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Statistics of Free-Radical Polymerizations Revisited Using a Fragment Approach. 2. Polyfunctional Monomers

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ABSTRACT: A fragment approach is used to derive statistical parameters of networks prepared from the free-radical polymerization of an $A_2 + A_f$ system, allowing different termination mechanisms to take place simultaneously. When the termination mechanism is shifted from chain transfer and/or disproportionation to combination, gelation is advanced by a factor 2/3, the amount of soluble material in the polymer fraction decreases, and the amount of elastic material in the polymer increases while showing a higher concentration of the cross-linking points of the highest possible functionality. Different macroscopic properties are, thus, expected for the resulting networks.

Introduction

Statistical parameters of networks arising from the free-radical polymerization of polyfunctional monomers have been derived by several authors,[1-6] using methods related to the theory of stochastic branching processes. A common limitation of these developments is that they do not consider, at least correctly, the case where different termination mechanisms take place simultaneously (the approximation used in ref 2 and 3, where termination by combination is considered statistically equivalent to propagation is not correct, as may be realized by analyzing the resulting expressions when combination is the exclusive termination mechanism).

Little is known about chain termination mechanisms for most monomers. Structural factors affecting the termination mechanism are the number of hydrogen atoms available for disproportionation and the bulkiness of substituents on the radical carbon atom. Increases in both factors enhance the termination by disproportionation. For example, in the case of styrene, it is generally agreed that termination takes place almost exclusively by combination over a wide range of temperatures. In the case of methyl methacrylate, both mechanisms are operative but the relative contribution of disproportionation increases with temperature (in this case there are bulky substituents and five hydrogens available for disproportionation). Chain transfer is obviously enhanced by adding a transfer agent. In any case, it is important to estimate the incidence of a shift in the termination mechanism on pre- and postgel properties of the polymer.

The aim of this part is to use the fragment approach previously developed[7] and to derive statistical parameters of networks prepared from the free-radical polymerization of an $A_2 + A_f$ system, allowing different termination mechanisms to take place simultaneously. As any double bond is a bifunctional unit, the functionality f of the polyfunctional monomer is always an even number. The present derivation retains the classical simplifying assumptions: (i) all double bonds are equally reactive, (ii) there are no substitution effects, and (iii) no intramolecular reactions occur in finite species. The validity of the last hypothesis may be questionable at the beginning of the reaction, when there is a finite probability for the radical at the end of a growing chain to react with double bonds pendant on its own chain.[8] The present analysis is then restricted to systems with a low concentration of the polyfunctional monomer A_f.

Fragment Approach

Table I shows the species and fragments that may be identified for a particular reaction extent p. An A_f molecule, with mass M_f, is fragmented into a skeleton with $f/2$ branches, devoid of mass, and $f/2$ double bonds, the mass of each one being $M_f(2/f)$. In order to regenerate the A_f structure, (α) linkages must be joined with (β) linkages.

The probability that a reacted double bond propagates the chain is defined as

$$q = r_p/(r_p + r_t + r_d + r_c) \qquad (1)$$

where r_p is the propagation rate and r_t, r_d, and r_c are termination rates by chain transfer, disproportionation, and combination, respectively.

The probability that termination occurs by combination is defined as

$$\xi = r_c/(r_t + r_d + r_c) \qquad (2)$$

By use of the definitions given by eq 1 and 2, the molar concentration of every species and fragment may be calculated, as is shown in Table I. In order to regenerate the structure, it must be taken into account that (+) linkages must be joined with (−) linkages, (α) linkages with (β) linkages, and arrows among themselves. As the concentration of (+) linkages must be equal to the one of (−) linkages, the concentration of initiator fragments must equal that of terminating units. Similarly, Table I shows that the concentration of (α) linkages is equal to the one of (β) linkages = $fA_f/2$.

At any reaction extent p, the unreacted A_f monomer verifies that not one of its $f/2$ double bonds has reacted. Then, its concentration is given by $A_f(1 - p)^{f/2}$, with an

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amount of unreacted double bonds equal to $(f/2)A_f(1 - p)^{f/2}$. At any reaction extent p, the total mass of the polymer fraction is given by

$$m_{\text{pol}} = A_2M_2p + A_fM_f[1 - (1 - p)^{f/2}] \tag{3}$$

Mass fractions of different fragments pertaining to the polymer are shown in Table I.

Pregel Stage

Calculations may be performed following the same lines discussed in part 1.[7] Let us call $Y(+)$, $Y(-)$, $Y(\alpha)$, $Y(\beta)$, and Z the average weights hanging from (+), (−), (α), and (β) linkages and arrows, respectively. For example, $Y(+)$ is defined as $Y(+) = \sum_{\text{fragments}}$(probability of joining a particular fragment having one or more (−) linkages)(average weight contributed by the particular fragment). Then, as the total concentration of (−) linkages is equal to $p[A_2 + (f/2)A_f]$, $Y(+)$ may be calculated as

$$\begin{aligned}Y(+) = \{1/p[A_2 + (f/2)A_f]\}\{&A_2pq[M_2 + Y(+)] + \\ &(f/2)A_fpq[(2/f)M_f + Y(+) + Y(\alpha)] + \\ &A_2p(1 - q)\xi[M_2 + Z] + \\ &(f/2)A_fp(1 - q)\xi[(2/f)M_f + Z + Y(\alpha)] + A_2p(1 - q) \times \\ &(1 - \xi)M_2 + (f/2)A_fp(1 - q)(1 - \xi)[(2/f)M_f + Y(\alpha)]\}\end{aligned} \tag{4}$$

By introducing

$$a_f = (fA_f)/(2A_2 + fA_f) \tag{5}$$

and rearranging, we get

$$Y(+) = [(1 - a_f)M_2 + a_f(2/f)M_f + a_fY(\alpha) + (1 - q)\xi Z]/(1 - q) \tag{6}$$

Similarly,

$$\begin{aligned}Y(-) = \{1/p[A_2 + (f/2)A_f]\}\{&A_2pq[M_2 + Y(-)] + \\ &(f/2)A_fpq[(2/f)M_f + Y(-) + Y(\alpha)] + \\ &p(1 - q)[A_2 + (f/2)A_f](0)\} = \\ &q[(1 - a_f)M_2 + a_f(2/f)M_f + a_fY(\alpha)]/(1 - q)\end{aligned} \tag{7}$$

As the total concentration of (β) linkages is equal to $(f/2)A_f$, then

$$Y(\alpha) = [2/(fA_f)]\{(fA_f/2)[(0) + (f/2 - 1)Y(\beta)]\} = (f/2 - 1)Y(\beta) \tag{8}$$

Similarly,

$$\begin{aligned}Y(\beta) = [2/(fA_f)]\{&(f/2)A_f(1 - p)(2/f)M_f + \\ &(f/2)A_fpq[(2/f)M_f + Y(+) + Y(-)] + \\ &(f/2)A_fp(1 - q)\xi[(2/f)M_f + Y(-) + Z] + \\ &(f/2)A_fp(1 - q)(1 - \xi)[(2/f)M_f + Y(-)]\} = \\ &(2/f)M_f + pqY(+) + pY(-) + p(1 - q)\xi Z\end{aligned} \tag{9}$$

Finally, as the total concentration of arrows is given by $[A_2 + (f/2)A_f]p(1 - q)\xi$, then

$$\begin{aligned}Z = \{1/[(A_2 + (f/2)A_f)p(1 - q)\xi]\}\{&A_2p(1 - q)\xi[M_2 + Y(-)] + (f/2)A_fp(1 - q)\xi[(2/f)M_f + Y(-) + Y(\alpha)]\} = \\ &(1 - a_f)M_2 + a_f(2/f)M_f + Y(-) + a_fY(\alpha)\end{aligned} \tag{10}$$

The set of five equations (eq 6–10) in five unknowns is solved to give

$$Y(+) = (1 + \xi)M^*/F(p,q,\xi) \tag{11}$$

$$Y(-) = qM^*/F(p,q,\xi) \tag{12}$$

$$Y(\alpha) = (1 - 2/f)M_f + p(2q + \xi)(f/2 - 1)M^*/F(p,q,\xi) \tag{13}$$

$$Y(\beta) = (2/f)M_f + p(2q + \xi)M^*/F(p,q,\xi) \tag{14}$$

$$Z = M^*/F(p,q,\xi) \tag{15}$$

where

$$M^* = (1 - a_f)M_2 + a_fM_f \tag{16}$$

$$F(p,q,\xi) = 1 - q - p(2q + \xi)a_f(f/2 - 1) \tag{17}$$

Gelation is attained when all the average weights go to infinite. This implies that $F(p_{\text{gel}},q,\xi) = 0$ or

$$p_{\text{gel}} = (1 - q)/[a_f(f - 2)(q + \xi/2)] \tag{18}$$

For $\xi = 0$, i.e., when termination takes place by chain transfer and/or disproportionation, the equation agrees with results reported by Gordon,[1] Macosko and Miller,[2] and Durand and Bruneau.[5]

Equation 18 is the general gelation condition for $\xi \neq 0$, i.e., when termination by combination also takes place. As q usually lies in the range 0.99–0.999, the ratio of gel conversions for the two limiting cases of termination mechanisms is given by

$$p_{\text{gel}}(\xi = 1)/p_{\text{gel}}(\xi = 0) = 2/3 \tag{19}$$

Then, when the termination mechanism shifts from chain transfer and/or disproportionation to combination, there is a significant decrease of the gel point.

The weight-average molecular weight of the whole system, i.e., including remaining monomers, is defined as

$$\begin{aligned}\bar{M}_{\text{w}} = &\textstyle\sum_{\text{fragments}}(\text{mass fraction of a particular fragment}) \times \\ &(\text{mass attached to a particular fragment})\end{aligned} \tag{20}$$

$$\begin{aligned}\bar{M}_{\text{w}} = [1/(A_2M_2 + A_fM_f)]\{&A_2M_2(1 - p)M_2 + \\ &A_fM_f(1 - p)[(2/f)M_f + Y(\alpha)] + A_2M_2pq[M_2 + Y(+) + \\ &Y(-)] + A_fM_fpq[(2/f)M_f + Y(+) + Y(-) + Y(\alpha)] + \\ &A_2M_2p(1 - q)\xi[M_2 + Y(-) + Z] + \\ &A_fM_fp(1 - q)\xi[(2/f)M_f + Y(-) + Y(\alpha) + Z] + \\ &A_2M_2p(1 - q)(1 - \xi)[M_2 + Y(-)] + \\ &A_fM_fp(1 - q)(1 - \xi)[(2/f)M_f + Y(-) + Y(\alpha)]\}\end{aligned} \tag{21}$$

Using eq 11 to 15 and rearranging, we get

$$\bar{M}_{\text{w}} = \{A_2M_2^2 + A_fM_f^2 + (2q + \xi)pZ[A_2M_2 + (f/2)A_fM_f]\}/(A_2M_2 + A_fM_f) \tag{22}$$

The weight-average molecular weight of the polymer fraction, $\bar{M}_{\text{w}}(\text{pol})$, may be calculated by recognizing that

$$\bar{M}_{\text{w}} = w_{\text{p}}\bar{M}_{\text{w}}(\text{pol}) + w_{\text{A}2}M_2 + w_{\text{A}f}M_f \tag{23}$$

where w_{p}, $w_{\text{A}2}$, and $w_{\text{A}f}$ are the mass fractions of polymer, monomer A_2, and monomer A_f, respectively. They are given by

$$w_{\text{p}} = \{A_2M_2p + A_fM_f[1 - (1 - p)^{f/2}]\}/(A_2M_2 + A_fM_f) \tag{24}$$

$$w_{\text{A}2} = A_2M_2(1 - p)/(A_2M_2 + A_fM_f) \tag{25}$$

$$w_{\text{A}f} = A_fM_f(1 - p)^{f/2}/(A_2M_2 + A_fM_f) \tag{26}$$

From eq 22–26, we get

$$\bar{M}_{\text{w}}(\text{pol}) = \{A_2M_2^2p + A_fM_f^2[1 - (1 - p)^{f/2}] + (2q + \xi)pZ[A_2M_2 + (f/2)A_fM_f]\}/\{A_2M_2p + A_fM_f[1 - (1 - p)^{f/2}]\} \tag{27}$$

When termination by combination does not take place ($\xi = 0$), eq 27 leads to the same result obtained by Durand and Bruneau.[5] When all mechanisms of termination are operative, eq 27 constitutes the general expression for the evolution of the weight-average molecular weight.

In order to calculate the number-average molecular weight, it is necessary to relate the number of chain ends with the number of moles in the polymer fraction. It is

Table I
Species and Fragments Identified in the $A_2 + A_f$ Free-Radical Polymerization

fragment	moles	mass	polymer mass fract.
unreacted A_2, $\circ$	$A_2(1-p)$	M_2	
unreacted double bond of an A_f, $\circ\!-\alpha$	$(f/2)A_f(1-p)$	$(2/f)M_f$	$A_fM_f[(1-p)-(1-p)^{f/2}]/m_{\rm pol}$
skeleton of an A_f, $\underset{\beta}{1}\,\underset{\beta}{\boxed{2}}\cdots\cdots\underset{\beta}{\boxed{f/2}}$	A_f	0	
propagating unit arising from an A_2,⁻ $-\bullet-^{+}$	A_2pq	M_2	$A_2M_2pq/m_{\rm pol}$
propagating unit arising from the double bond of an A_f,⁻ $\underset{\alpha}{-\bullet-}^{+}$	$(f/2)A_fpq$	$(2/f)M_f$	$A_fM_fpq/m_{\rm pol}$
unit terminated by combination (arising from an A_2),⁻ $-\bullet-$	$A_2p(1-q)\xi$	M_2	$A_2M_2p(1-q)\xi/m_{\rm pol}$
unit terminated by combination (arising from an A_f),⁻ $\underset{\alpha}{-\bullet-}$	$(f/2)A_fp(1-q)\xi$	$(2/f)M_f$	$A_fM_fp(1-q)\xi/m_{\rm pol}$
unit terminated by transfer or disproportionation (arising from an A_2),⁻ $-\bullet\dashv$	$A_2p(1-q)(1-\xi)$	M_2	$A_2M_2p(1-q)(1-\xi)/m_{\rm pol}$
unit terminated by transfer or disproportionation (arising from an A_f),⁻ $\underset{\alpha}{-\bullet\dashv}$	$(f/2)A_fp(1-q)(1-\xi)$	$(2/f)M_f$	$A_fM_fp(1-q)(1-\xi)/m_{\rm pol}$
initiator, $\square-^{+}$	$p(1-q)[A_2+(f/2)A_f]$	0	

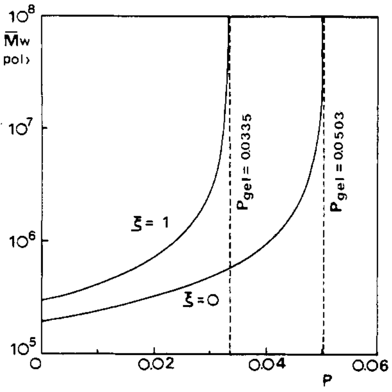


Figure 1. Weight-average molecular weight of the polymer fraction vs reaction extent, for the two limiting cases of $\xi = 0$ (termination by chain transfer and/or disproportionation) and $\xi = 1$ (termination by combination).

easily seen that, as intramolecular cyclization is neglected, any molecule of the polymer fraction has two chain ends (units terminated by transfer or disproportionation + initiators) plus twice the number of reacted branches of the A_f molecules in addition to the first one. Thus, number of moles in the polymer fraction = (moles of chain ends/2) − (moles of reacted branches of the A_f's, in addition to the first one). From Table I,

moles of chain ends = $p(1-q)(2-\xi)[A_2 + (f/2)A_f]$

moles of reacted branches of the A_f's in addition to the first one =

$$\sum_{m=2}^{f/2}(m-1)\binom{f/2}{m}p^m(1-p)^{(f/2)-m}A_f = \{(f/2)p - [1-(1-p)^{f/2}]\}A_f$$

Then, the number-average molecular weight of the polymer fraction may be obtained by dividing the polymer mass by the number of moles in the polymer fraction,

$$\bar{M}_n(\text{pol}) = \{A_2M_2p + A_fM_f[1-(1-p)^{f/2}]\}/\{(p/2)(1-q)(2-\xi)[A_2 + (f/2)A_f] - A_f[(f/2)p - (1-(1-p)^{f/2})]\} \quad (28)$$

When only a bifunctional monomer is used, eq 28 reduces correctly to the expression derived in the previous paper.[7]

Postgel Stage

In order to derive statistical parameters in the postgel stage, we have to determine the probability of having finite chains when leaving a fragment from (+), (−), (α), and (β) linkages and arrows. These probabilities will be called, respectively, $F(+)$, $F(-)$, $F(\alpha)$, $F(\beta)$, and G. For example, $F(+)$ is defined as $F(+) = \sum_{\text{fragments}}$(probability of joining a particular fragment having one or more (−) linkages) × (probability that all branches leaving the fragment, already linked by one of its (−) linkages, are finite). Similar definitions are valid for the remaining probabilities.

As the total concentration of (−) linkages is equal to $p[A_2 + (f/2)A_f]$, $F(+)$ is given by

$$F(+) = \{1/p[A_2 + (f/2)A_f]\}\{A_2pqF(+) + (f/2)A_fpqF(+)F(\alpha) + A_2p(1-q)\xi G + (f/2)A_fp(1-q)\xi GF(\alpha) + A_2p(1-q)(1-\xi) + (f/2)A_fp(1-q)(1-\xi)F(\alpha)\} \quad (29)$$

Similarly,

$$F(-) = \{1/p[A_2 + (f/2)A_f]\}\{A_2pqF(-) + (f/2)A_fpqF(-)F(\alpha) + p(1-q)[A_2 + (f/2)A_f]\} \quad (30)$$

$$F(\alpha) = F(\beta)^{f/2-1} \quad (31)$$

$$F(\beta) = [2/(fA_f)]\{(f/2)A_f(1-p) + (f/2)A_fpqF(+)F(-) + (f/2)A_fp(1-q)\xi F(-)G + (f/2)A_fp(1-q)(1-\xi)F(-)\} \quad (32)$$

$$G = \{1/[(A_2 + (f/2)A_f)p(1-q)\xi]\} \times \{A_2p(1-q)\xi F(-) + (f/2)A_fp(1-q)\xi F(-)F(\alpha)\} \quad (33)$$

Equations 29–33 may be rearranged and solved to give

$$F(+) = (1-X)(1-\xi X) \quad (34)$$

$$F(-) = 1 - qX \quad (35)$$

$$F(\alpha) = 1 - [(1-q)X]/[a_f(1-qX)] \quad (36)$$

$$F(\beta) = \{1 - [(1-q)X]/[a_f(1-qX)]\}^{2/(f-2)} \quad (37)$$

$$G = 1 - X \quad (38)$$

where X is the root between 0 and 1 of the following equation:

$$\{1 - [(1-q)X]/[a_f(1-qX)]\}^{2/(f-2)} = 1 - p + p(1-qX)^2(1-\xi X) \quad (39)$$

It may be seen that $X = 0$ is always a root of eq 39. It is the only root with physical meaning for $p \leqslant p_{\text{gel}}$. For $p > p_{\text{gel}}$, the only root with physical sense is the one lying between 0 and 1.

Now that we have the different probabilities of getting finite chains, any statistical parameter in the postgel stage may be easily calculated.

For example, the sol fraction of the whole system, i.e., including monomers, is given by $w_{\text{sol}} = \sum_{\text{fragments}}$(mass fraction of a particular fragment)(probability that all branches leaving the fragment are finite). Then,

$$w_{\mathrm{sol}} = [1/(A_2M_2 + A_fM_f)]\{A_2M_2(1-p) + A_fM_f(1-p)F(\alpha) + A_2M_2pqF(+)F(-) + A_fM_fpqF(+)F(-)F(\alpha) + A_2M_2p(1-q)\xi F(-)G + A_fM_fp(1-q)\xi F(-)F(\alpha)G + A_2M_2p(1-q)(1-\xi)F(-) + A_fM_fp(1-q)(1-\xi)F(-)F(\alpha)\} \quad (40)$$

Rearranging with the use of eq 34–39 leads to

$$w_{\mathrm{sol}} = \{1 - [A_fM_f(1-q)X]/[(A_2M_2 + A_fM_f)a_f(1 - qX)]\}[1 - p + p(1-qX)^2(1-\xi X)] \quad (41)$$

The sol fraction of the polymeric material, $w_{\mathrm{sol}}(\mathrm{pol})$, may be calculated by taking into account that

$$w_{\mathrm{sol}} = w_{\mathrm{sol}}(\mathrm{pol})w_{\mathrm{p}} + 1 - w_{\mathrm{p}} \quad (42)$$

where w_{p} is the polymeric mass fraction, given by eq 24. Then,

$$w_{\mathrm{sol}}(\mathrm{pol}) = (w_{\mathrm{sol}} + w_{\mathrm{p}} - 1)/w_{\mathrm{p}} \quad (43)$$

A particular fragment is part of a pendant chain if only one of its arms is joined to the gel. Thus, the mass fraction of pendant chains is given by

$$w_{\mathrm{pendant}} = [1/(A_2M_2 + A_fM_f)][A_fM_f(1-p)[1 - F(\alpha)] + A_2M_2pq\{F(+)[1-F(-)] + F(-)[1-F(+)]\} + A_fM_fpq\{F(+)F(-)[1-F(\alpha)] + F(+)F(\alpha)[1-F(-)] + F(-)F(\alpha)[1-F(+)]\} + A_2M_2p(1-q)\xi\{F(-)(1-G) + G[1-F(-)]\} + A_fM_fp(1-q)\xi\{F(-)F(\alpha)(1-G) + GF(\alpha)[1-F(-)] + GF(-)[1-F(\alpha)]\} + A_2M_2p(1-q)(1-\xi)[1-F(-)] + A_fM_fp(1-q)(1-\xi)\{F(-)[1-F(\alpha)] + F(\alpha)[1-F(-)]\}] \quad (44)$$

The mass fraction of pendant chains in the polymer fraction is given by

$$w_{\mathrm{pendant}}(\mathrm{pol}) = w_{\mathrm{pendant}}/w_{\mathrm{p}} \quad (45)$$

As the material that does not pertain to the sol or to pendant chains is part of elastic chains, its mass fraction is given by

$$w_{\mathrm{elastic}}(\mathrm{pol}) = 1 - w_{\mathrm{sol}}(\mathrm{pol}) - w_{\mathrm{pendant}}(\mathrm{pol}) \quad (46)$$

In order to calculate the fraction of cross-linking units of degree f, i.e., A_f units of the polymer fraction with its f arms going to the gel, one must look for the probability that the $f/2$ branches of the A_f skeleton, shown in Table I, are bonded to propagating units or units terminated by combination, both having its remaining two arms joined to the gel. Then, the fraction of cross-linking units of degree f in the polymer is given by

$$X_f = \{1/[1-(1-p)^{f/2}]\}\{pq[1-F(+)] \times [1-F(-)] + p(1-q)\xi(1-G)[1-F(-)]\}^{f/2} \quad (47)$$

The first factor represents the total moles of A_f divided by the moles in the polymer fraction. The second factor represents the simultaneous probability that the $f/2$ branches are joined to units having the two remaining arms going to the gel. Using eq 34, 35, and 38 and rearranging, we get

$$X_f = \{pqX^2[q(1-\xi X) + \xi]\}^{f/2}/[1-(1-p)^{f/2}] \quad (48)$$

In a similar way, one may calculate the fraction of cross-linking units of degree $(f-1)$, $(f-2)$, etc. For example, and following a similar reasoning, X_{f-1} is given by

$$X_{f-1} = \{1/[1-(1-p)^{f/2}]\}\{pq[1-F(+)] \times [1-F(-)] + p(1-q)\xi(1-G)[1-F(-)]\}^{f/2-1} \times \{pq(F(+)[1-F(-)] + F(-)[1-F(+)]) + p(1-q)\xi(F(-)(1-G) + G[1-F(-)]) + p(1-q)(1-\xi)[1-F(-)]\}(f/2) \quad (49)$$

Equation 49 is based on the fact that there are $(f/2)$ possibilities of combing $(f/2-1)$ branches going to infinite in two directions plus one branch going to infinite in only one direction. Using eq 34, 35, and 38, we get

$$X_{f-1} = \{(f/2)\{pqX^2[q(1-\xi X) + \xi]\}^{f/2-1}pX(1-qX) \times [2q(1-\xi X) + \xi]\}/[1-(1-p)^{f/2}] \quad (50)$$

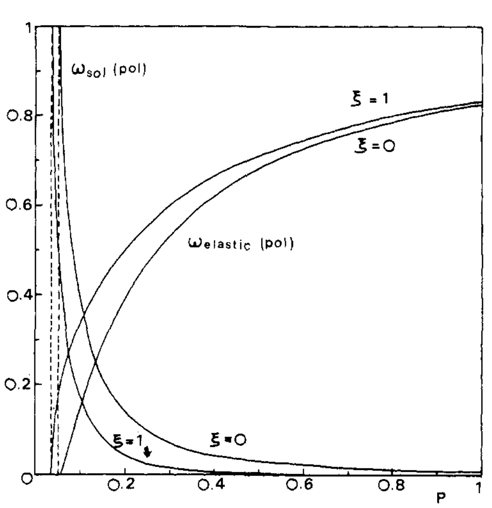
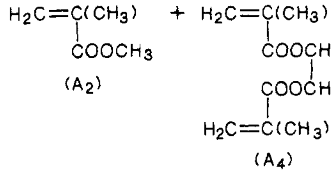


Figure 2. Mass fractions of soluble and elastic material of the polymer vs reaction extent, for the two limiting cases of $\xi = 0$ (termination by chain transfer and/or disproportionation) and $\xi = 1$ (termination by combination).

In order to show the implications of changes in the termination mechanism on the network structure, we will analyze the same system considered by Macosko and Miller[2,3] in two limiting cases: termination by combination ($\xi = 1$) and termination by chain transfer and/or disproportionation ($\xi = 0$).

Example

Consider the reaction of a vinyl with a divinyl such as methyl methacrylate with ethylene dimethacrylate:



$$\mathrm{H_2C{=}C(CH_3)(COOCH_3)} \; (A_2) \quad + \quad \mathrm{H_2C{=}C(CH_3)COOCH_2CH_2OOC(CH_3)C{=}CH_2} \; (A_4)$$

Assume $q = 0.999$ and $A_4/(A_2 + A_4) = 0.005$ ($a_f = 9.95 \times 10^{-3}$).

Figure 1 shows the evolution of the weight-average molecular weight of the polymer fraction, for the two limiting termination mechanisms. As expected, when chains are terminated by combination ($\xi = 1$), $\bar{M}_{\mathrm{w}}$ shows the highest values for every reaction extent and the polymer gels at the lowest conversion.

Mass fractions of soluble and elastic material belonging to the polymer are plotted in Figure 2, as a function of the reaction extent. Termination by combination leads to a decrease in the amount of sol and an increase in the amount of elastic material, when compared with termination by chain transfer and/or disproportionation. The fact that systems with $\xi = 1$ show practically no sol fraction in the polymer, at high reaction extents, may be of practical interest.

When $p = 1$, only a very small difference in the elastic mass fraction corresponding to $\xi = 0$ and 1 is observed. However, as is shown in Figure 3, the evolution of the concentration of cross-linking points (X_3 and X_4) in the polymer is significantly affected by the nature of the termination mechanism. At $p = 1$, termination by com-

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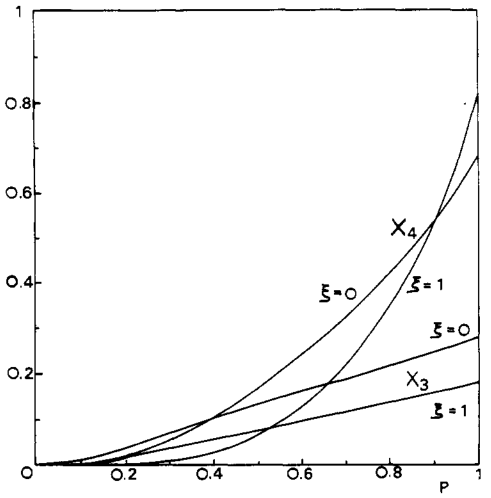

Figure 3. Fraction of A_4 molecules belonging to the polymer, with three (X_3) and four (X_4) arms going to the gel, as a function of reaction extent, for the two limiting cases of $\xi = 0$ (termination by chain transfer and/or disproportionation) and $\xi = 1$ (termination by combination).

bination leads to $X_3 = 0.177$ and $X_4 = 0.812$, while termination by chain transfer and/or disproportionation leads to the following values: $X_3 = 0.276$ and $X_4 = 0.679$. Thus, it may be reasonably expected that both types of networks will show different macroscopic properties. For example, it may be inferred that, due to the increase in the overall concentration of cross-linking points ($X_3 + X_4$) as well as in the relative amount of X_4 with respect to X_3, both the rubbery elastic modulus and the glass transition temperature will be higher for a network where termination takes place by combination (when compared with the same network with termination taking place by chain transfer and/or disproportionation).

Conclusions

By use of a fragment approach, statistical parameters of networks built up by a free-radical mechanism could be obtained both in pre- and postgel stages. This analysis introduces the effect of the nature of the termination mechanism on the network structure. When the termination mechanism is shifted from chain transfer and/or disproportionation to combination, gelation is advanced by a factor of 2/3, the amount of soluble material in the polymer fraction decreases, and the amount of elastic material in the polymer increases while showing a higher concentration of the cross-linking units with the highest possible functionality. It may, then, be inferred that a change in termination mechanism will be associated with variations in the macroscopic properties of the resulting network.

Registry No. Methyl methacrylate, 80-62-6; ethylene dimethacrylate, 97-90-5.

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Effect of Short-Range Correlation between Chain Elements on the Hydrodynamic Radius and the First Cumulant in Dilute Polymer Solutions

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ABSTRACT: It was checked how the first cumulant Ω and the hydrodynamic radius R_H of polymer dynamics in dilute solutions *in good solvent limit* were influenced by short-range correlation between the chain elements. For a scaling form of the element distribution and Oseen hydrodynamic interaction in the Kirkwood scheme, Ω at the q^3 regime was not affected by the short-range correlation, but R_H at smaller q was strongly affected. This result might indicate (1) an inadequacy of the Oseen description of hydrodynamic interaction in the Kirkwood formula and/or (2) the approximate nature (or a lack of accuracy) of the Kirkwood formula.

Introduction

The translational diffusion coefficient D (or the equivalent hydrodynamic radius R_H) and the first cumulant Ω of a single flexible polymer chain in dilute solutions have been made experimentally clear by dynamic light-scattering spectroscopy in wide ranges of the scattering vector (q) and the molecular weight.[1] It has recently been revealed that in the highly swollen state these characteristics were in apparent agreement with those of the nondraining Gaussian chain model with nonpreaveraged Oseen hydrodynamic interaction, i.e., the characteristic ratio R_H/R_G and the reduced first cumulant $\Omega/(q^3k_BT/\eta_0)$ were very close to the theoretical values in the unperturbed chain state.[2] Here R_G is the static radius of gyration of the polymer. However, this agreement is very curious since the element distribution in the swollen chain is not Gaussian at all. Use of the realistic element distribution,[3a] where the small-distance behavior is taken into consideration by a scaling form, may help this curious situation. In this paper, we investigate effects of the short-range correlation between chain elements on R_H and Ω through the scaling form.

Calculation and Results

According to the Akcasu–Gurol[4] treatment based on the general diffusion theory of Kirkwood,[5] the Ω of a chain

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