Studies in Network Formation. 6.[†] Populations of Species Produced on Cross-Linking Preformed Polymer: Random and Nonrandom Cross-Linking[‡]

Geoffrey C. Eastmond* and Julie E. Richardson[§]

Donnan Laboratories, University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K.

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ABSTRACT: This paper examines the populations of simple cross-linked species formed during the cross-linking of a preformed polymer by a free radical process. Reaction conditions are identified under which gelation kinetics are ideal and where cross-linking is assumed to be random and intermolecular; semidilute solutions and low rates of radical formation. Deviations from ideal kinetics found under other reaction conditions, dilute solutions and high rates of radical formation, are attributed to excess intramolecular cross-linking. Weight fractions of simpler cross-linked species, determined by gel-permeation chromatography under various reaction conditions and extents of cross-linking, are consistent with these generalizations and mechanisms are proposed to account for deviations in those weight fractions from values calculated from simple gelation theory.

Flory[1-4] and Stockmayer,[5,6] when developing gelation theory, derived equations to describe the distributions of molecular species formed during reaction. Relations were developed for (a) polymerizations of multifunctional monomers and (b) cross-linking of preformed polymer chains. While there have been subsequent developments in the theory of network formation and the modeling of cross-linking processes, there are few experimental studies of the populations of species of different complexity formed during cross-linking. Clarke et al.,[7] in a study of the cross-linking step polymerization of decamethylene glycol and benzene-1,3,5-triacetic acid, demonstrated that weight fractions of unreacted species and of the dimer conformed with the predictions of the statistical theory. Hess[8] obtained supporting data from an investigation of species present in silicate melts.

Quantitative information on species formed on cross-linking preformed polymers is sparse. Kells and Guillet[9] examined polystyrene cross-linked in the solid state. By use of an ultracentrifuge, Schlieren patterns showed the presence of un-cross-linked polymer and of species containing two and three primary chains but no quantitative data were obtained. Flory subsequently stated that while "the applicability of the statistical theory is well established .... Further definitive experiments are needed .... to assess its reliability in detail".[10]

For several years we have used free-radical graft polymerization to produce copolymers.[11] Bimolecular termination of propagating radicals in free radical polymerization occurs, at least in part, by radical–radical combination,[12,13] which, in graft polymerization, constitutes cross-linking and, on continued reaction, leads ultimately to network formation; free radicals are generated and terminated continuously during graft polymerization. We have used these processes to prepare copolymers[11,14-17] and for kinetic studies.[18-21] While we have gone some way to determining structural parameters of molecules formed prior to gelation (e.g., cross-link/branch ratios[22] and molecular weights of cross-links[23]), we have never been certain of the distribution of species of different complexity in the copolymers, e.g., the weight fractions of species consisting of z preformed chains cross-linked by $(z - 1)$ grafts. Nor have we been certain of the proportions of inter- and intramolecular cross-links formed under different experimental conditions. To answer some of these questions we have undertaken a model study of cross-linking.

This paper presents the results of an investigation of cross-linking functionalized preformed poly(*p*-methylstyrene) (P(pMeSt)) with a narrow molecular weight distribution. Cross-linking was achieved by the same free radical forming reaction as used to initiate graft polymerization. We have identified reaction conditions that, from gelation kinetics, appear to conform to random intermolecular cross-linking. Two sets of reaction conditions under which gelation kinetics deviate from random intermolecular cross-linking have also been identified; deviations are attributed to the occurrence of intramolecular cross-linking. Gel-permeation chromatography (GPC) was used to examine the products formed at different cross-link densities under different reaction conditions. Attempts have been made to deconvolute the chromatograms in order to examine how the weight fractions of simpler species formed vary with cross-link density under different reaction conditions; the resulting weight fractions of species are compared with those calculated by Flory. Preliminary data for samples cross-linked under "ideal" conditions (see below) have been published previously.[24]

Aspects of Gelation Theory. Flory[4] derived the critical condition for incipient gelation (network formation) for random cross-linking of preformed polymer chains of uniform molecular weight (uniform functionality of cross-linkable sites) as one cross-linked site per preformed chain, an average of one cross-link per two preformed chains. For such systems the number of cross-linked sites at the gel point is c/P where c is the base molar concentration of cross-linkable sites and P is their degree of polymerization. It follows that, if the rate of formation of cross-linked sites is $\mathcal{R}$, the time required to reach the gel point (the gel time, t_g) is given by

$$t_g = c/P\mathcal{R} \qquad (1)$$

for polymers with nonuniform molecular weight distri-

[†] Part 5: cf. G. C. Eastmond and J. E. Seymour.

[‡] Presented at Networks '90, Jerusalem, May 1990.

[§] Nee Seymour. Present address: Market Levington, Wilts.

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butions P is replaced by $\bar{P}_w$.

Flory also derived the weight fractions of soluble species formed during cross-linking. Weight fractions of species consisting of z preformed chains (linked by $(z-1)$ cross-links) are given by

$$w_z = \frac{z-1}{\gamma z!}(\gamma e^{-\gamma})^z \qquad (2)$$

where γ is the cross-linking index, defined as the average number of cross-linked units per preformed chain; $\gamma = 1$ at the gel point.

For individual species (2) can be linearized to give simple relationships. Thus, for $z \leq 3$, we derive for un-cross-linked species "monomer" ($z = 1$), "dimer" ($z = 2$), and "trimer" ($z = 3$)

$$z = 1 \qquad -\ln w_1 = \gamma \qquad (3a)$$

$$z = 2 \qquad -\frac{1}{2}\ln(w_2/\gamma) = \gamma \qquad (3b)$$

$$z = 3 \qquad -\frac{1}{3}\ln(2w_3/3\gamma^2) = \gamma \qquad (3c)$$

It is, in effect, the validity of these equations, the limits on their validity (in terms of experimental conditions), and the nature of any deviations from them that we examine in this paper.

Experimental Section

The polymer used in cross-linking studies was a brominated poly(*p*-methylstyrene) (P(BrpMeSt)); (P(pMeSt)) was prepared by anionic polymerization. Inhibitor was removed from *p*-methylstyrene (Mobile) by passing through neutral alumina. The monomer was dried with calcium hydride, distilled under vacuum, and stored under nitrogen. Immediately prior to use the monomer was further dried under vacuum with calcium hydride, distilled onto dibutylmagnesium, where it was allowed to react for 1 h, and then distilled into a reaction vessel into which dry benzene had been distilled. While under vacuum an appropriate amount of butyllithium and a few drops of tetrahydrofuran were added. Polymerization was allowed to proceed for 1 h and was then terminated by addition of methanol. The P(pMeSt) was precipitated into methanol.

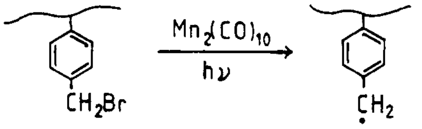
P(pMeSt) was brominated by using *N*-bromosuccinimide (NBS) and azobis(isobutyronitrile) (AIBN) in carbon tetrachloride;[25] extents of bromination were controlled by the amounts of NBS and AIBN used. Reactions were carried out under reflux under dry nitrogen and in the dark. The solution was filtered and the brominated polymer was precipitated into methanol and purified by repeated reprecipitation into methanol from dichloromethane solution; solutions in dichloromethane were filtered through a 0.4-μm filter. ^1H and ^{13}C NMR analyses showed that, under the reaction conditions used, bromination occurred exclusively at the *p*-methyl group. In different syntheses (reaction times) 8 and 34% of the methyl groups were brominated.

GPC showed several polymers to have narrow molecular weight distributions. Polymers were characterized by polystyrene standards with tetrahydrofuran as eluant; the flow rate was 1 cm^3 min^{-1}. Molecular weights of P(pMeSt) determined from polystyrene standards were multiplied by 128/114 to give the molecular weights of P(BrpMeSt); i.e., it was assumed that polystyrene and P(pMeSt) with identical degrees of polymerization will coelute. On bromination, elution volumes increased slightly. Molecular weights and degrees of polymerization used (e.g., in (1)) were based on values for the unfunctionalized polymers and extents of bromination; P in (2) is the degree of polymerization of cross-linkable sites, i.e., of brominated methyl groups. Polymers used in the cross-linking studies are identified in Table I.

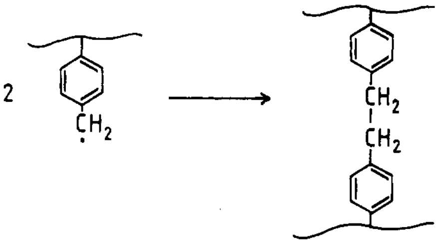
Table I
Characteristics of Poly(*p*-methylstyrene)s and Brominated Poly(*p*-methylstyrene)s

P(pMeSt)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	% bromination (methyl groups)	designation
A	65 600	73 500	1.12	8	A08
				34	A34
B	75 200	92 800	1.23	8	B08

Free radical formation, used in cross-linking and in initiating polymerizations (to assess rates of radical formation), was achieved through reaction of the photolysis products of dimanganese decacarbonyl (λ = 436 nm) with organic halides.[26] Reactions were carried out under vacuum in a laboratory illuminated with inactive sodium light. Essential features of the cross-linking process are shown in eqs 4a,b.



(4a)



(4b)

Dimanganese decacarbonyl ($Mn_2(CO)_{10}$) (Alpha Chemicals Ltd.) was purified by vacuum sublimation; the maximum concentration used in reaction mixtures was 1.54 × 10^{-3} mol L^{-1} to ensure uniform photon flux. α-Bromotoluene (Kodak) was used as received. Methyl methacrylate (MMA) (BDH Ltd) was purified by passing through neutral alumina and dried over calcium hydride.

Reaction mixtures for polymerization and cross-linking, using benzene as solvent, were prepared as described in previous studies. Neutral density filters were used to control incident light intensities and rates of radical formation. Reactions were performed at 25 °C. Rates of MMA polymerization were determined gravimetrically.

Viscosities of polymer solutions were determined in benzene solution at 25 °C on an Ubbelohde suspended-level viscometer.

Results and Discussion

Rates of Radical and Cross-Link Formation. Comparison of calculated and experimental values of t_g requires knowledge of $\mathcal{R}$; absolute values of $\mathcal{R}$ are potentially subject to error because they are not determined directly but from values of $\mathcal{R}^{1/2}$ extracted from other data.

Kinetic studies of free radical polymerizations,[26] photoinitiated by the same type of radical-forming process as used to generate cross-links in this study, demonstrated that (at constant [$Mn_2(CO)_{10}$] and incident light intensity I_0) rates of polymerization increase with increasing [halide] from zero to a plateau value achieved at "high" [halide], e.g., Figure 1. At high [halide], and under conditions of weak absorption, rates of radical formation $\mathcal{R}$ are given by

$$\mathcal{R} = kI_0[\mathrm{Mn_2(CO)_{10}}] \qquad (5)$$

Values of $\mathcal{R}$ have been determined from rates of free radical polymerization (ω) of MMA initiated by α-bromotoluene (as a model compound for the halogenated polymers) in conjunction with $Mn_2(CO)_{10}$ photolyzed at 436 nm. ω and $\mathcal{R}$ are related by

$$\omega = -\frac{\mathrm{d[MMA]}}{\mathrm{d}t} = \frac{k_p[\mathrm{M}]\mathcal{R}^{1/2}}{k_t^{1/2}}$$

where k_p and k_t are the rate coefficients for propagation

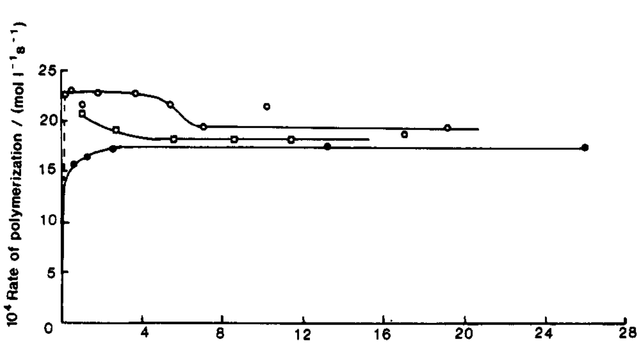


Figure 1. Variations in rate of polymerization of MMA at 25 °C photoinitiated by $Mn_2(CO)_{10}$ and organic halides at the same rate of photolysis. Organic halides used were (●) α-bromotoluene, (○) P(BrpMeSt) A08, and (□) P(BrpMeSt) A34. For polymeric reactants [halide] is in base mol L^{-1} of brominated residues.

and for overall termination; for MMA polymerization at 25 °C, $k_p/k_t^{1/2} = 0.055$ mol$^{-1/2}$ L$^{1/2}$ s$^{-1/2}$.[26]

Figure 1 shows the variations in ω with [halide] for α-bromotoluene and samples of P(BrpMeSt) used in gelation studies. Both types of halide show similar kinetic features but the plateau values of ω are slightly different. We have established that high rates of graft polymerization, initiated by macroradicals derived from a polymeric initiator, compared to those for initiation by small radicals are due to different rate coefficients for termination rather than to different rates of initiation.[23] Other workers have demonstrated that bimolecular termination of propagating radicals is a diffusion-controlled process[12,27] and that, at low degrees of polymerization, k_t is chain length dependent.[12,28] In graft polymerization the primary radical is large and there are no very small radicals with high k_t. Modified molecular weight distributions of grafts are consistent with this explanation.[23] We have therefore calculated values of $\mathcal{R}$ used in this study (for known values of I_0 and $[Mn_2(CO)_{10}]$) from rates of polymerization initiated by α-bromotoluene at [halide] $\geq 3 \times 10^{-3}$ mol L^{-1}.

Data in Figure 1 indicate that, kinetically, the polymeric halides behave similarly to small-molecule halides. Taking a relative value of k_t for bromotoluene-initiated polymerizations as unity, relative values of k_t for polymerizations initiated by the polymeric initiators A08 and A34 (Table I) are 0.935 and 0.824, respectively. For the difference between these values, and for the enhanced rates of polymerization at [halide] of about 1×10^{-3} mol L^{-1}, we have no explanation but consider they probably have a physical origin, which may influence the lifetimes of propagating radicals. We have no reason to believe they have any origin that will influence rates of radical formation and the numbers of cross-links formed in a given reaction time. Enhanced rates of polymerization at relatively low [halide] for polymeric initiation have been reported in related systems.[29]

The critical value for high [halide] of 3×10^{-3} mol L^{-1}, identified above, corresponds to polymer concentrations of about 0.5% (w/v). Polymerization data, however, indicate that the critical value of [halide] for polymeric initiators is $<1 \times 10^{-3}$ mol L^{-1} and possibly less than 0.1% (w/v), which is the lowest polymer concentration used in the cross-linking studies (0.1% (w/v) $\equiv 6 \times 10^{-4}$ base mol L^{-1} halide). Thus we believe that complications in cross-linking kinetics are possibly attributable to complications in rates of radical formation only at the very lowest polymer concentration used.

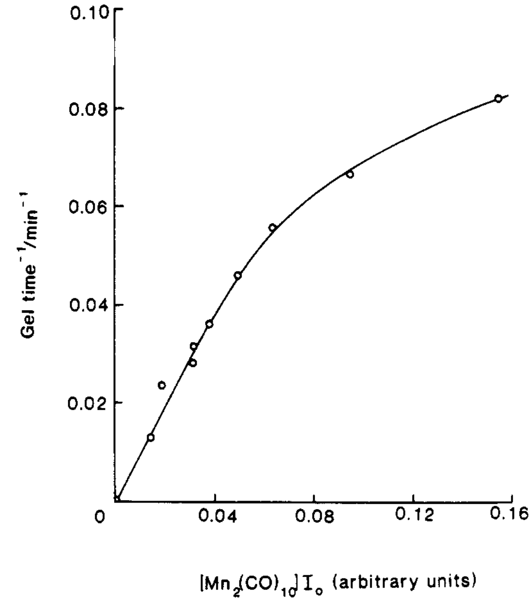


Figure 2. Dependence of reciprocal gel times on the product of $[Mn_2(CO)_{10}]$ and I_0; relative values of I_0 were determined from absorbances of neutral density filters.

The only other uncertainty in absolute values of $\mathcal{R}$ arises from possible solvent dependencies of $\mathcal{R}$ at constant $[Mn_2(CO)_{10}]$ and I_0. It is known that the quantum efficiency for radical formation in the presence of styrene is higher than for polymerizations in the presence of MMA[30] and is lower in the presence of ethyl acetate.[19] Values of $\mathcal{R}$ are independent of solvent in many systems including mixtures of MMA and benzene (the solvent used in this study) over a wider range of compositions.[18] It is possible that values of $\mathcal{R}$ are different in pure benzene but, in the absence of information to the contrary and in view of the agreement between observed and calculated values of t_g (see below), we take values of $\mathcal{R}$ calculated as described above to be the probable values.

It is possible that not all primary radicals lead to cross-link formation due to chain transfer. Chain transfer to polymer may be neglected because this has no influence on the number of radicals on preformed chains. Chain transfer to solvent reduces the rate of cross-link formation. Assuming the primary radical has similar reactivity to the styrene propagating radical and that radical lifetimes are comparable to those in polymerization, given the rate coefficient for transfer to benzene ($\sim 10^{-5}$)[12] and for bimolecular termination ($\sim 10^7$ mol^{-1} L s^{-1})[12] of polystyryl radicals and the concentrations of benzene and radicals, not more than 1% of primary radicals should undergo transfer to solvent.

Gelation Kinetics. In previous studies of gelation kinetics[18-21,23,24] we have taken reaction conditions under which the proportionalities between t_g and c and $1/\mathcal{R}$, required by (1), are obeyed simultaneously to correspond to random intermolecular cross-linking. We refer to these conditions as "ideal" cross-linking and now classify the systems as case I. Reaction conditions under which deviations from the above proportionalities occurred and under which values of t_g were greater than anticipated we considered to correspond to "nonideal" cross-linking through the creation of intramolecular cross-links. We retain this distinction.

Figures 2 and 3 show representative variations in $1/t_g$ with $[Mn_2(CO)_{10}]I_0$ ($[Mn_2(CO)_{10}]I_0 \propto \mathcal{R}$) and t_g with polymer concentration (equivalent to c in (1)), respectively, for cross-linking samples of P(BrpMeSt). Data show that

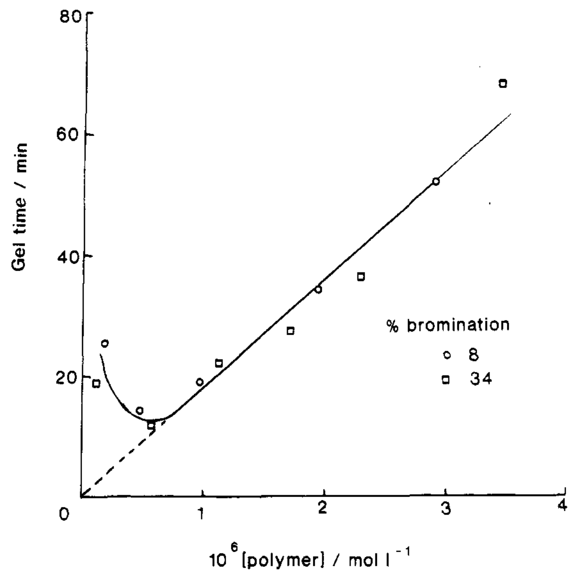


Figure 3. Gel times for cross-linking P(BrpMeSt) as a function of [polymer] for two samples of P(BrpMeSt): (○) A08; (□) A34. Experiments were performed at the same rates of photolysis of $Mn_2(CO)_{10}$.

the probabilities required by eq 1 are obeyed at relatively low $\mathcal{R}$ and [polymer] in excess of about 1% (w/v). It is the simultaneous agreement to these two dependencies that we use to classify reaction conditions as being "ideal".

Deviations from ideal behavior are in the form of extended values of t_g; at high $\mathcal{R}$ and low [polymer] (<1% (w/v)). These deviations, except possibly at the lowest polymer concentration used of 0.1% (w/v) (as explained above), are not consequences of changes in the kinetics of radical formation; data in Figure 3 show that deviations occur at the same polymer concentration rather than at the same bromide concentration. Thus, the deviations are not due to reduced rates of formation of cross-linking sites but possibly represent a loss of intermolecular cross-links, which lead to formation of a coherent network.

Under both sets of reaction conditions, where gelation kinetics are nonideal, the probability of forming a second radical on a chain already carrying a radical is increased and we have previously assumed that the origin of the deviations is probably due to the formation of such "wasted" intramolecular cross-links. We distinguish, however, between two types of deviation. In the one case, at low polymer concentrations, coherent gels are not formed in the early stages of gelation but rather gel particles are formed that form into coherent gels later. In the other, at high [polymer] and high $\mathcal{R}$, coherent gels are formed initially. We classify the former reaction conditions as case II and the latter as case III.

Incipient gelation under ideal cross-linking corresponds to $\gamma = 1$. For systems that deviate from ideal cross-linking, $\gamma \neq 1$ at the gel point and the actual value of γ is unknown. Under such conditions we calculate values of γ (γ_{calc}) from reaction times and the gel time that would have applied for ideal crosslinking at the same $\mathcal{R}$; i.e., we assume total rates of cross-link formation are identical whether or not cross-linking is ideal.

Further, quoted values of γ (or γ_{calc}) are reaction times expressed as fractions of t_g (for ideal cross-linking), implying that values of $\mathcal{R}$ are constant over the reaction times involved, which, at the low consumptions of $Mn_2(CO)_{10}$ involved, is essentially true.

Thus we have identified three sets of reaction conditions under which populations of species formed during reaction prior to gelation will be examined.

Case I: Ideal cross-linking, when gelation kinetics conform to relation 1. Calculated and experimental values of t_g were within 10%. Values of $\mathcal{R}$ were calculated from polymerization kinetics.

Case II: Nonideal cross-linking under conditions of low concentrations of preformed polymer. The solvent concentration regime relating to these experiments will be considered below.

Case III: Nonideal cross-linking under conditions of "high" concentrations of preformed polymer and high $\mathcal{R}$.

Solution Regimes. Polymer solutions exhibit distinct concentration regimes; one distinction is between dilute and semidilute solutions. This distinction is between one situation under which individual polymer molecules do not "see" each other in solution and where the segment density associated with an individual polymer coil is greater than the average segment density (dilute solution) and another under which the polymer coils do see each other in solution, where the coils of different molecules interpenetrate and the segment density through the solution is more uniform (semidilute solution).

The concentrations of preformed polymer used in these experiments fall in the region of the usual boundary between these two situations and we have examined the relevance of the boundary to our experiments.

In the dilute regime the viscosity of polymer solutions is determined by the molecular weight of the polymer and the concentration. In the semidilute regime polymer–polymer interactions increase the solution viscosity. For dilute solution behavior two common relations are (6a), the Huggins equation, and (6b), the Kramer relation; $k' = k - 0.5$. η_{sp}, η_r, and $[\eta]$ are respectively the specific,

$$(\eta_{sp}/c) = [\eta] + k[\eta]^2c \tag{6a}$$

$$(\ln \eta_r)/c = [\eta] + k'[\eta]^2c \tag{6b}$$

relative, and intrinsic viscosities. For a given polymer–solvent system, plots of the left-hand side of each relation as a function of polymer concentration should have a common intercept ($[\eta]$) and the slopes of the plots should change at a critical concentration (c^*), corresponding to the change from dilute to semidilute solution behavior.[31]

Figure 4 shows representative plots for polymer B08. In all cases a common intercept for the two plots was identified but, more importantly, both plots show a discontinuity in slope at about 1% (w/v) polymer. Table II gives values of c^*, defined as points of intersection for two of the polymers used in this study. From these and other data it was noted that c^* drifted with M_n in a manner consistent with observations of Gandhi and Williams on other systems.[32]

It is notable that c^* is, on average, very close to concentrations below which deviations from ideal gelation kinetics are observed. We discuss the relevance of this observation later.

Identification of Species. Figure 5 shows a representative set of gel-permeation chromatograms for reaction products from cross-linking polymer B08 at a concentration of 1% (w/v) to different degrees; a similar set of chromatograms for cross-linking A08 at 2% (w/v) was published in a preliminary report.[24]

Generally notable features on increasing cross-linking index are (i) the weight fraction of un-cross-linked species decreases steadily, (ii) a peak at about twice the molecular weight of the un-cross-linked species clearly develops in the early stages of cross-linking and retains some prominence throughout, and (iii) the weight fractions of species

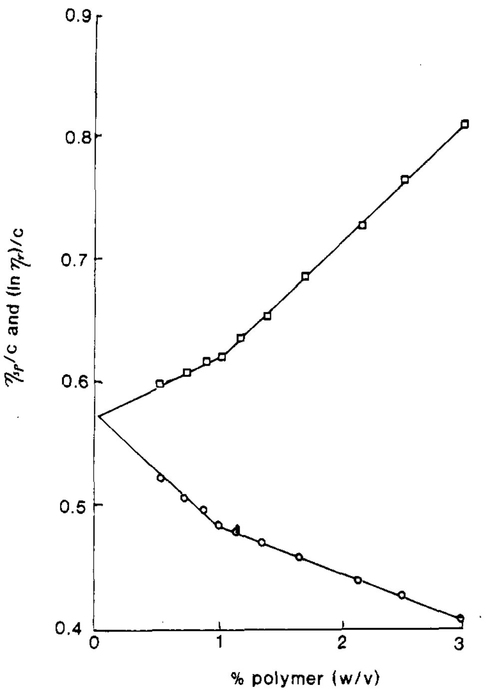


Figure 4. Huggins (□) and Kramer (○) plots, according to eqs 6a,b, for P(BrpMeSt) B08 in benzene solution at 25 °C.

Table II
Values of c^* for Samples of P(BrpMeSt) in Benzene Determined from Huggins and Kramer Relations

sample	c^*, % (w/v) Huggins	Kramer
A08	1.15	1.33
B08	1.15	1.02

of higher molecular weight gradually build up and the high molecular weight limit of species increases. The similarity between these data and those published previously indicates that, at the two polymer concentrations used, the distribution of species formed are approximately the same at equivalent cross-linking indices. In attempting to assess populations (or weight fractions) of individual species, it is necessary to attempt to deconvolute the chromatograms.

On cross-linking a polymer of uniform molecular weight, only species with discrete molecular weights (nM_0), which are simple multiples of the molecular weight of the initial polymer (M_0), are formed; n is an integer. Examination of gel-permeation chromatograms of known mixtures of selected calibration standards, with molecular weight distributions comparable to those of the brominated polymers, clearly demonstrated that weight fractions of monomeric and dimeric species can be assessed accurately for mixtures containing up to 20% dimer from the peak heights of the chromatograms; as we shall see, weight fractions of dimer relative to monomer hardly ever exceed 25%. At higher dimer contents a small overlap of the tail of the dimer affects the peak height of the monomer, introducing up to 14% error at a weight fraction of dimer of 0.5.

Thus, as described previously,[24] weight fractions of un-cross-linked polymer are readily assessed by extrapolating the sharp high molecular weight edge of the monomer peak in the chromatograms to the base line and determining the relative areas from un-cross-linked and all cross-linked species.

Estimation of weight fractions of individual larger species becomes progressively more difficult as the molecular weight and complexity of the species increase. Without any other factor, the logarithmic form of the calibration curve for the chromatograms results in a gradually increasing overlap of peaks as molecular weight increases. In addition, as molecular weights increase, distributions of species of a given molecular weight develop, which complicates the analysis.

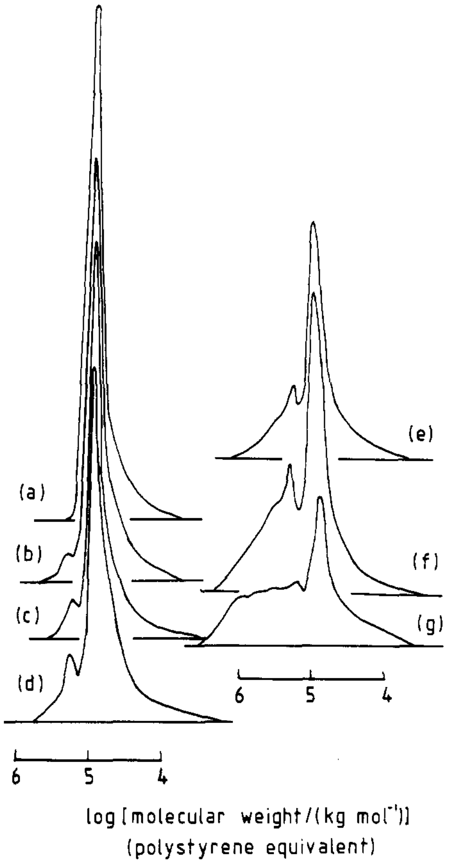


Figure 5. Gel-permeation chromatograms of samples of B08 (1% (w/v)) cross-linked to different extents: $\gamma = 0$ (a); 0.032 (b); 0.064 (c); 0.13 (d); 0.32 (e); 0.57 (f); 0.78 (g). Molecular weight scales are based on polystyrene standards.

Since there is no distribution between reaction sites on the monomeric species and radicals are produced randomly, all sites on a chain can be considered as having an equal probability of reaction. Thus, dimer species may have a variety of structures, according to the location of the cross-link between points on primary chains. One limiting structure with $z = 2$ is the linear molecule with molecular weight $2M_0$ (Figure 6a), formed by cross-linking two terminal units, and the other is the star molecule, formed by linking two central units (Figure 6b); this species has four equal arms with molecular weight $M_0/2$ and may be considered as a linear molecule of molecular weight M_0 carrying two branches, each with molecular weight $M_0/2$. The "average" species, and the most populous individual structure formed, has a maximum linear length of molecular weight $1.5M_0$ and two branches with a total molecular weight of $0.5M_0$ (Figure 6c); the branches may be at different points along the stem.

It is recognized that polymers of equal molecular weight but different geometry have different hydrodynamic volumes in solution. According to relations of Stockmayer and Fixman[33] the hydrodynamic volumes of linear dimer ($V_{2\text{-lin}}$) and symmetrical four-armed star ($V_{4\text{-star}}$) polymers are related by

$$V_{4\text{-star}}/V_{2\text{-lin}} = 0.71$$

Hydrodynamic volumes of other dimer species will be

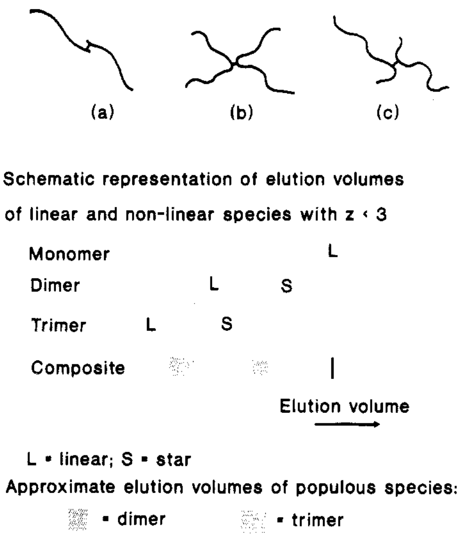


Figure 6. Forms of representative dimers formed by cross-linking two preformed chains: (a) between terminal units; (b) between central units; (c) in most probable form as described in the text. A schematic representation to show the approximate locations of linear, star-shaped, and most populous species on an elution volume scale and, in the latter case, to represent the form of a gel-permeation chromatogram of simple species in a reaction mixture after cross-linking.

between those for the limiting structures; a distribution of hydrodynamic volumes for dimers will therefore exist. Consequently, because gel-permeation chromatography separates species according to hydrodynamic volume, there will be a range of elution volumes for dimers. The maximum for the peak in the chromatogram corresponding to dimers is expected to be located at an elution volume determined by intermediate species rather than either of the limiting species. This is in accordance with experiments where a peak in the experimental chromatogram appears at an elution volume slightly greater than that expected for the linear dimer.

Trimer species generated will similarly have a range of hydrodynamic and elution volumes. From Stockmayer and Fixman[33] the equivalent ratio of hydrodynamic volumes of the limiting species, linear ($V_{3\text{-lin}}$) and symmetrical six-armed star ($V_{6\text{-star}}$), is given by

$$V_{6\text{-star}}/V_{3\text{-lin}} = 0.51$$

It is also anticipated that the peak in the chromatogram of trimer species will appear at some intermediate elution (hydrodynamic) volume. Trimer species will elute over a larger range of elution volumes than dimer species. Similar considerations will apply to more complex species.

The existence of the distribution of species with a given value of z, described above, will broaden the chromatograms for species with a given z. We have considered the consequences of attempting to separate mixtures of relative small species formed on cross-linking in conjunction with the calibration curve for the chromatographic columns used; the result is shown schematically in Figure 6. From Figure 6 it may be noticed that while the elution volumes of linear species with $z = 1$, 2 and 3 are well separated the separations of $z = 1$ and stars with $z = 2$ and 3 are not so well separated. Indeed the more symmetrical stars with $z = 3$ overlap with the more linear $z = 2$ species. A complete segregation of species, therefore, cannot be achieved. However, we note that overlaps are small and there should be points on the chromatogram, for intermediate species with $z = 3$, where there is no overlap between dimer and trimer and where the most populous species with $z = 3$ are likely to elute. Similarly, the most populous species with $z = 2$ are unlikely to overlap with species with $z \geq 2$; the anticipated elution volumes of more populous species are in the hashed regions of Figure 6.

Since the statistics of cross-link formation and the relative populations of species of different structure with the same z should remain constant throughout reaction, we have taken the peak height of the dimer species as proportional to the weight fraction of all species with $z = 2$. Although many chromatograms do not show a distinct peak for trimeric species (sometimes a shoulder is observed), we have identified an elution volume corresponding to peaks that appear at approximate elution volumes for trimers in some chromatograms as the elution volume of most populous species with $z = 3$ and have taken the peak height at that elution volume in all chromatograms to be proportional to the weight fraction of such species. To obtain estimates of w_2 and w_3 under various conditions, i.e., to relate w_z to chromatogram signal heights, we have adopted two methods. In method i we have assumed that, under conditions of ideal cross-linking, at the lowest value of γ used ($\gamma = 0.06$) values of w_2 and w_3 are given by (3) and $w_4 = 0$; the calculated value of $w_4 = 4.5 \times 10^{-4}$. In method ii we again assumed the calculated value of w_2 at the lowest γ and that values of w_2 and w_3 are proportional to signal heights at the identified elution volumes for $z = 2$ and 3. A comment on the use of data derived from (3) to test the predictions of (3) is included under Nonrandom Cross-Linking, case II.

Values of w_1, w_2, and w_3 obtained will be subject to some error. We consider values of w_1 to be most reliable and errors, which will increase with γ, are less than 10% at the highest γ used. Greatest uncertainty is in the separation of $z = 2$ and $z = 3$ and possible influence of star-shaped species with $z = 4$ on w_3 at high γ. We estimate that errors in evaluating w_2 and w_3 are unlikely to be greater than 15%. Even if values of w_2 and w_3 so obtained are subject to greater error, they are reproducible and allow comparisons to be made between populations of species obtained under these and other reaction conditions.

Populations of Species. Weight fractions of species with $z = 1, 2, 3$ were calculated, as described above, from several sets of chromatograms derived from samples of polymers cross-linked to different extents under different reaction conditions.

Case I. Random Cross-Linking. Parts A and B of Figure 7 present variations in w_1, w_2, and w_3 with γ for cross-linking preformed polymers B08 and A08 at 1 and 2% (w/v), respectively, where values of w_2 and w_3 were estimated according to method i. Within Figure 7 are data for one sample with values of w_3 estimated by method ii. Comparison may be made between experimental points and the curves calculated from (2).

In all cases values of w_1 agree closely with the calculated values over the whole range of γ studied. Data are consistent with random formation of free radicals and intermolecular cross-linking. That is, unreacted chains are converted to cross-linked species at rates consistent with the total functionalities of un-cross-linked and cross-linked species as calculated by Flory.[4] There is no evidence, under these reaction conditions, for intramolecular cross-linking or for other processes, such as chain transfer to solvent, which would reduce the rate of consumption of un-cross-linked species.

Values of w_2 and w_3 also agree well with calculated values from (2) for $\gamma < 0.5$, approximately. At higher γ, experimental values of w_z decrease more rapidly than calculated. Method ii gives better agreement between theory and experiment for $z = 3$ up to $\gamma = 0.8$; we are not

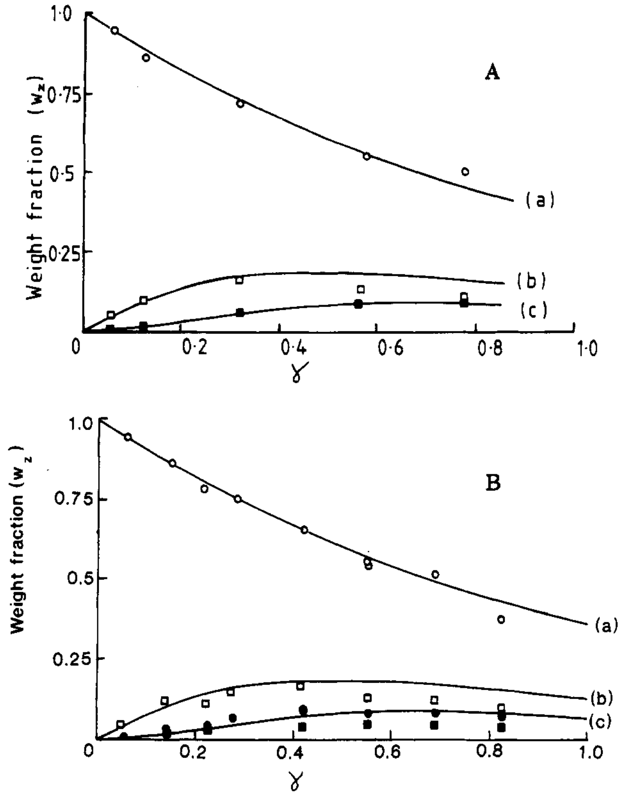


Figure 7. Variations in weight fractions (w_z) of cross-linked species having z primary chains with cross-linking index γ. Cross-linking of (A) B08 at 1% (w/v) and (B) A08 at 2% (w/v). In each case values of w_z are $z = 1$ (○), $z = 2$ (□), and $z = 3$ calculated by method i (■); (B) Points for w_3 calculated by method ii (●). Curves are calculated for (a) $z = 1$, (b) $z = 2$, and (c) $z = 3$ according to eq 2.

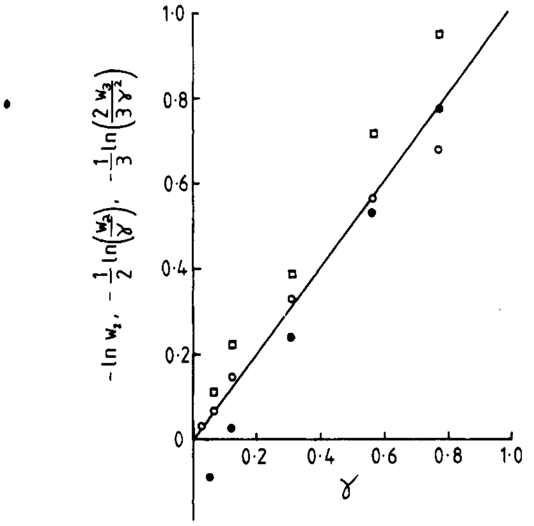


Figure 8. Variations in weight fractions (w_z) of cross-linked species with γ plotted according to eq (3) for cross-linking of B08 (1% (w/v)). $z = 1$ (○); $z = 2$ (□); $z = 3$ (●). Line is theoretical for all species.

certain that this method provides a more realistic comparison between theory and experiment.

An alternative approach to examining populations of species relative to calculated values is in terms of the linearized equations (3). Figure 8 shows such comparisons for cross-linking A08. Experimental points for each species may be compared with the common theoretical line. Both monomer and trimer give excellent agreement with theory except for small deviations for $z = 3$ at very low γ for B08, which may be due to experimental error; data for A08 do not show this deviation at small γ. The dimer also shows good agreement for γ up to 0.5, above which distinct deviations occur.

Deviations in w_2, under these reaction conditions, cannot be attributed to intramolecular cross-linking within dimeric species as a result of an increased probability of two radicals existing simultaneously on a single species because of their increased functionality. If this were the case species with $z = 2$ would be converted to $z = 3$ less rapidly than calculated and values of w_2 would exceed those calculated.

To begin to understand the deviations in w_2 at high γ, we consider the formation and consumption of the several species involved. We note that cross-linking does not occur directly between polymer chains but through the bimolecular reaction of macroradicals derived from the various polymeric species involved. The several reactions, for reactants with $z \leq 3$ and formation of species with z up to 4, are described by

$$\mathrm{M} \xrightarrow{h\nu} \mathrm{M}^{\bullet} \tag{7a}$$

$$2\mathrm{M}^{\bullet} \rightarrow \mathrm{D} \tag{7b}$$

$$\mathrm{D} \xrightarrow{h\nu} \mathrm{D}^{\bullet} \tag{7c}$$

$$\mathrm{D}^{\bullet} + \mathrm{M}^{\bullet} \rightarrow \mathrm{Tr} \tag{7d}$$

$$2\mathrm{D}^{\bullet} \rightarrow \mathrm{Tt} \tag{7e}$$

$$\mathrm{Tr} \xrightarrow{h\nu} \mathrm{Tr}^{\bullet} \tag{7f}$$

$$\mathrm{Tr}^{\bullet} + \mathrm{M}^{\bullet} \rightarrow \mathrm{Tt} \tag{7g}$$

where M, D, Tr, and Tt represent monomer, dimer, trimer, and tetramer, respectively, and M$^{\bullet}$ etc. their corresponding macroradicals. A common rate coefficient k_t is assumed for reactions 7b, 7d, 7e, and 7g. Species M, D, etc. are converted to more complex species at rates equal to rates of formation of M$^{\bullet}$, D$^{\bullet}$, etc. The excellent agreement between values of w_1 calculated and observed suggests that radicals are formed randomly throughout and all functional groups have equal probability of reaction at all stages of reaction. That is, radicals are formed on species according to their functionality and concentration. Rates of formation of M$^{\bullet}$, D$^{\bullet}$, and Tr$^{\bullet}$ are $\mathcal{R}F_{\mathrm{M}}$, $\mathcal{R}F_{\mathrm{D}}$, and $\mathcal{R}F_{\mathrm{Tr}}$, respectively; F_{Z} is the "functionality fraction" of species Z, a generalized species of z primary chains, defined as $F_{\mathrm{Z}} = zX_{\mathrm{Z}}/\sum zX_{\mathrm{Z}}$ where X_{Z} is the mole fraction of Z; $\sum F_{\mathrm{Z}} = 1$.

We have already argued that the probability of forming a second radical site on M$^{\bullet}$ during the lifetime of the first-formed radical, with consequent intramolecular cross-linking, is negligible. However, as the probability of diradical formation will increase with the functionality of complex species, we should consider the importance of such reactions as

$$\mathrm{D}^{\bullet} \xrightarrow{h\nu} \mathrm{D}^{\bullet\bullet} \tag{7h}$$

Intramolecular cross-link formation by D$^{\bullet\bullet}$ regenerates a dimer species D′. If the probability of this reaction was significant we would expect D to be converted to Tr at a reduced rate and, hence, values of w_2 to be higher than calculated. We might also expect the peak for species with $z = 2$ to drift to greater elution volumes as more compact species were produced. Neither of these effects are observed and (7h), and comparable reactions, can probably be neglected under these reaction conditions.

Thus, assuming a stationary state in total radical concentration ($[\mathrm{R}^{\bullet}] = \sum[\mathrm{Z}^{\bullet}]$), we can write for all species

$$d[R^\bullet]/dt = \mathcal{R} - k_t[M^\bullet]^2 - k_t[M^\bullet]\sum[Z^\bullet] - k_t'\sum([Z^\bullet]\sum[Z^\bullet]) = 0$$

where summations run over species z for $z \geq 2$. We introduce a different value of k_t (k_t') for reactions between radicals on species with $z \geq 2$ for reasons explained below.

In an attempt to specifically understand why observed values of w_2 fall below those calculated we first consider a simplified scheme involving only species with $z = 1$ (M) and $z = 2$ (D). Assuming a uniform value of k_t for all radical–radical reactions and a stationary state in each [radical], we can write

$$d[M^\bullet]/dt = \mathcal{R}F_M - k_t[M^\bullet]^2 - k_t[M^\bullet][D^\bullet] = 0 \quad (8a)$$

$$d[D^\bullet]/dt = \mathcal{R}F_D - k_t[D^\bullet]^2 - k_t[M^\bullet][D^\bullet] = 0 \quad (8b)$$

$$d[D]/dt = k_t[M^\bullet]^2 - \mathcal{R}F_D \quad (8c)$$

For a given starting distribution of species M, D, etc., their relative rates of removal, through macroradical formation, are fixed by the rate of photolysis of $Mn_2(CO)_{10}$ and their mole fractions. Any unexpected change in their absolute concentrations as the reaction progresses must reflect changes in their rates of formation. Thus, for the observed values of w_2 to decrease requires $k_t[M^\bullet]^2$ to decrease below its expected value.

As cross-linking progresses and the weight fractions of more complex species build up, the probabilities of reactions between macroradicals derived from those species should increase. For example, the probability of tetramer formation by coupling of two $D^\bullet$ should increase.

We propose that, at the low polymer concentrations involved ($[M_0]$ is at the lower end of the semidilute regime), the concentrations of D and especially $D^\bullet$ are sufficiently low that the probability of coupling of two $D^\bullet$s is reduced. Although we assume a uniform radical concentration overall, we suggest that restricted diffusion of $D^\bullet$ in an environment of M (and $M^\bullet$) prevents mutual termination between two $D^\bullet$ at the rate expected for the overall value of k_t. In effect, we propose that k_t for this reaction is replaced by an apparent rate coefficient k_t' ($k_t' < k_t$). From (8b) we have

$$2\mathcal{R}F_D = k_t[D^\bullet]^2 + k_t[D^\bullet][M^\bullet] \quad (8d)$$

and, if we now substitute k_t' for k_t in the first term on the right-hand side of (8d), to maintain the equality of (8d), then $k_t[D^\bullet][M]$ must increase. That is, the rate of trimer formation is increased at the expense of tetramer formation.

Similarly, from (8a), we have

$$\mathcal{R}F_M = k_t[M^\bullet]^2 + k_t[M^\bullet][D^\bullet] \quad (8e)$$

from which it follows that, if $k_t[M^\bullet][D^\bullet]$ is increased, then $k_t[M^\bullet]^2$ is decreased. Thus, the increase in rate of trimer formation decreases the rate of dimer formation.

From (8c) and (8e) it follows that

$$d[D]/dt = k_t[M^\bullet]^2 - k_t[D^\bullet]^2 - k_t[D^\bullet][M^\bullet] \quad (8f)$$

From (8f) it is seen that the rates of dimer, trimer, and tetramer formation are interlinked and the reduced rate of tetramer formation, through modification of k_t for the reasons proposed, reduces the rate of dimer formation and increases the rate of trimer formation as observed experimentally.

Similar considerations might apply to rates of formation and loss of other complex species. But the anticipated changes in rates of loss and formation of trimer would be counteracted by the increased rate of trimer formation through the enhanced rate of (7d). This is in accord with the smaller discrepancy between calculated and observed weight fractions of trimer relative to that of dimer at other than the lowest γ.

We conclude that, under "ideal" conditions, cross-linking occurs intermolecularly and essentially randomly. Thus, normal cross-linking kinetics and populations of species, as predicted by simple theory, are formed, at least in the early stages of reaction. In the later stages, but prior to gelation, the reaction kinetics and relative populations of complex species may be modified. There is no a priori reason to assume that discrepancies in the populations of more complex species would be observed if reactions were carried out in more concentrated solutions where the absolute concentrations of dimer etc. were higher and the probabilities of reactions between their macroradicals were not artificially reduced by being in a dilute solution regime within a semidilute solution when diffusion distorts reaction rates.

Confirmation of the proposed mechanism requires more extensive investigations. Preferably, higher polymer concentrations should be used. At constant M_0, this change requires formation of more cross-links and, using the current initiating system, increasing values of $[Mn_2(CO)_{10}]$, which might result in nonuniform light absorption. A different technique, which separates species according to mass rather than hydrodynamic volume (to obtain complete separation of species), would be preferred to confirm values of w_z and to ensure that any errors in current data analysis, through coelution of different species, do not compound discrepancies observed.

Even if there is some error in analyzing the weight fractions of cross-linked species, the above data act as a base line against which the populations of species formed under nonideal conditions for cross-linking may be assessed; see below.

Nonrandom Cross-Linking. Under conditions where gelation kinetics indicate nonrandom cross-linking, observed gel points do not correspond to an average of one cross-linked unit per prepolymer chain. Thus, absolute numbers of cross-links and values of γ cannot be estimated from observed gel times. We therefore estimate true values of γ (γ_{calc}) from rates of radical formation and concentrations of cross-linking sites. Values of γ_{calc} thus correspond to total numbers of cross-linked units per chain rather than numbers of units involved in intermolecular cross-links; values of γ_{calc} can exceed unity prior to the gel point. We now consider the populations of cross-linked species formed under the two sets of reactions conditions (cases II and III) for which deviations from normal cross-linking kinetics were observed.

(a) Case II. Low Concentrations of Preformed Polymer. Figure 9 shows gel-permeation chromatograms for two series of cross-linked mixtures, at varying extents of cross-linking, at preformed polymer concentrations of 0.25 and 0.5% (w/v). Similar sets of chromatograms were obtained for each of several concentrations in the range 0.01–0.6% (w/v).

Casual observation of the chromatograms indicates a strong similarity in the distributions of species formed at comparable values of γ_{calc} and γ for random cross-linking. More detailed comparison of the chromatograms, at identical values of γ, highlights differences in the distributions of species, Figure 10. These are seen under conditions of nonrandom cross-linking as (i) a smaller decrease in the monomer peaks for nonrandom cross-

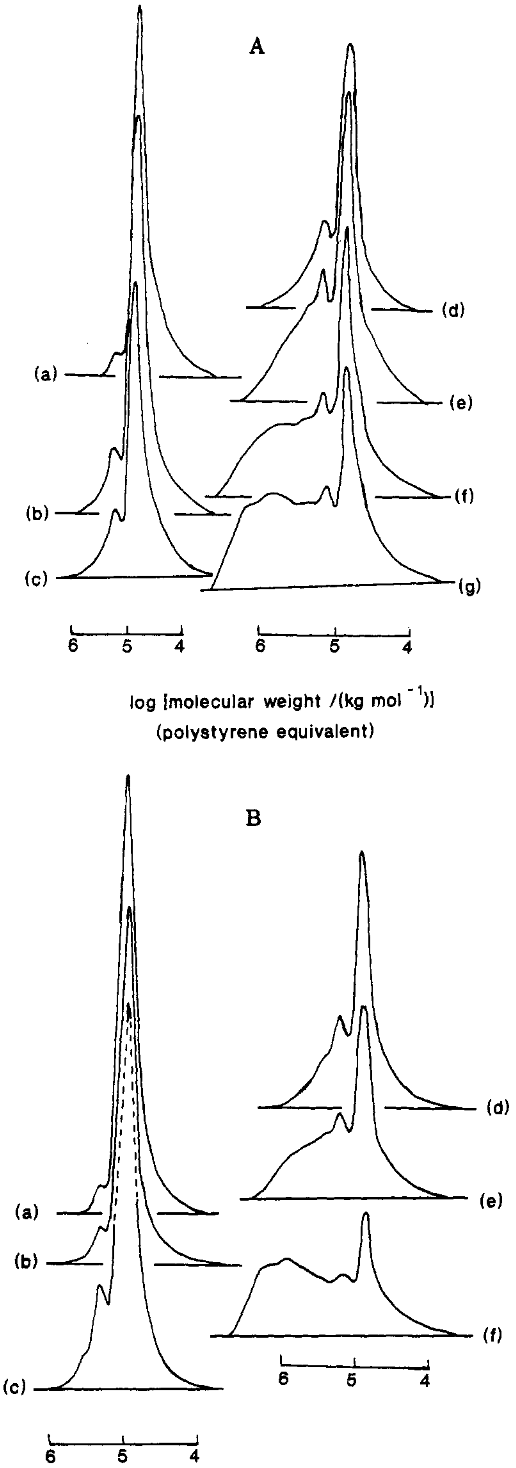


Figure 9. Gel-permeation chromatograms for samples of A08 cross-linked to different extents: (A) [polymer] = 0.25% (w/v); γ_{calc} = 0.056 (a); 0.11 (b); 0.22 (c); 0.44 (d); 0.89 (e); 1.33 (f). (B) [polymer] = 0.5% (w/v); γ_{calc} = 0.056 (a); 0.11 (b); 0.22 (c); 0.33 (d); 0.56 (e); 0.89 (f); 1.1 (g). Molecular weight scales determined by using polystyrene standards.

linking, (ii) a lower content of complex species, and (iii) chromatograms not extending to such high molecular weights. Together, the differences indicate reduced formation of species containing several preformed chains at comparable cross-link densities. While we shall attribute deviations from ideal kinetic behavior to intramolecular cross-linking and might expect this process to reduce the hydrodynamic volume of species of a given molecular weight, we see no indication of intramolecularly cross-linked material at long elution volumes in the chromatograms. Lack of such evidence is not surprising as intramolecular cross-linking would produce species with a distribution of loop and arm sizes and, hence, of different elution volumes that would be superimposed on a large elution peak.

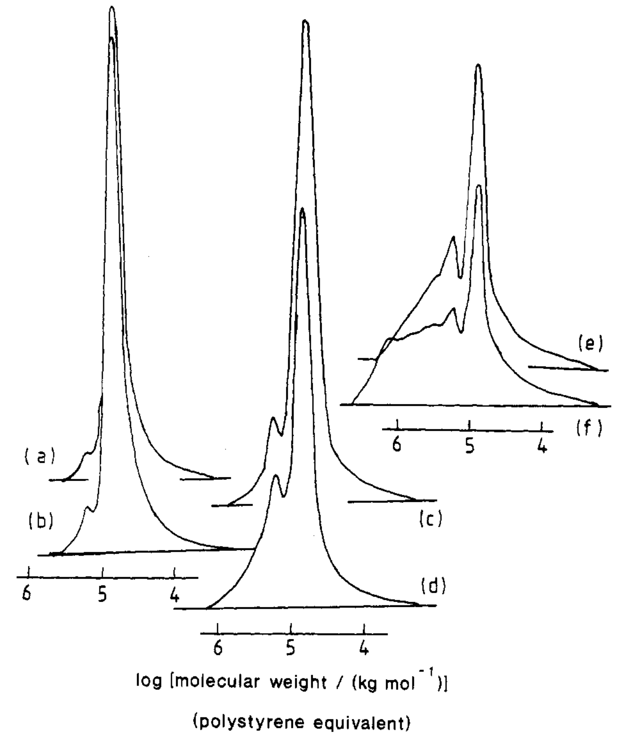


Figure 10. Comparison of chromatograms obtained from samples cross-linked under case I (b, d, f) and case II (a, c, e) conditions for cross-linking of B08 at identical values of γ (or γ_{calc}): γ = 0.066 (a, 0.25% (w/v); b, 1% (w/v)); γ = 0.37 (c, 0.1% (w/v); d, 1% (w/v)); γ = 0.78 (e, 0.25% (w/v); f, 1% (w/v)).

Using procedures described previously, values of w_z for several species, as functions of cross-linking index, are represented in Figure 11 for several values of [polymer]. These data confirm that, at low [polymer], rates of conversion of monomer to dimer decrease with decreasing [polymer]. Consistent with this observation are reduced dimer and trimer contents, compared with calculated values, at low γ_{calc}, although this discrepancy is partially lost at higher γ_{calc}; this is consistent with reduced formation of more complex species at higher γ_{calc}, cf. Figure 11.

Comparison of experimental data, at different [polymer] and γ_{calc}, on the linearized plot for w_1 (Figure 12) shows a distinct trend in reducing rates of formation of dimer as [polymer] decreases. Figure 13 shows the variation in slope of the lines in Figure 12 with [polymer]. From these data it is clear that at low [polymer], in spite of sustained rates of radical formation, the rates of formation of complex species decrease with decreasing [polymer].

Chain transfer to solvent could, in principle, give rise to the type of deviations observed. However, for reasons presented above and due to the coincidence that both the nature of crosslinking kinetics and the agreement between experimental and calculated values of w_2 change at c^*, we currently discount the possibility that the deviations described are a consequence of chain transfer. Furthermore, very similar deviations have been observed previously at comparable [polymer] in the presence of monomers as radical scavengers[18] and in studies of radiation cross-linking of poly(vinyl alcohol).[34]

We consider the possibility that the above deviations from ideal behavior arise from competition between in-

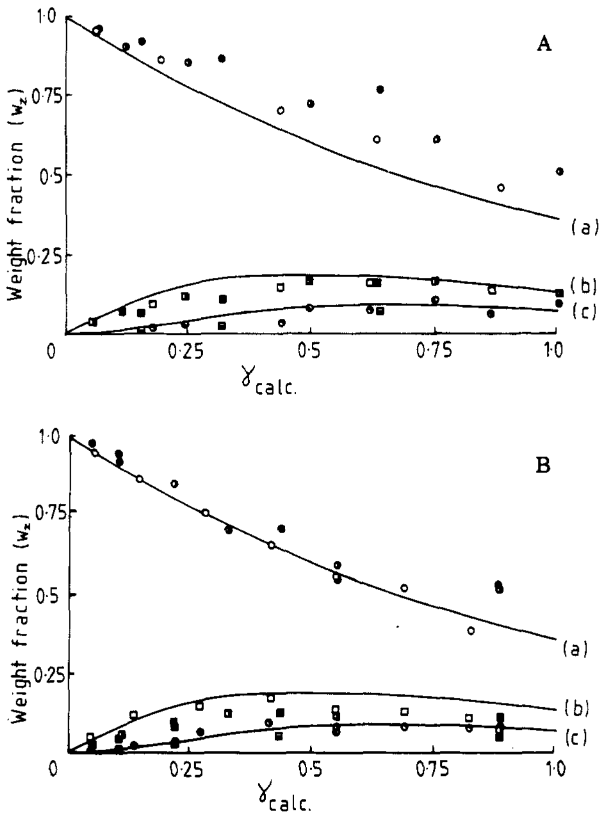


Figure 11. Weight fractions (w_z) of species with z primary chains, formed by cross-linking polymers A08 (A) and B08 (B) at different concentrations, as functions of the cross-linking index. Designations of experimental points are presented in the table. Curves are calculated from eq 2 for (a) $z = 1$, (b) $z = 2$, and (c) $z = 3$.

	[polymer], % (w/v)	z: 1	2	3
A	0.1	●	■	▣
	0.25	◐	◧	◕
	0.6	○	□	◕
B	2	○	□	◕
	0.5	◐	◧	◕
	0.25	●	■	▣

termolecular cross-link formation by reaction of M$^\bullet$ with other macroradicals and further reaction on M$^\bullet$ to form diradical M$^{\bullet\bullet}$, with consequent intramolecular cross-link formation through preferential termination of two radicals on the same polymer molecule. Intramolecular cross-linking regenerates M but in the form of a loop (M′).

$$M^\bullet \xrightarrow{h\nu} M^{\bullet\bullet} \qquad (7i)$$

$$M^{\bullet\bullet} \rightarrow M' \qquad (7j)$$

We therefore add (7i,j) to the previous mechanism. The rate of intramolecular cross-link formation is, we assume, given by the rate of (7i). Thus, since both types of cross-link are formed by reactions of M$^\bullet$ and a stationary state in [R$^\bullet$] is assumed, the fraction of termination leading to intermolecular cross-links (f_{inter}) is given by

$$f_{\text{inter}} = \frac{k_t[M^\bullet][R^\bullet]}{k_t[M^\bullet][R^\bullet] + \mathcal{R}F_{M^\bullet}} = \frac{k_t[M^\bullet][R^\bullet]}{k_t[M^\bullet][R^\bullet] + \mathcal{R}[M^\bullet]P/c} = \frac{1}{1 + P\mathcal{R}^{1/2}/(ck_t^{1/2})} \qquad (8)$$

Equation 8 and Figure 13, therefore, reflect competition between inter- and intramolecular cross-linking. The extent of intramolecular cross-linking is predicted to increase with the ratio $P\mathcal{R}^{1/2}/ck_t^{1/2}$, which is in agreement with observation. We have seen, in Figures 2 and 3, that deviations from ideal gelation kinetics occur at high $\mathcal{R}$ and low c. Comparison with previous studies indicate that, at comparable [halide], deviations are more prevalent when high molecular weight preformed polymers are used.[18,34] We have no direct evidence to test the dependency on

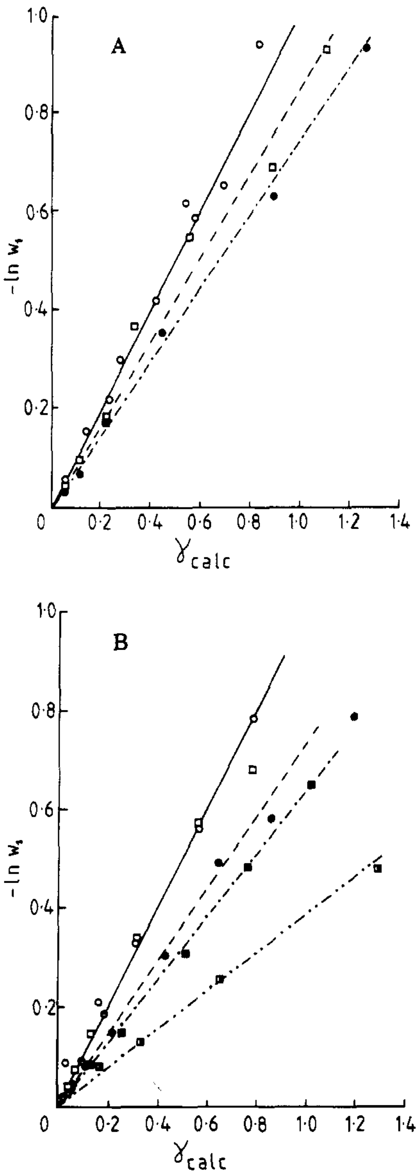


Figure 12. Variations in w_1 with γ_{calc} according to eq 3a for (A) A08 at 2% (w/v) (○), 0.5% (w/v) (□), 0.25% (w/v) (●) and (B) B08 at 5% (w/v) (◒), 2% (w/v) (○), 1% (w/v) (□), 0.6% (w/v) (●), 0.25% (w/v) (■), 0.1% (w/v) (◧). The solid line is theoretical. Other lines are used in construction of Figure 13.

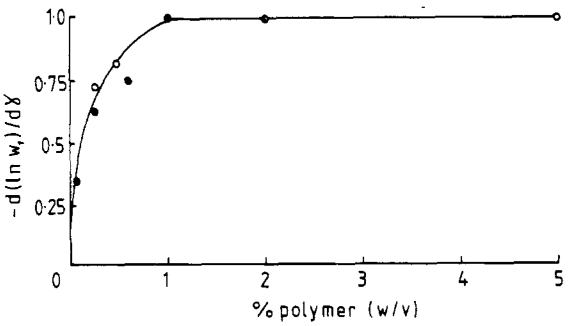


Figure 13. Variations in $-\mathrm{d}(\ln w_1)/\mathrm{d}\gamma$ with polymer concentration for A08 (○) and B08 (●); ◕ is a common point.

$k_t^{1/2}$ and this is the only factor that reflects an influence of the chemical structure of the preformed polymer. Nevertheless, this dependence is sensible in predicting that relatively high values of k_t, in flexible polymers, will reduce the average radical lifetime and the probability that a second radical will form on a chain during the lifetime of a preformed radical.

Enhanced formation of intramolecular cross-links occurs in dilute solutions, where polymer concentrations are not uniform throughout, as identified in a preceding section. We attribute the effect to the sustained rates of radical formation, through photolysis of $Mn_2(CO)_{10}$, producing diradicals at a significant rate because, in dilute solution, the macroradical diffusion and termination with another macroradical does not compete effectively with diradical formation at the photolysis rates used. In practice this effect is seen in the formation of small gel particles at long reaction times. The particles form by gradual accretion of polymer species, further enhancing the nonuniformity of polymer concentration through the reaction medium.

Plots of (3b) and (3c), using values of γ_{calc}, also gave linear plots for each species in each series of experiments. However, many of those lines did not pass through the origin and their slopes were not equal to those calculated. No systematic trends in slopes or intercepts have been identified.

It should be recognized that data derived from (3), in the very earliest stages of cross-linking, have been used to assess weight fractions of species that have been used to test the applicability of (3); we believe that, under the circumstances, this procedure is justified. Suppose there had been, say, some intramolecular cross-linking under the reaction conditions used to establish the procedure applied (see Identification of Species) and under which gelation kinetics were normal. For agreement between experiment and theory to be observed with several species (z = 1, 2, 3) under random cross-linking conditions the deviations from intermolecular cross-linking would have to persist over a range of cross-linking indices in such a way as to modify the weight fractions of all species and the gel time under a variety of reaction conditions, such as different concentrations of preformed polymer, in a consistent manner. The apparent agreement would then have to fail when deviations from normal kinetics were observed. We find this coincidence highly unlikely and suggest that the procedure used is justifiable.

(b) Case III. High Rates of Radical Formation. Figure 14 presents gel permeation chromatograms for assemblies of species produced by cross-linking polymer B08 (2% (w/v)) at "high" rates of initiation. The value of $\mathcal{R}$ in this series of experiments, calculated from rates of polymerization of MMA, was 1.78×10^{-6} mol L^{-1} s^{-1}, compared with values of about 1.2×10^{-7} mol L^{-1} s^{-1} used in other experiments; values of γ_{calc} are based on calculated gel times, assuming ideal cross-linking at high $\mathcal{R}$. The chromatogram clearly demonstrate that, as cross-linking proceeds, the weight fractions of complex species do not build up, at the expense of monomer, as rapidly as for ideal cross-linking. In addition, very small proportions of more complex species are formed; i.e., chromatograms do not extend to elution volumes as low as, for example, in Figure 5.

Plots of weight fractions of M, D, and Tr with γ are shown in Figure 15 and are compared with calculated values at equivalent γ. Data clearly show that, even at high rates of macroradical formation and in semidilute solutions of preformed polymer, monomeric species are not converted to more complex structures at the rate anticipated. Deviations in this case cannot be attributed to chain transfer as, at the high values of $\mathcal{R}$ employed, radical lifetimes and probabilities of chain transfer would be reduced. Clearly, under these reaction conditions, a large proportion of the radicals generated must be "wasted" in intramolecular cross-link formation. Linearized plots, based on (3), do not show any understandable trends and even the plot of $-\ln w_1$ does not pass through the origin. Thus, the statistics of cross-linking and formation of complex species are quite different under these reaction conditions than for both random cross-linking and nonrandom cross-linking at low $\mathcal{R}$ and high [polymer].

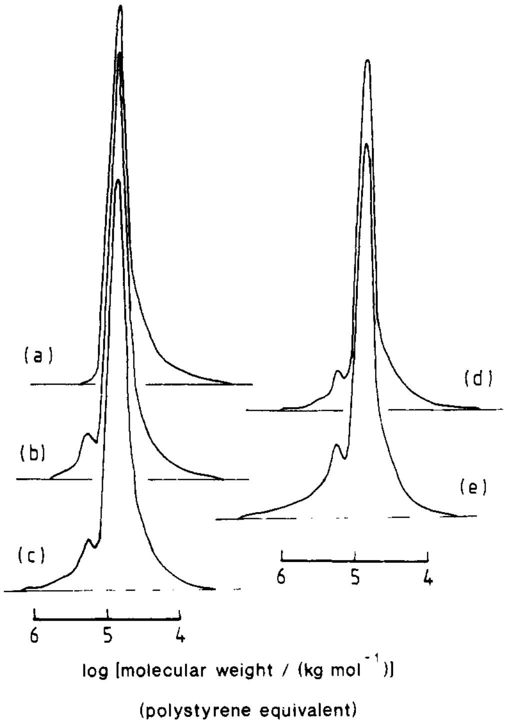


Figure 14. Gel-permeation chromatograms for samples of B08 cross-linked to values of γ_{calc} of (a) 0, (b) 0.08, (c) 0.17, (d) 0.33, and (e) 0.5. The molecular weight scale is based on polystyrene standards.

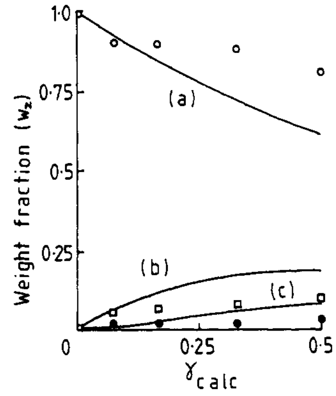


Figure 15. Variations in weight fraction (w_z) for z = 1 (○), z = 2 (□), and z = 3 (●), as functions of γ_{calc}, calculated from chromatograms in Figure 14. Curves calculated from eq 2 for (a) z = 1, (b) z = 2, and (c) z = 3.

We attribute these several observations to relatively high rates of reaction 7i and rapid formation of cross-links in (7j) at high $\mathcal{R}$. That is, we assume that at the high $\mathcal{R}$ used in these experiments the radical lifetimes are still sufficiently long that a significant proportion of diradicals are formed, in competition with intermolecular cross-link formation, and that these diradicals preferentially undergo intramolecular cross-link formation. These observations and conclusions are consistent with trends predicted in eq 8.

Conclusions

The cross-linking of preformed polymers, with reactive side groups, by a free radical process has been investigated. Studies of gelation kinetics identified three regimes.

Case I: Ideal cross-linking kinetics, consistent with eq 1, in semidilute solutions of polymer with relatively low rates of radical formation.

Case II: nonideal cross-linking in dilute solutions of preformed polymer.

Case III: nonideal cross-linking in semidilute polymer solutions with high rates of radical formation.

In cases II and III experimental gel times were longer than calculated by (1).

Weight fractions of simpler species (monomer, dimer, and trimer species) were assessed for cases I–III as functions of the cross-linking index. Data were compared with weight fractions calculated from network theory assuming purely intermolecular cross-linking.

From the above comparisons it was concluded that, under case I conditions: (i) free radical formation on preformed chains is random; (ii) un-cross-linked species are converted to cross-linked species at a rate commensurate with theory; (iii) cross-linking is intermolecular at least up to cross-linking indices of 0.8; (iv) at cross-linking indices up to 0.5 dimer and trimer weight fractions are consistent with statistical theory and random intermolecular cross-linking; and (v) at higher cross-linking indices, but prior to gelation, deviations from calculated weight fractions of dimer species are a consequence of reaction between dimeric radical species and monomeric radical species in preference to mutual reaction of dimer radicals with other complex radical species; i.e., we suggest that dimer–dimer termination is hindered, relative to dimer–monomer termination, by restricted diffusion to a greater extent than predicted on purely statistical grounds.

Irrespective of the validity of the explanation for deviations from theory in (v) above, comparison of the above results with data obtained under nonideal reaction conditions allows useful conclusions on the statistics of cross-linking under different reaction conditions to be made.

Under case II conditions, (i) monomeric species are converted to complex species at a lower rate than predicted from network theory; (ii) intramolecular cross-linking competes with intermolecular cross-linking and the proportion of intramolecular cross-linking increases as the concentration of preformed polymer decreases; and (iii) in dilute solutions diradicals and intramolecular cross-links are formed because of the extended lifetime of monomeric radicals in the dilute solution regime and the time required for molecules to undergo translational diffusion to terminate mutually.

Under case III conditions, (i) very extensive intramolecular cross-linking occurs at high rates of radical formation because of the increased probability of diradical formation and (ii) intramolecular cross-linking severely retards the buildup of complex intermolecularly cross-linked species.

In practice, many cross-linking processes involve the cross-linking of preformed chains with a distribution of chain lengths, typically $\bar{M}_w/\bar{M}_n \sim 2$. Stockmayer's equations[6] allow calculation of the weight fractions of the various cross-linked species for such systems with intermolecular cross-linking. Given currently available procedures, it does not appear feasible to test these general equations. However, in view of the current results, we are probably justified in using these equations, under reaction conditions where (1) applies, to estimate the populations of various species formed during cross-linking and graft polymerization processes.[11]

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