Cyclization in vinyl–divinyl copolymerization

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It was found by analysis of the composition and n.m.r. behaviour of low-conversion soluble copolymers of styrene (S) with 5–60 wt% of ethylene dimethacrylate (EDMA) that cyclization strongly predominates in crosslinking copolymerization. The results suggest that, especially at a higher content of the divinyl component, compact structures are formed with the character of microgel-like particles. At a higher EDMA content, this component is incorporated into the copolymer only as a unit with a pendant double bond and the content of crosslinks (EDMA units with both vinyls reacted) does not further increase with increasing EDMA content. The pendant vinyls in the particle cores are already so immobilized or sterically hindered that they are unable to react even with small molecules of the monomer. Procedures for the determination of copolymerization parameters for pairs of mono- and divinyl monomers, usually neglecting cyclization, were revised. An analysis of the theoretical model of crosslinking copolymerization with weak cyclization and experimental results obtained with the S–EDMA system with prevailing cyclization show that the copolymerization parameters need not be too much distorted, if they have been determined from the content of the mono- and divinylic components of the copolymer.

INTRODUCTION

The intensity of formation of intramolecular bonds (cyclization) depends on the relative probability of meeting between two reactive groups which have been connected already by at least one sequence of bonds. If the extent of cyclization, σ, is measured relatively with respect to the extent of the intermolecular reaction, α, the smallest extent of cyclization can be expected for stepwise reactions of components (monomers) that cannot form cycles by reactions between their groups; a somewhat higher cyclization is expected and observed in the crosslinking of primary chains, while the most intensive cyclization occurs at the beginning of chain crosslinking copolymerizations. σ/α in the limit of zero degree of crosslinking (onset of reaction) is zero for stepwise reactions, finite for the crosslinking of primary chains and infinite for chain reactions.

The extent of cyclization thus expressed is so high for crosslinking chain copolymerizations because, at the beginning of the reaction, the individual chains (dissolved in the monomer) are virtually isolated from each other; hence, the probability of a reaction between the growing macroradical and one of the pendant double bonds attached to it is finite, while the probability of a reaction between this macroradical and the double bond on another chain approaches zero as the reaction conversion goes to zero. With increasing polymerization conversion, the chain concentration increases; consequently, the fraction of crosslinks consumed in the cycles, and thus also σ/α, decrease.

This extent of cyclization in the chain crosslinking copolymerization is evident from many experimental results[1–11] concerning a relatively low content of unreacted double bonds at low conversions, or a shift of the gel point by an order of magnitude towards higher conversions. Some of these results also indicate the reduced reactivity of pendant vinyls at a high content of the divinyl component. Theoretical descriptions include cyclization into kinetic equations through the cyclization factor, which is regarded either as independent of conversion and of the length of the macroradical[9,10], or approximates these dependences e.g. in the approach based on the theory of branching processes, which has been applied to the polymerization of a bisunsaturated monomer[12].

In all the theoretical procedures, all the pendant double bonds in branching or cyclization reactions have so far been assumed accessible; the ability of the pendant double bonds to react intermolecularly has been assumed independent of the structure of the polymer which carries them. In the theory of branching processes based on the graph model and cascade substitution, the cyclization probability is derived from the probability of meeting between the reacting sites joined by a single sequence of bonds in the absence of the excluded volume. The application of this procedure fitted experimental results well for systems with weak cyclization (stepwise reactions, crosslinking of primary chains) and has been successfully extended also beyond the gel point[13]. A reasonable fit has been reached for more strongly crosslinked systems[12], but only because of some compensation for the neglected correlation with the existing cycles by raising the chain flexibility factor.

In some cases, the cyclization has been neglected altogether, e.g. in the determination of the copolymerization parameters for pairs of mono- and divinyl monomers[14–19], although the rate of addition of the pendant double bond differs, depending on whether that bond is attached to the given macroradical or not. It is questionable whether the copolymerization parameters are really determined by the relative reactivities of monomers towards the given type of the free radical or not. We analysed the problem by comparing results of a simple statistical model with those of experimental studies on the copolymerization of styrene and ethylene dimethacrylate and on the structure of low-conversion copolymers by n.m.r. methods. Th study had as its objectives

(1) to explain what error may be made in the determination of the copolymerization parameters while neglecting cyclization, and whether procedures can be found to eliminate the effect of cyclization;

(2) to characterize the mechanism of network formation, considering changes in the copolymer structure.

EXPERIMENTAL

Materials and preparation of copolymers

Monomers. Styrene (S), methyl methacrylate (MMA) and ethylene dimethacrylate (EDMA) were shaken with 5%

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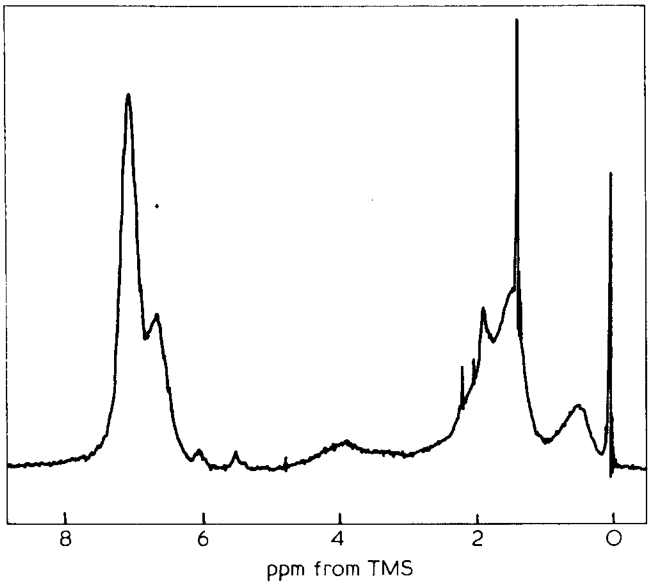


Figure 1 ^1H n.m.r. spectrum of copolymer of styrene with ethylene dimethacrylate in CCl_4 (conc. 10% (w/v)) measured at 100 MHz and 65°C

NaOH, washed with water, dried with anhydrous Na_2SO_4, stabilized with n-octylpyrocatechol (S, EDMA) or 2,2′-methylene-bis(4-methyl-6-tert.-butylphenol), and redistilled under reduced pressure in nitrogen. Purity was checked by gas chromatography.

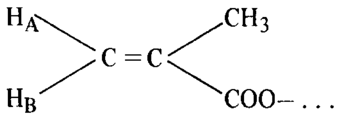
Other chemicals. Benzoyl peroxide was recrystallized from acetone solution; the other chemicals, reagent grade, were used as recieved.

Copolymerization. The copolymerization was carried out in glass ampoules. The solution was bubbled through with nitrogen for approximately 2 min. The ampoules were sealed and placed in a thermostat. The polymerization was initiated with 0.1–1.5% benzoyl peroxide (related to the monomers) and proceeded at 60°–75°C depending on the styrene and diluent concentration. After a reaction time which kept conversion below the critical conversion at gelation, the ampoules were removed from the thermostat and quickly cooled to 0°C. The ampoules were opened and the contents were poured into methanol in excess containing 0.1% of 2,6-ditert.-butyl-4-methylphenol (antioxidant K4), which inhibited the polymerization of pendant double bonds. The ampoule was rinsed with CCl_4 containing 0.1% of K4. The precipitate was once more reprecipitated from CCl_4 with methanol; the solvent and the precipitant again contained 0.1% of the antioxidant K4. The precipitate was dried at room temperature and reduced pressure (100 Pa). In the absence of K4, the drying was accompanied by crosslinking and loss of copolymer solubility. No inhibitor was added in the process of isolation of the copolymers S–MMA during the reprecipitation.

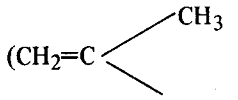
N.m.r. measurements

Solutions of copolymers S–EDMA or S–MMA, 10% w/v concentration, were prepared in measuring cells. CCl_4 containing 0.1% of the antioxidant K4 was used as solvent. With the exception of measurements, the sealed cells with copolymer solutions were kept in a refrigerator. ^1H n.m.r. spectra were recorded with a JEOL-PS-100 spectrometer at 100 MHz and 65°C. Integrated intensities were measured with a built-in integrator with a relative accuracy of ±1%.

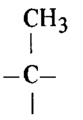
For illustration, the ^1H n.m.r. spectrum of one of the S–EDMA samples studied is given in *Figure 1*. The band at the extreme right corresponds to HMDS; a sharp band at 1.4 ppm and weaker sharp bands at 2.05 and 2.2 ppm are due to the antioxidant K4. The range 6.5–7.3 ppm comprizes bands of the aromatic protons of S units. The aliphatic protons of S units contribute to the wide band in the range 1.0–2.5 ppm. EDMA units may exist for the S–EDMA copolymers in two forms, namely, as EDMA units with the pendant double bond or with both reacted double bonds. The vinyl protons yield bands at 5.5 ppm (H_A) and 6.0 ppm (H_B) denoted as H_A, H_B, which can be seen in the formula:



(the assignment follows from an analogy with MMA)[20]. The protons of $-OCH_2$ yield a wide band at ~4 ppm. The $-CH_2-$ protons contribute to the wide band in the range 1.0–2.5 ppm, while those of the CH_3 group in the immediate vicinity of the double bond



give the band at 1.9 ppm. Contribution to the wide band at 0.6 ppm is due to CH_3 groups of the type



$$-CH_2-\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}-$$

The composition of copolymers S–EDMA characterized by the molar fractions of styrene, x_1, and ethylene dimethacrylate, x_{DV}, or of ethylene dimethacrylate units with the pendant double bond, x_2, and with both reacted vinyls, x_3, was determined from:

$$x_{DV} = (I_{EDMA}/14)/(I_{EDMA}/14 + I_{S-ar}/5)$$

$$x_2 = (I_{CH_2=}/2)/(I_{EDMA}/14 + I_{S-ar}/5)$$

$$x_3 = x_{DV} - x_2,\; x_1 + x_2 + x_3 = 1$$

where I_{S-ar} is the integrated intensity of the band of the aromatic protons of S units, $I_{CH_2=}$ is the integrated intensity of bands of the vinyl protons. I_{EDMA} is given by:

$$I_{EDMA} = I_{tot} - (8/5)I_{S-ar} - I_{K4}$$

where I_{tot} is the total integrated intensity of the recorded spectrum (except HMDS), and I_{K4} is the integrated intensity corresponding to the antioxidant K4 in CCl_4 determined by measuring the solvent with K4 under the same conditions as those used in measurements of the copolymers.

The composition of the copolymers S/MMA was determined from:

$$x_{MMA} = (I_{MMA}/8)/(I_{MMA}/8 + I_{S-ar}/5)$$

where I_{MMA} is defined analogously as I_{EDMA}.

RESULTS AND DISCUSSION

Model

A usual assumption is that a bond may be formed when reactive groups meet in an elementary reaction volume. We start with such an assumption, extending our speculations concerning the course of copolymerization of the mono- and divinyl monomer at low conversions (no compositional drift) to include cyclization. The model is based on the following assumptions.

(a) The rate of intermolecular reactions (addition of monomers, and addition of pendant double bonds leading to intermolecular crosslinks, i.e. between chains so far unlinked) is given by the average concentration of the addition partners in the system and their reactivities and is independent of the degree of polymerization of the particle to which the reaction sites are attached (the usual assumption in the copolymerization).

(b) The local concentration around a free radical of those double bonds that already are connected with that radical through at least one bond sequence determines the rate of cyclization.

(c) The local concentration of cyclizable bonds is given by the probability that the ends of a single sequence of bonds separating the reaction sites meet in the reaction volume. This probability is defined by the statistics of the equivalent chain. The effect of possibly existing cycles is neglected.

It may be expected that the above assumptions hold at low extent of cyclization. At a high extent of cyclization, the assumptions (a) and (c) need not be fulfilled.

In the Appendix, the assumptions just described are used to derive relationships between composition and the copolymerization parameters r_1, r_2 for copolymerization of a monovinyl monomer with a symmetrical divinyl monomer having vinyls with independent reactivity. Such a treatment yields a modified relationship between the composition of the monomers and of the copolymer (equation (A8)):

$$F_1 = [f_1(f_1r_1 + 1 + Y)]/(f_1 + r_2 + Yr_2) \qquad (1)$$

where F_1 is the concentration ratio of the mono- and divinyl monomer units in the polymer and f_1 is the concentration ratio of double bonds in the mono- (M_1) and divinyl (M_2) monomer, M_1/M_2. The factor $Y = Pm_2/M_2C_0$ expresses the effect of cyclization. It is proportional to the cyclization constant P, which is dependent on the chain flexibility and on the size of the smallest ring (equation (A17)), and to the fraction of units with pendant double bonds m_2 (equation (A10))*, being inversely proportional to the initial concentration C_0 of double bonds in the system (equation (A18)) and to the molar fraction M_2 of double bonds belonging to the divinyl monomer. In the ring-free system, $P = 0$, and also $Y = 0$, and equation (1) assumes a form usual for binary copolymerization systems.

After substitution for m_2 from equation (A10), the expression for F_1 (equation 1) may be expanded in power series with respect to $(1/C_0)$, and by extrapolating to $(1/C_0) = 0$, one obtains copolymerization parameters, and also the cyclization constant P. The plot against $1/C_0$ is equivalent to the plot against $1/\nu_0$, in which ν_0 is the volume fraction of monomers in the system at the beginning of the reaction. The extrapolation to $(1/\nu_0) = 0$, suggested by Jacobson and Stockmayer[21], suggests that cyclization increases with increasing dilution of the system. Successful application of the procedure depends on the reliability of extrapolation over the experimentally inaccessible range $(1/\nu_0) = 1$ to 0, where $\nu_0 = 1$ corresponds to undiluted monomers.

Model calculations (*Figure 1*) show that:

(1) the polymer composition with respect to the content of units of the mono- and divinyl monomer should not vary too much with dilution, while the fraction of units with pendant double bonds should decrease considerably at the expense of the formation of intramolecular crosslinks;

(2) the major part of the expected change of composition with dilution corresponds to the experimentally inaccessible range $1/\nu_0 \epsilon (0,1)$, which impedes reliable, extrapolation. The model described should be asymptotically valid at zero cyclization and should thus describe the network formation at very low concentrations of the divinyl monomer. In the next section, we examine the applicability of the model for systems not complying with the condition of low divinyl concentration.

Copolymerization of styrene with ethylene dimethacrylate

Toluene was selected as diluent for the copolymerizations; the copolymerization of styrene with methyl methacrylate was studied first, in order to verify that the diluent did not affect the copolymerization behaviour. Within the range studied, 0–60 vol% of toluene, the copolymer composition determined by ^{1}H n.m.r. spectrometry and elemental analysis was independent, within experimental error, of the content of the diluent. In *Table 1*, the calculated copolymerization parameters are given, along with several reported data. For this reason in the copolymerization of styrene (S) with ethylene dimethacrylate (EDMA) the diluent should affect the copolymerization behaviour only by its diluting effect, i.e. by the fact that dilution raises cyclization.

The molar fractions of EDMA units (x_{DV}) and of EDMA units with the pendant double bond (x_2) or with both reacted double bonds (x_3) were determined at various dilutions ν_0 and compositions. *Table 2* and *Figures 2* and *3* summarize results from at least three independent experiments; the reproducibility was ±1%. The weight polymerization conversions varied from 0.01 to 0.04; the example given in *Table 3* indicates, however, that even within a broader range of conversions the copolymer composition is virtually conversion-independent. The results show that the overall copolymer composition given by x_{DV} or f_1 in equation (1)

Table 1 Copolymerization parameters of styrene (S) with methyl methacrylate (MMA) and of styrene with ethylene dimethacrylate (EDMA)

	r_1	r_2	T(°C)	Source
S–MMA	0.55	0.58	90	ref 22
	0.52	0.46	60	ref 23
	0.54	0.50	60	ref 21
	0.52	0.49	60	ref 25
	0.51	0.49	75	This paper
S–EDMA	0.35	0.65	60	ref 14
	0.42	0.37	75	This paper bulk, exp.
	0.40	0.51	75	This paper extrapolated to $1/\nu_0 = 0$

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* the relations between x_i and m_i values are: $m_1 = x_1/(x_1 + x_2 + 2x_3)$, $m_2 = x_2/(x_1 + x_2 + 2x_3)$, $m_3 = 1 - m_1 - m_2$

Table 2 Composition of copolymers of styrene with ethylene dimethacrylate as a function of dilution

	Initial volume fraction of monomers, v_0				
$w_{2,0}$	1	0.8	0.6	0.4	0.2
Molar fraction of EDMA, x_{DV}					
0.05	0.12_0	0.11_5	0.12_5	0.11_0	–
0.10	0.18_5	0.19_0	0.18_5	0.16_5	–
0.20	0.28	0.26_5	0.26_0	0.25_0	0.22
0.40	0.43_0	0.42_0	0.40_0	0.39_0	–
0.60	0.55_5	0.55_5	0.53_0	0.53_0	0.46
Fraction of EDMA units in cycles, σ					
0.05	0.62	0.65	0.55	0.70	–
0.10	0.60	0.57	0.53	0.58	–
0.20	0.46	0.52	0.46	0.51	0.54
0.40	0.31	0.34	0.34	0.36	–
0.60	0.25	0.25	0.23	0.21	0.30

$w_{2,0}$, weight fraction of EDMA in the polymerizing system; $\sigma = x_3/x_{DV}$

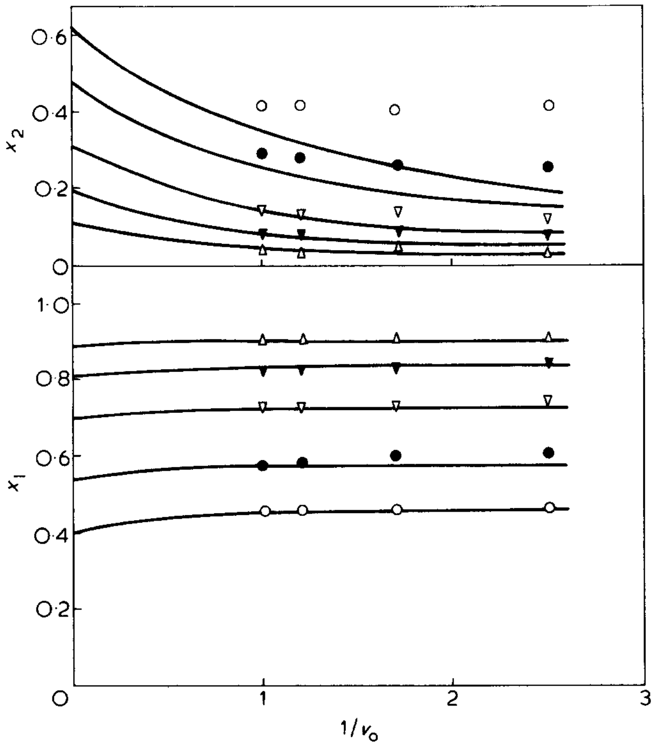

Figure 2 Dependence of molar fraction of styrene units (x_1) and ethylene dimethacrylate units with pendant double bond (x_2) in copolymer on dilution. Initial weight fraction of EDMA, $w_{2,0}$: △, 0.05; ▲, 0.10; ▽, 0.20; ●, 0.40; ○, 0.60. Curves are calculated according to equation (1) for $r_1 = 0.4$, $r_2 = 0.52$, $q = 3$, $k_m = 3$, $l = 0.25$ nm

is only slightly dependent on the dilution of the system, which is also predicted by the simple model (cf. *Figure 1*). The slight increase in the styrene content with dilution also satisfies such a prediction. The copolymerization parameters determined by double plots according to Finneman–Ross[26] from the composition at copolymerization in bulk (*Table 1*) ($r_1 = 0.42$, $r_2 = 0.37$) and from linearly extrapolated values to $1/v_0 = 0$ ($r_1 = 0.40$, $r_2 = 0.51$) differ from each other, but not too much. It seems, therefore, that neglecting cyclization in the determination of r_1 and r_2 need not be wrong if they are calculated from the content of the mono- or divinyl component. A more detailed analysis would be required, however, for pairs of monomers differing more distinctly from ideality in their copolymerization behaviour.

The result just mentioned seems also to suggest that the simple model discussed here is a tolerable approximation. Changes in the content of EDMA units with the pendant double bond and with both reacted bonds (*Figures 2* and *3*) show, however, that this is not so. Evidence for this is:

(a) the content of pendant double bonds considerably exceeds expected values, especially at a high EDMA content (*Figure 1*);

(b) with increasing EDMA content in the mixture, the content of EDMA units with both double bonds reacted tends towards a limiting value beyond approximately 20 wt% of EDMA in the mixture; during the further rise in the EDMA concentration, this component is incorporated into the copolymer only as a unit with the pendant double bond (*Figure 2*).

Such a course cannot be obtained by adjusting the value of the cyclization constant *P*. In the low concentration range of the divinyl monomer, the change in composition approaches the expected course, and one may assume a better agreement with the model, which after all should be exactly valid in the limit of zero concentration of the divinyl

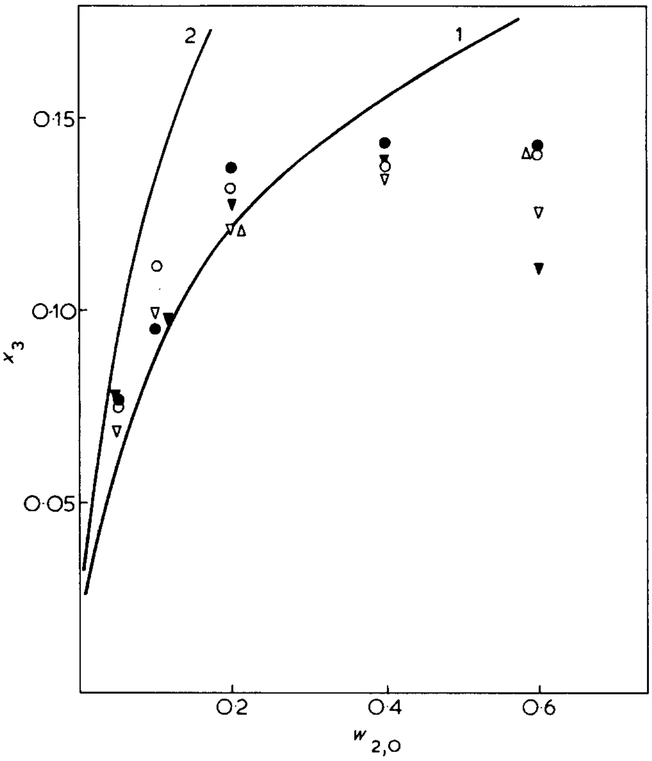

Figure 3 Dependence of molar fraction of ethylene dimethacrylate units with both reacted double bonds (x_3) on initial weight fraction of divinyl monomer at various dilution. v_0: ○, 1.0; ●, 0.8; ▽, 0.6; ▲, 0.4; △, 0.2. Curves were calculated using the procedure described in the Appendix for $v_0 = 1$ (curve 1) and $v_0 = 0.4$ (curve 2) for $r_1 = 0.4$, $r_2 = 0.52$, $q = 3$, $q = 3$, $k_m = 6$, $l = 0.25$ nm

Table 3 The dependence of the composition of the copolymer S–EDMA on weight conversion ξ at $w_{2,0} = 0.20$, $v_0 = 0.6$

ξ	0.011	0.022	0.026	0.055	0.069	0.081
x_{DV}	0.25_5	0.26_5	0.27_0	0.25_5	0.24_0	0.26_5
x_2	0.14_5	0.15_0	0.13_5	0.13_5	0.15_0	0.14_0

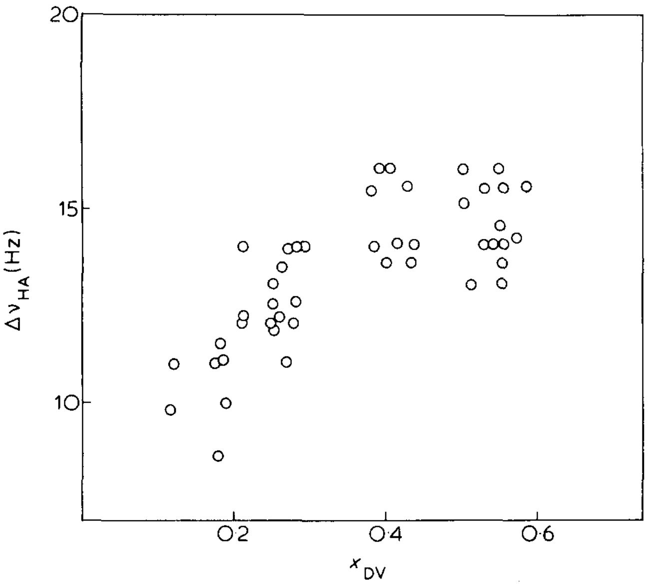

Figure 4 Line width $\Delta\nu$ of vinyl protons H_A in high-resolution n.m.r. spectra *versus* content of ethylene dimethacrylate units (x_{DV}) in copolymer

component. The results also show that the degree of cyclization remains virtually unchanged with dilution and decreases with increasing EDMA content, at variance with the usual views on the effects of these factors on cyclization.

Network formation in vinyl–divinyl copolymerization

The observations described above indicate the invalidity of assumptions employed in the formulation of a simple model at a higher content of the divinyl component. Certainly, there is a breach of the validity of assumption (b) about the functional form for the positional probabilities of two reactionable sites but the predominant effect is due to the invalidity of assumption (a). Intermolecular reactions are no more controlled by the average concentration of reacting species, and the independence of reaction ability for groups attached to particles of varying size and symmetry is not valid either: some of the pendant double bonds are buried inside the compact intramolecularly-crosslinked structure and have only a limited chance to react even with small molecules of the monomer. Minnema and Staverman call this effect shielding[7]. A considerable drop in the reaction ability of pendant double bonds in microgel particles has also been observed by Funke *et al.*[27]. The content of pendant vinyls in the copolymer does not change with conversion at a high content of the divinyl component[11]. The compactness of the internally highly crosslinked particles is supported by recent findings of Shah *et al.*[28], who found that the content of pendant vinyls decreased and polymerization rate increased in crosslinked styrene copolymers with increasing separation of vinyls in the crosslinking agent. The increasingly flexible bridge in the crosslinking agent lowers the stiffness (compactness) of the structure and allows more pendant vinyls to take part in polymerization.

The compactness of structures (having the character of small microgel particles with a diffuse boundary, forming homogeneous solutions), which arise in the crosslinking copolymerization at its very beginning, is also documented by a detailed analysis of n.m.r. measurements. *Figure 4* shows that the line widths $\Delta\nu$ of vinyl protons H_A (at 5.5 ppm) increase with increasing x_{DV} and do not seem to change much at x_{DV} higher than 0.3–0.4. At the same time, broadening of the bands of H_A protons indicates a limited mobility of these protons.

The integrated intensity of high resolution bands corresponding to the S or EDMA protons is smaller than that adequate for the mass of copolymer present. This contention is supported by comparing the intensities with those found for poly(methyl methacrylate) or copolymers of styrene and methyl methacrylate. Thus, for copolymers prepared from a mixture with 5 wt% EDMA ($w_{20} = 0.05$, $x_{DV} = 0.12$), only 70% of protons present in the copolymer are seen in the spectrum, while at 60 wt% EDMA ($x_{DV} = 0.54$), this fraction drops to 30%. The mobility of a large part of protons is considerably restricted, similarly as in swollen PMMA or PS gels[29,30], so that these protons yield a broad band, which cannot be detected in the ^1H n.m.r. high resolution spectrum. It is questionable whether the composition of the part of mass 'seen' by the ^1H n.m.r. high resolution spectra is different from that of the remaining part. That this is *not* so in systems studied by us can be demonstrated by a comparison with other analytical methods. Results of elemental analysis show that the total content of the S and EDMA units coincides with n.m.r. data within the limits of experimental error. Further more, from a comparison between the results obtained by analysis of ^1H n.m.r. spectra and infra-red spectra, x_2 values determined independently by the two methods *are* the same.

Combining these and published results, it is possible to formulate the initial process of the vinyl–divinyl crosslinking copolymerization at higher contents of the crosslinking agent.

Owing to a strongly developed cyclization, densely internally crosslinked and microgel-like formations arise even at the beginning of copolymerization. In these formations, a majority of pendant vinyls are so immobilized that they cannot participate easily in inter- and intramolecular crosslinking reactions. The reaction rate for double bonds in the surface layer is much higher than that for internal double bonds, and the particles are linked only through these reaction sites (cf ref 27). Dilution does not raise the fraction of intramolecular bonds to any important degree, even if it shifts critical conversion at the gel point towards higher values, by increasing the multiplicity of connections of particles. Such a mechanism also operates in the formation of macroporous systems, in which strong cyclization is combined with effects of the thermodynamic instability of the system and with the formation of phase boundaries[31]. With the exception of the range of very low contents of the divinyl component, assumptions allowing a theoretical treatment of the crosslinking copolymerization, usually employed for systems with mild cyclization (tree-like models and spanning-tree approximation), are not fulfilled. Therefore,deviations from the assumed dependence, e.g. of the average molecular weights, on conversion and on the degree of polymerization of primary chains P_0, or of critical conversion on P_0 and dilution may be expected. A system involving spherical formations with an interacting surface layer would probably be a better approximation of reality.

In spite of the strong cyclization and deviations in crosslinking copolymerization from the usual view, the copolymerization parameters determined with neglection of cyclization need not be too distorted. Consequently, many data reported in the literature may be regarded, cautiously, as an approximate measure of the reactivity of vinyl groups.

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APPENDIX

Low-conversion copolymerization of the mono- and divinyl monomer with cyclization

Let us consider the copolymerization of the monovinyl and symmetrical divinyl monomers with an independent reactivity of vinyls in the limit of zero conversion. Three types of vinyls exist in the system: monovinyl monomer (component 1, molar fraction M_1), divinyl monomer (component 2, M_2), and pendant vinyl on the formed polymer (component 3, M_3). m_1, m_2, m_3 denote fractions of reacted vinyls in the polymer, m_2 being related to reacted vinyls in the divinyl unit with the pendant double bond, and m_3 denoting reacted vinyls in the divinyl unit with both bonds reacted. The concentrations of the corresponding free radicals are denoted with R_1, R_2, R_3.

The kinetic equations for the change of m_i with time are given by:

$$v'_1 = \mathrm{d}m_1C_p/\mathrm{d}t = M_1C_0(k_{11}R_1 + k_{21}R_2 + k_{31}R_3) \quad \text{(A1)}$$

$$v'_2 = \mathrm{d}m_2C_p/\mathrm{d}t = -M_3C_0(k_{13}R_1 + k_{23}R_2 + k_{33}R_3) - Pm_2(k_{13}R_1 + k_{23}R_2 + k_{33}R_3) + M_2C_0(k_{12}R_1 + k_{22}R_2 + k_{32}R_3 \quad \text{(A2)}$$

$$v'_3 = \mathrm{d}m_3C_p/\mathrm{d}t = 2C_0M_3(k_{13}R_1 + k_{23}R_2 + k_{33}R_3) + 2Pm_2(k_{13}R_1 + k_{23}R_2 + k_{33}R_3) \quad \text{(A3)}$$

where P is the probability of cyclization and has the meaning of a local concentration of segments provided by the same chain, C_0 is the initial number of vinyls, and C_p is the number of reacted vinyls in unit volume.

Units with the pendant double bond (m_2) are formed by the addition of the divinyl monomer and disappear either due to crosslinking reactions (M_3C_0) or due to cyclization reactions (Pm_2). Similarly, units with both reacted double bonds are formed both by crosslinking and by cyclization reactions.

If the reaction proceeds to a low conversion of vinyls, i.e. $M_3 \to 0$, then, from the condition of the symmetry and independence of the reactivity of vinyls in the divinyl monomer we obtain:

$$k_{i3} = k_{i2} \text{ and } k_{3j} = k_{2j}$$

Under stationary state conditions for radical concentrations R_1, R_2, R_3, we obtain:

$$R_3/R_2 = Y \quad \text{(A4)}$$

$$R_2/R_1 = k_{12}/k_{21}f_1 \quad \text{(A5)}$$

$$R_3/R_1 = (k_{12}/k_{21})(Y/f_1) \quad \text{(A6)}$$

where

$$f_1 = M_1/M_2 \text{ and } Y = Pm_2/M_2C_0$$

The concentration ratio of monovinyl and divinyl units in the polymer:

$$F_1 = m_1/(m_2 + m_3/2) = \mathrm{d}m_1/(\mathrm{d}m_2 + \mathrm{d}m_3/2) \quad \text{(A7)}$$

is obtained by substituting (A4)–(A6) into equations (A1)–(A3):

$$F_1 = f_1(f_1r_1 + 1 + Y)/(f_1 + r_2 + Yr_2) \quad \text{(A8)}$$

where $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are the copolymerization parameters. By ruling out cyclization, $P = 0$, (A8) becomes the usual copolymerization equation for a binary copolymer.

In equation (A8), f_1 is given by the initial concentration of vinyls of types 1 and 2, but the relation for m_2 and the cyclization factor P are still to be found. The fraction m_2 in the limit of zero conversion is given by:

$$m_2 = v'_2/(v'_1 + v'_2 + v'_3) \quad \text{(A9)}$$

which, after substitution for R_i, gives:

$$m_2 = \{[1 + (r_2/f_1)(1 + Y)](1 - Y)\}/\{f_1r_1 + (1 + Y)[2 + (r_2/f_1)(1 + Y)]\} \quad \text{(A10)}$$

i.e. a cubic equation with respect to m_2 as a function of r_1, r_2, M_1, M_2, P and C_0.

For a ring-free case ($P = 0$ or $C_0 \to \infty$):

$$\lim_{\substack{P=0\\C_0\to\infty}} m_2 = (f_1 + r_2)/(r_1 f_1^2 + 2f_1 + r_2) \tag{A11}$$

as also follows from the solution of the system (A1)–(A3) for $P = 0$. By expanding m_2 (equation (A10) into a power series of $1/C_0$, we obtain:

$$Y = b_1/C_0 - b_2/C_0^2 + \ldots.. \tag{A12}$$

where:

$$b_1 = [(f_1 + r_2)/(f_1^2 r_1)]\,(P_2/M_2)$$

$$b_2 = [(f_1 + r_2)(f_1^3 r_1 + 4f_1^2 + 5f_1 r_2 + 2r_2^2)/ (f_1^2 r_1 + 2f_1 + r_2)^3]\,(P/M_2)^2$$

By substituting equation (A12) into equation (A–8) and expanding into a series, we obtain:

$$F_1 = a_0 + a_1/C_0 - a_2/C_0^2 + \ldots. \tag{A13}$$

where:

$$a_0 = f_1(f_1 r_1 + 1)/(f_1 + r_2)$$

$$a_1 = f_1^2 b_1 (l - r_1 r_2)/(f_1 + r_2)^2$$

Hence, by plotting F_1 against $1/C_0$ and using intercepts on the y-axis for various f_1, it would be possible to determine r_1, r_2, and, by using the limiting slope also, the probability P.

The cyclization probability may be guessed from the conformational statistics of the equivalent chain. For the meeting between the kth and mth segments, where $|k - m| = i$, in the reaction volume δV it holds that:

$$P_i \delta V = (3/2\pi i l_s^2)^{3/2} \delta V \tag{A14}$$

where l_s is the length of the statistical segment, which contains $q = n/n_s$ of monomeric segments. The total probability of cyclization by reaction of the growing macroradical with the pendant double bond on any chain segment, is:

$$P = q \sum_{i=k}^{n_s-1} P_i \tag{A15}$$

Since the growing macroradical may be of different length from 1 to $n_s - 1$ (of ref 32), it holds that:

$$P = (3/2\pi l_s^2)^{3/2} (q/n_s) \sum_{i=k}^{n_s-1} (n_s - i)\, i^{-4/2} \tag{A16}$$

where k is the number of segments in the smallest ring.

For high n_s, the sum may be replaced by the integral to obtain:

$$P = 2(3/2\pi l^2)^{3/2} q^{-3/2} k_m^{-1/2} \tag{A17}$$

where l is now the length of the monomer unit, and k_m is the number of monomer units in the smallest ring.

The total initial concentration of double bonds in the volume unit is derived as:

$$C_0 = N_a (f_1 + 1)/(V_1 f_1 + V_2/2) v_0 \tag{A18}$$

where N_a is the Avogadro number, V_1, V_2 are the molar volumes of components 1 and 2, and v_0 is the initial volume fraction of monomers in the system.