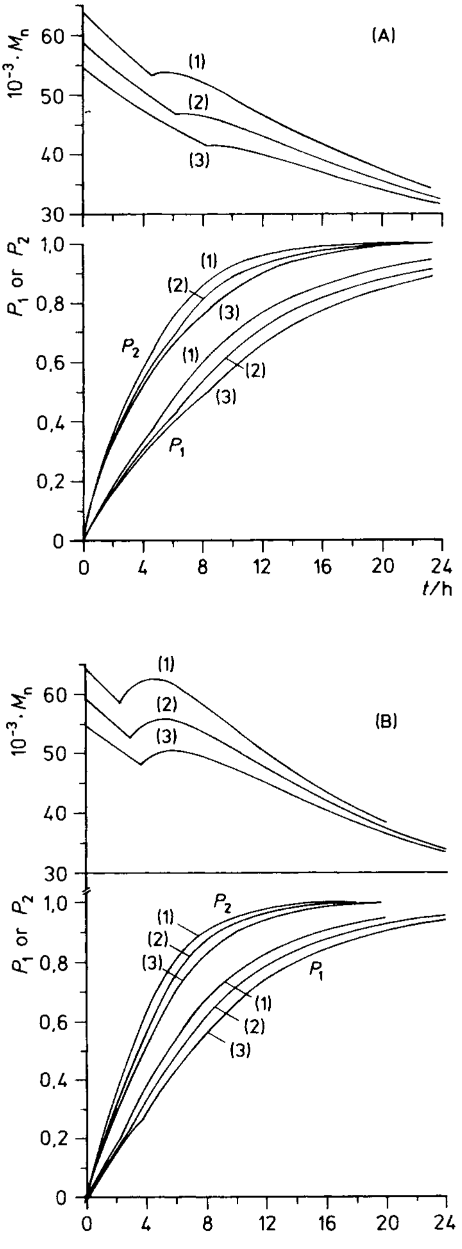

Fig. 7. Calculated conversions for styrene P_1, for the DVB isomers P_2, and the number-average molecular weight of the primary chains $\overline{M}_n$ shown as a function of the polymerization time t. DVB content = 0,35 (A) and 0,53 mol-% (B). ν_2^{00} = 1,000 (1); 0,833 (2); 0,714 (3)

Beyond the gel point, the rate of monomer conversion is accelerated and the molecular weight of the chains is increased due to the gel effect in the polymerization system. The time-conversion curves predicted by theory, however, do not fit the experimental data in the reaction period after the gel point (Fig. 1). For instance, at 0,35 mol-% DVB and $v_2^{00} = 1{,}00$, the amount of gel fraction remains unchanged for reaction times longer than 6 h, indicating that 94% of the monomers are consumed within 1,5 h after gelation (vitrification point). However, theory predicts a post-gelation time of 18,7 h. The considerable difference observed can be explained as follows: As termination and crosslinking are reactions between polymer chains, the rate constants of these reactions are reduced more significantly after the gel point than the rate constants of the other elementary reactions. Moreover, the reduction in the rate constants (i.e., the decrease in the mobility of the polymer chains) would be proportional to the viscosity of the reaction medium, whereas the latter depends on the crosslinking density of the gel, and is not proportional to the average crosslinking density of the whole system (gel + sol). Consequently, in the expression of the mobility factor (Eq. (A15)), only primary chains with $v_e \geq 2$ should be considered.

It must be pointed out that the number of crosslinks per chain and the number-average molecular weights calculated using the kinetic model refer to the whole volume of the polymer system, i.e., they are average values of sol and gel fractions of crude networks. The characteristics of the gel fractions are discussed in the next section.

Structural characteristics of the networks

The characterization of the networks was performed by applying Flory's swelling equation for tetrafunctional networks[26)]

$$\ln(1 - v_2) + v_2 + \chi v_2^2 = -(\xi/V_0)\, V_1\, v_2^{1/3}\, (v_2^0)^{2/3}\, [1 + K(\lambda^2)] \tag{3}$$

where χ is the polymer-solvent interaction parameter, ξ is the cycle rank or number of independent circuits in the network, V_0 is the volume of the network in the reference state, V_1 is the molar volume of solvent, v_2^0 is the volume fraction of the gel at the end of network formation, and $K(\lambda^2)$ is a factor characterizing the extent to which the deformation upon swelling approaches the affine limit. $K(\lambda^2)$ is a function of v_2 and also of the network parameter κ which is a measure of the entanglement constraints. The two extreme cases for $K(\lambda^2)$ are[25,29)] $K(\lambda^2) = 0$ for a network of phantom chains and $K(\lambda^2) = 1 - v_2^{2/3}$ for the case of an affine network.

At large deformations, i.e., at high swelling ratios (such as those of the networks prepared in this study), restrictions on the fluctuations of the junctions by neighboring chains are expected to vanish, so that the value $K(\lambda^2)$ can be taken as zero. The required values of χ for the polystyrene-toluene system were obtained from published results, which indicate[20,30)]

$$\chi = 0{,}455 - 0{,}155\, v_2 \tag{4}$$

in the range of interest. Assuming that the densities of sol and gel are the same, the volume fraction of the gel at the end of network formation, v_2^0, was calculated from W_g and v_2^{00} as

$$v_2^0 = \frac{W_g}{1 + \rho\,(1 - v_2^{00})/(v_2^{00}\, d_M)} \tag{5}$$

where d_M is the density of the monomers.

The cycle rank ξ is a fundamental characteristic value of any network, regardless of the functionalities of the network junctions and of the pattern of imperfections (i.e., free chain ends) it may contain$^{31)}$. The phantom reduced force or the modulus of the network in the range of large deformations, $[f^*]_{ph}$, can be correlated with the cycle rank density using the equation$^{32,33)}$

$$[f^*]_{ph} = (\xi/V_0)\, R\, T (v_2^0)^{2/3} \tag{6}$$

where R is the gas constant and T the absolute temperature (298 K).

Taking $V_1 = 106{,}3\ \mathrm{cm^3 \cdot mol^{-1}}$, $d_M = 0{,}91\ \mathrm{g \cdot cm^{-3}}$ and using the limiting W_g and v_2 values listed in Tab. 1, the phantom moduli of the networks swollen in toluene were calculated using Eqs. (3) – (6), and are shown in column 5 of Tab. 1. It seems that the modulus of the networks decreases with increasing initial dilution and decreasing DVB concentration.

S-DVB networks can be considered as a network with four and three functional junctions because of the existence of free chain ends in the system. Consequently, for such networks, the relationships between the cycle rank ξ, the total number of junctions μ, the number-average of segments between successive junctions x_c and that of the primary chains y can be expressed as follows$^{33-35)}$.

$$\xi/V_0 = \frac{1}{2x_c\, V_1}\left(1 - \frac{3x_c}{y}\right) \tag{7}$$

$$\mu/V_0 = \frac{1}{2x_c\, V_1}\left(1 - \frac{x_c}{y}\right) \tag{8}$$

The total number of junctions μ depends on the initial DVB concentration and on the crosslinking efficiency E, which is the number of intermolecular crosslinks formed per DVB molecule. Assuming that approximately half of a monomeric unit occupies a volume equal to that of a solvent molecule along the backbone, while the other half forms a branch$^{36)}$, the density of junctions can be given by

$$\mu/V_0 = \frac{2\rho N_x E}{M_1} \tag{9}$$

where N_x is the mole fraction of DVB isomers in the monomer mixture, and M_1 is the molecular weight of a monomeric unit taken as $104\ \mathrm{g \cdot mol^{-1}}$.

From Eqs. (7) to (9), it follows

$$\xi/V_0 = \mu/V_0 - \frac{1}{V_1\, y} \tag{10}$$

$$\xi/V_0 = \frac{2\rho N_x E}{M_1} - \frac{1}{V_1\, y} \tag{10'}$$

The crosslinking efficiency E and the number-average of segments per primary chain, y, may be assumed to be constant at a given dilution and over the range 0,35 to 0,53 mol-% DVB. Consequently, when the cycle rank density is plotted against $(\mu/V_0)E^{-1}$, straight lines can be obtained, for a given degree of initial dilution. On this basis, the slope of the lines corresponds to the crosslinking efficiency E, and the intercept for zero DVB concentration can be taken as the product $(V_1 y)^{-1}$. In Fig. 8,

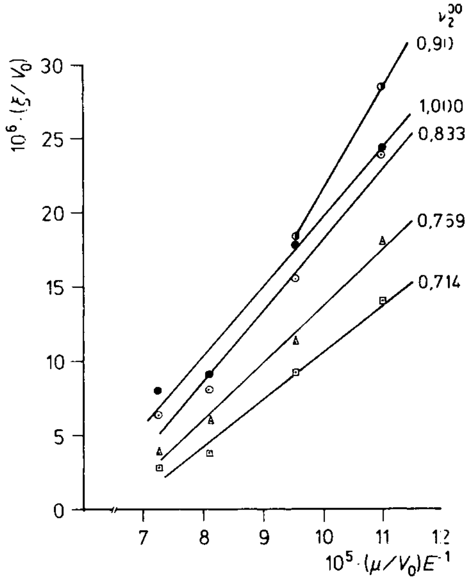

Fig. 8. Dependence of the cycle rank density (ξ/V_0) on the product $(\mu/V_0)E^{-1}$ according to Eq. (10). v_2^{00} = 1,000 (●); 0,90 (◑); 0,833 (○); 0,769 (△); 0,714 (□)

(ξ/V_0) is plotted against $(\mu/V_0)E^{-1}$ for the networks presented in Tab. 1. It seems that the (ξ/V_0) vs. $(\mu/V_0)E^{-1}$ curves can be expressed by a linear relationship at all diluent concentrations, within the limits of experimental error. The values E and y, calculated from the slope and intercept of the least-squares lines, are collected in Tab. 2, together with the correlation coefficients. For comparison, the number-average of segments per primary chain of crude (unextracted) networks y' was calculated using the equation

$$y' = \frac{\overline{M}_n}{2\rho V_1} \tag{11}$$

where $\overline{M}_n$ is the number-average molecular weight of primary chains calculated using the kinetic model at 95% monomer conversion. The values for y' are also shown in Tab. 2.

It can be seen that the value of y ranges from 200 to 450, depending on the degree of dilution. The average size of the primary chains of the network is much larger than that of the crude network and, furthermore, the difference between them increases with increasing degree of dilution (Fig. 9). These results are reasonable since for the

Tab. 2. The crosslinking efficiency E and the number-average of segments per primary chain of extracted and unextracted networks, y and y', respectively, for various degrees of initial dilution. r: the correlation coefficients of the lines shown in Fig. 8

v_2^{00}	E	y	r	y'
1,000	0,47	350	0,989	150
0,900	0,69	200	[a]	145
0,833	0,48	310	0,991	140
0,769	0,38	380	0,995	130
0,714	0,31	450	0,990	120

[a] Calculations were performed using two data points.

polymer chains in the sol, the higher the molecular weights, the higher the probability to be linked to the gel. It follows that the larger species in the sol are preferentially connected to the gel, which results in an increase in y with respect to y'. Moreover, with increasing dilution, only larger species can be attached to the gel due to the increase of the sol fraction, which results in the observed increase of y as well as $(y - y')$. On the other hand, the crosslinking efficiency decreases with increasing dilution because of the larger number of crosslinks and of pendant vinyl groups wasted in the sol fraction. The anomalous behaviour observed in the range between $v_2^{00} = 1{,}00$ and 0,90 is expected to originate from vitrification, as explained in the previous section.

The number-average of segments between successive junctions, x_c, and the density of junctions, μ/V_0, calculated using Eqs. (7) and (8) are also shown in Tab. 1. The variation of x_c and μ/V_0 with dilution is similar to that of y and E, respectively. According to the gel-sol probability approach, the weight fraction of gel, together with the molecular weight distribution of the primary chains, are correlated with the crosslinking index, that is, with the number of junctions per weight-average mole-

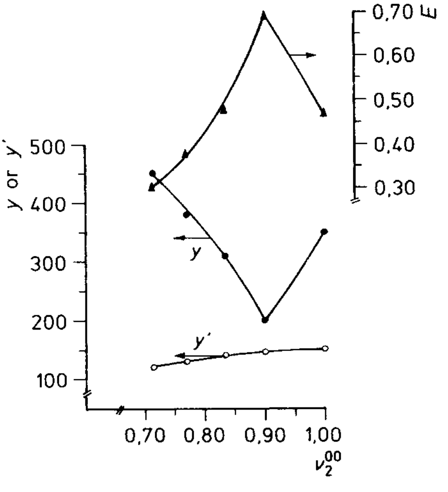

Fig. 9. The number-average of segments per primary chain of extracted (y) and unextracted networks (y'), and the cross-linking efficiency E shown as a function of the degree of initial dilution v_2^{00}. (●): y; (○): y'; (▲): E

cule[14]. Since the equilibrium swelling values of the gels, v_2, are also correlated with the number of junctions (Eqs. (3) and (10)), the dependence of W_g on v_2 should be universal, as it was found experimentally with the present networks (Fig. 3).

Conclusions

The free-radical copolymerization of styrene with small amounts of a commercial DVB in the bulk or in toluene solution yields loosely crosslinked networks, together with varying amounts of soluble polymer. It was found that gel formation is retarded by rising dilution, and the networks thus formed exhibit a larger degree of swelling and a smaller gel fraction as the dilution increases. Neglecting the cyclization reactions due to the low DVB concentrations used, the experimental results can be explained with the kinetic mechanism of S-DVB copolymerization (see Appendix). In the range of rather low degrees of dilution (v_2^{00} = 1,00 – 0,90), the properties of the networks are determined by the combination of two opposing effects of the diluent, namely dilution and plasticizing effects. Whereas the first effect tends to lower the reaction rates of the monomers and the number of pendant vinyl groups, the latter shifts the vitrification point of the system toward higher conversions, and thus ensures prolonged reaction times. Furthermore, for all the networks studied, the dependence of the gel fraction on the equilibrium degree of swelling was found to be universal, regardless of conversion, initial dilution, as well as DVB and initiator concentration.

Calculations performed using the theory of rubber elasticity indicate that the average number of segments per primary chain of the network varies between 200 and 450, depending on the degree of initial dilution. This corresponds to a number-average molecular weight of primary chains (as polystyrene) of about 50000 to 100000 g · mol^{-1}. Consequently, considerable amounts of free chain ends are present in such networks, which do not contribute to the elasticity of the gel. For $v_2^{00} < 0{,}90$, namely for systems which are always in the rubbery state during the copolymerization, the crosslinking efficiency was found to decrease, but the sizes of the primary chains and of the network chains increase as the dilution increases.

Appendix

Kinetic mechanism of S-DVB copolymerization

Recently, Mikos et al. developed a kinetic model for free-radical monovinyl-divinyl monomer copolymerization reactions[22]. The model neglects the cyclization reactions and is therefore valid for low divinyl monomer concentrations. Here this model is applied to the copolymerization of styrene with small amounts of a commercial DVB, with following assumptions:

1) Since the DVB concentration is very low, the concentration of growing chains with a DVB terminal group is zero. Furthermore, ethylvinylbenzenes (present in commercial DVB) is taken as styrene.
2) The monomers and the pendant vinyl groups are mostly consumed in the propagation rather than in the initiation step. Thus the latter is neglected.

3) The reactivity of vinyl groups is independent of the size of molecules to which they are attached.
4) Chain transfer to monomer and solvent is ignored in the calculations. The termination reaction rate by disproportionation is zero.
5) The reactor volume is constant during the copolymerization.

The following radical chain mechanism is assumed for the copolymerization of styrene and commercial DVB:

Initiation step:

$$\mathrm{I} \xrightarrow{k_\mathrm{d}} 2\mathrm{A}$$

$$\mathrm{M}_1 + \mathrm{A} \xrightarrow{k_{\mathrm{i}_1}} \mathrm{P}_{1,0,0}$$

$$\mathrm{M}_2' + \mathrm{A} \xrightarrow{k_{\mathrm{i}_{2'}}} \mathrm{P}_{0,1,0}$$

$$\mathrm{M}_2'' + \mathrm{A} \xrightarrow{k_{\mathrm{i}_{2''}}} \mathrm{P}_{0,1,0}$$

$$\mathrm{P}_{p,q,r} + \mathrm{A} \xrightarrow[\text{and } k_{\mathrm{i}_{3''}}]{k_{\mathrm{i}_{3'}}} \mathrm{P}_{p,q-1,r+1} + \mathrm{P}_{0,0,1}$$

$$\mathrm{M}_{p,q,r} + \mathrm{A} \xrightarrow[\text{and } k_{\mathrm{i}_{3''}}]{k_{\mathrm{i}_{3'}}} \mathrm{M}_{p,q-1,r+1} + \mathrm{P}_{0,0,1}$$

Propagation and crosslinking steps:

$$\mathrm{P}_{p,q,r} + \mathrm{M}_1 \xrightarrow{k_{\mathrm{p}_1}} \mathrm{P}_{p+1,q,r}$$

$$\mathrm{P}_{p,q,r} + \mathrm{M}_2' \xrightarrow{k_{\mathrm{p}_{2'}}} \mathrm{P}_{p,q+1,r}$$

$$\mathrm{P}_{p,q,r} + \mathrm{M}_2'' \xrightarrow{k_{\mathrm{p}_{2''}}} \mathrm{P}_{p,q+1,r}$$

$$\mathrm{P}_{p,q,r} + \mathrm{P}_{x,y,z} \xrightarrow[\text{and } k_{\mathrm{p}_{3''}}]{k_{\mathrm{p}_{3'}}} \mathrm{P}_{p,q,r+1} + \mathrm{P}_{x,y-1,z+1}$$

$$\mathrm{P}_{p,q,r} + \mathrm{M}_{x,y,z} \xrightarrow[\text{and } k_{\mathrm{p}_{3''}}]{k_{\mathrm{p}_{3'}}} \mathrm{P}_{p,q,r+1} + \mathrm{M}_{x,y-1,z+1}$$

Termination step:

$$\mathrm{P}_{p,q,r} + \mathrm{P}_{x,y,z} \xrightarrow{k_\mathrm{tc}} \mathrm{M}_{p+x,q+y,r+z}$$

(I = initiator, A = primary initiating radical, M_1 = styrene, M_2' = *m*-DVB, M_2'' = *p*-DVB, $\mathrm{P}_{p,q,r}$ or $\mathrm{P}_{x,y,z}$ = growing polymer chain, $\mathrm{M}_{p,q,r}$ = dead polymer chain. Three subscripts refer to the number of styrene units $p(x)$, pendant vinyl groups $q(y)$ and crosslinks $r(z)$ per chain. k_d, k_p and k_tc are the rate constants for the decomposition of the initiator, propagation and termination by combination, respectively. Subindices 1,2′ and 2″ relate to styrene, *m*-DVB and *p*-DVB, respectively, whereas 3′ and 3″ refer to pendant double bonds originating from *m*- and *p*-DVB units, respectively)

From the above reactions, the reaction rates of initiator, styrene, *m*-DVB, and *p*-DVB may be written as follows*):

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*) Italics were used to denote concentrations of the species of the same symbols.

$$\frac{dI}{dt} = -k_d I \tag{A1}$$

$$\frac{dM_1}{dt} = -k_{p_1} PM_1 \tag{A2}$$

$$\frac{dM_2'}{dt} = -2k_{p_{2'}} PM_2' \tag{A3}$$

$$\frac{dM_2''}{dt} = -2k_{p_{2''}} PM_2'' \tag{A4}$$

where P is the concentration of total active polymer, i.e.,

$$P \equiv \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} P_{p,q,r} \tag{A5}$$

Using the steady state approximation for radicals, P can be given as:

$$P = \left(\frac{2fk_d I}{k_{tc}}\right)^{1/2} \tag{A6}$$

where f is the initiator efficiency factor.

The rate expressions for the total divinyl monomer can be calculated from Eqs. (A3) and (A4) as

$$\frac{dM_2}{dt} = -2k_{p_1} PM_2 \left(\frac{x_2'}{r_{12'}} + \frac{x_2''}{r_{12''}}\right) \tag{A7}$$

where M_2 is the total concentration of the DVB isomers, x_2' and x_2'' are the mole fractions of *m*- and *p*-DVB in the DVB mixture, respectively, $r_{12'}$ and $r_{12''}$ are the reactivity ratios of styrene with the first double bond of *m*- and *p*-DVB, respectively.

According to theory[22], the moments of the molecular weight distribution, $\psi_{i,j,k}$, of crosslinked copolymer, defined as

$$\psi_{i,j,k} \equiv \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \sum_{r=0}^{\infty} p^i q^j r^k (P_{p,q,r} + M_{p,q,r}) \tag{A8}$$

can be used to predict the gel point and the number-average molecular weight of the primary chains. The rate equation for the first and the zeroth moment of the molecular weight distribution of total polymer can be written as:

$$\frac{d\psi_{0,0,0}}{dt} = 2fk_d I - 0{,}5 k_{tc} P^2 \tag{A9}$$

$$\frac{d\psi_{1,0,0}}{dt} = k_{p_1} PM_1 \tag{A10}$$

$$\frac{d\psi_{0,1,0}}{dt} = 2k_{p_1} PM_2 \left(\frac{x_2'}{r_{12'}} + \frac{x_2''}{r_{12''}}\right) - k_{p_3} PM_3 \tag{A11}$$

$$\frac{d\psi_{0,0,1}}{dt} = 2k_{p_3} PM_3 \tag{A12}$$

where M_3 is the concentration of pendant vinyl groups, i.e., $M_3 \equiv \psi_{0,1,0}$, and k_{p_3} is the average propagation rate constant of the reaction between a growing polymer chain and a pendant vinyl group. It must be pointed out that the value k_{p_3} depends on the ratio of the pendant double bonds in *m*- and *p*-positions because of the different reactivities of these vinyl groups. In Eqs. (A11) and (A12), the ratio of the *m*- and *p*-DVB units with pendant vinyl groups was assumed to be constant.

The average number of effective crosslinks per primary chain, ν_e, and the number-average molecular weight of the primary chains, $\bar{M}_n$, can be calculated, using the moments of the molecular weight distribution of the crosslinked copolymer, as follows[22]:

$$\nu_e = \frac{\psi_{0,0,1}}{\psi_{0,0,0}} \tag{A13}$$

$$\bar{M}_n = \frac{104\,\psi_{1,0,0} + 130(\psi_{0,1,0} + 0{,}5\,\psi_{0,0,1})}{\psi_{0,0,0}} \tag{A14}$$

The equations given above are valid for copolymerization reactions up to gel point, assuming that the reactions occurring before the gel point are reaction-controlled. For the reaction period beyond gelation, the change in the polymerization rate constants of the diffusion-controlled steps are described by a mobility factor, μ', defined as[22,23]:

$$\mu' = 1/\nu_e \tag{A15}$$

Consequently, the rate equations for the distribution moments of the crosslinked polymer are modified as follows:

$$\frac{d\psi_{0,0,0}}{dt} = 2fk_d I - 0{,}5\mu' k_{tc} P^2 \tag{A16}$$

$$\frac{d\psi_{1,0,0}}{dt} = k_{p_1} P M_1 \tag{A17}$$

$$\frac{d\psi_{0,1,0}}{dt} = 2k_{p_1} P M_2 \left(\frac{x_2'}{r_{12'}} + \frac{x_2''}{r_{12''}}\right) - \mu' k_{p_3} P M_3 \tag{A18}$$

$$\frac{d\psi_{0,0,1}}{dt} = 2\mu' k_{p_3} P M_3 \tag{A19}$$

with

$$P = \left(\frac{2fk_d I}{\mu' k_{tc}}\right)^{1/2} \tag{A20}$$

Calculations

Eqs. (A1) – (A20) can be solved numerically to predict the average number of crosslinks per chain, monomer conversions and number-average molecular weights as a function of time, DVB concentration and initial dilution. The following values of the kinetic constants and the reactivity ratios have been used[12,22]: $k_d = 7{,}57 \cdot 10^{-6}\ s^{-1}$, $k_{p_1} = 330\ l \cdot mol^{-1} \cdot s^{-1}$, $k_{tc} = 1{,}07 \cdot 10^8\ l \cdot mol^{-1} \cdot s^{-1}$, $r_{12'} = 0{,}88$ and $r_{12''} = 1{,}18$. The initiator efficiency factor f was taken as 0,5. The mole fractions of *m*- and *p*-DVB in the DVB mixture, i.e., x_2' and x_2'', were taken as 0,75 and 0,25, respectively. The only unknown parameter, k_{p_3}, was calculated using the experimental data of copolymerization reactions with 0,35 mol-% DVB for $\nu_2^{00} = 1{,}00$. Fig. 1 indicates a gelation time of 4,5 – 5,0 h. At the gel point, the average number of crosslinks per chain is equal to 2. Thus, for a polymerization time of 4,75 h, the kinetic model predicts $\nu_e = 2$ if $k_{p_3} = 508\ l \cdot mol^{-1} \cdot s^{-1}$. This value of k_{p_3} was used for further calculations.

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