

MECHANISM OF NETWORK FORMATION BY RADICAL COPOLYMERIZATION

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Abstract - Radical copolymerization of two monomers, one of them being bifunctional, has been widely used for the synthesis of polymer networks. However, the actual structure of such networks is still controversial, and it has never been related accurately with the copolymerization parameters.

It has been assumed that large fluctuations of the length of the elastic chain originate, at least in part, from the fact that the consumption of the two monomers follow different rate laws. It occurred to us that the decisive factor in that respect is not the consumption of the bifunctional monomer, but it is the ability of the pendant double bonds to undergo reaction with growing radicals and to form the actual branch points. This is clearly evidenced by recent works carried out on the system styrene-divinylbenzene in which it was shown that, once the gel point has been reached, crosslinking goes on; more links between individual chains are formed, whereby the crosslink density increases and the average length of the elastically effective network chain decreases.

A kinetic investigation of the radical copolymerization was carried out on several systems of this type: styrene-divinylbenzene, styrene-diisopropenylbenzene, styrene-ethylene dimethacrylate, methylmethacrylate-ethylene dimethacrylate. In some cases, a chain transfer agent was added to the system to delay the occurrence of network formation. From the conversion curves of each individual monomer - that were obtained from vapor phase chromatography taken at regular time intervals - the instantaneous composition of the copolymers formed were determined. Thus, the values of the radical reactivity ratios of the two monomers involved could be calculated. It was confirmed that the bifunctional monomer is more reactive and therefore more readily consumed than the monofunctional monomer. In addition, it was shown that the rate of polymerization of styrene is enhanced noticeably in the presence of a small amount of divinylbenzene. Also it was established that the rate of crosslinking does not parallel the rate of consumption of the divinyl monomer.

To give account of all results it has to be assumed that in the early stages of the reaction most of the bifunctional monomer reacted gives yield to pendant double bonds (and, perhaps, to a much lesser extent, to cyclization). The reactivity of these pendant unsaturations is far lower than that of the monomers involved, consequently the pendant double bonds are still numerous, once the gel point has been reached. As these double bonds are slowly consumed in the later stages of the reaction (when not much monomer is left over), the network becomes tighter, its swelling ratio decreases and its modulus increases.

These findings throw new light into the problem of the structural homogeneity of network synthesized by radical copolymerization. It cannot be stated anymore that the crosslink density is bound to be inhomogeneous in such networks, nor that once the bifunctional monomer is consumed pendant chains are formed solely. In fact it appears that these species are far more homogeneous in structure that it had been assumed previously, and the crosslink density can be related with the composition of the monomer mixture, provided the reaction was pursued until all double bonds have been consumed.

INTRODUCTION

Polymer networks are commonly obtained by radical copolymerization of two monomers, one of them being bifunctional (Ref. 1-3). It is a method of great industrial interest, which was applied to a large number of systems. However, even in the absence of syneresis (solvent expulsion during the

process) the homogeneity of the networks has been questioned and their actual structure is still controversial. The mode of formation of the crosslinks has been examined in a rather speculative way, and the proportions of structural elements that do not contribute to the network elasticity (dangling chains, intramolecular cyclization) have been subject to debates (Ref. 4&5). No accurate relation was found between the parameters of network formation (Ref. 6&7) (concentration used and copolymerization parameters) and the structure of the species obtained.

The kinetics of styrene-divinylbenzene copolymerization has been studied in a number of papers (Ref. 8-10). It has been observed that the conversion of the two monomers follows different rate laws, DVB being consumed more readily. It cannot be concluded that as the DVB content of the remaining monomer mixture gets a smaller the degree of crosslinking decreases: a DVB molecule incorporated gives yield to a pendent double bond; when this pendent unsaturation reacts in turn with a growing radical a branch point is formed that may contribute to the crosslinking of the system (unless this latter reaction occurs intramolecularly whereby a cyclization is formed (Ref. 11). Thus, these decisive factor is the ability of pendent double bonds to undergo reaction with growing radicals.

In this paper, two different approaches of this problem will be presented and discussed:

- 1) A kinetic investigation is meant to establish the conversion rates at various stages of the reaction. The composition of the species formed, their molecular weight and molecular weight distribution, their double bond content were studied as a function of time, until gelation occurs. Once a network is formed the composition of the remaining monomer mixture (that is part of the swelling solvent) cannot be determined easily any more; that is why in some experiments a transfer agent is added, to delay the occurrence of the gel point (Ref. 8 & 12): The number of crosslinks necessary to achieve gelation is increased as the "primary" molecules that are formed in the presence of a transfer agent are smaller in size. The kinetics of the process is not affected appreciably by the transfer agent (Ref. 13).
- 2) Another type of investigation aimed at a more accurate determination of the phenomena occurring at the gel point. Experiments on the time dependence of the viscosity of the reaction medium have shown (Ref. 14) that the percolation theory is able to give account of the gelation process considered.

Beyond the gel point the variation of the elasticity modulus was studied as a function of time, to get an estimate of the crosslink density (i.e. of the number of elastically effective network chains existing at any given time). Equilibrium swelling measurements have also been used for the same purpose (Ref. 12 & 15). Both these experiments show that crosslinking goes on far beyond the gel point, even though most of the bifunctional monomer has been converted prior to the gel point. Thus, it can be confirmed that crosslinking is commanded by the reactivity of pendent unsaturations upon attack by growing radicals.

A KINETIC INVESTIGATION OF THE RADICAL COPOLYMERIZATION OF STYRENE WITH VARIOUS BIFUNCTIONAL MONOMERS

Some general considerations

Upon studying the radical copolymerization of styrene (S) with a bifunctional comonomer (D) account must be taken of the fact that either of the two double bonds of D can be attacked by a growing radical. The classical rate equation must therefore be modified as follows :

$$\begin{aligned} - \frac{dS}{dt} &= k_{SS} [S\cdot] [S] + k_{DS} [D\cdot] [S] \\ - \frac{dD}{dt} &= 2 k_{SD} [S\cdot] [D] + 2 k_{DD} [D\cdot] [D] \end{aligned} \quad (1)$$

Here k_{SD} and k_{DD} are the rate constants characterizing the attack of either double bonds of D by a $S\cdot$ or $D\cdot$ radical. k_{SS} and k_{DS} are the rate constants of addition of styrene onto a $S\cdot$ or $D\cdot$ radical. The stationary state condition can be written as:

$$k_{DS} [D\cdot] [S] = 2 k_{SD} [S\cdot] [D]$$

whereupon equation (1) can yield the following expression :

$$\frac{dS}{dD} = \frac{[S]}{[D]} \cdot \frac{k_{SS} [S] + 2 k_{SD} [D]}{2 k_{DD} [D] + 2 k_{DS} [S]} \quad (2)$$

If the radical reactivity ratios are defined as usual by:

$$r_S = \frac{k_{SS}}{k_{SD}} \quad r_D = \frac{k_{DD}}{k_{DS}}$$

and inserted in equation (2) one gets:

$$\frac{dS}{dD} = \frac{[S]}{[D]} \cdot \frac{\frac{1}{2} r_S [S] + [D]}{2 r_D [D] + [S]} \quad (3)$$

The factors 1/2 and 2 take account of the fact that there are two double bonds on each D molecule, $[D]$ being the real molar concentration of D in the reaction medium.

In all the experiments that were carried out, the proportion of D was very low. In most of them, D amounted to 2% of the styrene concentration. This implies that:

$$\begin{aligned} \frac{1}{2} r_S [S] &\gg [D] \\ 2 r_D [D] &\ll [S] \end{aligned}$$

and equation (3) reduces to:

$$\frac{dS}{dD} = \frac{1}{2} r_S \frac{[S]}{[D]} \quad (4)$$

It follows that if one of the monomers is converted into polymer according to a first order law, the same should be true of the second monomer (see Note a).

Techniques used

The kinetic investigation of the radical copolymerization of styrene S, with various bifunctional comonomers D was carried out at 60°C, in benzene solution, with azo-2,2'-isobutyronitrile (AIBN) as initiator. In some experiments CCl₄ was added as a transfer agent. Comparative experiments were carried out⁴ with 2% comonomer, and in absence of transfer agent.

At given time, some of the solution was sampled out, and the remaining concentrations of the monomers S and D were determined by gas liquid chromatography (GLC). Simultaneously an aliquot of the reaction mixture was treated with excess methanol to precipitate out the copolymer formed. The overall conversion was thus established gravimetrically, and also calculated from the amounts of S and D consumed, as determined by GLC. Both values are in good agreement.

The polymer samples were submitted to a characterization involving light scattering measurements (to determine the weight average molecular weight), gel permeation chromatographic evaluation of the apparent polydispersity (see Note b) and analytical determination of the double bond content of the dry samples.

Note a - Equation (4) is identical with that found for a so-called "ideal" system, characterized by $r_a \cdot r_b = 1$ (Ref.16). In the present case, however, equations (4) is valid only in the range of compositions very low in D.

b - The molecules formed are branched, and the branching degree increases with conversion, until a network is formed. Even if the universal calibration is used (Ref.17) and in spite of the low D contents, the polydispersity indices are only apparent values, as the branching degrees increases with molecular weight, within a sample.

From the GLC investigation of the monomers remaining in the reaction medium, the plots of the monomer concentration versus time can be drawn. From the slopes of the curves (dS/dt and dD/dt) at any given time the instantaneous copolymer composition can be calculated. The overall copolymer composition can be obtained either by integration, or from the amounts of monomers S and D converted into polymer from time 0 until time t.

Attention should be called to the fact that chromatographic detection applies merely to the monomers D and S. The third polymerizable species, namely the pendent double bonds is entirely overseen in the kinetic experiments. That is why double bond titration (Ref.18) was carried out on the polymer samples obtained at various stages of the reaction. From the remaining double bond content the proportion of unsaturations that have been consumed can be calculated. Unfortunately, the accuracy of the experimental method is insufficient, and it is merely possible to state qualitatively that at early stages of the reaction the proportion of double bonds that have been used for crosslink formation is rather low. In a first approximation, the effect of crosslink formation on the observed kinetic results can be neglected during the first hours of reaction.

The method of Fineman and Ross (Ref.19) was used to get the reactivity ratios characterizing the various binary S-D mixtures investigated. The classical expression of the linearization of the composition equation has to be modified to take account of the fact that monomer D has two reactive double bonds:

$$Y = -2 r_D + X \frac{r_S}{2}$$

with

$$Y = \frac{2 F_S - 1}{F_S} \frac{f_s}{f_d} \quad X = \frac{1 - F_S}{F_S} \cdot \frac{f_S^2}{f_D^2}$$

and

$$F_S = \frac{dS}{dS + dD} \quad f_S = \frac{S}{S + D}$$

To get a better accuracy the values of the derivatives dS/dt and dD/dt were determined by computer calculation on curves smoothed using the least square method.

The values of Y and X define a straight line, (the correlation coefficient being better than 0.995), and in all cases the slope is well defined, thus giving accurate values of r_S . The ordinate intercept is also computed but its value is subject to some uncertainty, which is due to the low D content of the system investigated. Experiments carried out with higher D contents would not have helped much in that matter, because gelation would have intervened earlier, and the domain of composition considered in each experiment would have been narrower.

DISCUSSION OF THE RESULTS OBTAINED

1 - Preliminary experiments (Ref.12) have been run in the presence of CCl_4 , with purified DVB as bifunctional monomer. Its DVB content amounts to 92% (roughly 38% para and 54% meta isomer), with about 5% of ethylvinylbenzenes. It was possible to follow by GLC the consumption of styrene, of p.DVB and of m.DVB. The conversion curves are shown on Fig.1. It is confirmed that DVB is consumed more readily than styrene, and that the p.isomer is more reactive than the meta isomer.

It was observed that the conversion of all three monomer species obey first order laws, within experimental accuracy: Fig.2 shows the plot of $\ln = [M_0] / [M]$ as a function of time (see Note c).

Note c - If the duration of an experiment is higher than approximately 10 hours (half the half time of AIBN under the conditions chosen $\ln \frac{[M_0]}{[M]}$ should be plotted versus $[1 - \exp(-k_d t/2)]$ instead of t (Ref.13).

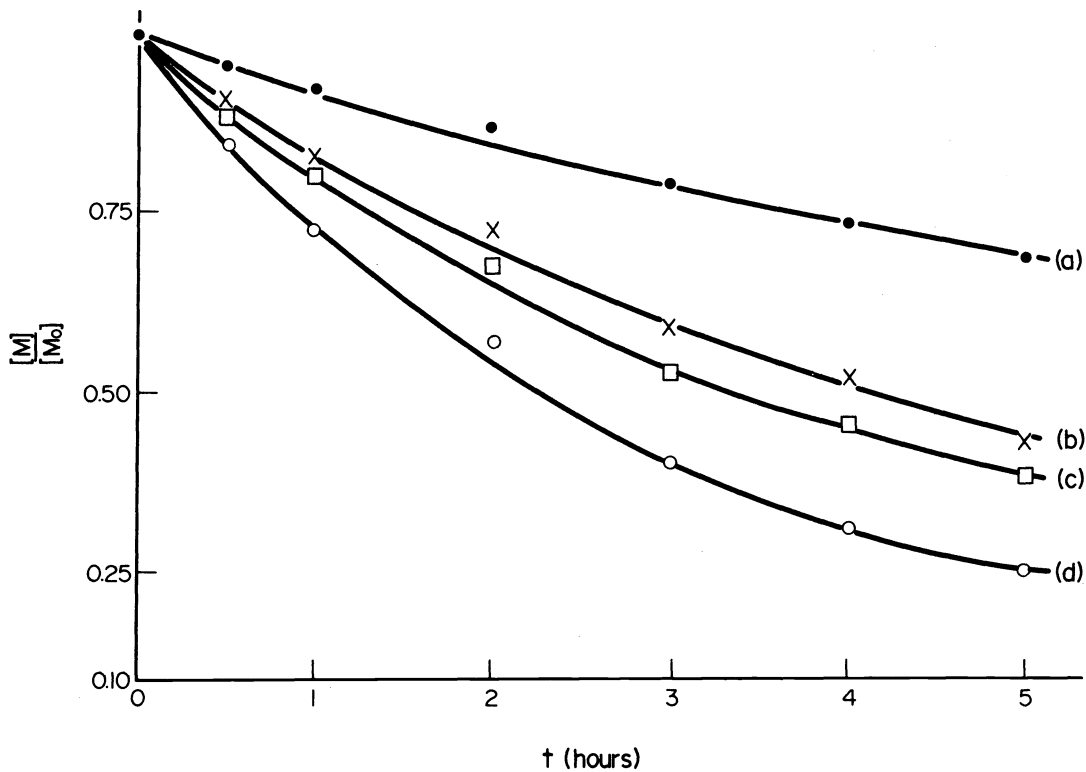


Fig.1 - Radical copolymerization of styrene and DVB:

Monomer conversion versus time
 (a) styrene (b) m.DVB
 (c) DVB total (d) p.DVB

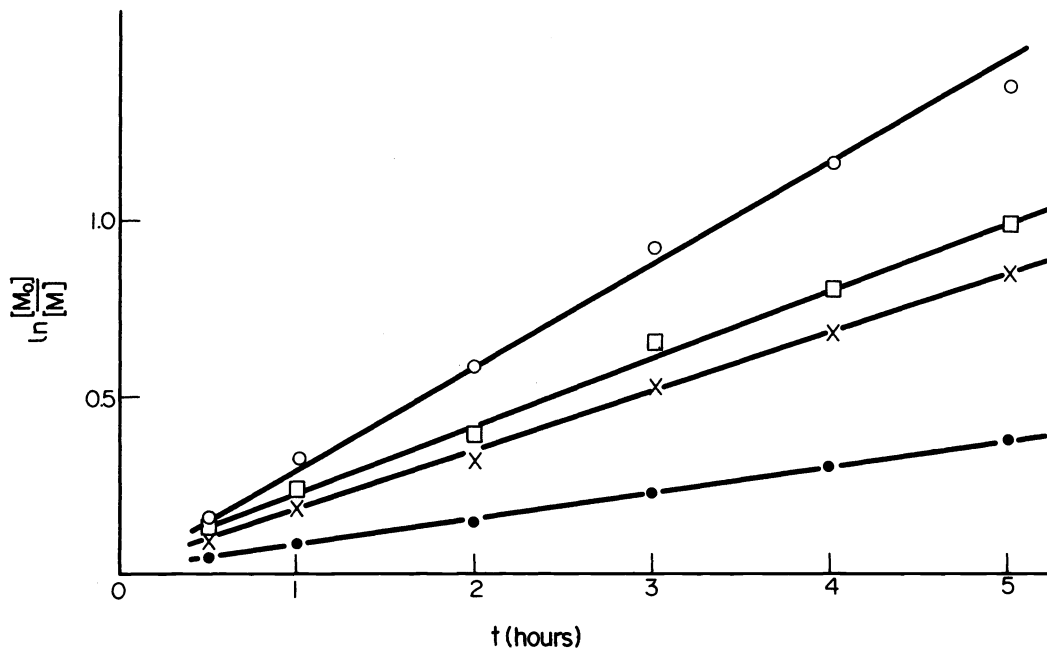



Fig.2 - Radical copolymerization of styrene and DVB:
 First order plots $\ln [M_0] / [M]$ versus time t


• styrene x m.DVB
 □ DVB total o p.DVB

From these conversion curves the instantaneous compositions of the copolymers obtained were calculated. Considering implicitly DVB as a single constituent - which is a very rough approximation - a Fineman - Ross diagram was set up, and the value of the reactivity ratio for the styrene radicals was found to be 0.76.

2 - Kinetic results - This first set of data prompted us to carry out more precise experiments on truly binary systems. Styrene was copolymerized under standard conditions in benzene solution, at 60°C, with constant proportions (2 mole %) of five different pure comonomers:

- . meta-divinylbenzene (m.DVB)
 - . para-divinylbenzene (p.DVB)
 - . meta-diisopropenylbenzene (m.DIB)
 - . para-diisopropenylbenzene (p.DIB)
 - . ethylenedimethacrylate (DME)
- 

DVB



DIB
- $$\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-\text{CH}_2-\text{CH}_2-\text{OCO}-\text{C}(\text{CH}_3)=\text{CH}_2$$

In each case, AIBN was used as radical initiator, and no chain transfer agent was added in this set of experiments.

The conversion of the individual monomers was followed gas chromatographically as a function of time, and the curves of the percentual conversion with time are shown on Fig. 3,4,5,6,7 and 7b. As indicated above these curves, have been used for the calculation of the instantaneous compositions of the copolymers formed, at various times. An example of the numerical data obtained is shown on Tab. 1,2,3 for the system styrene-m.DVB. The Fineman-Ross diagrams established from the data computed on these 5 systems are shown on Fig. 8,9,10,11,12 and the values of the radical reactivity ratios obtained for these systems are shown on Tab. 4.

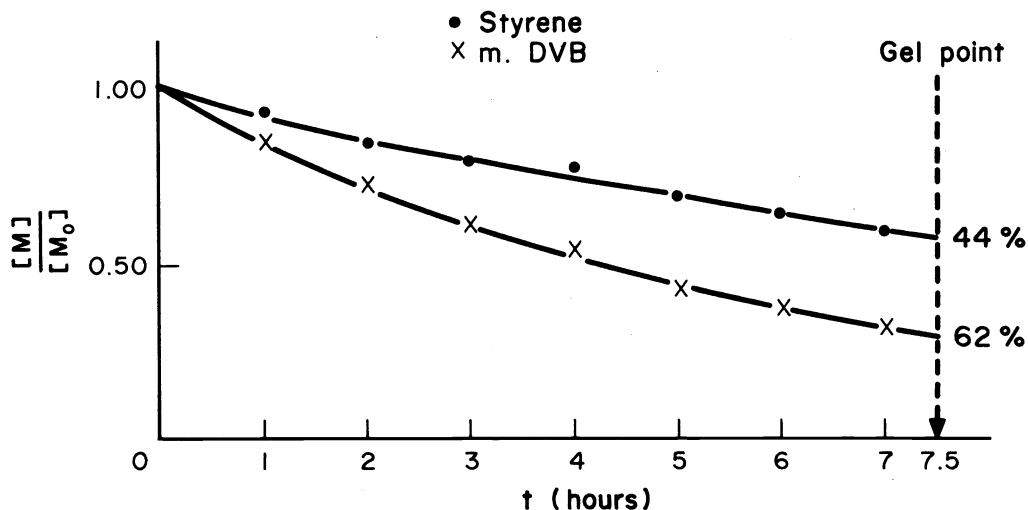


Fig.3 - Radical copolymerization of styrene and m.DVB (2 mole %) Conversion curves

As already mentioned the values of r_D lack precision, whereas the values of r_S can be considered accurate.

In all 5 cases the consumption of the difunctional monomer is faster than that of the styrene, although there are obvious differences in reactivity between the individual comonomers. The system styrene-m.DIB is the one exhibiting the smallest difference in rates of consumption of the monomers. The largest differences are observed for the system styrene-DME and styrene-p.DVB.

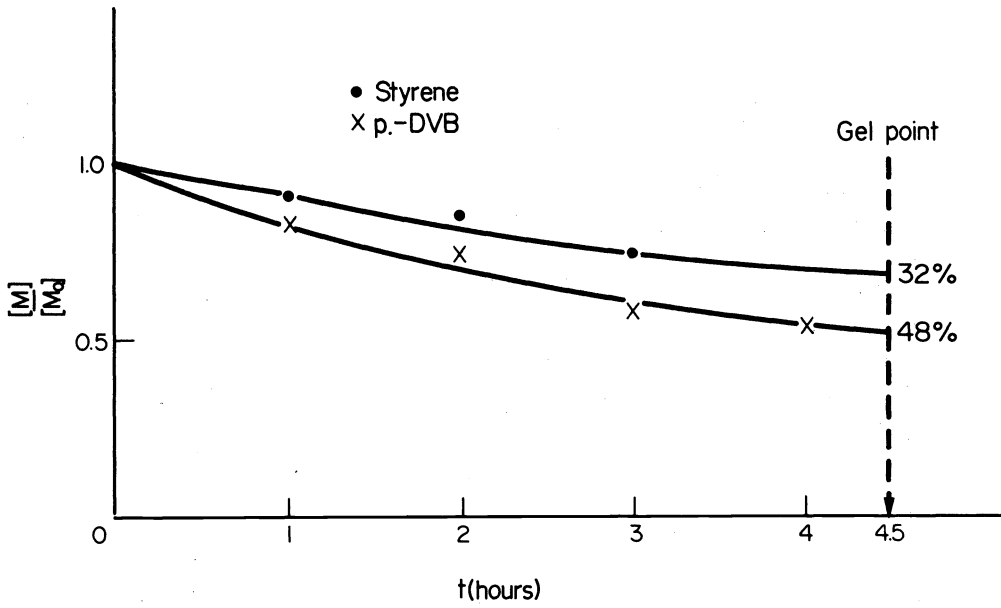


Fig. 4 - Radical copolymerization of styrene and p.DVB (2 mole %) Conversion curves

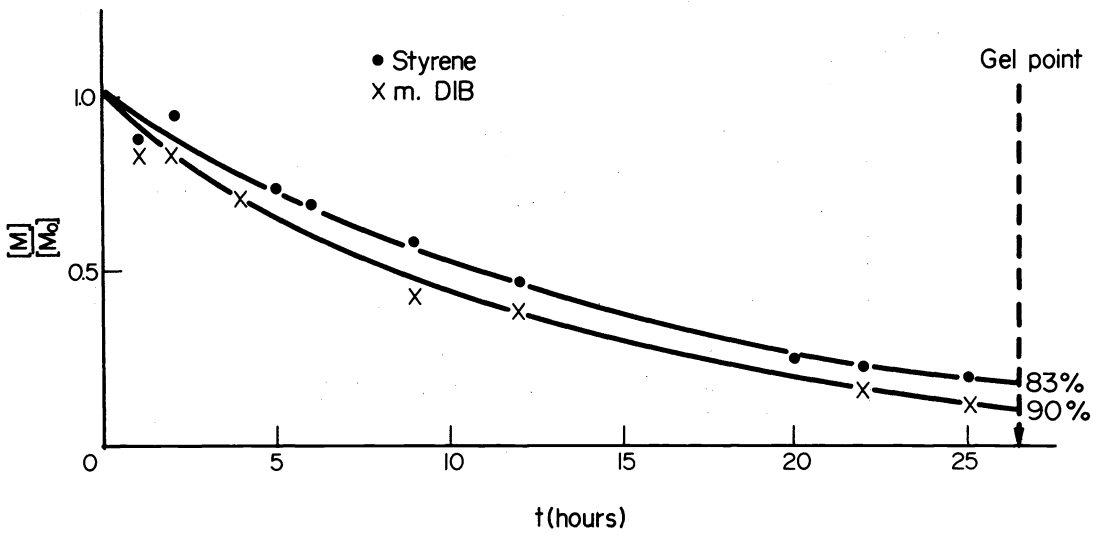


Fig. 5 - Radical copolymerization of styrene and m.DIB (2 mole %) Conversion curves

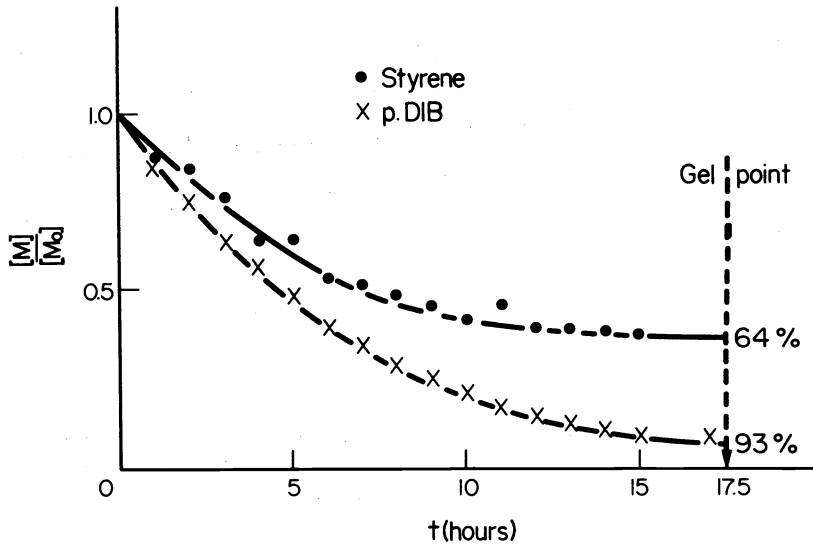


Fig. 6 - Radical copolymerization of styrene and p.DIB (2 mole %) Conversion curves

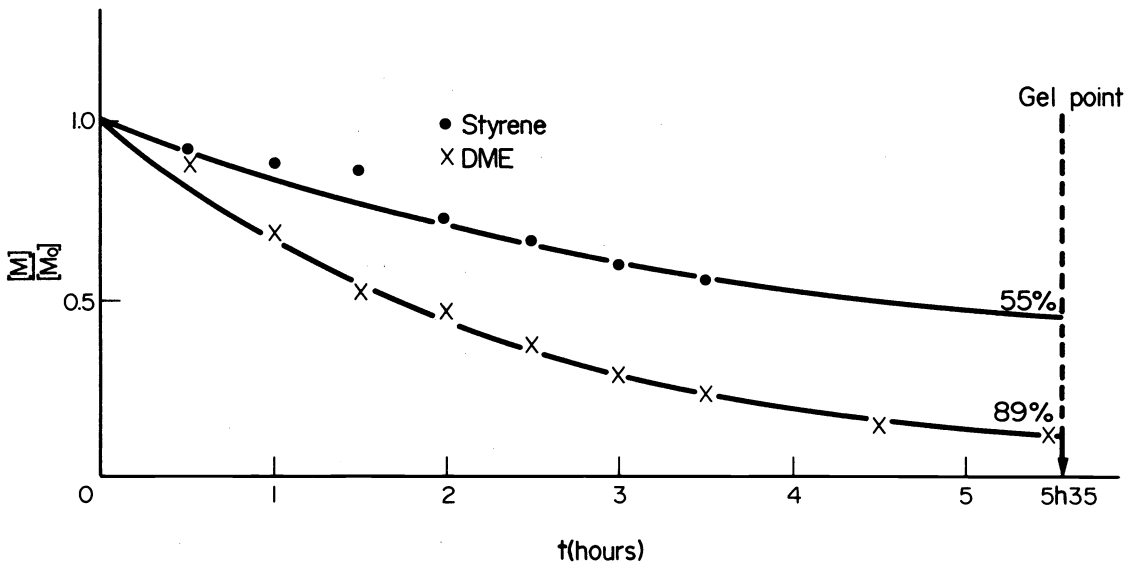


Fig. 7a - Radical copolymerization of styrene and DME (2 mole % DME) Conversion curves

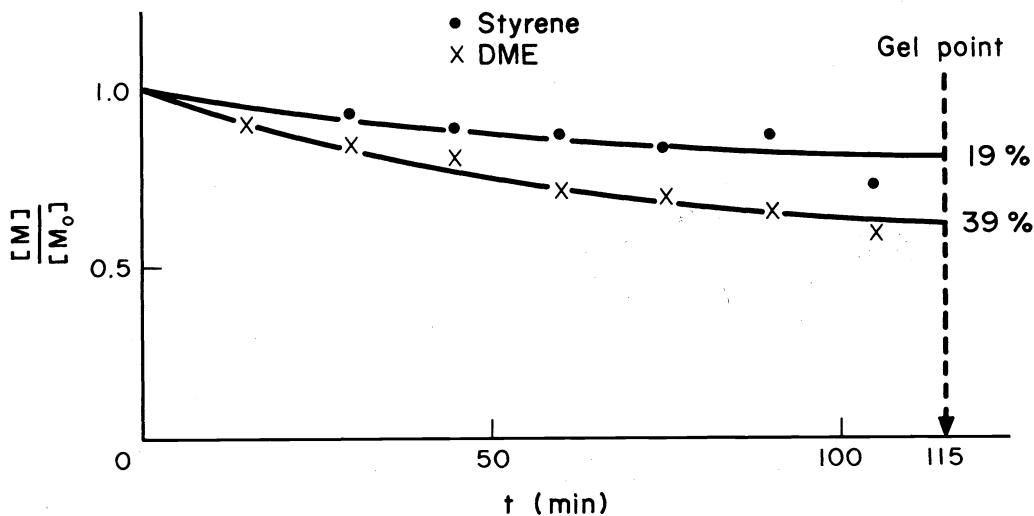


Fig. 7b - Radical copolymerization of styrene and DME
Conversion curves (5 mole % DME)

Time (hours)	[S]	Styrene d[S]	ΔS	Meta-DVB [D]	d[D]	ΔD	Y	X
0	4.000			0.080			47.7	115.1
1	3.723	0.273	0.273	0.067	0.0122	0.012	52.6	126.4
2	3.465	0.257	0.534	0.057	0.0103	0.022	58.0	138.8
3	3.225	0.239	0.774	0.048	0.0087	0.031	63.8	152.1
4	3.002	0.223	0.997	0.041	0.0074	0.038	70.2	166.6
5	2.794	0.207	1.205	0.035	0.0063	0.044	77.3	183.2
6	2.601	0.193	1.398	0.029	0.0054	0.055	85.3	202.0
7	2.421	0.180	1.572	0.025	0.0045	0.054	93.8	221.3

Table 1 - Composition of the soluble copolymers formed during the early stages of the radical copolymerization of styrene and meta DVB (Gel point : $t_c = 7.5$ h)

[S] and [D] are the instantaneous concentrations of styrene and m.DVB
d[S] and d[D] are the amounts of monomers incorporated during the last time interval considered
 ΔS and ΔD are the cumulated variations of these values

Time (hours)	X_1 %	X_2 %	DB %	$\bar{M}_{w,LS}$	$\bar{M}_{w,GPC}$	$\bar{M}_{n,GPC}$	$\left(\frac{\bar{M}_w}{\bar{M}_n}\right)_{GPC}$
1	7.70	7.71	2.56	38 500	39 500	15 500	2.5
2	14.01	16.00	2.45	50 500	46 000	20 000	2.1
3	19.84	21.68	2.80	71 000	67 000	18 500	3.6
4	25.34	23.32	2.56	109 000	71 000	16 000	4.4
5	30.60	31.40	2.54	203 000	159 500	28 000	5.7
6	36.56	35.67	2.21	560 000	305 000	29 500	~ 10
7	37.52	41.92	1.51	6 800 000	1 550 000	31 500	~ 50

Table 2 - Characterization of the soluble copolymers formed during the copolymerization of styrene and meta-DVB

X_1 and X_2 are the conversion degrees determined by gravimetry and by gaz liquid chromatography respectively
DB ... is the weight percentage of double bonds $>C=C<$
 $\bar{M}_{w,LS}$.. are the weight average molecular weights determined by light scattering
 $\bar{M}_{w,GPC}$ and $\bar{M}_{n,GPC}$ are the weight and number average molecular weights determined by gel permeation chromatography

Time (hours)	Instantaneous composition of the monomers mixture		Instantaneous composition of the formed copolymers		Integrated composition of the formed copolymers	
	% styrene	% DVB	% styrene	% DVB	% styrene	% DVB
1	98.03	1.97	-	-	-	-
2	98.21	1.79	95.77	4.23	95.77	4.23
3	98.37	1.63	96.15	3.85	95.95	4.05
4	98.51	1.49	96.49	3.51	96.12	3.88
5	98.64	1.36	96.78	3.22	96.27	3.73
6	98.761	1.24	97.05	2.95	96.40	3.60
7	98.87	1.13	97.28	2.72	96.52	3.48
8	98.99	1.03	97.56	2.44	96.64	3.36

Table 3 - Composition of the copolymers obtained in the radical copolymerization of styrene and m.DVB

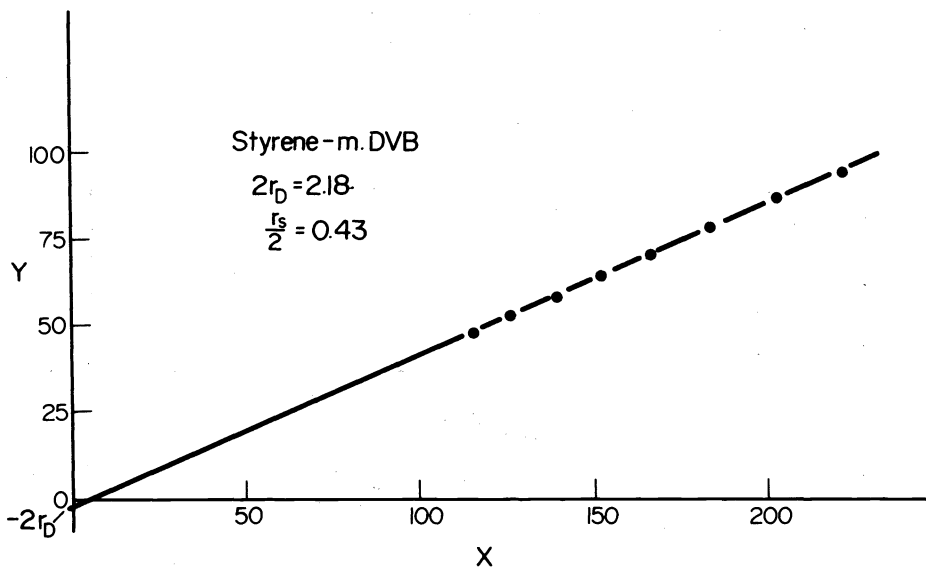


Fig. 8 - Fineman-Ross diagram for the system styrene-m.DVB

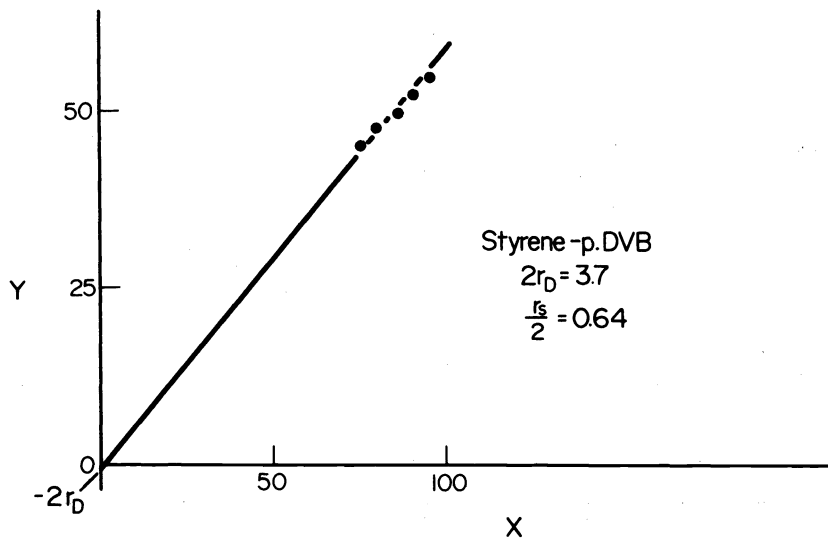


Fig. 9 - Fineman-Ross diagram for the system styrene-p.DVB

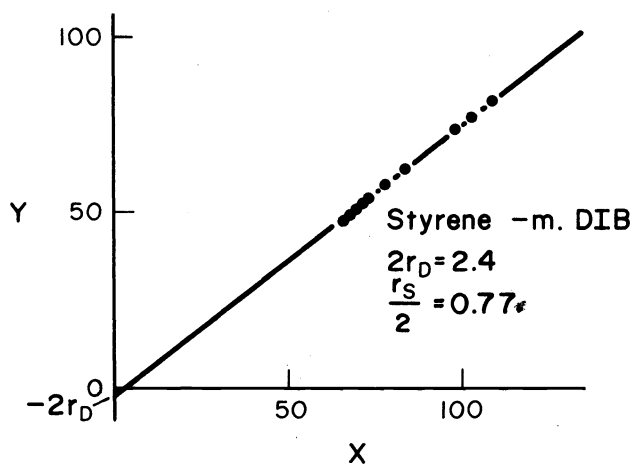


Fig. 10 - Fineman-Ross diagram for the system styrene-m.DIB

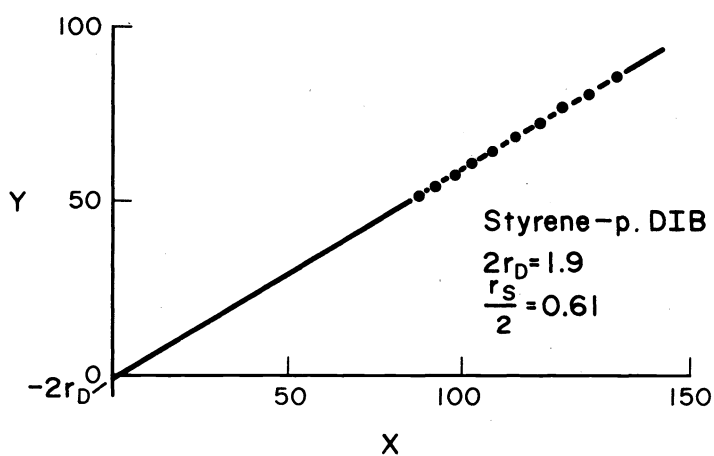


Fig. 11 - Fineman-Ross diagram for the system styrene-p.DIB

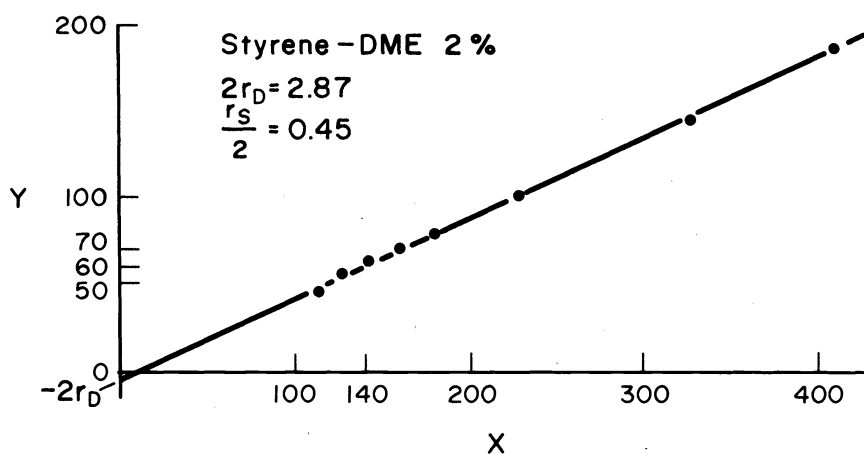


Fig. 12 - Fineman-Ross diagram for the system styrene-DME

System	r_s	r_D
Styrene-m.DVB	0.86	1.1
" -p.DVB	1.28	1.7
" -m.DIB	1.54	1.2
" -p.DIB	1.22	1.0
" -DME	0.90	1.4

Table 4 - Values of the reactivity ratios found from the Fineman-Ross diagram

It is striking that in two cases both reactivity ratios are higher than unity, which is considered exceptional. However it should be remembered that the bifunctionality of D-monomers introduce a factor 2 (resp.1/2) into the Fineman-Ross linearization equation, and that the values of r_D lack accuracy.

It has been emphasized at this stage that the time t_c which is required for gelification to occur is very different from system to system. Similarly the conversion at which the gel point is reached, under the same experimental conditions, and with identical amounts of bifunctional monomer (2 moles %) are quite different. When m.DIB is the comonomer gelification occurs after 26.5 hours of reaction, at a time at which 83% of the system and 90% of the DIB initially present have reacted (Fig.5). On the contrary, with p.DVB gelification is observed after only 4.5 hours of reaction, the conversion at t_c amounting to 32% for styrene and 48% for p.DVB (Fig.4). In the range of styrene-DME system (with 2% DME) 5.5 hours are necessary to reach the gel point, and 55% of the styrene and 89% of the DME have been converted by then (Fig.7). These results are of major importance, since they give a qualitative indication on the reactivity of pendent double bonds. The unsaturations arising from m.DIB (once incorporated in the chain) are the least reactive with respect to styrene radicals, whereas the pendent unsaturation originating from either p.DVB or DME are the most reactive ones. It would have been of great interest to double-check these results by means of accurate double bond analysis. Unfortunately, the analytical precision is not good enough to calculate the percentage of double bonds remaining untouched in the copolymers.

Nevertheless, it is likely that the reactivity of the pendent unsaturations - though different from system to system - is comparatively low, and in the beginning of the copolymerization their concentration tends to increase: the number of pendent double bonds formed exceeds by far the number of pendent double bonds reacted (to form crosslinks). It should be objected that if intramolecular reaction were privileged these double bonds would be consumed without formation of elastically effective crosslinks (Ref.11). But the results presented in the next section show that intramolecular cyclization can only be of minor importance, as many pendent double bonds are still available in later stages of the reaction, to establish more and more crosslinks, at times at which the amount of bifunctional monomer remaining has become quite negligible.

Finally it should be pointed out that in all these binary systems the conversion of both monomer species follow first order law, as it is exemplified for a system in Fig.13.

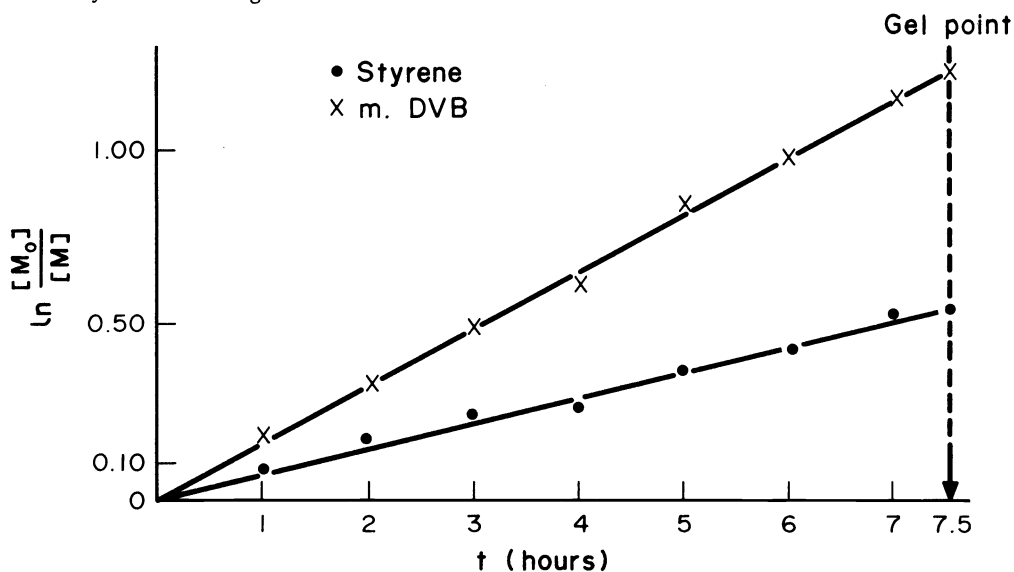


Fig.13 - Radical copolymerization of styrene and m.DVB. First order plots

AN INVESTIGATION OF VISCOSITY AND MODULUS OF THE REACTION MIXTURE DURING THE RADICAL COPOLYMERIZATION OF STYRENE AND DIVINYLBENZENE

The main purpose of this investigation was to establish whether a gelation process resulting from such a copolymerization can be analyzed in terms of a percolation process. The analogy between percolation and gelation as was first suggested by Stauffer (Ref.20) and by DE GENNES (Ref.21 & 22). New bases have been set to the gelation theory, and it is now possible to take both cyclization and excluded volume effects into account, which was not possible in classical treatments of Flory and Stockmayer (Ref.23).

If percolation occurs at the gel point, it implies that the viscosity of the reaction medium has diverged. The viscosity η of the reaction medium is measured in situ, as a function of reaction time t , by means of an automatic sphere rheometer, which has been described elsewhere (Ref.14). On the basis of the percolation theory a power law between viscosity and reduced time (defined as $(t_c - t)/t_c$, t_c being the time at which the gel point is reached) should be expected:

$$\eta \sim \left(\frac{t_c - t}{t_c} \right)^{-s}$$

The value of the exponent s can be computed using a Monte Carlo simulation, and its value should be close to 0.7 (± 0.07).

Experimentally, it was observed (Fig.14) that the viscosity of the reaction medium increases noticeably only during the last half hour before gelation (t_c being in that case of the order of 9 hours). If plotted in a double logarithmic scale (Fig.15) it is evidenced that two domains have to be considered:

- near the gel point the best fitting exponent is 0.78 in satisfactory agreement with the value expected.
- farther from the gel point the exponent of the scaling law is close to unity (1.05 ± 0.04).

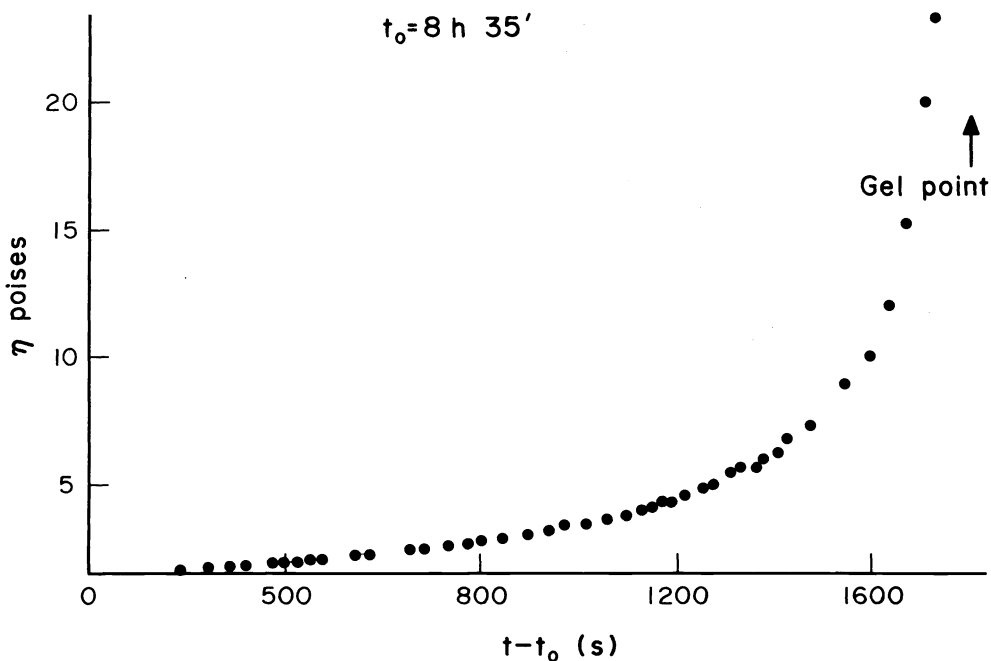


Fig. 14 - Variation of the viscosity of the reaction medium with reaction time (η_r is a reference viscosity): ($\eta_r \approx 30$ poises)

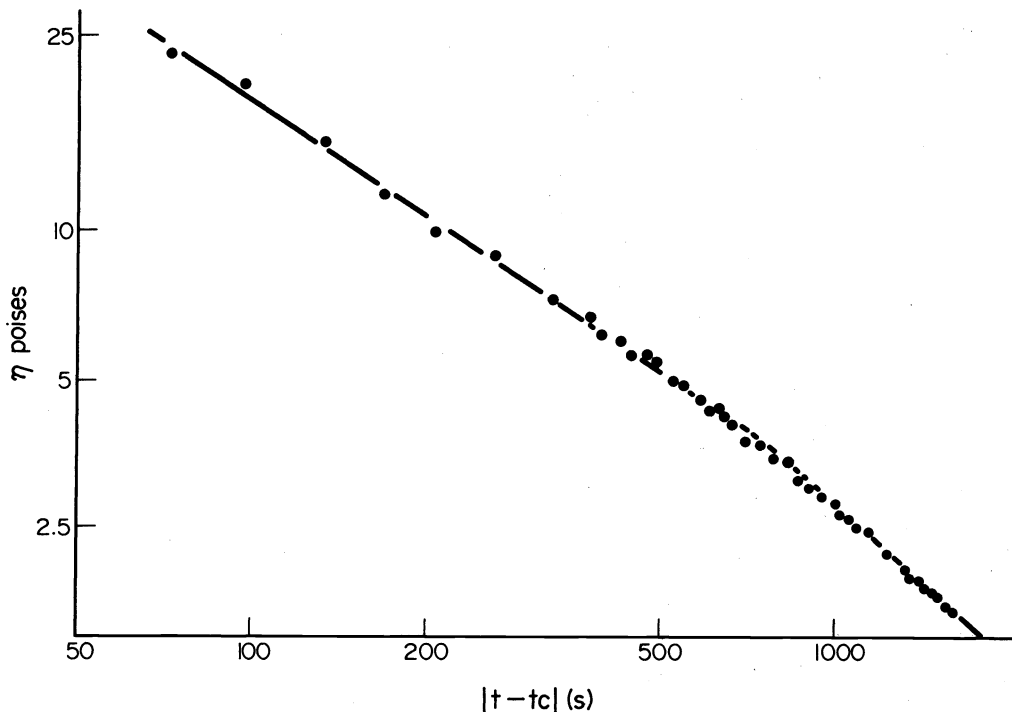


Fig. 15 - Log-Log plot of the viscosity as a function of time difference ($t - t_c$)

This shows that the so-called "effective medium approximation" (Ref.24) gives acceptable results far from the gel point. This may mean that cyclization and excluded volume effects do not play a major role. But, when gelation is about to happen, during the radical copolymerization of styrene and divinylbenzene, the observed divergence of the viscosity of the reaction medium can be analyzed in terms of a percolation process.

The second aim of this investigation was to measure the modulus of the gel (once it is formed) as a function of time (or conversion), in order to establish to what extent the network becomes tighter, in spite of the fact that most of the DVB has been consumed at this stage. The magnetic sphere rheometer can be used both for viscosity measurements (prior to gelation) and for the determination of the elastic modulus of the swollen gel (beyond the gel point); the accuracy of the latter measurements is not very high, though.

From the experimental results (Ref.25) it appears that the modulus increases by at least 3 orders of magnitude over 5 hours of reaction time beyond the gel point. This qualitatively confirms that many more crosslinks are formed by reaction of pendent double bonds with growing radicals.

Similar conclusions can be drawn from equilibrium swelling measurements performed on gels obtained by radical copolymerization of styrene and DVB carried out to various conversions. Fig. 16 shows that the results obtained for 3 different systems, containing respectively 1,2 and 3 mole % DVB with respect to styrene. In these experiments the occurrence of the gel point had been delayed by the presence of CCl_4 . It appears clearly that the equilibrium swelling degree of the networks formed (in benzene) decreases when the reaction time increases, thus evidencing again that additional crosslinks are formed in later stages of the reaction.

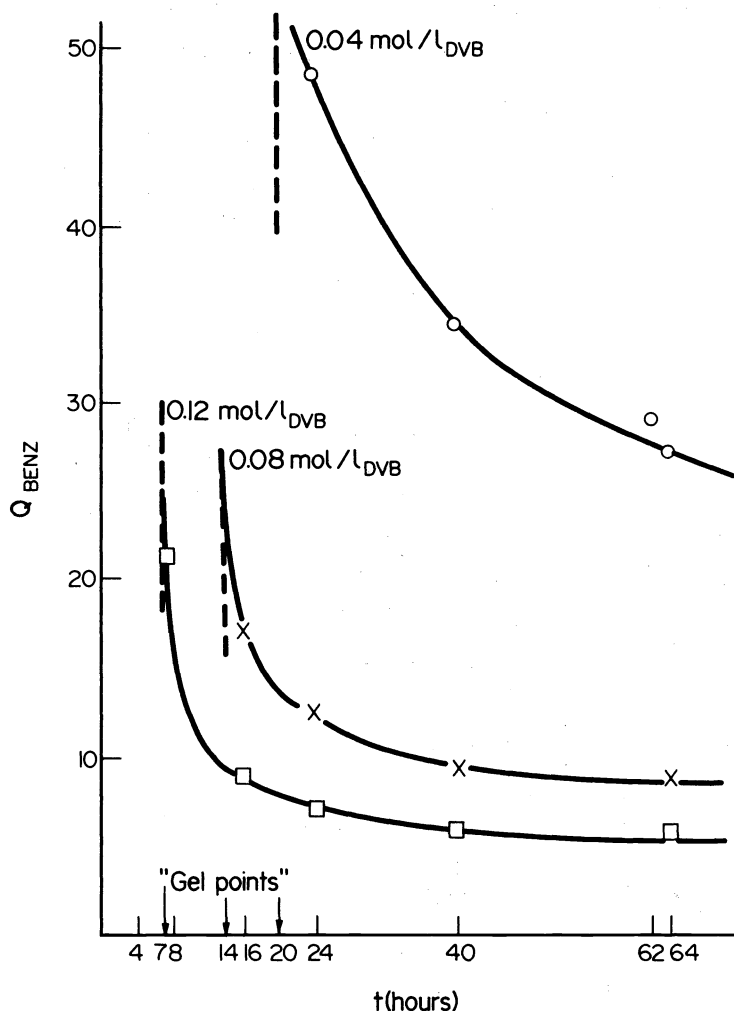


Fig. 16 - Variation of the equilibrium swelling degree in benzene of styrene-DVB network as a function of reaction time

- 1 mole % DVB
- × 2 mole % DVB
- 3 mole % DVB

(experiments performed in the presence of CCl_4)

CONCLUSION

The results that were displayed in this paper bring new light onto the mechanism of network formation by radical copolymerization of two monomers, one of which is bifunctional and present only in small proportion. Some of the ideas commonly held in the structure of such networks have to be reconsidered, and this investigation contributes to a better understanding of network structure versus network formation.

During the early stages of the reaction (prior to the gel point), the copolymerization process yields so called "primary" macromolecules, that are branched, and the size of which increases with conversion. When a bifunctional monomer molecule D is attacked by a growing radical a pendent double bond is formed. When such a pendent double bond reacts in turn a branch point is formed. However, it is shown here that the reactivity of these pendent unsaturations with respect to radicals is lower than that of both monomers D and S. Therefore, their concentration increases in the early stages of the reaction. Intramolecular reactions can occur (to yield cyclization) but

such reactions are not probable, and most of the double bonds will give yield to branch points connecting two "chains".

The gel point can be analyzed in terms of a percolation process, and it is characterized by the divergence of the viscosity of the reaction medium. At this point, molecules of infinite molecular weight have been built up, next to many others of finite size. However, all macromolecules present bear still unreacted unsaturations: thus many more crosslinks are formed in the later stages of the reaction. As the concentrations of monomers D and S decrease the probability for pendent unsaturations to react with growing radicals increases, and the network becomes tighter. This is shown clearly by the decreasing equilibrium swelling ratios and by the increasing values of the elastic moduli as reaction progresses beyond the gel point. It is thus demonstrated, though in a qualitative fashion, that the chain formed in the latter stages of the process contribute efficiently to the network elasticity and that the number of crosslinks steadily grows until all unsaturations have reacted.

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