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Cyclization and Reduced Pendant Vinyl Group Reactivity during the Free-Radical Cross-Linking Polymerization of 1,4-Divinylbenzene

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ABSTRACT: Free-radical cross-linking polymerization of 1,4-divinylbenzene (1,4-DVB) has been investigated in toluene. The monomer concentration was less than 5 w/v %. Conversion of monomer and pendant vinyl groups, weight-average molecular weight $\bar{M}_w$, and intrinsic viscosity $[\eta]$ of the polymers were measured as a function of the reaction time up to the onset of macrogelation. A kinetic model was used to calculate the extent of cyclization and reduced pendant reactivity from the experimental data. Fraction of pendant vinyls in cycles, number of multiple cros-linkages, and the reactivity ratio of pendant to monomeric vinyl were evaluated as a function of the polymerization temperature, initial concentrations of 1,4-DVB and the initiator as well as the amount of styrene as a comonomer. The results indicate that 30−60% of pendant vinyls are used by cyclization reactions and, on average, 100−800 multiple cross-linkages occur per one intermolecular cross-link formed. The average pendant reactivity for intermolecular links is 2−3 orders of magnitude lower than the monomeric vinyl reactivity. These results were found to be in accord with the observed weak $\bar{M}_w$ dependence of $[\eta]$ of the polymers and their stability against degradation by ultrasonic waves. The critical exponent γ suggests non-mean-field behavior in the vicinity of the gel point.

Introduction

Carothers first pointed out that gelation is the result of the linking process of polymer molecules into a three-dimensional network of infinitely large size.[1] The term "infinitely large size" refers, according to Flory,[2] to a molecule having dimensions of an order of magnitude approaching that of the containing vessel. Thus, "such molecules are finite in size, but by comparison with ordinary molecules they may be considered infinitely large".[2] However, by decreasing the dimension of the containing vessel we can reduce the size of the gel formed until it approaches to that of the ordinary molecules. For example, cross-linking polymerization in a micelle produces a gel with a diameter of 50 nm and a molecular weight of about 40 × 10^6 g/mol.[3] Such gel particles of colloidal size are called microgels.[4−7] Besides the technical interest in microgels as materials to improve the properties of binders and coatings,[8,9] they are used as model systems for studying structures of polymer networks.[10−12]

In analogy with the macroscopic gel formation, the microgels formed by emulsion polymerization spread through the whole available volume, which is here the latex particles.[13] A different type of microgel can be obtained by homogeneous free-radical cross-linking (co)-polymerization. Since increasing dilution during cross-linking increases the probability of cyclization, the growing polymer chains in a highly dilute solution become intramolecularly cross-linked and their structure approaches the microgels formed within the micelles. Thus, contrary to the classical gelation theory[2] which assumes the initial formation of essentially linear primary molecules, intramolecularly cross-linked primary particles called microgels may form at moderate to high concentrations of cross-linker or solvent.[14−16] As polymerization proceeds new microgels are continuously generated. The interparticular reactions namely the cross-linking reactions are responsible for the agglomeration of the microgels leading to the macrogel formation. Thus, macrogel formation process via microgels may be described by Smoluchowski's coagulation equation:[17,18]

$$\frac{\mathrm{d}c_k}{\mathrm{d}t} = \frac{1}{2}\sum_{i+j=k} k_{ij}c_ic_j - c_k\sum_{j=1}^{\infty}k_{jk}c_j \tag{1}$$

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

where c_i is the concentration of i-mer and k_{ij} is the interparticle cross-linking rate constant to form $(i+j)$-mer from i-mer and j-mer.[19−23] If all microgels are mutually penetrable, that is, if all functional groups are able to react, α becomes unity and gelation occurs according to the Flory−Stockmayer model.[2,24−26] If only a certain fraction of the functional groups is able to react, for example those on the surface of the particles, α is less than unity. Thus, the structure of the microgels seems to be important in the cross-linking process which in turn depends on the extent of the intramolecular cross-linking reactions.

The effect of intramolecular cross-linking reactions on the polymer structure can be found in the literature already as early as 1935. Staudinger and Husemann[27] could isolate a soluble polymer by polymerizing divinylbenzene (DVB) alone in very dilute solutions. From the low specific viscosity of this polymer with respect to linear polystyrene of similar molecular weight, they concluded that the isolated polymer should be a colloidal molecule having the shape of a spherical particle. Later on, Walling[28] observed that the actual gel point in the bulk polymerization of ethylene glycol dimethacrylate (EGDM) exceeds that predicted using the classical theory of gelation[2] by more than 2 orders of magnitude (2.9% vs 0.022% in terms of critical conversion). He

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explained this deviation due to the fact that "the growing chains undergoes so many cross-linking reactions within itself that its ability to swell is reduced".[28] Zimm et al.[29] observed that the molecular weight dependence of the intrinsic viscosity of branched styrene-DVB copolymers is quite weak; they found an exponent $a = 0.25$, which is between the value of massive spheres ($a = 0$) and the unperturbed Gaussian chain ($a = 0.50$). Malinsky et al.[30] observed that in styrene-DVB copolymerization the fraction of pendant vinyl groups is lower than calculated at low conversions, whereas at high conversions the copolymers contain a large excess of these groups. They explained the results in terms of cyclization and reduced mobility of segments where the latter dominates at high conversions and reduces the reactivity of pendant vinyl groups. Cyclization during the gel formation was also studied by many researchers.[31–46] Another explanation for the discrepancy between the observed and predicted behavior of free-radical cross-linking copolymerizations is the reduced reactivity of pendant vinyl groups during the reactions.[28,47–54] It is now generally agreed that both cyclization and reduced pendant reactivity coexist in free-radical cross-linking copolymerizations and they are related to each other.[16,55–57]

At the moment there exist no theory of network formation by free-radical cross-linking copolymerization that takes into account extensive cyclization. On the other hand, the experimental data reported in the literature for the extent of cyclization are rather scarce and some of them are conflicting probably due to the inaccuracy of the method of measurements.[45] It is the purpose of this paper to present new measurements which will enable us to estimate the magnitude of cyclization and reduced pendant reactivity depending on the reaction conditions. In this way, we hope to develop a deeper insight into the microscopic phenomena occurring during free-radical cross-linking polymerizations.

In this work, conversion of monomers and pendant vinyl groups were determined experimentally in free-radical polymerization of 1,4-DVB in toluene solution. The monomer concentration was less than 5 w/v%. The weight-average molecular weight, $\bar{M}_w$, and intrinsic viscosity $[\eta]$ of the polymers were measured as a function of the reaction time up to the onset of macrogelation. In usual cross-linking polymerizations, gel points are determined by observing the time at which the reaction mixture would no longer flow. For example, a gas bubble or glass ball moving gently through the polymerizing mixture suddenly becomes immobilized at this critical point.[15,55,58] However, in the present system because of the high degree of dilution such a transition cannot be observed and the viscosity of the reaction mixture remained finite at the gel point. Instead, insoluble macrogel particles, i.e., agglomerates of the microgels started to appear at the gel point, i.e., at the transition point from micro- to macrogelation. A kinetic model is also used to study the experimental data and to evaluate the extent of cyclization, multiple cross-linking, and reduced pendant reactivity as a function of the reaction conditions.

It must be pointed out that commercial DVB is generally used as cross-linker in free-radical copolymerizations. Commercial DVB has a fundamental drawback in that it typically consists of a mixture of four main isomers: 1,4-DVB, 1,3-DVB, 1-ethyl-4-vinylbenzene, and 1-ethyl-3-vinylbenzene. Walczynski[42] has demonstrated that in free-radical polymerization the apparent rate constants of these components differ substantially. These different reactivities cause a drift in the copolymer composition during the polymerization and thus, bring difficulties and uncertainties in the analysis of experimental results. Therefore we decided to synthesize polymers using pure 1,4-DVB monomer, which can be separated from the commercial mixture by a bromination–debromination sequence.

Table 1. Synthesis Conditions of Polymers[a]

series	T, °C	c, w/v %	$10^3[\mathrm{I}]_0$, M	DVB, wt %
I	v	5	2.6	100
II	70	v	8.0	100
III	70	2	v	100
IV	70	5	2.6	v

[a] Abbreviations: v, variable; c, initial monomer concentration in w/v %; $[\mathrm{I}]_0$, initial concentration of AIBN in mol L^{-1}; DVB, wt % of 1,4-DVB in styrene-1,4-DVB monomer mixture.

Experimental Section

Materials. 1,4-Divinylbenzene (1,4-DVB) was isolated from the commercial mixture, which contained 55–60% DVB with a ratio of 1,3 to 1,4 isomer of about 2.5, by bromination.[15,59,60] A 1-L portion of the commercial DVB mixture was combined with 0.5 L of benzene, to which was added dropwise 0.55 L of bromine, with stirring and cooling to keep the temperature below 10 °C. Then the tetrabromide crystals formed were filtered, washed with methanol and crystallized twice from chloroform. The debromination of the tetrabromide thus obtained was carried out by dissolving 68 g of tetrabromide and 1.8 g of N-phenyl-2-aminonaphthalene in a mixture of 390 mL of tetrahydrofuran and 30 mL of water under heating and then adding 18.5 g of zinc dust during 15 min at such a rate as to keep the reaction mixture boiling. The reaction mixture was then cooled to room temperature, 500 mL of ether was added and then filtered to remove excess zinc. The organic layer was washed six 300 mL portions of water and dried over anhydrous sodium sulfate, and ether was removed under reduced pressure. The residue, 1,4-DVB, was sublimated twice under reduced pressure. Yields were about 80% of theory. Purity was checked by GC and found to be better than 99.5%. Styrene was shaken with 10% NaOH, washed with water, dried with anhydrous $\mathrm{CaCl_2}$, and finally distilled under reduced pressure. The initiator 2,2′-azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. The polymerization solvent, toluene, was distilled over sodium under nitrogen atmosphere.

Polymerization. 1,4-DVB was freshly sublimated prior to polymerization. The appropriate amounts of 1,4-DVB, styrene, and AIBN were dissolved in toluene and this was divided and transferred into a series of glass tubes of 5-mm diameter and 20-cm length. To eliminate oxygen from the system, three freeze–pump–thaw cycles were used. The glass tubes were then placed in a thermostated bath for a predetermined polymerization time. Homologous series of polymers were obtained in this way allowing systematic variation of the temperature, monomer and initiator concentrations, and comonomer composition. Synthesis conditions of each series of polymers are collected in Table 1. After reaction, the tubes were removed from the bath and cooled rapidly in an ice–water bath. The solution was then precipitated dropwise into an agitated solution of methanol to which a small amount of hydroquinone has been added. The precipitated polymer was dissolved in a small amount of benzene, and the solvent was then removed by freeze-drying. The conversion of monomer was determined by weighing the polymer. The gel point was determined as the midpoint between the last time at which a soluble polymer was obtained and that at which the polymer was not soluble in toluene. For ascertaining the insoluble gel components of samples, the latter were treated with an approximately 50-fold excess of toluene at room temperature. The formation of insoluble polymer was detected visually from the appearance of gel particles in toluene.

Characterization. All solvents were purified and distilled prior to use. Solvent purity was checked by GC and found to be nearly 100%. The weight-average molecular weight of the polymers was determined by small-angle light scattering (Chromatix KMX-6) at 25 °C with a laser source at 633 nm. Toluene was used as the solvent. The refractive index increments (dn/dc) were measured with a Chromatix KMX-16 refractometer. Quasielastic light-scattering (QELS) experiments were performed using PCS 100 spectrometer and K 7027 "Loglin" correlator (Malvern Ins. Ltd.) with a Spectra-Physics argon ion laser (Model 2020-03) at 488 nm. The scattering angle was 90°. The data were analyzed and the z-average hydrodynamic diameter (D_z) were calculated using the method of cumulants. Dilute solution viscosities of the polymers were measured in toluene at 20 °C by AVS 400 Schott. Intrinsic viscosities ($[\eta]$) were obtained by extrapolating plots of η_{sp}/c vs c to zero concentration where η_{sp} is the specific viscosity of a solution of concentration c(in grams per milliliter). Degradation experiments on microgels were carried out by ultrasonic waves using Sonifier 250 high-frequency generator (Branson). Solutions of microgels in benzene were irradiated at 20 kHz and at room temperature in the presence of *N,N*-diphenyl-*N'*-picrylhydrazine as radical scavenger.

The content of pendant vinyl groups and copolymer composition were measured by IR spectroscopy (Philips SP3-200) using chloroform solution of the polymers. The absorption peak at 1630 cm^{-1} due to the C=C stretching vibration was used for the determination of the pendant vinyl groups. Calibration was carried out using 4-isopropylstyrene as a model substance. Batzilla[61] showed that the extinction coefficient of 4-isopropylbenzene is close to that of DVB units in the polymer bearing pendant vinyls. A standard deviation of ±0.1 mmol pendant vinyl group/gram of polyDVB was found for the method of measurement. The composition of styrene-1,4-DVB copolymers was determined using the absorption peaks at 760 and 838 cm^{-1} due to the monosubstituted phenyl ring of styrene and the para-disubstituted phenyl ring of DVB units respectively.[62] Calibration was carried out using mixtures of polystyrene and polyDVB.

Kinetic Modeling

There are several theories of network formation used to describe the relations among the molecular weight of polymers and the conversion or reaction time during cross-linking. These theories include statistical[2,24–26,63–66] and kinetic[44,67–75] methods, and simulation in *n*-dimensional space, such as the percolation method.[76–78] In the past half century, statistical and kinetic approaches have been extensively used to describe polymeric gelation. These approaches consider the average properties of the reaction system, and therefore, they cannot deal exactly and directly with long-range correlations such as cyclization and with the resulting heterogeneities. On the other hand, the percolation theory that belongs to a non-mean-field theory can take into account the heterogeneities but at present the result of this theory is unrealistic due to the difficulty of introduction of realistic mobilities. The critical region seems to be the main domain of application of percolation techniques to polymer networks. Thus, at the moment there exist no exact theory of network formation that takes into account heterogeneities and microgel formation due to the extensive cyclization. The experimental data obtained in the present study were organized and studied within the framework of a kinetic model which includes constants for cyclization and pendant reactivity. In this way we hope to obtain information on the magnitude of cyclization and reduced pendant reactivity depending on the reaction conditions.

A kinetic scheme for free-radical cross-linking copolymerization of vinyl/divinyl monomers can be written as follows. The polymerization system involves three types of vinyl groups; those on vinyl and divinyl monomers and those on polymer chains, i.e., pendant vinyls. Accordingly, the polymerization system can be considered as a special case of terpolymerization in which one of the vinyl groups (pendant vinyls) is created during the course of the reaction when the vinyl on divinyl monomer reacts. The pendant vinyl groups thus formed can then react by cyclization, cross-linking, or multiple cross-linking reactions, or remain pendant. With cyclization the cycle is formed when the macroradical attacks the pendant vinyl groups in the same kinetic chain, while with multiple cross-linking it is formed if the radical attacks double bonds pendant on other chains already chemically connected with the growing radical[68,79] (Figure 1). It should be noted that cyclization and multiple cross-linking were recently redefined as primary and secondary cyclizations, respectively.[44] In the following text the classical definitions will be used.

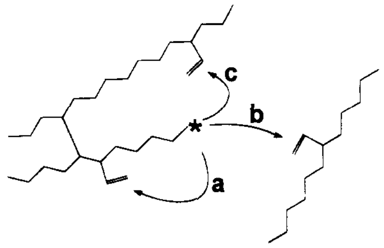

Figure 1. Schematic picture of cyclization (a), cross-linking (b), and multiple cross-linking (c) in free-radical cross-linking copolymerization.

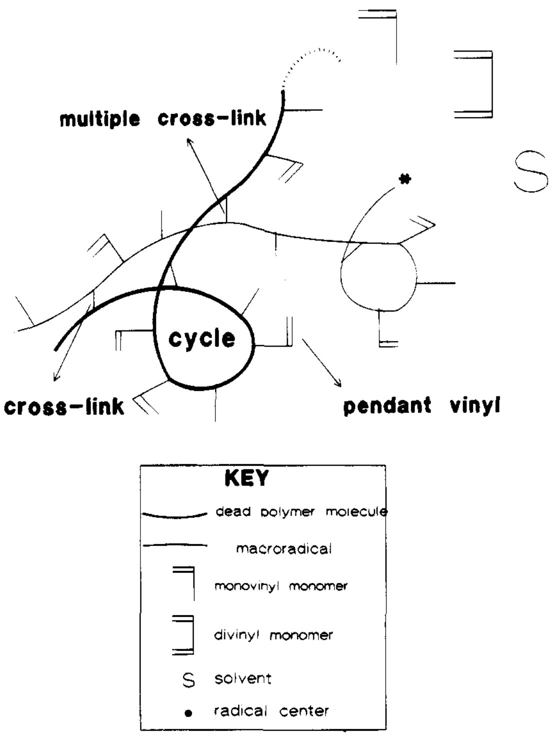

Figure 2. Schematic representation of the pregelation period in free-radical cross-linking copolymerization.

A schematic representation of the polymerization system prior to gelation is shown in Figure 2. The divinyl monomer can be found in the polymer as units bearing pendant vinyl groups, cycles, cross-links, or multiple cross-links. Since according to the classical theory of gelation[2] only one cross-link per weight-average primary molecule is necessary for the onset of a macrogelation, the content of pendant vinyls is a

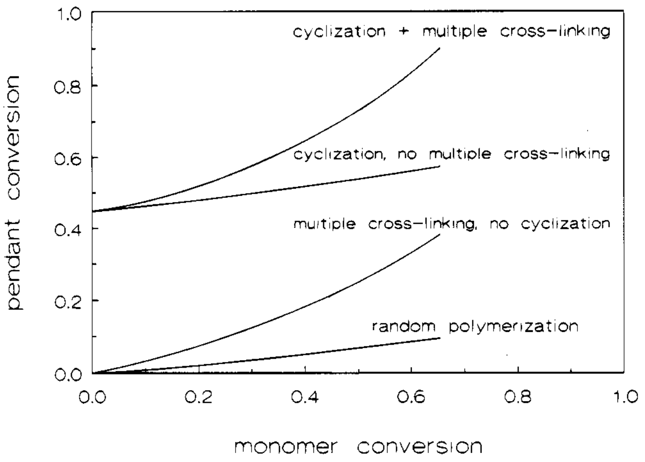

Figure 3. Graphical representation of variation of pendant vinyl conversion x_3 with the monomer conversion x for various types of intramolecular reactions.

highly sensitive indicator for the formation of cycles and multiple cross-links in finite species.[44-46,68,79,80] Here, we define the pendant conversion, x_3, as the fraction of divinyl monomer units with both vinyl groups reacted, i.e., the fraction of fully reacted divinyl monomer units in the polymer. Theories neglecting cyclization predict that 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 cross-linking is a second-order reaction, deviation from zero indicates the existence of cyclization. On the other hand, the rate of change of pendant conversion x_3 with the monomer conversion x or with the reaction time t is a measure of the extent of multiple cross-linkages.[44,79] The greater the slope of x_3 versus x or t curve, the higher the number of multiple cross-links formed per cross-link. Thus, the occurrence of multiple cross-linking will be reflected in a greater decrease in the polymer unsaturation as conversion proceeds than would otherwise occur. Figure 3 shows schematic representation of variation of pendant vinyl conversion x_3 with monomer conversion x for various types of intramolecular reactions.

Let k_{cyc} be the fraction of pendant vinyls in cycles at zero conversion and k_{mc} be the average number of multiple cross-linkages per cross-link, then, on the basis of the kinetic equations given previously,[44,68,69-75] the following rate equations for the weight-average molecular weight $\bar{M}_{\mathrm{w}}$ and the pendant conversion x_3 can be written:

$$\frac{\mathrm{d}(x\bar{M}_{\mathrm{w}})}{\mathrm{d}x} = \bar{M}^{\bullet}_{\mathrm{w}}\left[1 + \frac{r_{21}\bar{r}_{32}(1 - x_3)\bar{F}_2}{1 + (2r_{21} - 1)f_2}\left(\frac{x}{1 - x}\right)\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{u}}}\right]^2$$

$$\bar{M}_{\mathrm{w}}(0) = \bar{M}^{\bullet}_{\mathrm{w},0} \qquad \bar{M}_{\mathrm{w}}(x_{\mathrm{c}}) = \infty \tag{2}$$

$$\frac{\mathrm{d}x_3}{\mathrm{d}x} = \frac{r_{21}}{1 + (2r_{21} - 1)f_2}\left[\frac{\bar{r}'_{32}(1 - x_3)}{(1 - x)} - \frac{2f_2}{\bar{F}_2}\frac{(x_3 - k_{\mathrm{cyc}})}{x}\right]$$

$$x_3(0) = k_{\mathrm{cyc}} \tag{3}$$

where r_{21} is the reactivity ratio of vinyls on divinyl to monovinyl monomers, $\bar{r}_{32}$ and $\bar{r}'_{32}$ are the actual and apparent reactivity ratio of pendant vinyl to monomeric vinyl on divinyl monomer, respectively, f_2 and $\bar{F}_2$ are the accumulated mole fraction of divinyl monomer in the reaction mixture and in the copolymer, respectively, $\bar{M}_{\mathrm{u}}$ is the molecular weight of the repeating unit, $\bar{M}^{\bullet}_{\mathrm{w}}$ is the weight-average molecular weight of the primary chains, and x_{c} is the critical conversion at the gel point. It should be noted that the apparent reactivity ratio of pendant to monomeric vinyl $\bar{r}'_{32}$ includes both the contributions of cross-linking and multiple cross-linking reactions, and is related to the actual reactivity ratio through the equation

$$\bar{r}'_{32} = \bar{r}_{32}(1 + k_{\mathrm{mc}}) \tag{4}$$

Moreover the weight-average molecular weight of the primary chains $\bar{M}^{\bullet}_{\mathrm{w}}$ is not constant but a function of conversion due to the depletion of monomer and initiator and due to the diffusion controlled termination reactions. Assuming that the propagation rate constant remains unchanged during polymerization, the drift in the primary chain length can be calculated as follows:

$$\frac{\bar{M}^{\bullet}_{\mathrm{w}}}{\bar{M}^{\bullet}_{\mathrm{w},0}} = \frac{(\mathrm{d}x/\mathrm{d}t)}{(\mathrm{d}x/\mathrm{d}t)_0}\exp(k_{\mathrm{d}}\,t) \tag{5}$$

where the subscript 0 denotes the initial values at the start of the reaction and k_{d} is the decomposition rate constant of the initiator (for AIBN;[81] $k_{\mathrm{d}} = 1.58 \times 10^{15} \exp(-15560/T)$ in s^{-1}).

For 1,4-DVB polymerization, since $f_2 = \bar{F}_2 = 1$, eqs 2 and 3 simplify to

$$\frac{\mathrm{d}(x\bar{M}_{\mathrm{w}})}{\mathrm{d}x} = \bar{M}^{\bullet}_{\mathrm{w}}\left[1 + 0.5\bar{r}_{32}(1 - x_3)\left(\frac{x}{1 - x}\right)\frac{\bar{M}_{\mathrm{w}}}{\bar{M}_{\mathrm{u}}}\right]^2 \tag{6}$$

$$\frac{\mathrm{d}x_3}{\mathrm{d}x} = 0.5\bar{r}'_{32}\left(\frac{1 - x_3}{1 - x}\right) - \frac{x_3 - k_{\mathrm{cyc}}}{x} \tag{7}$$

Analytical solution of eq 7 and its comparison with the statistical theory are given in the Appendix. It can be seen that by using homopolymerization of divinyl monomers, the uncertainty due to the reactivity ratio r_{12} can be avoided. Note that the derivation of the equations given above makes the following assumptions: (1) steady-state approximation for the radical species (the reactivities are independent of the type of the radical end); (2) both cyclization and multiple cross-linking reactions occur at constant rates; (3) every polymer radical possesses only one radical center; (4) the mole fraction of pendant vinyl groups is independent of chain length of the polymer molecules; and (5) chain transfer reactions do not occur. As shown recently by Tobita,[82] the assumptions 3 and 4 may be reasonable approximations under ideal conditions. However, the validity of these assumptions for the present system involving microgels is not guaranteed. On the other hand, assumption 2 means that the parameters k_{cyc} and k_{mc} are constant throughout the polymerization. Because of the high degree of dilution of the present polymerization systems, it is reasonable to assume the independence of the extent of cyclization, represented by k_{cyc}, on the monomer conversion in the pre-gel period. However, since multiple cross-linking is a second-order reaction, one may expect that k_{mc} is zero at zero monomer conversion and it increases as the reaction proceeds because multiple cross-linking becomes more probable the greater the molecules formed.[79] Indeed, the kinetic gelation model proposed recently by Anseth and Bowman[83] also indicates this trend. The conversion dependence of the extent of multiple cross-linking may be represented empirically by the equation

$$\bar{r}'_{32} = \bar{r}_{32} \exp(A_1x + A_2x^2 + ...) \qquad (8)$$

where A_1, A_2, etc. are adjustable parameters. However, calculations using eq 8 instead of eq 4 would lead to no change in the present results for the extent of the pendant reactivity and cyclization but the number of multiple cross-links would increase from 0 to much higher values at the gel point than the average values k_{mc} calculated using eq 4.

The kinetic model represented by eqs 6 and 7 may be used for the calculation of the cyclization parameters k_{cyc} and k_{mc} as well as of the average reactivity ratio of pendant to monomeric vinyls for intermolecular reactions $\bar{r}_{32}$ as follows: With the use of experimental x_3 vs x data eq 7 (or eq A1 given in the Appendix) may be solved for k_{cyc} and $\bar{r}'_{32}$. In the second step, since $\bar{M}_w$ diverges at the gel point, the value of $\bar{r}_{32}$ satisfying $\bar{M}_w(x_c) = \infty$ may be obtained numerically using simultaneous solution of eqs 6 and 7. The drift in the primary chain length can be included into the calculations by fitting experimental time-conversion data using eq 5. The values of $\bar{M}^{\circ}_{w,0}$ (weight-average chain length of zero conversion polymers) may be obtained from the $\epsilon = 1$ intercept in the experimental $\bar{M}_w$ vs ϵ plots, where ϵ is the dimensionless distance to the gel point and is defined as

$$\epsilon = 1 - (x/x_c) \qquad (9)$$

Thus, in order to calculate the number of cycles and multiple cross-links per structural unit and the average reactivity ratio of pendant to monomeric vinyls, experimental monomer and pendant conversions, weight-average molecular weights versus time data together with the gel point conversions must first be obtained.

Results and Discussion

Cyclization. It is known that in free-radical polymerization cross-linking enhances the gel effect significantly and the autoacceleration in polymerization rate starts right down to zero conversion.[80,84–87] Figures 4 and 5 show plots of fractional monomer conversion, x, vs polymerization time, t, for different monomer and initiator concentrations up to the onset of macrogelation. For the systems studied here the gel effect seems to be insignificant up to the gel point, probably due to the high degree of dilution. Similar time-conversion curves were also obtained at different temperatures between 60 and 80 °C and at different 1,4-DVB/styrene ratios.[88] By using the numerical fit of the experimental time-conversion data and by using eq 5, the ratio of the weight-average molecular weight of the primary chains at conversion x to that at $x = 0$, $\bar{M}^{\circ}_w/\bar{M}^{\circ}_{w,0}$, were calculated. The results indicate only a small drift in the primary chain length during the course of the pregelation period (Figure 6).

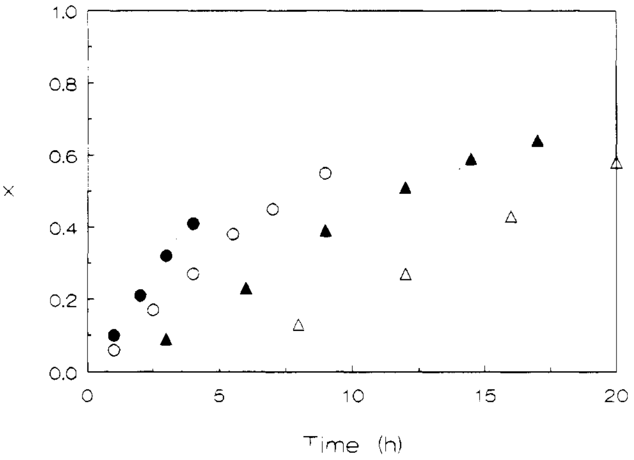

Figure 4. Variation of the conversion versus polymerization time in free-radical cross-linking polymerization of 1,4-DVB. Initial monomer concentration c = 5 (●), 2 (○), 1 (▲), and 0.5 w/v % (△). Reaction conditions: see series II in Table 1.

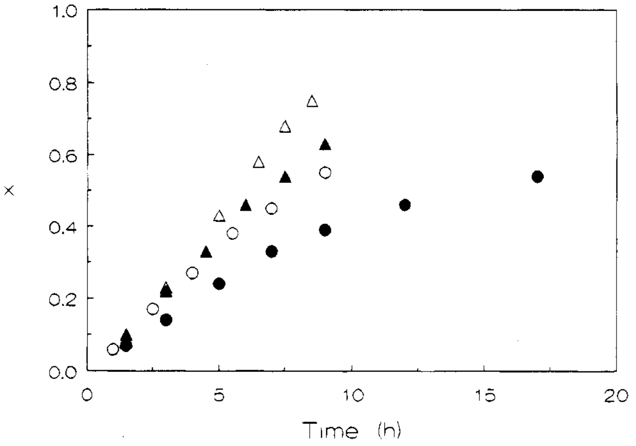

Figure 5. Variation of the conversion versus polymerization time in free-radical cross-linking polymerization of 1,4-DVB. Initial concentration of AIBN in mmol L^{-1} = 2.6 (●), 8 (○), 16 (▲), and 32 (△). Reaction conditions: see series III in Table 1.

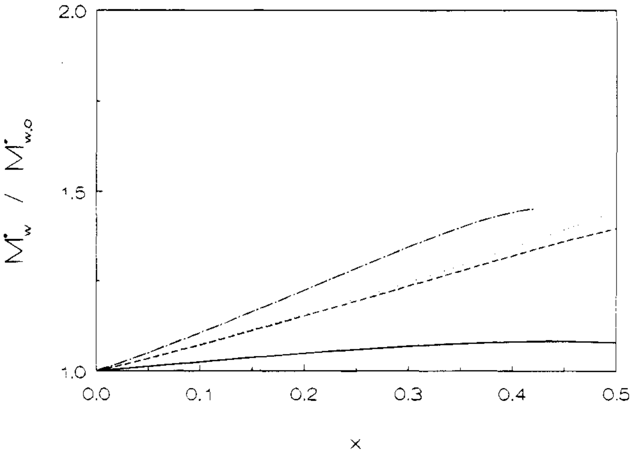

Figure 6. Drift in the primary chain length as a function of monomer conversion x. Reaction conditions: Polymerization systems of series II at c = 5(—) and 2 w/v % (- -); and series III at $[I]_0$ = 2.6 (-··-) and 16 mmol L^{-1} (···) (Table 1).

Figures 7–9 show plots of pendant vinyl conversion versus monomer conversion for different temperatures, monomer and initiator concentrations. Note that the pendant conversion is the fraction of fully reacted divinyl monomer units in the polymer. The experimental data points are shown as symbols. Error bars indicate 95% confidence interval derived from the standard deviation for the method of measurements. The curves in the figures were computed with eq A1 given in the Appendix by a least-squares curve-fitting method. The parameters k_{cyc} and $\bar{r}'_{32}$ found are collected in the first and second columns of Table 2. The agreement of theoretical curves with the experimental data seems satisfactory. From Figure 7 it can be seen that within this range of temperature (60–80 °C) increasing the temperature does not change much the extent of cyclization. Figure 8 shows the effect of the initial monomer concentration on cyclization. As the

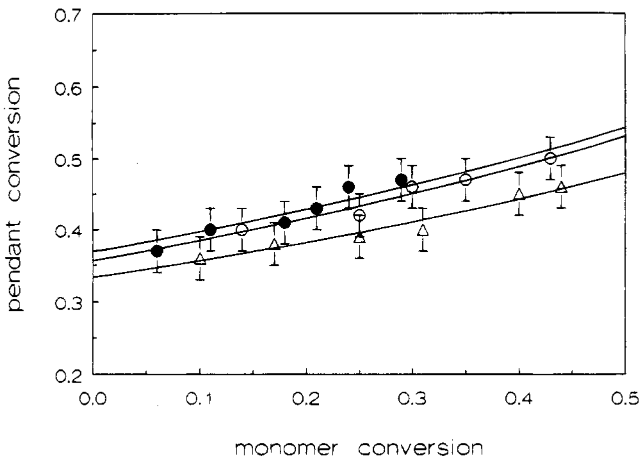

Figure 7. Pendant vinyl conversion versus monomer conversion for different polymerization temperatures. Polymers of series I in Table 1: 60 °C (●), 70 °C (△), and 80 °C (○).

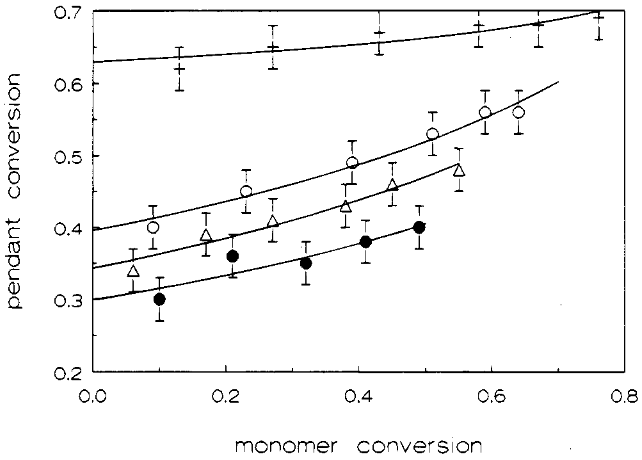

Figure 8. Pendant vinyl conversion versus monomer conversion for different degrees of initial dilution. Polymers of series II at $c = 5$ (●), 2 (△), 1 (○), and 0.5 w/v % (+).

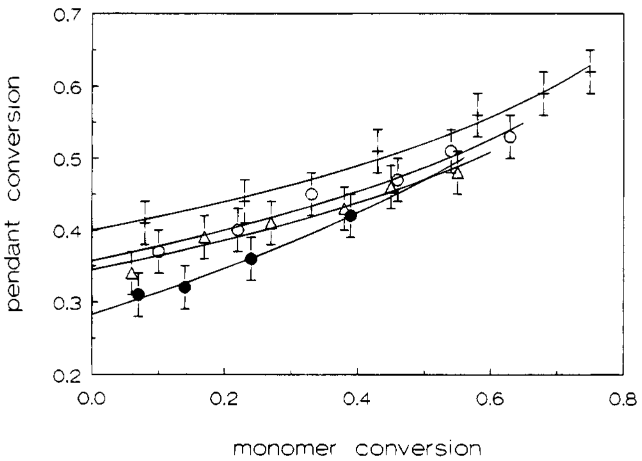

Figure 9. Pendant vinyl conversion versus monomer conversion for different initial concentration of the initiator AIBN. Polymers of series III at 2.6 (●), 8.0 (△), 16 (○), and 32 mmol L^{-1} AIBN (+).

monomer concentration decreases from 5 to 0.5 w/v %, the fraction of units in cycles, k_{cyc}, increases from 0.30 to 0.63. Figure 9 shows that with increasing initiator concentration the fraction of units in cycles k_{cyc} increases. This may be due to the more efficient consumption of pendant vinyl groups by cyclization in small particles (short chains) rather than in large particles due to steric reasons. However, as will be shown later, since the decrease in the primary chain length is faster than the increase in k_{cyc}, less cycles per primary chain form as the initiator concentration increases. Figure 10 shows the pendant vinyl conversion vs monomer conversion plots at different 1,4-DVB/styrene ratio. Because there are only two data points for each system, the lines only show the trend of data and did not allow calculations. However, it can be seen that at DVB contents higher than 40 wt %, almost the same proportion of pendant vinyls are used by cyclization. In other words, at high DVB contents the number of cycles formed per DVB unit is independent of the cross-linker concentration in the monomer mixture. However, as the DVB concentration decreases, the number of cycles decreases but, as can be seen from the slope of the lines, that of multiple cross-links increases (Table 2). This may be due to a looser microgel structure with decreasing DVB concentration, which makes the pendant vinyls more accessible for the macroradicals of other particles. Previous works of Malinsky et al.,[30,68] Soper et al.,[37] and Walczynski et al.[42] with the same system support this result. Comparison of these studies indicates that k_{cyc} is a function of the DVB content at low amounts of cross-linker, whereas it becomes insensitive at high cross-linker contents. Experimental data of Mrkvickova and Kratochvil also show the same trend.[89]

The cyclization constants k_{cyc} in Table 2 indicate that 30 to 60% of the pendant vinyl groups are used by cyclization reactions. The fraction of pendant vinyls used by cyclization increases as the dilution increases, the primary chain length decreases, or the cross-linker concentration in the monomer mixture increases up to a critical level. The apparent pendant reactivity ratio $\bar{r}'_{32}$ is about unity. However, this does not mean an equal reactivity of pendant and monomeric vinyls because $\bar{r}'_{32}$ includes the contributions of both cross-linking and multiple cross-linking reactions (eq 4).

Reduced Pendant Vinyl Reactivity and Multiple Cross-linkages. The monomer conversions at the gel point, x_c, are given in column 3 of Table 2. As expected, gelation occurs at a lower conversion as the initiator concentration decreases or monomer concentration increases (series III and II respectively). In the styrene-DVB copolymerization (series IV) the conversion at the gel point shows a minimum around 40 wt % DVB and it increases below and above with increasing content of DVB. Similar results were also obtained by Storey[15] in bulk polymerization conditions; he reported the minimum of the gel point at 20 wt % DVB.

By using the gel point data, the contributions of cross-linking and multiple cross-linking reactions to the apparent pendant vinyl reactivity ratio $\bar{r}'_{32}$ can now be separated. The value of $\bar{r}_{32}$ satisfying $\bar{M}_{\mathrm{w}} = \infty$ at $x = x_c$ may be obtained numerically by using simultaneous solution of eqs 6 and 7. In the calculations the drift in the primary chain length was taken into account by using eq 5 and the weight-average molecular weights at zero conversion $\bar{M}^{\circ}_{\mathrm{w},0}$ were calculated from the $\epsilon = 1$ intercept of experimental $\bar{M}_{\mathrm{w}}$ vs ϵ plots.

Calculation results of $\bar{M}^{\circ}_{\mathrm{w},0}$, $\bar{r}_{32}$, and k_{mc} are shown in columns 4–6 of Table 2. A 2–3 orders of magnitude decrease in the average reactivity of pendant vinyl for intermolecular reactions compared to monomeric vinyl is seen from Table 2. This drastic decrease in the pendant reactivity may predominantly be due to the extensive cyclization which decrease the mobility of segments by decreasing the size of polymer coils. On the other hand, the average number of multiple cross-

Table 2. Characteristics of the Polymerization Systems Studied[a]

series	parameter	k_{cyc}	r'_{32}	x_c	$10^{-3}M'_{w,0}$	$10^3 r_{32}$	$10^{-2}k_{mc}$	γ
I	T, °C							
	60	0.37 ± 0.03	1.8 ± 0.1					
	70	0.33 ± 0.03	1.3 ± 0.1	0.42 ± 0.015	240	2	6	1.4 ± 0.3
	80	0.36 ± 0.04	1.7 ± 0.1	0.45 ± 0.02	165	2	8	1.7 ± 0.5
II	c, w/v %							
	5	0.30 ± 0.04	0.9 ± 0.1	0.43 ± 0.02	113	6	2	1.3 ± 0.4
	2	0.34 ± 0.03	1.1 ± 0.1	0.59 ± 0.04	44	8	1	1.6 ± 0.3
	1	0.40 ± 0.03	1.2 ± 0.1	0.70 ± 0.06	30	7	2	2.1 ± 0.4
	0.5	0.63 ± 0.03	0.5 ± 0.1	(0.79)[d]	46	2	2	
III	10^3 [I], M							
	2.6	0.28 ± 0.05	1.6 ± 0.2	(0.56)[d]	77	5	3	
	8.0	0.34 ± 0.03	1.1 ± 0.1	0.59 ± 0.04	44	8	1	1.6 ± 0.2
	16	0.36 ± 0.03	1.2 ± 0.1	(0.65)[d]	46	7	2	
	32	0.40 ± 0.03	1.2 ± 0.1	(0.75)[d]	16	13	1	
IV	DVB, wt %							
	100	(0.32)[b]	(0.20)[c]	0.42 ± 0.03	240			1.4 ± 0.3
	80	(0.35)[b]	(0.15)[c]	0.41 ± 0.01	290			1.1 ± 0.3
	70	(0.37)[b]	(0.15)[c]	0.38 ± 0.02	135			1.5 ± 0.2
	60	(0.36)[b]	(0.17)[c]	(0.36)[d]	104			
	40	(0.33)[b]	(0.44)[c]	(0.35)[d]	86			
	20	(0.25)[b]	(1.07)[c]	(0.44)[d]	48			

[a] Abbreviations: k_{cyc}, fraction of pendant vinyls in cycles; k_{mc}, number of multiple cross-links per cross-link; r'_{32} and r_{32}, apparent and actual reactivity ratio of pendant to monomeric vinyl; x_c, gel point conversion; $\bar{M}'_{w,0}$, weight-average molecular weight of zero conversion polymers; and γ, critical exponent of $\bar{M}_w$ vs ϵ (a dimensionless distance to the gel point) plot. Error bars indicate 95% confidence interval. [b] Estimated from the y intercept of x_3 vs x lines in Figure 10. [c] Slope of x_3 vs x lines in Figure 10. [d] Calculated by drawing perpendicular asymptote to the experimental $\bar{M}_w$ vs x curves.

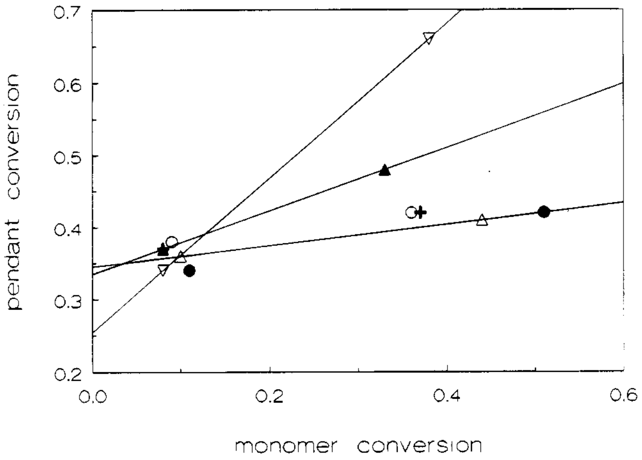

Figure 10. Pendant vinyl conversion versus monomer conversion for different 1,4-DVB/styrene ratio. Polymers of series IV at 100 (●), 80 (△), 70 (○), 60 (+), 40 (▲), and 20 wt % 1,4-DVB (▽). The lines only show the trend of data.

links formed per cross-link varies between 100 and 800. The pendant vinyl reactivity decreases further by increasing dilution (series II). The trend of data also indicates that increasing primary chain length decreases the reactivity of pendant vinyl groups and increases the number of multiple cross-links (series III). At first sight this result seems to contradict the inverse dependence of k_{cyc} on the primary chain length. However, calculations show that, although k_{cyc} decreases, the number of cycles per weight-average primary chain increases from 50 to 165 with increasing chain length, which would lead to the formation of denser structures, as seen from the decrease in the pendant vinyl reactivity.

Table 2 also indicates an interesting feature of free-radical cross-linking copolymerization: the weight-average molecular weight of zero conversion polymers, $\bar{M}'_{w,0}$, increases with the DVB concentration. This unusual behavior was also observed recently by several researchers[87,90-92] and can be explained as a result of cyclization, which decreases the mobility of segments and suppresses the diffusion-controlled termination due to steric reasons.

According to the results given above, a large number of multiple cross-links form between two polymer chains after they link together in the reaction mixture by a single cross-link. This means that there exist highly cross-linked regions in the pregel polymers which must be stable against degradation into the primary chains. In order to prove these results, degradation experiments were carried out by ultrasonic waves using polymer samples dissolved in benzene. Polymers of molecular weights $\bar{M}_w = (2-10) \times 10^6$ g/mol were used for this purpose. Figure 11a shows the variation of $\bar{M}_w$ and hydrodynamic diameter D_z measured by QELS with the degradation time for a polymer of $\bar{M}_w = 2.2 \times 10^6$ g/mol. Both $\bar{M}_w$ and D_z decrease first abruptly but then slowly until finally they reach limiting values. The final $\bar{M}_w$ was found to be about 0.64×10^6 g/mol compared to the molecular weight of zero conversion polymers, i.e., that of the "individual microgels", $\bar{M}_{w,0}$, of 0.11×10^6 g/mol (shown as dotted line in Figure 11a). Under the same experimental conditions, poly(4-methylstyrene) chains could be degradated to a molecular weight of 0.08×10^6.[93] Several experiments with polymers of different molecular weights showed a decrease in their molecular weight up to the region 1 shown in Figure 11b. Thus, there exist highly cross-linked regions in the pregel polymers due to the extensive multiple cross-linking reactions and only the large clusters formed shortly prior to gelation can be degradated. In other words we can speculate that the agglomerates of the microgels are stable due to the multiple cross-linking reactions and they form highly cross-linked regions of the polymer products.

The densely packed structure of microgels and microgel agglomerates due to the extensive cyclization and multiple cross-linking is manifested in the intrinsic viscosity $[\eta]-\bar{M}_w$ plots. Figure 12 shows such a plot for microgels obtained at different monomer concentrations. Calculation of the exponent a for each monomer concentration indicates a gradual decrease from 0.25 to 0.20 as the dilution increases. Moreover, the average value

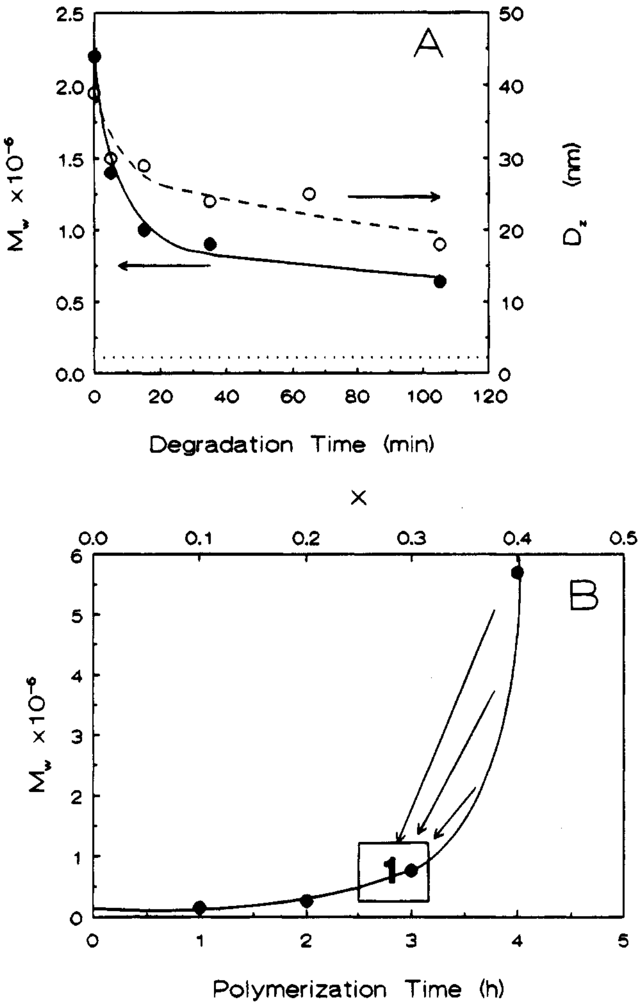

Figure 11. (A) Variation of the weight-average molecular weight, $\bar{M}_w$ (●), and hydrodynamic diameter, D_z (○), of a polymer sample from series II at $c = 5$ w/v % with time of ultrasonic degradation. The initial $\bar{M}_w$ of the polymer sample is 2.2×10^6 g/mol. The curves only show the tendency of data. The dotted horizontal line shows $\bar{M}_w$ of zero conversion polymers ("individual microgels"). (B) Variation of $\bar{M}_w$ with the polymerization time t and monomer conversion x in the synthesis of the polymers from Series II at $c = 5$ w/v %. The region 1 in the box represents the limiting $\bar{M}_w$ reached by degradation experiments.

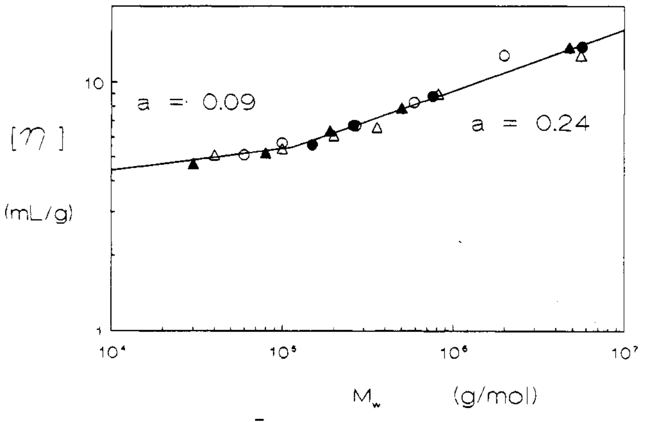

Figure 12. [η] versus $\bar{M}_w$ for series II at $c = 5$ (●), 2 (○), 1 (▲), and 0.5 w/v % (△).

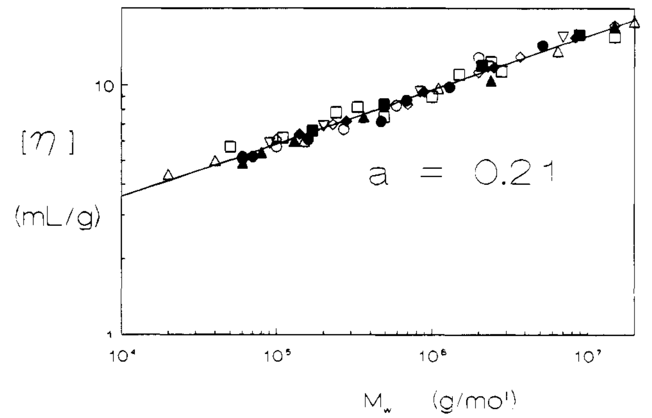

Figure 13. [η] versus $\bar{M}_w$ for series III at 2.6 (●), 8 (○), 16 (▲), and 32 mmol L^{-1} AIBN (△) and, for series IV at 100 (■), 80 (□), 70 (◆), 60 (◇), 40 (▽), and 20 wt % 1,4-DVB (▼).

of the exponent a is close to zero for $\bar{M}_w < 10^5$ as seen in Figure 12 due to the predominant cyclization and multiple cross-linking, and becomes 0.24 above this molecular weight, compared with the value $a = 0.7$ for linear polystyrene in benzene. Thus, the exponent a agrees well with the calculation results for the extent of cyclization. Figure 13 shows the same plot with a slope of 0.21 ± 0.01 for different intiator concentrations and 1,4-DVB/styrene ratios. This value of the exponent a is close to the value of 0.25 reported by Zimm et al.[29] for styrene-DVB copolymers.

In Figure 14, parts a–d, plots of $\bar{M}_w$ versus the distance to the gel point ϵ are shown for different reaction conditions. The error bars were estimated from the uncertainty in the determination of the gel point and they are smaller than the point symbol itself at $\epsilon \cong 1$. The values of the critical exponent γ are collected in column 7 of Table 2. It must be noted that the microgel formation prior to gelation requires a change in the exponent γ during the course of the polymerization. Obviously, more measurements at $\epsilon \cong 1$ are needed to derive a definite conclusion to this problem. Experimental data indicate a critical exponent γ varying between 1.1 and 2.1, depending on the conditions of synthesis. Moreover, calculation of ϵ in terms of vinyl group conversion p instead of monomer conversion[94] shifts the exponents 5–10% upward. However, calculations using eq 6 give exponents between 0.8–1.0 depending on the reaction conditions. Since all the kinetic aspects of cross-linking polymerization (unequal reactivity and drift), cyclization, and multiple cross-linking were taken into account in the calculations, the difference between the results of calculations and experiments can be accounted for the non-mean-field behavior. It must be noted that the incipient gel point is probably the region where the non-mean-field nature of the reaction system makes its greatest contribution and thus, a kinetic theory is least likely to hold because of its mean-field character. Indeed, the critical exponents γ reported in the literature for free-radical cross-linking polymerization systems are varying between 1.5 and 1.8,[92,95,96] which are much closer to the percolation value[97] of 1.74 than to the classical value[24] of 1.

Conclusions

Experimental data indicate the following features of free-radical cross-linking polymerization of 1,4-DVB in toluene solutions:

(1) The extrapolated value of pendant vinyl conversion to zero monomer conversion is always not zero, indicating the existence of cyclization. Calculations show that 30–60% of pendant vinyls are used by cyclization reactions and, on average, 100–800 multiple cross-linkages occur per one intermolecular cross-link formed. A drastic decrease in the average pendant vinyl reactiv-

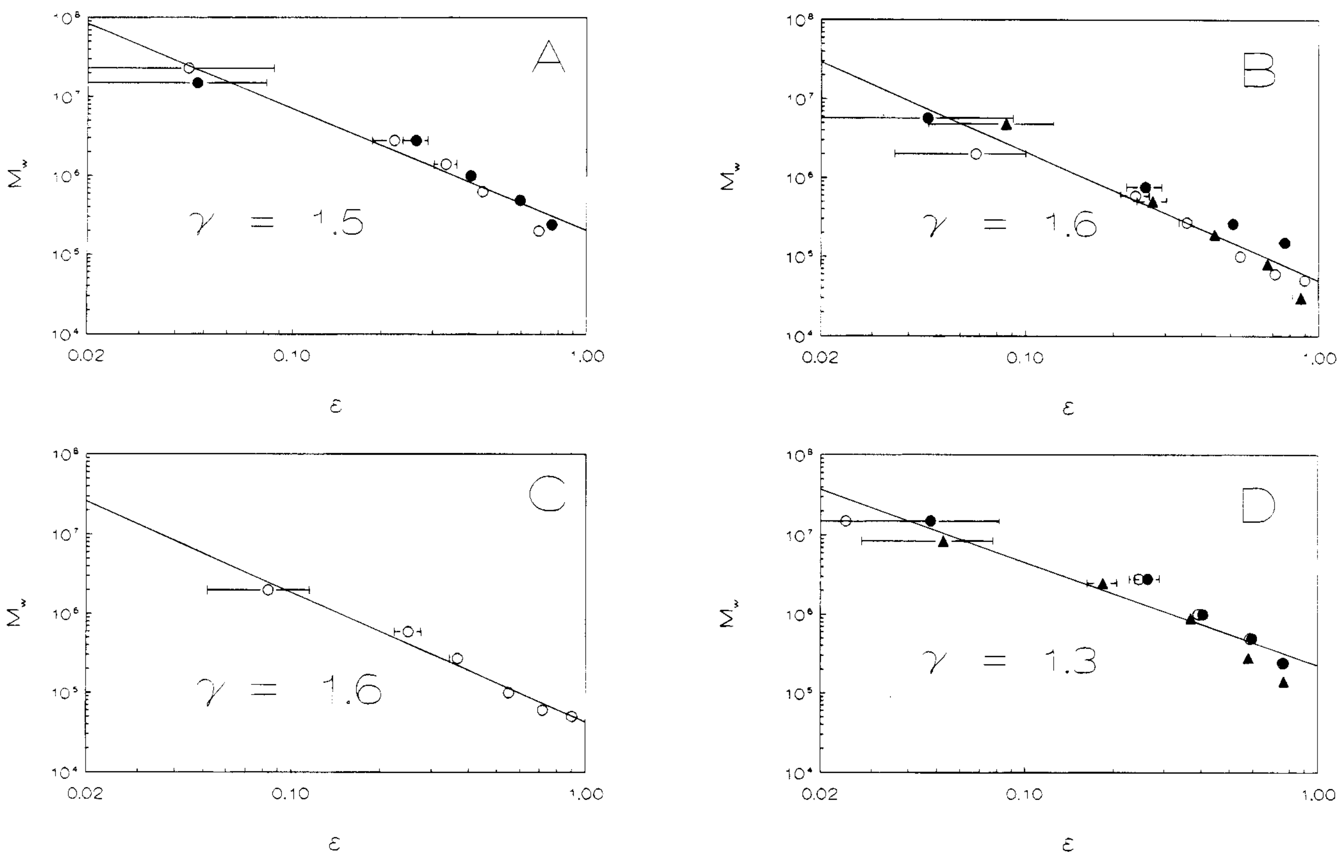

Figure 14. $\bar{M}_w$ versus ϵ plots for series I (A), II (B), III (C), and IV (D). (A) Temperature = 70 °C (●) and 80 °C (○). (B) c = 5 (●), 2 (○), and 1 w/v % (▲). (C) $[I]_0$ = 8 mmol L^{-1} AIBN. (D) DVB wt % = 100 (●), 80 (○), and 70 (▲). The critical exponents shown in the Figures are the average values for each series.

ity for intermolecular links compared to monomeric vinyl is observed. These findings agree with the observed weak $\bar{M}_w$ dependence of $[\eta]$ of the polymers and their stability against degradation to the primary particles. Thus, macrogelation in free-radical polymerization of 1,4-DVB proceeds via formation of internally cross-linked primary particles in which the reactivity of pendant vinyls is drastically reduced. It must be pointed out that, if we include cyclization and multiple cross-linking reactions, the pendant vinyl group has an apparently enhanced reactivity compared to monomeric vinyls. This is due to the much higher concentration of pendant vinyl groups than average in the vicinity of the radical end of a growing chain.

(2) Increasing dilution promotes cyclization and thus reduces further the pendant vinyl reactivity for intermolecular links.

(3) Decreasing initiator concentration decreases the fraction of units in cycles k_{cyc}. However, since the primary chain length increases faster than k_{cyc} decreases, more cycles per primary chain form as the initiator concentration decreases. This causes the reduction of the pendant vinyl reactivity and to an increase of the number of multiple cross-linkages.

(4) Increasing cross-linker concentration increases cyclization and reduces the number of multiple cross-links up to a certain level. Later on, they become insensitive to the cross-linker concentration. This behavior seems to be similar to the dependence of the critical conversion at the gel point on the amount of cross-linker in the initial monomer mixture.

Due to the sensitive dependence of the gel point on the average reactivity of pendant vinyl groups represented by $\bar{r}_{32}$, eq 6 seems to be particularly convenient for determining the value of $\bar{r}_{32}$, following the finding cyclization and multiple cross-linking parameters by using eq 7. It is to be noted that as the kinetic theories neglect excluded volume effects and the concentration fluctuations, which should play an important role in the vicinity of the gel point, the calculated critical exponent γ differs drastically from the experimental value.

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Appendix: Analytical Evaluation of Pendant Conversion, x_3, as a Function of Monomer Conversion x

Solution of eq 7 gives

$$x_3 = \left(\frac{1-x}{x}\right)\left(\frac{k_{\mathrm{cyc}} - 0.5\bar{r}'_{32}}{0.5\bar{r}'_{32} - 1}\right) + \frac{1}{x} + \frac{(1-k_{\mathrm{cyc}})}{(0.5\bar{r}'_{32} - 1)}\,\frac{(1-x)^{0.5\bar{r}'_{32}}}{x} \qquad \text{for } \bar{r}'_{32} \neq 2 \quad \text{(A1)}$$

$$x_3 = (1 - k_{\mathrm{cyc}})\left(\frac{1-x}{x}\right)\ln(1-x) + 1 \qquad \text{for } \bar{r}'_{32} = 2 \quad \text{(A2)}$$

$$x_3 \cong x/4 \qquad \text{for } \bar{r}'_{32} = 1,\ k_{\mathrm{cyc}} = 0, \text{ and } x \ll 1 \quad \text{(A3)}$$

Thus, in random free-radical cross-linking polymerization the pendant conversion becomes one-fourth of the monomer conversion, i.e., half of the vinyl group conversion, as predicted by the statistical theories.[24]

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