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INFLUENCE OF THE STYRENE RATIO ON THE COPOLYMERIZATION KINETICS OF DIMETHACRYLATE OF DIGLYCIDYL ETHER OF BISPHENOL A VINYLESTER RESINS CROSSLINKED WITH STYRENE

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Key Words: Vinylester matrix; Methyl methacrylate; Styrene; Copolymerization kinetics; Sequence distribution; Crosslink density

ABSTRACT

Infrared spectroscopy was used in this work to investigate the copolymerization characteristics of systems based on a dimethacrylate of diglycidyl ether of Bisphenol A combined with styrene in variable proportions ranging from 25 to 60% by weight. Particular attention has been paid to determination of the theoretical monomer sequence distributions obtained from copolymerization theory. The results show that the final structure of these materials is probably diphasic, with a first phase consisting of a vinylester network and a second phase rich in polystyrene. The influence of the monomer sequence distribution on the final crosslink density has been evaluated.

INTRODUCTION

It is generally recognized that the average crosslink density and its spatial distribution are important structural factors governing certain use properties (for instance, mechanical strength) of thermoset materials. In the case of networks based on styrene copolymerization with polyfumarate (unsaturated polyester, UP) or dimethacrylate (vinylester resins, VE), these factors are first controlled by such copolymerization characteristics as initial molar ratio, final conversion, and sequence distribution of each comonomer. Traditionally, physical measurements such as residual cure exotherm [1], glass transition temperature [2], or rubbery elastic modulus [3] have been used to give a more or less precise image of the "average" network structure through more or less empirical structure-property relationships.

A more refined approach (but difficult to use ordinarily) consists of splitting off at the ester groups by hydrolysis in order to obtain a linear styrene unsaturated acid copolymer. In principle, it is possible to determine the concentration of chain ends resulting from the interruption of the copolymerization process (through molecular weight measurements) and the styrene sequence distribution (through classical NMR measurements). This method was successfully applied to UP systems [4]; however, it would probably be more difficult to apply it to VE systems owing to their high hydrolytic stability.

Indeed, the sequence distribution can be deduced in principle from the concentrations of reacted and unreacted monomeric species by using the copolymerization theory [5], but useful analytical data utilizing such calculations are very scarce in the case of UP and practically nonexistent in the case of VE. Concerning UP, the most detailed data involving careful FTIR quantitative determinations were published recently [6]. These studies showed that the simplest "azeotropic" copolymerization model is not adapted to describe the styrene-fumarate copolymerization which is characterized by considerable changes of the apparent reactivity ratios (and consequently sequence length distributions) during the cure.

A very interesting feature of these systems—and a supplementary source of structural heterogeneity—is due to the occurrence of a phase separation, linked to microgel formation, at relatively low conversion. This process, first described by Dusek and coworkers [7], was later mathematically modeled by Boots [8] and then experimentally confirmed, in the case of unsaturated polyester, by Lee and coworkers [9].

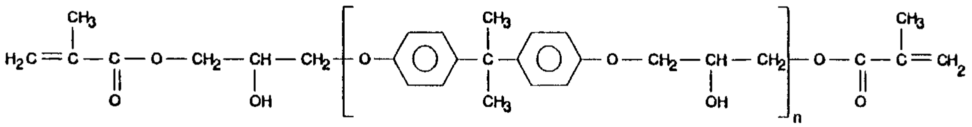
One of the consequences of phase separation involves a molecular shielding effect on fumarate double bonds present in the precipitated phase. In the extreme case—for instance, room temperature crosslinking of UP—20 to 30% of these double bonds would become practically inaccessible to styrene, which essentially homopolymerizes in the latter stage of the curing process. In probably all cases, microgelation will result in a change of the apparent reactivity ratios, e.g., in the sequence distribution of styrene and unsaturated ester structural units.

The aim of this work is to investigate the copolymerization characteristics of systems based on a dimethacrylate of diglycidyl ether of Bisphenol A (DGEBA) combined with styrene in variable proportions ranging from 25 to 60% by weight. Particular attention will be paid to the determination of theoretical monomer sequence distributions from analytical (FTIR) data conversions by using the copolymerization theory.

EXPERIMENTAL

Materials

The dimethacrylate vinylester prepolymer under study was supplied by Dow Chemical. Its chemical structure can be represented as follows:



Its number-average molecular weight is 1100 g·mol^{-1}, which corresponds to $n = 3$. Eight mixtures were prepared with styrene to obtain resins with a styrene ratio ranging from 25 to 60% by weight. The corresponding codes and styrene weight fractions S are given in Table 1. In a typical commercial recipe, $S = 45\%$. The initiator system was composed of methyl ethyl ether ketone peroxide (1%), dimethyl aniline (0.06%) and cobalt octoate (0.018%).

Crosslinking Procedure

Just after the addition of the initiator system to the monomer mixture and its homogenization, one drop of the reactive mixture was placed between two KBr windows placed in the sample holder of the FTIR spectrophotometer. The cure was monitored at ambient temperature. Due to the very low thickness (10 μm) of the reactive layer, it is believed that the system remains in almost isothermal conditions over the duration of cure.

Analytical Measurements

A Perkin-Elmer FTIR 1725X spectrometer was used for the determination of double bond concentrations. The unreacted double bonds were determined at 910 and 945 cm^{-1} for styrene and methacrylate monomeric species, respectively. The absorbance was determined by the tangent baseline method, and the phenyl peak of styrene at 700 cm^{-1} was used as an internal standard. From measurements on the unreacted monomer mixtures, it was verified that both bands under study obey the Beer-Lambert law. The monomer concentrations will be expressed in mol·L^{-1}, neglecting, in a first approximation, the volumetric change due to crosslinking.

TABLE 1. Samples under Study and Corresponding Weight Fractions

Sample	A	B	C	D	E	F	G	H
S (%)	26	30	35	40	45	50	55	60

RESULTS

Kinetic Stages

The experimental results are summarized in Fig. 1 where the residual styrene concentration [S] has been plotted against the residual methacrylate concentration [M]. Three distinct stages, schematized pictorially in Fig. 2, can be distinguished.

In the first stage, both rates of monomer consumption are of the same order of magnitude:

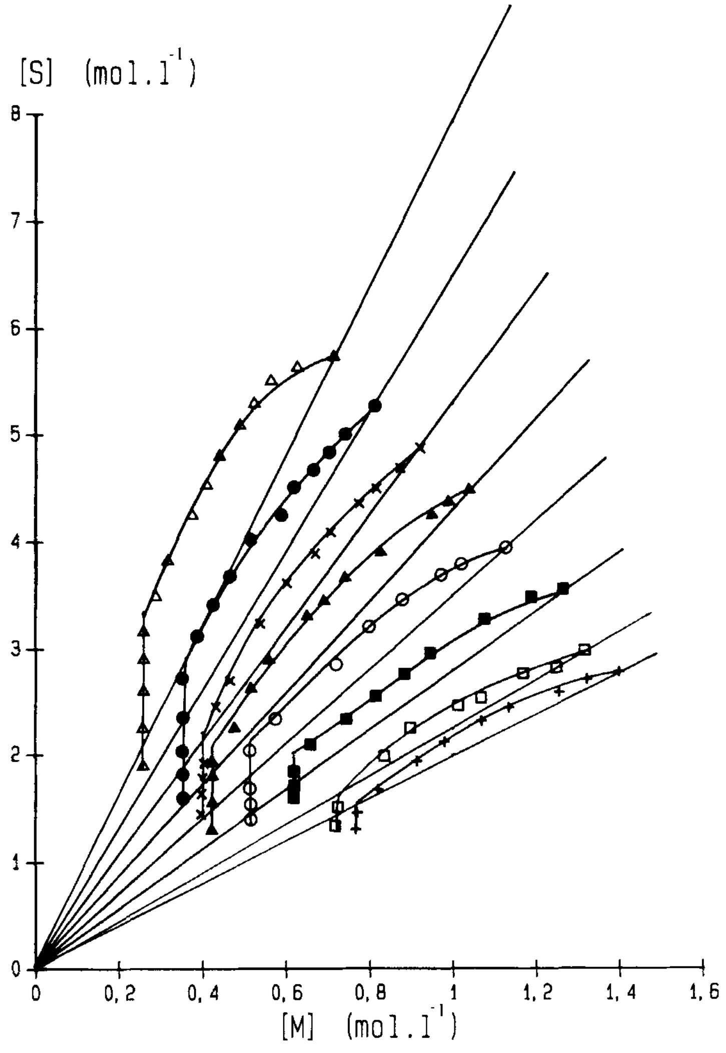


FIG. 1. Residual styrene concentration versus the residual methacrylate concentration. Sample A, +; Sample B, □; Sample C, ■; Sample D, ○; Sample E, ▲; Sample F, ×; Sample G, ●; Sample H, △.

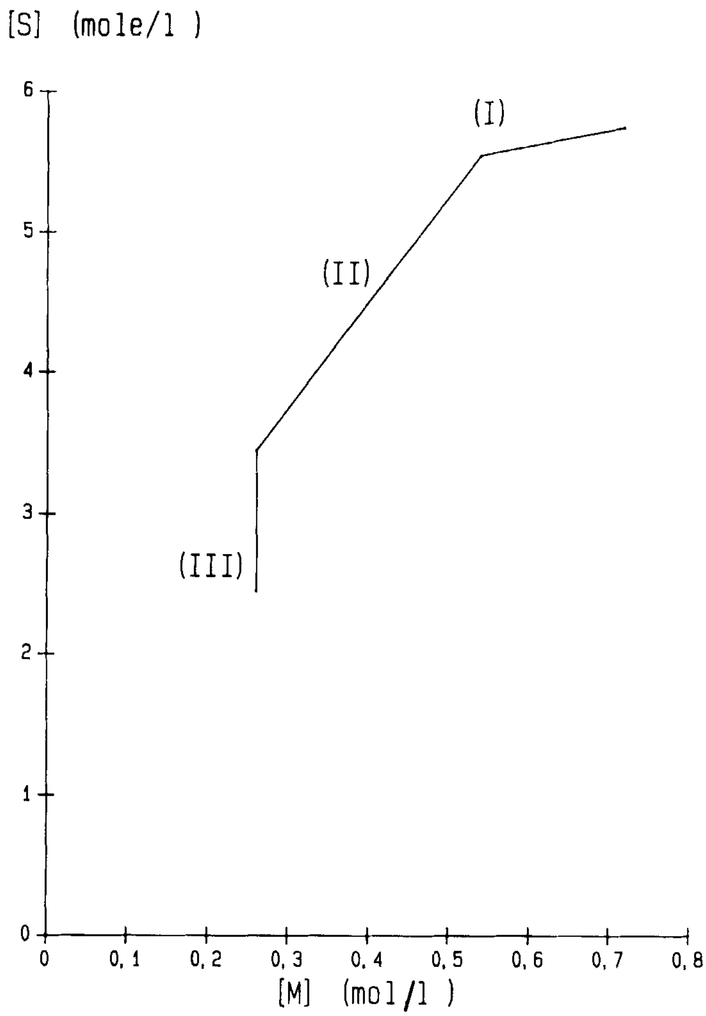


FIG. 2. Schematic shape of a copolymerization plot showing the existence of three kinetic stages.

$$V_1 = \left(\frac{d[\mathrm{S}]}{d[\mathrm{M}]}\right)_1 \approx 1$$

where V_1 is the ratio of monomer disappearance rates in Stage 1

$\frac{d[\mathrm{S}]}{dt}$ is the rate of styrene disappearance

$\frac{d[\mathrm{M}]}{dt}$ is the rate of methacrylate disappearance

The end of Stage 1 coincides more or less with gelation as visually observed and confirmed by solubility experiments.

The second stage begins when the conversion ratio reaches about 20–30%. It is characterized by a slope practically equal to the initial concentration ratio:

$$V_2 = \left(\frac{d[\mathrm{S}]}{d[\mathrm{M}]}\right)_2 \approx \frac{[\mathrm{S}]_0}{[\mathrm{M}]_0}$$

where V_2 is the ratio of monomer disappearance rates in Stage 2.

The third stage is characterized by an interruption of methacrylate copolymerization and continued styrene consumption. It begins at a conversion of about 50–60% and stops when the residual styrene concentration reaches a value ranging from 1.2 mol·L^{-1} (Sample A) to 1.9 mol·L^{-1} (Sample H), and varies almost linearly with the initial styrene molar ratio. Some kinetic data are summarized in Table 2.

Reactivity Ratios

The reactivity ratios r_s and r_m can be estimated from the well-known [5] copolymerization equation

$$V = \frac{d[\mathrm{S}]}{d[\mathrm{M}]} = \frac{[\mathrm{S}]}{[\mathrm{M}]} \times \frac{r_s[\mathrm{S}] + [\mathrm{M}]}{[\mathrm{S}] + r_m[\mathrm{M}]} \tag{1}$$

which can be rearranged to

$$r_s = \frac{V}{x^2} r_m + \frac{V - 1}{x} \tag{2}$$

where $x = [\mathrm{S}]/[\mathrm{M}]$.

A graphical determination of r_s and r_m was attempted in Figs. 3 and 4 for the first and the second stages, respectively ($r_s \rightarrow \infty$ for all the cases in the third stage).

Each straight line corresponds to Eq. (2) for a given sample. In the ideal case, all the straight lines must intersect at a single point whose coordinates are r_s and r_m.

TABLE 2. Coordinates of the Beginning of the Three Copolymerization Stages and the Corresponding Rate Ratios

Sample	A	B	C	D	E	F	G	H
S (%)	26	30	35	40	45	50	55	60
$[\mathrm{S}]_0$ (mol/L)	2.82	3.0	3.6	4.0	4.5	4.9	5.3	5.75
$[\mathrm{M}]_0$ (mol/L)	1.4	1.38	1.26	1.14	1.04	0.92	0.82	0.72
V_1	1.19	1.19	0.87	1.31	1.92	2.61	3.41	1.06
$[\mathrm{S}]_2$ (mol/L)	2.35	2.4	3.45	3.8	4.0	4.3	4.45	5.55
$[\mathrm{M}]_2$ (mol/L)	1.125	0.99	1.11	0.97	0.83	0.77	0.58	0.54
V_2	1.72	2.26	2.9	3.5	4.14	5.0	6.5	7.5
$[\mathrm{S}]_3$ (mol/L)	1.74	1.79	2.0	2.19	2.24	2.45	2.95	3.45
$[\mathrm{M}]_3$ (mol/L)	0.77	0.72	0.61	0.51	0.41	0.40	0.35	0.28
V_3	∞	∞	∞	∞	∞	∞	∞	∞
P_3 (%)	15	14	11	20	21	21	26	28

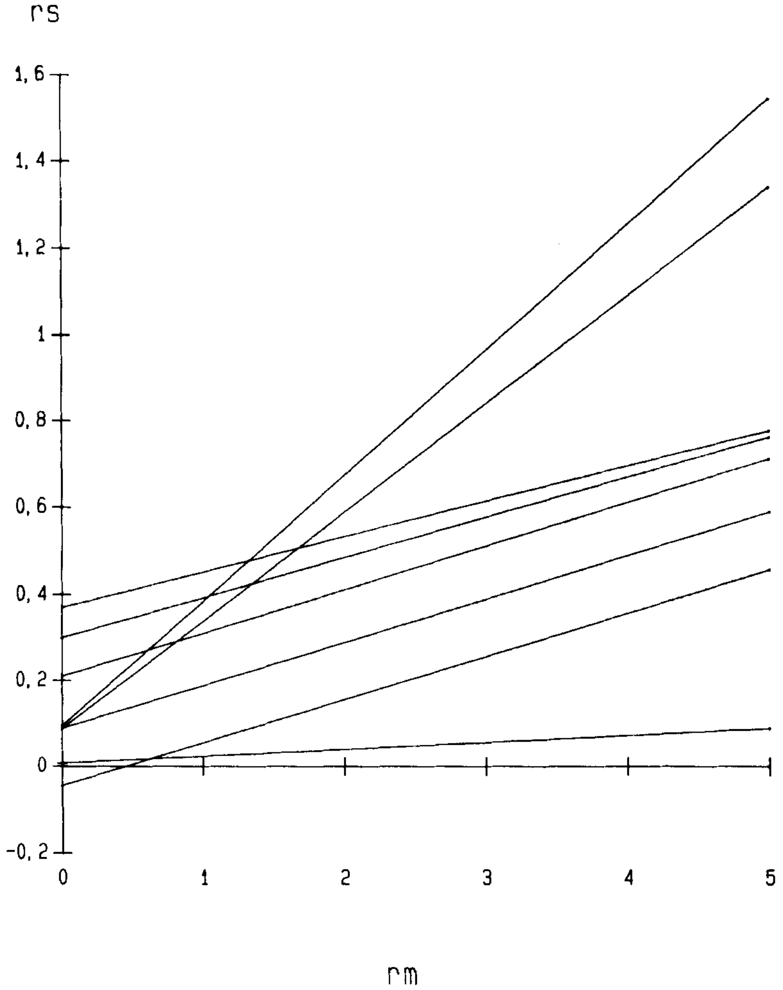


FIG. 3. Graphical determination of r_s and r_m during Stage 1.

In the case of the second stage (Fig. 4), most of the straight lines do indeed intersect in the vicinity of the point with coordinates $r_{s2} = 0.8$ and $r_{m2} = 0.7$.

The situation is noticeably less clear in the case of the first stage (Fig. 3). Average values for the intercept coordinates in the first stage can be estimated as $r_{s1} = 0.4 \pm 0.1$ and $r_{m1} = 1.2 \pm 0.5$.

Styrene Sequence Distribution

The probability p that styrene will add to a styrene ending growing macroradical is given by

$$p = \frac{xr_s}{xr_s + 1} \tag{3}$$

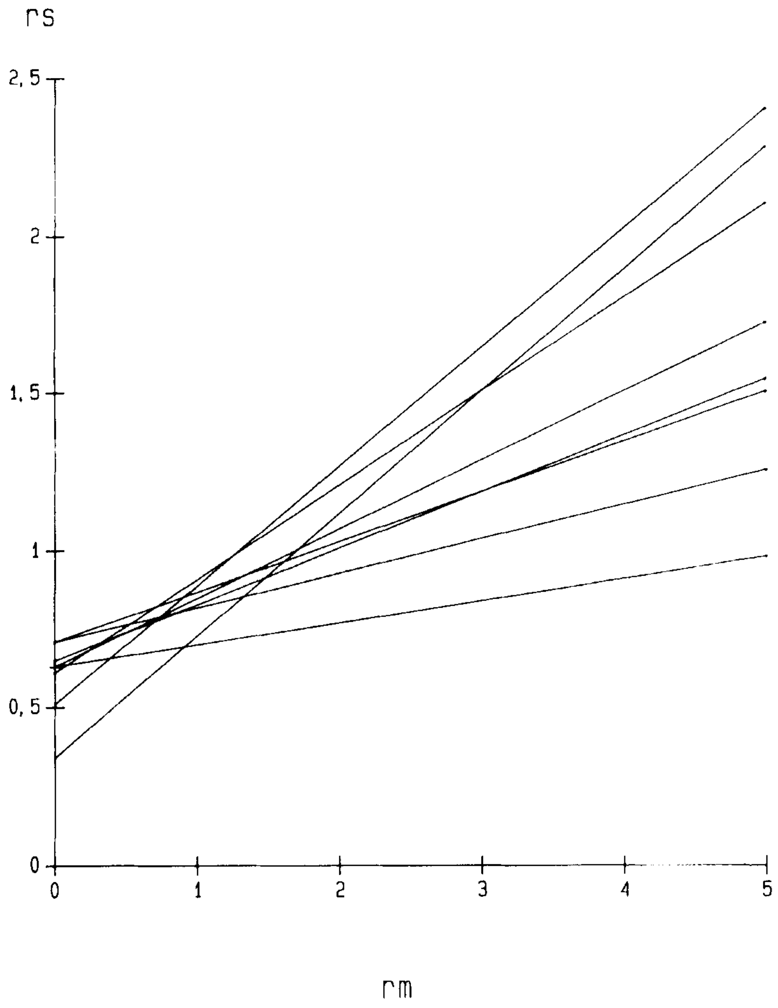


FIG. 4. Graphical determination of r_s and r_m during Stage 2.

From this probability it is possible to determine, according to Bovey [10], the molar fraction of styrene monomer units F_i present in sequences of a given length i by

$$F_i = i \times p^{i-1} \times (1 - p)^2, \qquad -\mathrm{M}-(\mathrm{S})_i-\mathrm{M}- \tag{4}$$

The sequence length distribution will change from one kinetic stage to another as a result of reactivity changes.

Equations (3) and (4) were applied to the data obtained at the end of both the first and second stages. The styrene molar fraction in a given type of sequence was computed up to $i = 8$ and plotted against the sequence length in Figs. 5 (first stage) and 6 (second stage).

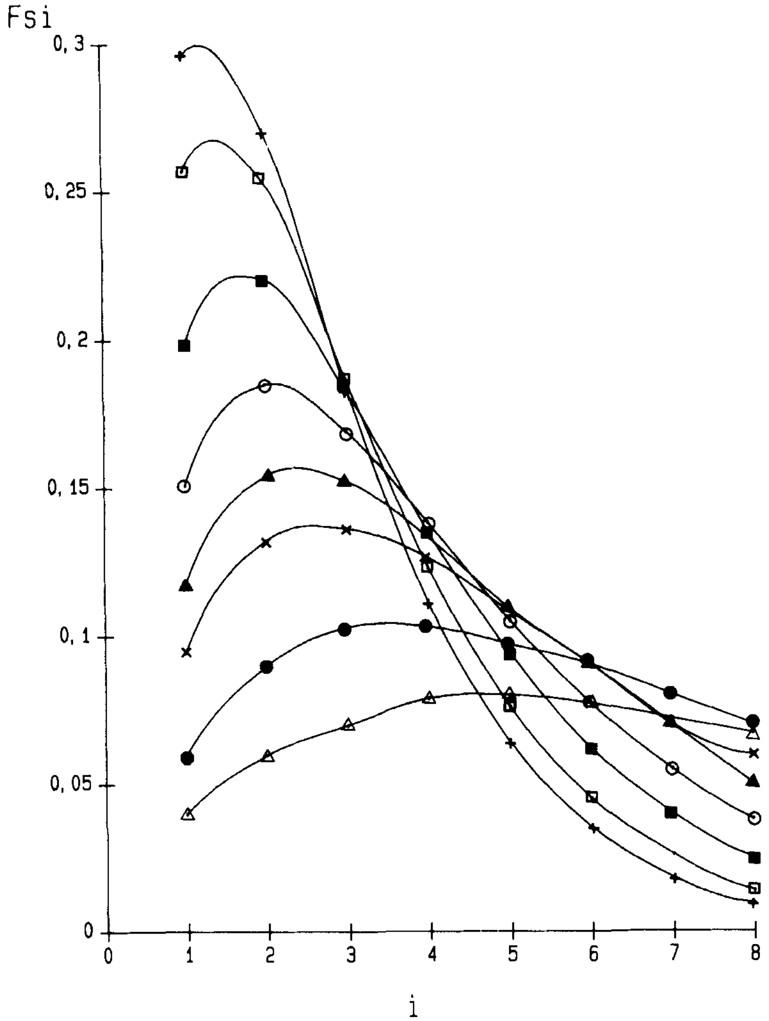


FIG. 5. Molar fraction of styrene monomer units present per type of sequence at the end of Stage 1. Sample A, +; Sample B, □; Sample C, ■; Sample D, ○; Sample E, ▲; Sample F, ×; Sample G, ●; Sample H, △.

Methacrylate Sequence Distribution

The above relationships were applied to methacrylate monomer units, using $r_{m1} = 1.2$ and $r_{m2} = 0.7$ for the first and second stages, respectively. The computed molar fractions, F_i for $i = 1$ to 5, are plotted against the sequence length in Figs. 7 and 8.

Structure of the Final Cured Network at Ambient Temperature

To illustrate general trends, the following characteristics were computed:

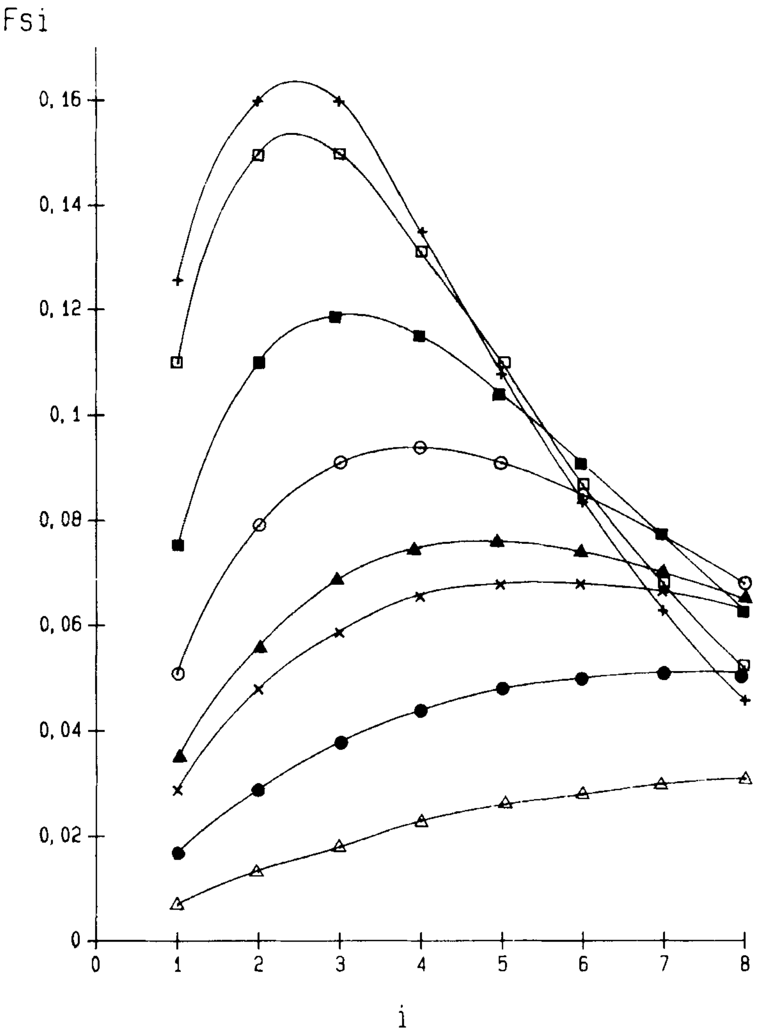


FIG. 6. Molar fraction of styrene monomer units present per type of sequence at the end of Stage 2. Sample A, +; Sample B, □; Sample C, ■; Sample D, ○; Sample E, ▲; Sample F, ×; Sample G, ●; Sample H, △.

$$F_{ss} = \frac{s_1}{[S]_0} \sum_{i=1}^{i=j} (F_i)_{\text{Stage 1}} + \frac{s_2}{[S]_0} \sum_{i=1}^{i=j} (F_i)_{\text{Stage 2}}$$

where F_{ss} is the molar fraction of styrene for sequences shorter than the average sequence length

s_1 and s_2 are the quantities of styrene consumed during the first and second stages

$j = \mathrm{Int}(x_0)$, x_0 being the initial number of styrene units per methacrylate unit and j the integer part of x_0

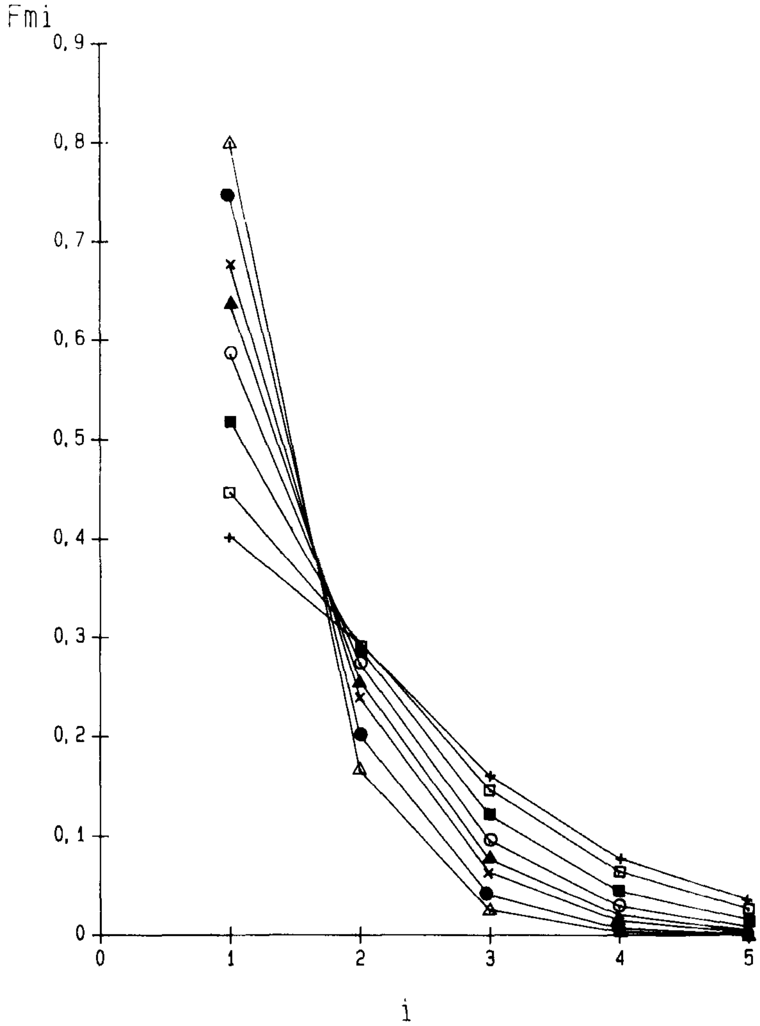


FIG. 7. Molar fraction of methacrylate monomer units present per type of sequence at the end of Stage 1. Sample A, +; Sample B, □; Sample C, ■; Sample D, ○; Sample E, ▲; Sample F, ×; Sample G, ●; Sample H, △.

$$F_{s1} = \frac{s_1}{[S]_0} \sum_{i>8} (F_i)_{\text{Stage 1}} + \frac{s_2}{[S]_0} \sum_{i>8} (F_i)_{\text{Stage 2}}$$

where F_{s1} is the molar fraction of styrene in sequence length greater than 8.

F_{m1}, F_{m2}, and F_{m3} are the molar fractions of methacrylate in monads, diads, and triads (it is considered that values for F_{mk} with $k \geq 4$ are negligible).

The calculations were made on the basis of the conversion data in Table 2, assuming that the sequence length distribution remains constant during a given kinetic

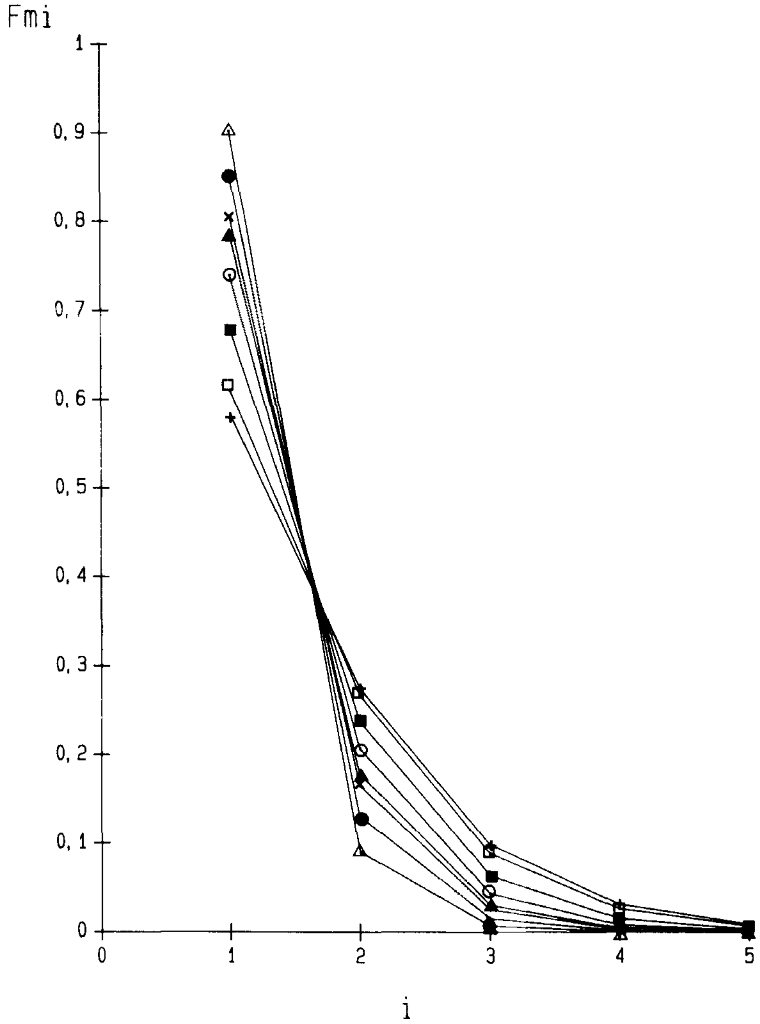


FIG. 8. Molar fraction of methacrylate monomer units present per type of sequence at the end of Stage 2. Sample A, +; Sample B, □; Sample C, ■; Sample D, ○; Sample E, ▲; Sample F, ×; Sample G, ●; Sample H, △.

stage. The results are summarized in Table 3. Indeed, a part of the residual methacrylate units are present as dangling chains, the remaining being in unreacted dimers.

The concentration of each species can be estimated assuming equireactivity of mono- and direacted species. Let us consider the three types of DGEBA vinylester units and the equation relating them:

$$c_2 + c_1 + c_0 = 1 \tag{5}$$

where Unreacted → c_2
Monoreacted → c_1
Direacted → c_0

TABLE 3. Final Sequence Length Distribution Characteristics in the Networks Polymerized at Ambient Temperature (F_{sr} and F_{mr} are the residual concentrations of unreacted styrene and methacrylate units, respectively)

Sample	A	B	C	D	E	F	G	H
S (%)	26	30	35	40	45	50	55	60
F_{ss} (%)	15.6	15.5	14.7	11.4	15.4	17.5	15.1	8.5
F_{s1} (%)	17.6	17	20	34.8	41	43	50.7	52
F_{m1} (%)	22	24	33	38	44.7	43	45	52
F_{m2} (%)	12	13	12	12	12	10	9.5	7.6
F_{m3} (%)	5.6	5.8	3.9	3.1	2.7	2	1.6	0.92
F_{mr} (%)	55	52	48	44.7	39.4	43.5	42.6	39
F_{sr} (%)	47	46	45	35	29	29	30	32

and where the concentration of a given species is linearly related to its probability of formation (c_0, c_1, and c_2).

The probability ratio of reaction for a monoreacted DGEBA vinylester can be expressed by

$$\frac{c_i\,(\text{probability to give a monoreacted species again})}{c_0\,(\text{probability to give a direacted species})} = \frac{2c_2}{c_1} \tag{6}$$

The conversion ratio X_m is given by

$$X_m = \frac{c_1 + 2c_0}{2}$$

We thus have a system of three equations with three unknown quantities whose resolution leads to the following relationships:

$$c_0 = X_m + 0.5 - 0.5\sqrt{\delta}$$

$$c_1 = \sqrt{\delta} - 1 \qquad \text{with} \quad \delta = 1 + 4X_m - 4X_m^2$$

$$c_2 = \frac{3}{2} - X_m - 0.5\sqrt{\delta}$$

These equations are used to generate the results in Table 4.

TABLE 4. Molar Fractions of DGEBA Units in Dangling Chains (c_1) and Unreacted Monomer (c_2) at the End of the Polymerization Process

Sample	A	B	C	D	E	F	G	H
X_m	0.45	0.48	0.52	0.55	0.61	0.56	0.57	0.61
c_1	0.41	0.41	0.41	0.41	0.40	0.41	0.41	0.40
c_2	0.34	0.31	0.27	0.25	0.19	0.23	0.23	0.19

Overall Conversion

The overall conversion ratio is plotted against the initial styrene weight fraction in Fig. 9. It appears that the maximum conversion is attained for Sample E, e.g., for the styrene weight fraction (45%) most frequently used in industrial applications.

DISCUSSION

The above results call for the following comments.

1. The change of kinetic regime from Stage 1 to Stage 2 is obviously due to gelation. During the first stage, the coppolymerization kinetics are presumably governed by the intrinsic reactivity of styrene and methacrylate double bonds. The

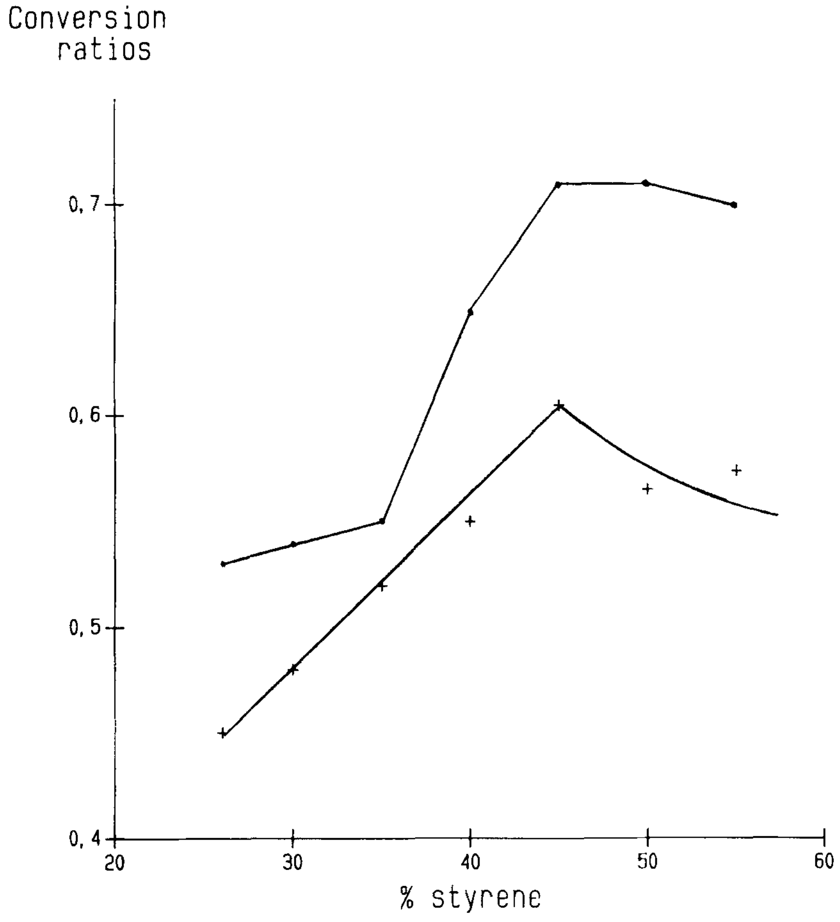


FIG. 9. Overall conversion ratios of methacrylate and styrene versus the initial styrene weight fraction. Conversion ratio of styrene, ●; conversion ratio of methacrylate, +.

gelation is essentially characterized by a marked decrease of the inherent reactivity of methacrylate units with other methacrylate units and by an increase of the styrene reactivity ratio. Both trends are consistent with the hypothesis that, during Stage 2, styrene monomer molecules can move relatively unrestricted within the network, whereas methacrylate groups, owing to their considerably higher molar volume, become immobilized and are less prone to homopolymerization as illustrated by the shift of sequence length distributions from the first to the second stage (Figs. 5–8). Furthermore, we note the large polydispersity of the polystyrene chain lengths formed in cases where the styrene level exceeds 40% initially: the distribution sequence curves become flat, whereas they are sharp for the low styrene level resins.

2. At the end of Stage 2, 45 ± 10% of the initially present methacrylate double bonds remain unreacted, among which only 20% ($c_1/2$) are bound to the network. Nonetheless, the methacrylate copolymerization stops. The first explanation which comes to mind is that, during the second stage, the diffusivity of the reactive species decreases as the crosslink density increases and eventually a state is attained where no additional conversion is observed.

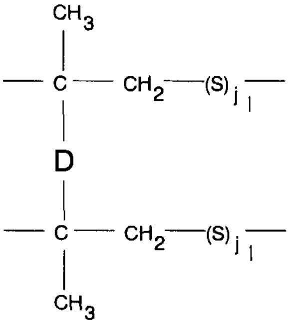
The fact that only styrene continues to react during Phase 3 is, however, difficult to explain in the case of a simple homogeneous reaction since, in principle, there must be access to reactive methacrylate double bonds. It thus seems reasonable to suppose that some separation, presumably initiated during Stage 2, has occurred, leading to a two-phase structure. The first phase would contain essentially the copolymer network swelled by the unreacted dimethacrylate monomer and, perhaps, a part of the residual styrene monomer. The second phase would essentially contain the remaining unreacted styrene. It can then be hypothesized that the copolymerization in the first phase stops at the end of the second stage as a result of its vitrification. The styrene homopolymerization continues during the third stage, until presumably vitrification also occurs in the second phase. However, it is necessary to point out the difference between the behavior of the high styrene level resins and the behavior of the low styrene level resins. The percentages P of polystyrene formed during the final stage of the crosslinking of each resin are given in Table 2. If the polystyrene percentage formed at the end of crosslinking is still low (about 10%) for the low styrene ratio resins, it increases suddenly for the resins with a styrene ratio greater or equal to 40%. In fact, for the resins with a low initial styrene content, all the reactions are more or less stopped at the beginning of Stage 3, thus leading to a network containing a large content of unreacted species.

3. Consequences of the monomer sequence distribution on the final crosslinked density. A detailed study of the crosslink density of the networks described in this report will be published shortly. Here, only the effects of the irregular sequence distribution of styrene and methacrylate will be examined by using a simplified model of the network structure. The model employed is based upon two assumptions.

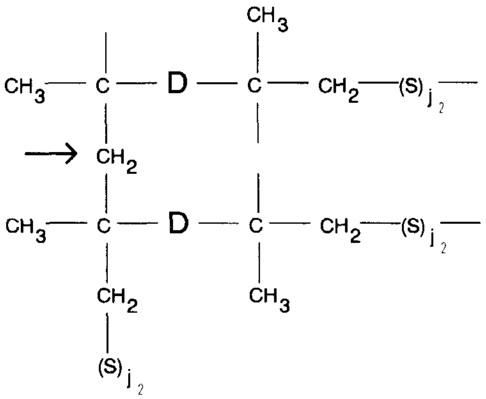
a. Changes of the styrene sequence length distribution do not alter the average crosslink density. In other words, monads are not qualitatively different from p ads ($p > 1$).

b. In contrast, changes of methacrylate sequence length distribution can affect the average crosslink density because monads and p ads are eventually different.

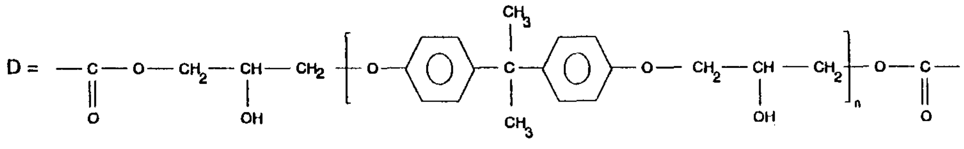
Let us consider, for instance, the "average network cell" or constituent repeat unit (CRU) of two networks respectively based on methacrylate monads and diads (with the same overall composition).



I (monad)



II (diad)



If s is the number of styrene units per methacrylate unit, it can be written that

$$j_1 = s \quad \text{and} \quad j_2 = \frac{4}{3}s$$

where j_1 and j_2 are the average numbers of styrene monomer units in polystyrene chains of monad and diad respectively.

In the Network I based on monads, the crosslink density (number of network segments per mass unit) is given by

$$(\overline{M_c^{-1}})_0 = \frac{3}{\overline{M}_d + 2s\overline{M}_s}$$

where $\overline{M}_d$ and $\overline{M}_s$ are the respective molecular weights of the dimethacrylate and styrene repeat units. $\overline{M}_s = 104\ \mathrm{g\cdot mol^{-1}}$ and $\overline{M}_d \approx 1100\ \mathrm{g\cdot mol^{-1}}$ in the case under investigation in this paper.

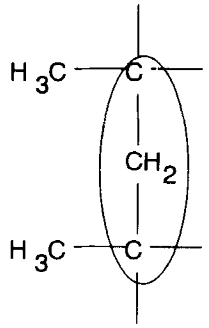
In the Network II we have the following alternative:

1. The methylene connecting the two dimethacrylate units (arrow) is considered to be a network chain (all the crosslinks are trifunctional). In this case the crosslink density is given by

$$(\overline{M_c^{-1}})_1 = \frac{6}{2\overline{M}_d + 3j_2\overline{M}_s} = \frac{3}{\overline{M}_d + 2s\overline{M}_s}$$

This crosslink density would be the same as in the case of a network uniquely based on methacrylate monads.

2. The methylene is not considered to be a chain. In other words, this network contains a tetrafunctional crosslink of structure



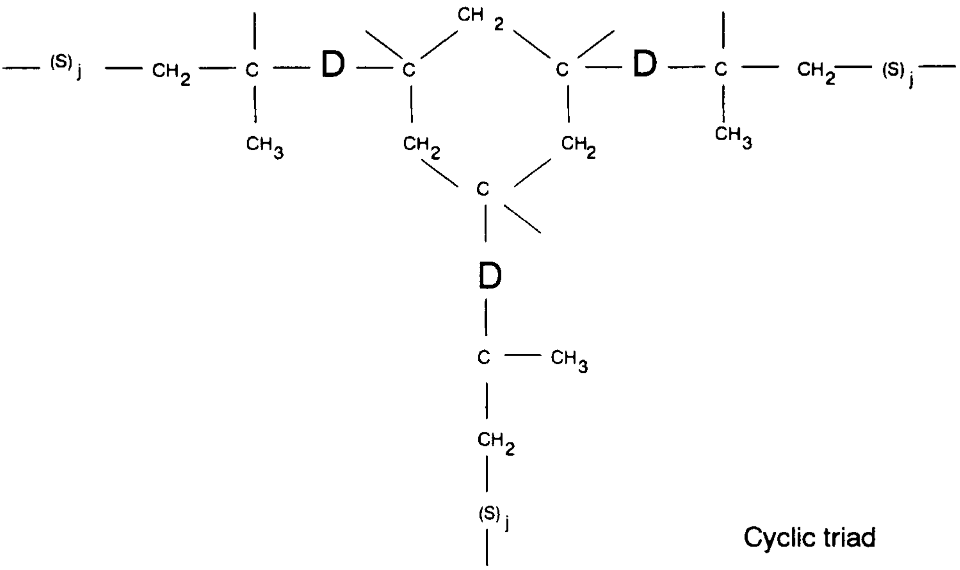
In this case, the crosslink density would be given by

$$(\overline{M_c^{-1}})_2 = \frac{5}{2\overline{M}_d + 4s\overline{M}_s} = \frac{5}{6}\,(\overline{M_c^{-1}})_0$$

For a methacrylate triad, the same hypothesis would lead to

$$(\overline{M_c^{-1}})_2 = \frac{7}{9}\,(\overline{M_c^{-1}})_0$$

An extreme case is represented by the cyclic triad:

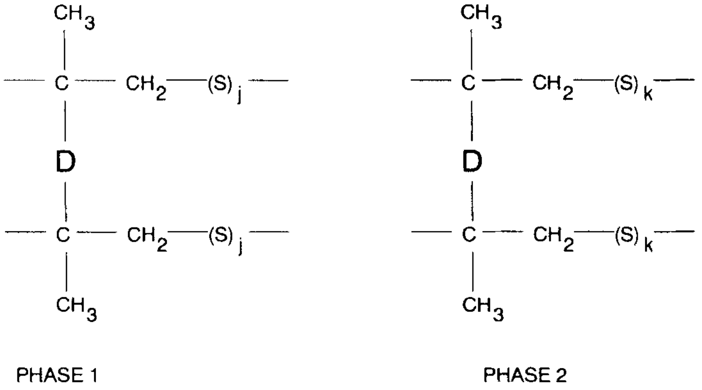


Cyclic triad

$$(\overline{M_c^{-1}})_2 = \frac{6}{3\overline{M}_d + 6s\overline{M}_s} = \frac{2}{3}\,(\overline{M_c^{-1}})_0$$

In the networks under study, the molar fraction of methacrylate units in *p* ads is always less than 30%. In other words, the change in average crosslink density (relative to the monad-based network), due to the presence of these sequences, is largely lower than 16% and presumably undetectable with the usual physical methods of analysis such as rubber elasticity measurements employed for monophasic systems.

4. Spatial distribution of the crosslink density. It has been shown that the systems under study are probably diphasic or, at least, that significant spatial heterogeneities of the monomer sequence distribution occur. Let us consider a diphasic system constituted of two phases differing by the styrene weight fraction



If Φ is the mass fraction of Phase 1 and s is the average number of styrene units per methacrylate unit, from the mass balance it can be written that

$$\Phi = \frac{1 + 2\mu j)(s - k)}{(1 + 2\mu s)(j - k)} \quad \text{where} \quad \mu = \frac{\overline{M}_s}{\overline{M}_d}$$

where $\overline{M}_s/\overline{M}_d = 0.1$. Thus, considering a system close to the commercial recipe with $s = 5$, we obtain

$$\Phi = 0.5(1 + 0.2j)\frac{(5 - k)}{(j - k)}$$

An interesting application of this relationship is for the case where the final morphology results in the growth of nodules having a composition close to the average one and a weight fraction, Φ, close to unity:

$$\Phi = 1 - \epsilon \quad \text{with} \quad \epsilon \ll 1$$

The internodular phase would result essentially in large polystyrene sequences or even polystyrene homopolymers ($k \gg s > j$).

The above relationship can then be approximated by

$$\Phi = 0.5(1 + 0.2j)\left(1 - \frac{s - j}{k}\right) \quad \text{with} \quad \frac{s - j}{k} \ll 1$$

resulting in a value of j given by

$$j = 10\Phi - 5$$

Thus, the nodular structure is close to the "azeotropic" network since the mass fraction $(1 - \Phi)$ of the internodular phase is low.

In principle, values of Φ lower than 0.9 would be relatively easy to determine by using the glass transition characteristic of a diphasic structure.

In contrast, values of Φ between 0.9 and 1.0 would be more difficult to determine. A value of Φ between 0.9 and 1.0 would correspond to a value of j (in the nodular phase) between 4 and 5, and the corresponding effect on the crosslink density would be low since, according to the above relationship:

$$\overline{M}_c^{-1} = \frac{3}{\overline{M}_d + 2j\overline{M}_s} \rightarrow \frac{\Delta\overline{M}_c^{-1}}{\overline{M}_c^{-1}} = -0.5\,\frac{\Delta j}{j}$$

It is noteworthy that this relationship can also describe the crosslink density fluctuations within the nodular phase.

CONCLUSIONS

FTIR was used to study the copolymerization characteristics of DGEBA vinylester resins containing variable initial styrene ratios. By using the copolymerization theory and a statistical treatment, it is possible to obtain the monomer sequence distributions at the end of each of three stages of crosslinking. It is shown that, for these systems, the final structure is probably diphasic, with a first phase consisting of the vinylester network and a second phase rich in polystyrene.

The influence of the monomer sequence distribution on the final crosslink density is probably undetectable by classical methods used for monophasic systems. On the other hand, in the case of a diphasic system, the fluctuations of crosslink density induced by the presence of a second phase depend on the importance of the second phase. A detailed study of the crosslink density of these networks to be published in the near future will give more information about the structure of such networks.

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