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Cyclization in Chain-Crosslinking Copolymerization

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Summary

Styrene and ethylene dimethacrylate were polymerized in benzene solutions to high conversions. Gels were prepared from critical concentrations of the divinylidene monomer and the fractions of the divinylidene units engaged in intermolecular crosslinks were estimated. The fractions were found to be very small, viz. 5, 10 and 18 % at the total monomer concentrations 1, 2 and 3 mol/dm^3, respectively. Behaviour of pregel polymers suggests that cyclization of primary chains and multiple crosslinking are responsible for the low efficiency of the crosslinking agent.

Introduction

A copolymerization process involving divinyl (or multivinyl) monomers is one of the most widely used methods for preparation of polymer networks. As in the other methods, the reaction proceeds through a certain conversion at which a viscous flow disappears and an elastic modulus appears instead. This critical conversion - a gel point - is a very characteristic and sensitive measure reflecting the actual mechanism of crosslinking in the system.

Gelation in polymerization systems is recently the subject of controversy among physicists (STAUFFER 1976). The controversy concerns the behaviour of gelling systems near to the gel point. Classical theory due to FLORY (1953), STOCKMAYER (1944) and GORDON (1962) predicts proportionality between weight average degree of polymerization and reciprocal distance from the gel point while the percolation theory (STAUFFER 1976) gives a different exponent. Chemists, on the other hand, seem to be more interested in the mechanism of polymer formation in crosslinking polymerization. Indeed, recently published data brought a new light on the complexity of vinyl-divinyl copolymerization (KAST and FUNKE 1979, WHITNEY and BURCHARD 1980, GALINA et al. 1980, DUŠEK et al. 1980). It has become understood that in the systems where a fraction of divinyl monomer is

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moderate or high (i.e. above several percent) both a high extent of cyclization and a decrease of apparent reactivity of pendant vinyl groups become significant. Moreover, the extent of cyclization and apparent reactivity of pendant vinyl groups seem to depend on size of molecules and therefore on conversion (WHITNEY and BURCHARD 1980). So far, neither classical nor percolation theory is able to deal with those effects properly.

In this paper, experimental results are reported on vinyl-divinyl copolymerization in which the fraction of crosslinking agent is small. Experiments were designed to minimize the effect of the reactivity of pendant vinyl groups. Therefore, the effect of cyclization should be more clear.

Experimental

Monomers - styrene and ethylene dimethacrylate (EDMA) - were purified in the usual way and redistilled prior to use. Benzene was dried with sodium and distilled through an efficient rectification column. Benzoyl peroxide was recrystallized from chloroform.

All polymerizations were carried out in ampules at 60°C for at least 48 h. The air was removed from the ampules by several freeze-thawing cycles and finally argon was used to fill up the ampules.

The polymers were isolated from the solutions by precipitation with methanol and were purified in several dissolution-precipitation cycles.

Viscosities of the polymer solutions were measured in a suspension-level Ubbelohde viscometer.

The GPC spectra were recorded with a Waters-200 instrument calibrated by standard polystyrene samples.

No bands due to unreacted double bonds were found in the IR spectra of the polymers.

Results and Discussion

1. Critical Concentration of Divinyl Monomer

Three series of styrene-EDMA copolymers were prepared. The total concentrations of vinyl groups were 1,2 and 3 mol/dm^3. Critical concentrations (just sufficient to produce gelation) of divinyl monomer were determined for each total concentration of the monomers. It was found that the critical concentration was easier to determine than a critical conversion. Whenever a gel had been produced, its presence could be detected without doubts by lack of flow of the ampule content. Any danger of mechanical disruption of weak links which always exists in the falling ball experiments (GORDON and ROE 1956, ADAM et al. 1979, WHITNEY and BURCHARD 1980) was then avoided. The gels in ampules were uniform - no wall effect was observed.

Critical concentrations of vinyl(idene) groups are shown in Table 1. The values given after the numbers indicating the critical concentrations show the distance from the nearest concentration at which the polymer solutions remained liquid.

TABLE 1

Critical concentrations of vinylidene groups of EDMA at which the gel is formed in the course of styrene-EDMA copolymerization (60°C)

Total concentration of vinyl groups mol/dm³	Critical concentration of EDMA vinylidene groups mmol/dm³
1.00	140.4 (1.8)
2.00	73.8 (4.0)
3.00	40.8 (1.8)

Calculated and experimental averages of the molecular weights of styrene homopolymers which were prepared simultanously are listed in Table 2. Calculations were performed using literature data (POLYMER HANDBOOK 1975) following a simple kinetic scheme of radical polymerization to high conversion (BAMFORD et al. 1958). Good agreement of calculated and measured data indicate lack of major side effects in the course of polymerization.

TABLE 2

Calculated and measured averages of the molecular weight of polystyrenes prepared at different concentrations of the monomer in benzene at 60°C. Concentration of benzoyl peroxide was 0.01 mol/dm³. Viscosity averages were calculated numerically and from intrinsic viscosities measured in (a) cyclohexane at 34.5°C and (b) benzene at 25°C.

Concn.of styrene mol/dm³	M_n 10^{-3} calc.	M_w 10^{-3} calc.	$M_\eta^{(a)}$ 10^{-3} calc.	$M_\eta^{(b)}$ 10^{-3} calc.	$M_\eta^{(a)}$ 10^{-3} expl.	$M_\eta^{(b)}$ 10^{-3} expl.	M_n 10^{-3} GPC	M_w 10^{-3} GPC
1.00	8.9	20.3	17.5	18.8	15	20	-	-
2.00	17.6	40.5	34.9	37.5	27	34	31	47
3.00	26.3	60.6	52.2	56.1	51	56	43	63

2. Crosslinking efficiency of ethylene dimethacrylate

Since the critical concentration of EDMA is much higher than sufficient to introduce one unit per chain and no unreacted double bonds were detected, it is clear that a large fraction of crosslinking monomer is wasted in cycle formation. Therefore, in systems containing a small amount of divinyl monomer, OKASHA's et al. (1979) argument that a decrease of reactivity of pendant double bonds rather than cyclization is responsible for delay of gelation has not been confirmed.

Using cascade theory (classical theory approach) it is possible to estimate the effectiveness of the divinyl monomer. The condition for the gel point reads (see Appendix):

$$\begin{vmatrix} 1-a(1-q) & 0 & -aq & 0 & 0 \\ 0 & 1-a(1-s) & 0 & -as & 0 \\ -b(1-s) & 0 & 1-bs & 0 & -p \\ 0 & -b(1-q) & 0 & 1-bq & -p \\ -b(1-s) & -b(1-q) & -bs & -bq & 1 \end{vmatrix} = 0 \qquad (1)$$

where:

a is the probability of a propagation step involving monovinyl monomer,

b is the probability of a propagation step involving the vinyl of divinyl monomer,

q is the chance that a radical terminated with a monovinyl unit reacts with the vinyl of divinyl monomer,

s is the chance that a radical terminated with a unit belonging to a divinyl monomer reacts with the vinyl of another divinyl monomer,

p is the chance that the link between two vinyls of divinyl monomer is intermolecular.

The set of probabilities a,b,q and s may be derived from the kinetic scheme of copolymerization (GALINA and RUPICZ 1979). The parameter p which describes the effectiveness of crosslinking may be extracted from equation (1) to give:

$$p = A/bB \qquad (2)$$

where

$$A = (1-a)^2(1-bq)(1-bs)+(1-a)a(1-b)\left[q(1-bq)+s(1-bs)\right]+a^2qs(1-b)^2 \qquad (2a)$$

and

$$B = (1-a)^2\left[q(1-bs)+s(1-bq)\right]+(1-a)a\left[(1-b)(s^2+q^2)+s(1-bs)+q(1-bq)\right]+2a^2qs(1-b) \qquad (2b)$$

Due to the limitation of cascade theory (GORDON and SCANTLEBURY 1966) equation (2) provides only approximative values. It helps, however, to estimate the magnitude of fractions of divinyl monomer units which are wasted in cycles. From their values, listed in Table 3, one can see also that dilution leads to decrease of effectiveness of divinyl monomer. Indeed, dilution may affect the extent of cyclization in three ways. It favours intramolecular linking in ring-chain competition during formation of primary chains, may lead to multiple crosslinking in the reaction of growing molecule with pendant bonds of already existing one, and, in later stages of the reaction, may favour formation of cyclized cluster structures involving several primary chains.

It seems that cyclization of primary chains and multiple crosslinking are the most important features in the copolymerization. EDMA is a monomer having relatively flexible joint linking two vinylidene groups, therefore, the probability of short-range cycles is relatively high.

With a small amount of the divinyl monomer, only a small fraction of doubled and tripled primary chains is formed and the distribution of chain sizes is slightly broadened. This is illustrated by GPC spectra of the copolymers shown in Fig.1. Increased amount of EDMA produces spectra in which large molecules are seen. The latter give maxima at the limiting region of the spectra where no retention and, therefore, no separation takes place.

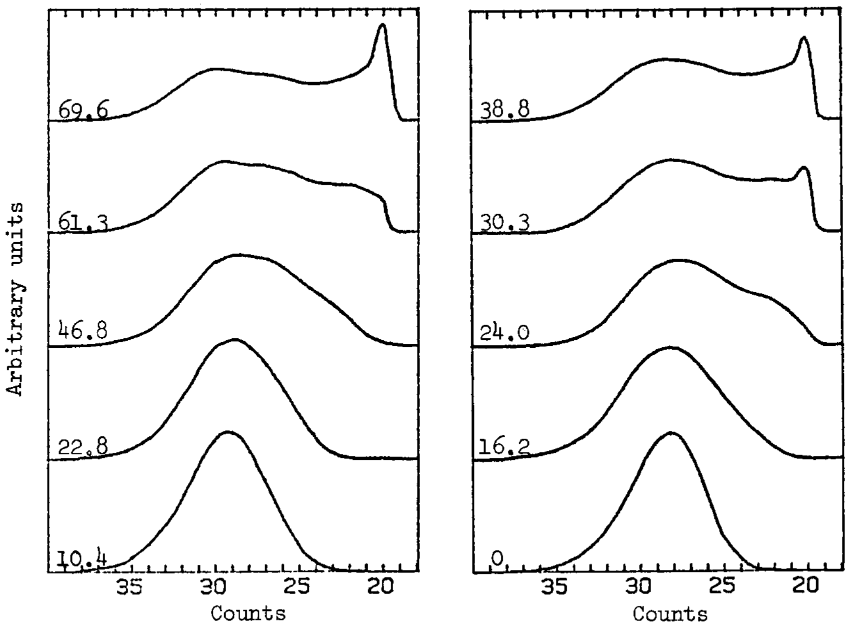
TABLE 3

Numerical values of kinetic probabilities appearing in equations (1) and (2). Calculations were based on literature data (POLYMER HANDBOOK 1975) with experimental critical concentrations of EDMA. Kinetic constants of methyl methacrylate polymerization were used to calculate the probabilities describing the reaction of the vinylidene groups of EDMA.

Concentration of vinyl groups mol/dm^3	a	b	q	s	p
1.00	0.988	0.978	0.219	0.062	0.053
2.00	0.994	0.962	0.069	0.017	0.098
3.00	0.996	0.936	0.027	0.006	0.178

3. Viscosities

Limiting viscosity numbers of styrene-EDMA copolymers in benzene increase with increasing fraction of crosslinking monomer as it is shown in Table 4. Only at the lowest concentration of the monomers was the intrinsic viscosity measured to be lower than that of linear polystyrene. Increasing fractions of large molecules heavily influence intrinsic viscosities covering a possible effect of cyclization on dimensions of primary chains. Moreover, only large cycles (as produced e.g. by random intramolecular crosslinking) may considerably decrease dimensions of molecules (ALLEN et al. 1973, GORDON et al. 1977) while short-range cycles which are more likely to be formed in the vinyl-divinyl copolymerization (GORDON and ROE 1956) seem to have the opposite effect. Dimensions of molecules having only short-range cycles were found to be larger than those of linear analogues during simulation of the vinyl-divinyl copolymerization on a cubic lattice (MIKEŠ 1979 see also DUŠEK et al.(1980).



a b

Fig. 1. GPC spectra of styrene-EDMA copolymers obtained at two different total concentrations of the monomers: (a) 2 moles/dm^3 and (b) 3 mol/dm^3. The concentrations of vinylidene groups (in mmol/dm^3) are given for each spectrum

TABLE 4

Intrinsic viscosities of benzene solutions of styrene-EDMA copolymers at 25°C. C_{EDMA} is the concentration of EDMA vinylidene groups.

Total concentration of vinyl groups (mol/dm^3): 1.00		2.00		3.00	
C_{EDMA} mmol/dm^3	$[\eta]$ cm^3/g	C_{EDMA} mmol/dm^3	$[\eta]$ cm^3/g	C_{EDMA} mmol/dm^3	$[\eta]$ cm^3/g
0	15.5	0	22.9	0	33.2
21.2	15.1	10.4	24.2	16.2	37.4
60.8	18.5	22.8	26.1	24.0	50.8
84.8	23.3	46.8	39.1	30.3	69.5
101.3	26.1	61.3	48.2	38.8	80.6
138.6	63.2	69.6	70.8		

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Appendix

In a collection of chains obtained in vinyl-divinyl copolymerization let us split all the links joining reacted vinyls in divinyl monomer which form intramolecular cycles. Only the fraction p of intermolecular links remains. The five states at which one may find the reacted vinyls in the resulting molecular tree are shown in Fig. A.1.

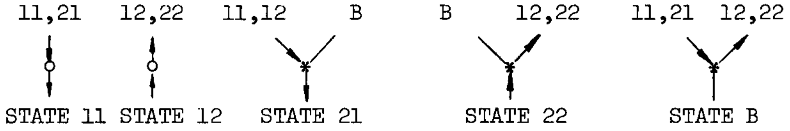

Fig. A.1. Different states of reacted vinyls in n-th generation of the molecular tree. The states in which links arrive in (n+1)-th generation are also shown. Arrows indicate direction of growth of primary molecules. Symbols (o) and (*) denote reacted vinyls belonging to mono- and divinyl monomer, respectively.

Assuming that the concentration of pendant vinyls is uniform throughout the system and making no restriction on possible ring sizes, the following link probability generating functions for each state may be formulated (see e.g. BURCHARD et al. 1974):

$$f_{11}(\underline{\theta}) = 1-a + a(1-q)\theta_{11} + aq\theta_{12} \qquad (A.1)$$

$$f_{12}(\underline{\theta}) = 1-a + a(1-s)\theta_{21} + as\theta_{22} \qquad (A.2)$$

$$f_{21}(\underline{\theta}) = \{1-b + b(1-q)\theta_{11} + bq\theta_{12}\}(1-p + p\theta_B) \qquad (A.3)$$

$$f_{22}(\underline{\theta}) = \{1-b + b(1-s)\theta_{21} + bs\theta_{22}\}(1-p + p\theta_B) \qquad (A.4)$$

$$f_B(\underline{\theta}) = \{1-b + b(1-q)\theta_{11} + bq\theta_{12}\}\{1-b + b(1-s)\theta_{21} + bs\theta_{22}\} \qquad (A.5)$$

with

$$\underline{\theta} = (\theta_{11},\theta_{12},\theta_{21},\theta_{22},\theta_B) \qquad (A.6)$$

and probabilities a,b,q,s and p defined in the text.
The probability generating function for the number of descendants of a given unit in the n-th generation is:

$$\underline{F}_n(\underline{\theta}) = (f_{11}(\underline{\theta}),f_{12}(\underline{\theta}),f_{21}(\underline{\theta}),f_{22}(\underline{\theta}),f_B(\underline{\theta})) \qquad (A.7)$$

According to the cascade theory (GOOD 1960, GORDON 1962), the condition of gelation reads:

$$\det\{\underline{1} - (d\underline{F}_n(\underline{\theta})/d\underline{\theta})_{\underline{\theta}=\underline{1}}\} = 0 \qquad (A.8)$$

Differentiation followed by putting all θ's equal to 1 gives equation (1).

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