(34) Dautzenberg, H. *J. Polym. Sci., Polym. Symp.* **1977**, *61*, 83.
(35) Altenberger, A. R.; Tirrell, M.; Dahler, J. S. *J. Chem. Phys.* **1986**, *84*, 5122.
(36) von Meerwall, E. D.; Amis, E. F.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260.
(37) Miyaki, Y.; Einaga, Y.; Fujita, H. *Macromolecules* **1978**, *11*, 1180.
(38) Phillies, G. D. J. *Macromolecules* **1987**, *20*, 558.
(39) Brown, W.; Rymdén, R. *Macromolecules* **1986**, *19*, 2942.
(40) Daoud, M.; de Gennes, P.-G. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1971.
(41) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(42) Amis, E.; Han, C. C. *Polymer* **1982**, *23*, 1042.
(43) Wang, D. H.; Cohen, C. *Macromolecules* **1984**, *17*, 1679, 2890.
(44) Brown, W. *Macromolecules* **1984**, *17*, 66.
(45) Chang, T.; Yu, H. *Macromolecules* **1984**, *17*, 115.
(46) Eisele, M.; Burchard, W. *Macromolecules* **1984**, *17*, 1636.
(47) Huber, K.; Bantle, S.; Burchard, W.; Fetters, L. J. *Macromolecules* **1986**, *19*, 1404.
(48) Antonietti, M.; Coutandin, J.; Sillescu, H. *Macromolecules* **1986**, *19*, 793.
(49) Subsequent to submission of this paper, Benmouna et al.[50] have presented a theory of dynamic scattering from ternary systems as employed here. They predict two relaxation processes: cooperative (D_c) and interdiffusional (D_I) modes, where the latter refers to the relative motions of the chains. The amplitude of the cooperative mode becomes significant, however, only above a weight fraction of about 0.5.
(50) Benmouna, M.; Benoit, H.; Duval, M.; Akcasu, Z. *Macromolecules* **1987**, *20*, 1107, 1112.
(51) Brown, W.; Štěpánek, P. *Macromolecules*, in press.

Cyclization and Reduced Reactivity of Pendant Vinyls during the Copolymerization of Methyl Methacrylate and Ethylene Glycol Dimethacrylate

D. T. Landin and C. W. Macosko*

Department of Chemical Engineering, University of Minnesota, Minneapolis, Minnesota 55455. *Received December 5, 1986; Revised Manuscript Received August 29, 1987*

ABSTRACT: Methyl methacrylate was copolymerized with small amounts of ethylene glycol dimethacrylate. Monomer and pendant vinyl conversion as a function of time was measured up to the gel point. Pendant vinyl conversion was determined by ^{1}H NMR. Plots of pendant conversion versus monomer conversion exhibit a positive y-intercept indicating the tendency to cyclize during the formation of a primary chain. For bulk systems, this amounted to approximately 3–4% of pendant vinyls and the cyclic proportion increased with dilution. The slope of the pendant versus monomer conversion plot is attributed to the formation of cross-links and subsequent cycles. A kinetic model is developed which includes constants for cyclization and pendant reactivity. Values for these constants for the chemical systems studied are evaluated. The average pendant vinyl reactivity is found to be approximately half that of monomeric vinyl reactivity.

Introduction

Understanding the behavior of pendant vinyls is key to the study of network formation by addition polymerization involving multifunctional vinyl monomers. During such a polymerization, pendant vinyls are created when the first vinyl unit of a multifunctional vinyl monomer reacts and the group is added to a polymer chain. The pendant vinyl can then react or remain pendant. The reactivity of the pendant vinyl may be the same as that of the monomeric vinyl or it may be increased or reduced. If it reacts with a growing chain to which it is not already chemically attached, it forms a cross-link. Cyclization occurs if the pendant vinyl is already attached to the chain with which it reacts.

The behavior of pendant vinyls affects the prediction of network properties such as cross-link density, sol fraction, and critical conversion for gelation. The first theories which connected structural properties and extent of reaction were those of Flory[1,2] and Stockmayer.[3,4] These theories assumed equal reactivity of monomeric and pendant vinyls and all reacted pendant vinyls were cross-links (no cyclization). Walling[5] showed that for the methyl methacrylate–ethylene glycol dimethacrylate and vinyl acetate–divinyl adipate systems there was a large discrepancy between the gel point calculated from the Flory–Stockmayer theory and that found experimentally. He attributed the discrepancy to diffusion control of the reaction. In a series of papers, Gordon and Roe[6] disputed this explanation and instead attributed the discrepancy to the formation of cycles. There is extensive experimental evidence of the inadequacy of the Flory–Stockmayer theory for several systems.[7-15] Two explanations for the discrepancy between observed and theoretical gel points are the formation of cycles[16] and a reduced reactivity of the pendant functional group.[14,17]

In this work, conversion of monomeric and pendant vinyls and the gel point are determined experimentally for the vinyl–divinyl system of methyl methacrylate with small amounts of ethylene glycol dimethacrylate. A simple model is proposed which includes the possibility for both cyclization and reduced reactivity. This provides a framework within which to organize and study the data.

Table I
Chemical Systems Investigated

system	mol % EGDMA	% dodecanethiol	vol % in tol
0N	0.00	0	100
0T	0.00	1	100
1N	0.57	0	100
2N	1.14	0	100
2N-50	1.14	0	50
2N-25	1.14	0	25
2T	1.14	1	100
3N	1.70	0	100

Experimental Section

Methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) were obtained from Aldrich. MMA was washed with a 10% aqueous potassium hydroxide solution and

0024-9297/88/2221-0846$01.50/0

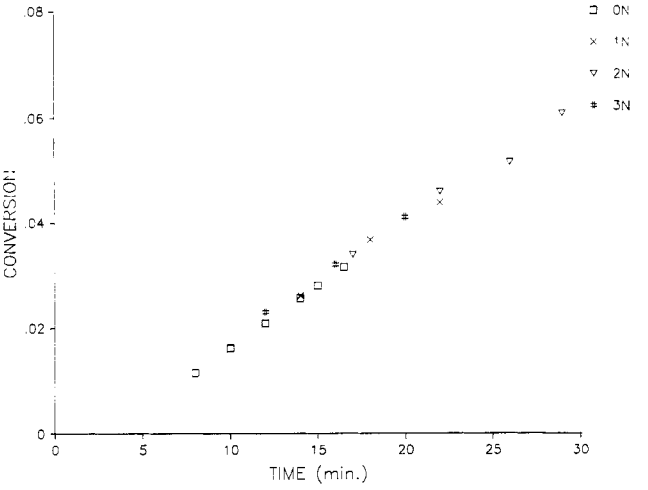

Figure 1. Monomer conversion versus time of four systems investigated.

Table II
Slope and *y*-Intercept of Pendant Conversion Plot, Gel Point Conversion, Pendant Vinyl Reactivity, and Secondary Cyclization Constant for Chemical Systems Studied

system	*y*-intercept	slope	gel point	r_3	k_{ps}
1N	0.0276	3.573	0.097	1.86	9.74
1T	0.0465	0.252	0.409	1.80	0.10
2N	0.0345	4.852	0.061	2.22	19.70
2N-50	0.0724	3.064			
2N-25	0.1695	0.692			
2T	0.0389	0.783	0.295	2.26	2.70
3N	0.0313	5.550	0.033	2.38	29.23

EGDMA was used as received. The monomers were mixed to give the chemical systems shown in Table I. Azobis(isobutyronitrile) (AIBN) from Kodak was added in the amount 0.3% by weight. To some of the chemical systems, 1% by volume of dodecanethiol was added as a transfer agent. Toluene was used as solvent for the solution polymerizations. The reaction mixture was poured into several 6-in. glass test tubes each capped with a rubber septum. The tubes were placed in a 60 °C water bath for varying amounts of time. Tubes were removed from the bath and polymer was precipitated in methanol to which a small amount of *N,N*-diphenyl-*N'*-picrylhydrazyl (DPPH) had been added.

The conversion of monomer was determined by drying and weighing the precipitated polymer. Conversion versus time data for the polymerization under these conditions are shown in Figure 1. Neither the addition of EGDMA or the addition of transfer agent changed the conversion versus time results.[18]

Gel points were determined by observing the time at which the reaction mixture would no longer flow. The gel point conversion was then obtained from the conversion versus time plot. These results are listed in Table II.

Proton nuclear magnetic resonance, ^{1}H NMR, was used to determine the conversion of pendant vinyls. The precipitated polymer was dissolved in chloroform and then reprecipitated in methanol. The polymer was dried and then dissolved in deuteriated chloroform with 1% v/v tetramethylsilane (TMS). This solution was used for NMR analysis. NMR spectra were obtained with a Nicolet NT-300 WB (Nicolet Analytical Instruments). A one-pulse sequence was used with a 45° pulse, 2-s delay time, and 2.05-s acquisition time. Approximately 100 acquisitions were obtained per spectrum. Quadrature detection was used and the spectral window was 4000 Hz. The spectra were machine integrated.

An NMR spectrum for sample 2N is shown in Figure 2. A blowup of the region from 4.0 to 6.5 ppm is shown in Figure 3. The three peaks from 0.7 to 1.25 ppm are from methyl groups adjacent to reacted vinyl groups. The peaks from 4.0 to 4.5 ppm are from the OCH_2 protons on EGDMA monomeric units in the polymer. The two peaks at 5.65 and 6.2 ppm are from unreacted vinyl groups. The peak at 3.55–3.7 ppm is due to OCH_3 protons on MMA monomeric units in the polymer.

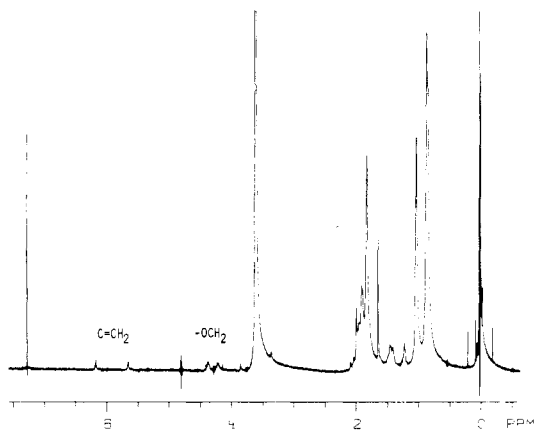

Figure 2. ^{1}H NMR spectrum of sample from chemical systems 2N. OCH_2 peaks are in the 4.0–4.5 ppm region. $C{=}CH_2$ peaks are in the 5.5–6.5 ppm region.

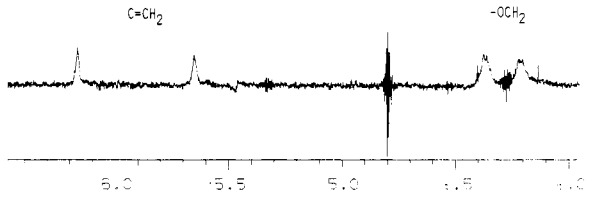

Figure 3. Enlargement of the 4.0–6.5 ppm region of spectrum in Figure 2.

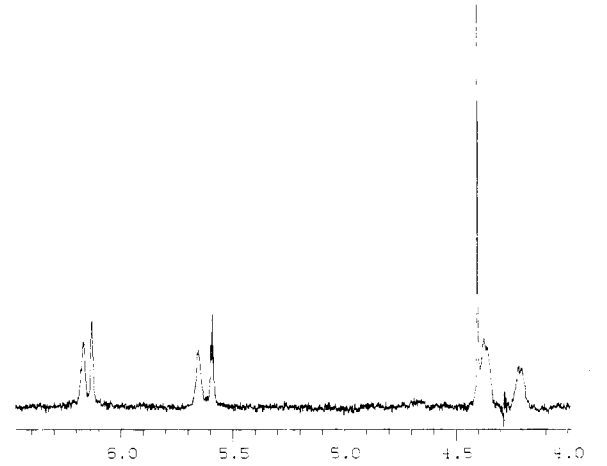

Figure 4. ^{1}H NMR spectrum, 4.0–6.5 ppm region, of 2N sample with residual monomer still in it. Peaks at 5.58 and 6.13 ppm are due to monomeric $C{=}CH_2$ and the sharp peak at 4.4 ppm is due to monomeric OCH_2.

The areas under the OCH_2 and OCH_3 peaks are used to determine copolymer composition through the equation

$$\frac{[\text{EGDMA}]}{[\text{MMA}]} = \frac{\sum A(\text{OCH}_2)/4}{A(\text{OCH}_3)/3} \tag{1}$$

where $A(OCH_2)$ and $A(OCH_3)$ are the areas under the peaks. From eq 1, the polymer ratio is found to be identical with the monomer ratio (Table I) indicating monomeric vinyl reactivities are equal as found by previous workers.[15] Pendant conversion is given by the equation

$$p_p = 1 - \frac{\sum A(\text{C}{=}\text{CH}_2)/2}{\sum A(\text{OCH}_2)/4} \tag{2}$$

where p_p denotes pendant conversion.

In some cases, it was very difficult to eliminate all of the monomer from the polymer. When this happened, the spectrum appeared as in Figure 4. It was difficult to separate the monomer

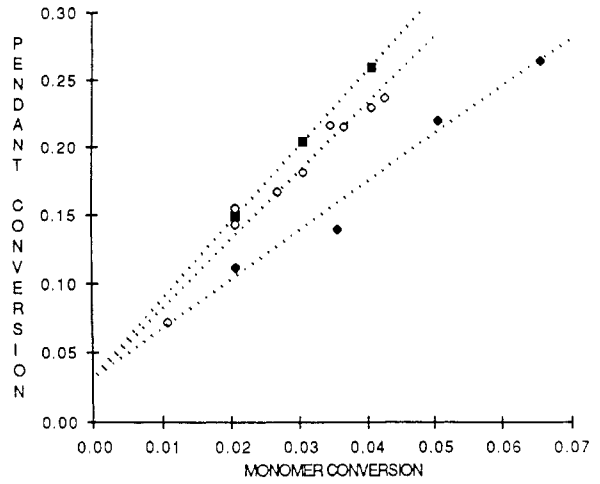

Figure 5. Pendant conversion vesus monomer conversion for increasing cross-linker concentration 1N (◆) (0.57 mol % EGDMA, Table I), 2N (◇) (1.14%), and 3N (■) (1.70%). Dotted lines represent least-squares fit to data.

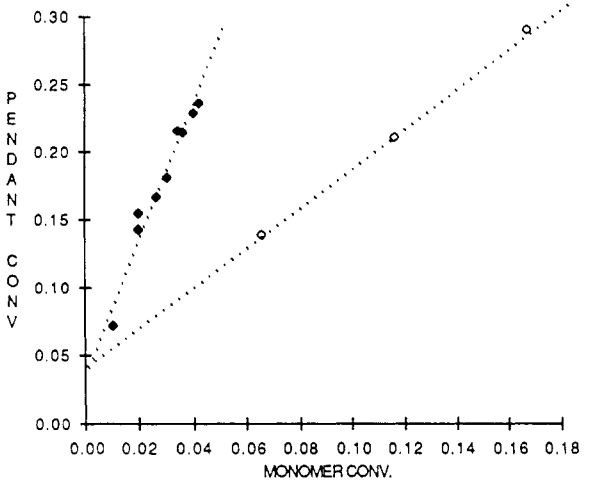

Figure 6. Pendant conversion versus monomer conversion for different primary chain molecular weight 2N (◆) (247 000) and 2T (△) (52 100).

and polymer OCH_2 peaks so an alternative analysis was used. This analysis used the equation

$$p_p = \frac{\alpha - \beta(\gamma + 1)}{\alpha + \beta} \tag{3}$$

where $\alpha = \sum A(CH_3)/3$, $\beta = \sum A(C{=}CH_2)/2$, and $\gamma = [MMA]/[EGDMA]$.

Intrinsic viscosity was used to determine the molecular weight of PMMA with no EGDMA polymerized under the same conditions as those with EGDMA. Measurements were made at 30 °C with a 0.46-mm diameter Ubbelhode viscometer. Ethyl acetate (EtOAc) was used as solvent. From the equation

$$[\eta] = KM^a$$

where K and a for MMA in EtOAc at 30 °C are[19]

$$K = 6.75 \times 10^{-3} \qquad a = 0.72$$

the molecular weights were $M = 2.47 \times 10^5$ for MMA without any transfer agent (sample 0N in Table I) and $M = 5.21 \times 10^4$ for MMA with transfer agent (0T, Table I).

Results and Discussion

Plots of pendant vinyl conversion versus monomer conversion are shown in Figures 5–7. Figure 5 shows the effect of increasing amounts of EGDMA. Lines have been drawn through the data points by using a least-squares fit to better show the trend of the data. All systems show a positive y-intercept. This indicates that in the limit of zero conversion, pendant vinyls have reacted or in other words as the first polymer chains are forming, pendant vinyls are reacting. Since cross-linking is a second-order reaction and in the limit of zero conversion polymer chains are infinitely dilute, this loss of pendant vinyls must be due to cyclization. Cyclization during the formation of a primary chain will be called primary cyclization.

From Figure 5, it can be seen that within this range of cross-linker concentration, increasing the EGDMA does not change the proportion used up in primary cycles. The effect of a different primary chain length is shown in Figure 6. Samples with and without transfer agent have the same proportion of pendant vinyls in primary cycles; however, the slopes are much different.

Figure 7 shows the effect of dilution. Although there are only two data points for the 25% monomer case, the trend seems to be that a greater proportion of pendant vinyls are used in primary cycles as the dilution is increased. This is expected. Although a good solvent will expand the chain slightly it will not reduce the concentration of pendant vinyls near the radical on the end of a primary chain nearly as much as it does the monomer concentration. The slopes in Figure 7 decrease with dilution, indicating less secondary cycles, also expected with dilution.

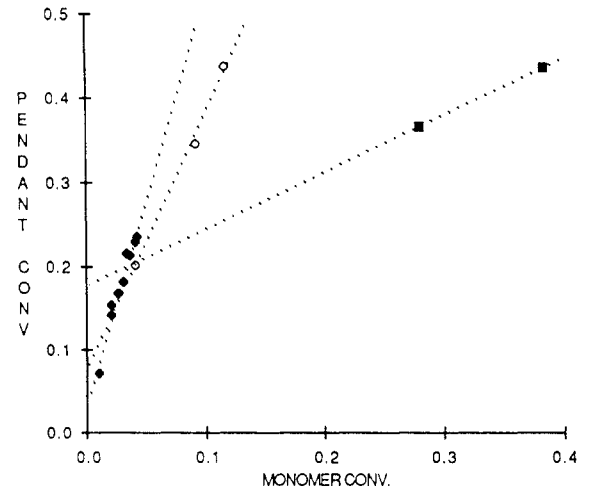

Figure 7. Pendant conversion versus monomer conversion showing the effect of dilution 2N (◆), 2N-50 (◇) (50% toluene), and 2N-25 (■) (75% toluene).

The y-intercept and slope from each pendant conversion curve and the gel point conversion for each chemical system investigated are listed in Table II.

In developing a model to describe this behavior, the slope of the pendant conversion curve is attributed to the formation of cross-links and to secondary cycles. Secondary cycles are those formed with a pendant vinyl attached to a polymer chain which has just been connected to the propagating radical chain by a cross-link. The process of cross-linking and secondary cyclization is illustrated in Figure 8. The contributions of cross-linking and secondary cyclization to the slope can be separated at the gel point since the conversion of pendant vinyls to cross-links necessary for gelation is known theoretically.

Kinetic Model

A detailed development of the kinetic model is found in the Appendix. Three constants of concern are r_3, reactivity ratio of pendant vinyl to monomeric vinyl; k_{pp}, proportion of pendant vinyls used in primary cyclization; and k_{ps}, number of pendant vinyls used in secondary cyclization per cross-link. The primary cyclization constant

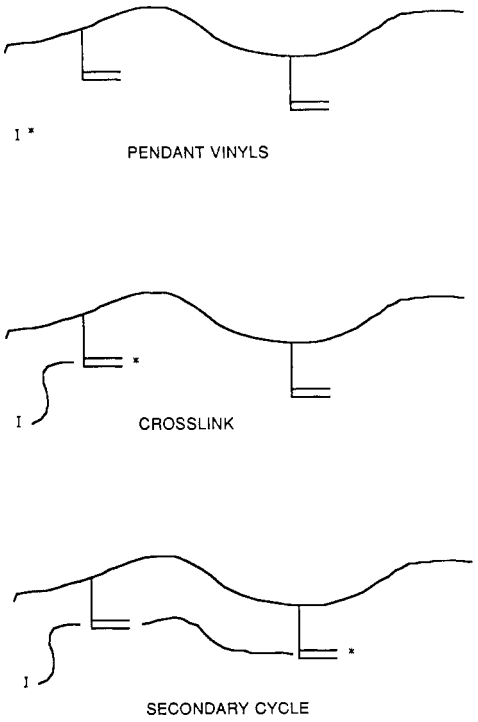

Figure 8. Schematic drawing of the process of cross-link and secondary cycle formation.

is obtained from the y-intercept of the pendant conversion versus monomeric conversion plot. The slope of this plot is not enough information to determine r_3 and k_{ps} alone. A further piece of information is needed. This is obtained by using the network theory. The pendant conversion to cross-links necessary for gelation is obtained theoretically from the equation[20]

$$p = \frac{1 - q}{2a_4q} \tag{4}$$

where p is the conversion of pendant vinyls to cross-links necessary for gelation, q is the probability that a monomeric unit incorporated in a polymer chain is not a chain end, and a_4 is the proportion of vinyl functional groups which are on divinyl monomer units.

To obtain a unique pair (k_{ps},r_3) of values which gives both the correct slope and the correct cross-link conversion at gelation, k_{ps} versus r_3 giving the correct slope and k_{ps} versus r_3 giving the cross-link conversion are plotted.

The k_{ps} versus r_3 plot for pairs giving the correct slope of the pendant conversion plot is determined by using the kinetic model developed in the Appendix. A value for r_3 is chosen and the slopes obtained by using three different values for k_{ps} with the r_3 values are used to find the k_{ps} value giving the correct slope by linear regression. This is repeated for several different r_3 values.

The k_{ps} versus r_3 plot for pairs giving the correct conversion to cross-links at gelation is also determined by using the kinetic model. Once again, a value for r_3 is chosen. The conversion to cross-links at the experimentally determined monomer conversion of gelation is calculated with this r_3 value and three different k_{ps} values. The k_{ps} value giving the cross-link conversion predicted by eq 4 is determined by linear regression. This is repeated for several r_3 values.

The intercept of the two curves gives the values for r_3 and k_{ps}. Figure 9 shows this plot for sample 2T. With and without transfer agent, the reactivities are similar but the amounts of secondary cyclization are very different. Table II shows r_3 and k_{ps} as determined for several of the systems

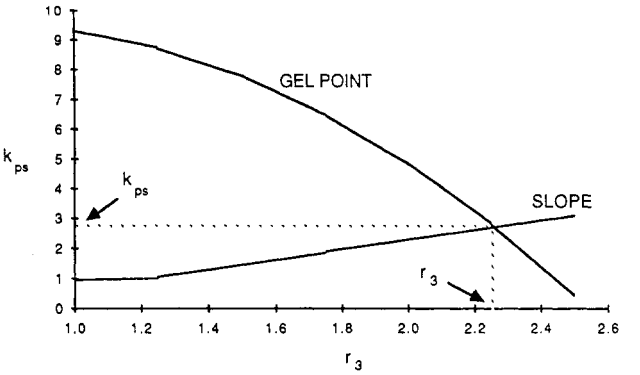

Figure 9. Plot determination of k_{ps} and r_3 for system 2T. GEL POINT line represents (k_{ps},r_3) pairs from the model giving the theoretical cross-link conversion necessary for gelation. SLOPE line represents (k_{ps},r_3) pairs from the model giving the same pendant conversion versus monomer conversion slope as found experimentally.

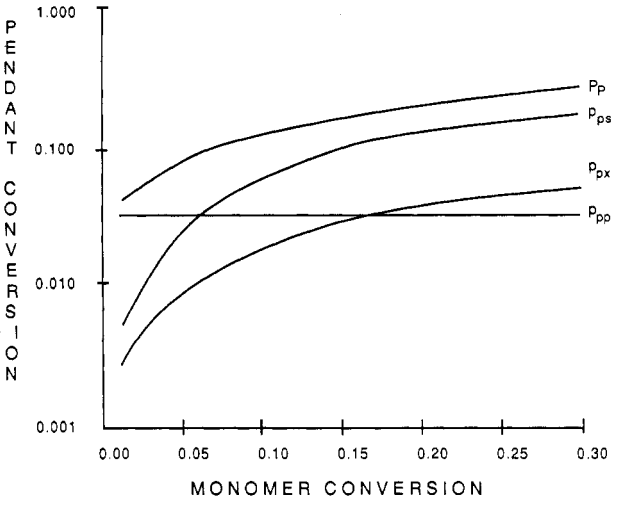

Figure 10. Conversion of pendant vinyls (p_p) to cross-links (p_{px}) or primary cycles (p_{ps}) as predicted by the kinetic model for system 2T.

investigated. When the amount of cross-linker is held constant and the chain length varied, the pendant reactivity is fairly constant while the number of secondary cycles per cross-link increases with increasing chain length. This may be so because a longer chain has a greater concentration of pendant vinyls surrounding a radical end. In the case of systems 2N and 2T, the system with transfer agent has a k_{ps} equal to 2.7 and the system without transfer agent a value of 19.7. This is reasonable because the primary chain length in the system without transfer agent is nearly 6 times larger than in the system with transfer agent. Both the pendant reactivity and the number of secondary cycles change as the primary chain length is held constant and the amount of cross-linker is varied. Pendant reactivity decreases as the amount of cross-linker is increased. This is probably due to an increase in steric screening effects caused by increasing the number of branches in the vicinity of a pendant vinyl as well as decreasing the mobility of the macromolecule. The number of secondary cycles increases as the amount of cross-linker is increased. This is once again due to the greater concentration of pendant vinyls surrounding a radical end.

Once the constants have been determined, the model can be used to predict total conversion of pendant vinyls and conversion to cross-links, primary cycles, and secondary cycles. These predicted conversions are shown as a function of monomer conversion in Figure 10 for system 2T. These conversions can now be used in a branching

theory to predict molecular parameters.[18,21]

Conclusions

Vinyl–divinyl network formation has been investigated by determining the conversion of pendant vinyls as a function of monomeric vinyl conversion, using this information to shape the concept of cyclization and cross-linking, and formalizing these concepts by incorporating them in a kinetic model for the rate of polymerization. Plots of pendant conversion versus monomer conversion exhibited a positive y-intercept, indicating the loss of pendant vinyls during the formation of a primary chain. This loss was attributed to the formation of primary cycles. Primary cyclization increased with increasing dilution. The slope of the plot indicated the formation of secondary cycles with the formation of cross-links. The kinetic model along with experimental conversion curve data provided a means to estimate the number of secondary cycles and the reactivity of the pendant vinyl. The amount of secondary cyclization increased with increasing length of the primary chain. The pendant vinyl reactivity was found to be approximately half that of monomeric vinyls.

This approach to understanding network formation is that of developing a model which is consistent with the available experimental data, and it is only an approximation. Primary cyclization has been assumed to occur at a constant rate. This is probably not so since as the reaction progresses, the concentration of pendant vinyls not connected by a primary chain to a particular radical end increases and provides competition. As the reaction approaches the gel point, the amount of secondary cyclization will also increase, especially in the largest clusters. In this analysis, the rate of secondary cyclization, k_{ps}, has been assumed to be constant. Pendant reactivity in this model is not that of an isolated vinyl in a very dilute system. Instead it must include steric contributions from neighboring portions of the chain. It is not surprising then that it is less than the reactivity of monomeric vinyls.

Acknowledgment. This research was supported by a grant from the Army Research Office, Polymer Chemistry Program.

Appendix

With the concept of primary and secondary cyclization in mind, a kinetic scheme for the vinyl–divinyl copolymerization can be written. In this scheme, A = vinyl on monovinyl monomer, B = vinyl on divinyl monomer, P = pendant vinyl, a = vinyl in polymer from monovinyl monomer, b = first vinyl from divinyl monomer incorporated in polymer, p = pendant vinyl incorporated in polymer, pp = pendant vinyl in primary cycle, px = pendant vinyl in cross-link, and ps = pendant vinyl in secondary cycle. The propagation steps are written as

$$\begin{array}{llll} A^* + A \rightarrow A^* & (k_{11}) & A^* + B \rightarrow B^* & (k_{12}) \\ A^* + P \rightarrow P^* & (k_{13}) & B^* + A \rightarrow A^* & (k_{21}) \\ B^* + B \rightarrow B^* & (k_{22}) & B^* + P \rightarrow P^* & (k_{23}) \\ P^* + A \rightarrow A^* & (k_{31}) & P^* + B \rightarrow B^* & (k_{32}) \end{array}$$

$$P^* + P \rightarrow P^* \quad (k_{33})$$

The equations for the time rate of appearance and disappearance of species A and B are

$$-\frac{d[A]}{dt} = k_{11}[A^*][A] + k_{21}[B^*][A] + k_{31}[P^*][A] \quad (5)$$

$$-\frac{d[B]}{dt} = 2(k_{12}[A^*][B] + k_{22}[B^*][B] + k_{32}[P^*][B]) \quad (6)$$

Pendant vinyls are both produced and consumed so an equation for the time rate of change has terms for both. Contributions to the term for disappearance come from reaction to cross-links, primary cycles, and secondary cycles. The equation for P becomes

$$-\frac{d[P]}{dt} = (1 + k_{ps})(k_{13}[A^*][P] + k_{23}[B^*][P] + k_{33}[P^*][P]) + \frac{k_{pp}}{2}\frac{d[B]}{dt} - (k_{12}[A^*][B] + k_{22}[B^*][B] + k_{32}[P^*][B]) \quad (7)$$

where k_{pp} is the fraction of pendant vinyls in primary cycles and k_{ps} is the average number of secondary cycles formed per cross-link. Differential equations are also written for the appearance of species in the polymer. These are

$$\frac{da}{dt} = -\frac{d[A]}{dt} \quad (8)$$

$$\frac{db}{dt} = -\frac{1}{2}\frac{d[B]}{dt} \quad (9)$$

$$\frac{d(pp)}{dt} = -\frac{k_{pp}}{2}\frac{d[B]}{dt} \quad (10)$$

$$d(px)/dt = k_{31}[P^*][A] + k_{32}[P^*][B] + k_{33}[P^*][P] \quad (11)$$

$$\frac{d(ps)}{dt} = k_{ps}\frac{d(px)}{dt} \quad (12)$$

Combining eq 5 and 6 gives

$$\frac{d[A]}{d[B]} = \frac{[A](k_{11}[A^*] + k_{21}[B^*] + k_{31}[P^*])}{2[B](k_{12}[A^*] + k_{22}[B^*] + k_{32}[P^*])} \quad (13)$$

Assuming quasi-steady state and using the accompanying equations

$$\begin{aligned} k_{12}[A^*][B] &= k_{21}[B^*][A] \\ k_{23}[B^*][P] &= k_{32}[P^*][B] \\ k_{31}[P^*][A] &= k_{13}[A^*][P] \end{aligned} \quad (14)$$

eq 11 becomes

$$\frac{d[A]}{d[B]} = \frac{[A](k_{11}/k_{12}[A] + [B] + k_{13}/k_{12}[P])}{2[B]([A] + k_{22}/k_{21}[B] + k_{23}/k_{21}[P])} \quad (15)$$

If r_{ij} is defined as

$$r_{ij} = k_{ii}/k_{ij}$$

Equation 15 becomes

$$\frac{d[A]}{d[B]} = \frac{r_{12}[A]([A] + [B]/r_{12} + [P]/r_{13})}{2r_{21}[B]([A]/r_{21} + [B] + [P]/r_{23})} \quad (16)$$

Equation 6 and 7 combine to give

$$\frac{d[P]}{d[B]} = \frac{(1 + k_{ps})r_{32}[P]([A]/r_{31} + [B]/r_{32} + [P])}{2r_{23}[B]([A]/r_{21} + [B] + [P]/r_{23})} - \frac{1 - k_{pp}}{2} \quad (17)$$

Expressions for the relative changes in the polymer content are also obtained. Dividing eq 8 by eq 9 gives the expression

$$\frac{da}{db} = 2\frac{d[A]}{d[B]} \quad (18)$$

Equation 10 divided by eq 9 result in

$$d(pp)/db = -k_{pp} \quad (19)$$

Equation 11 divided by eq 9 and eq 12 divided by eq 9 give

$$\frac{d(px)}{db} = \frac{r_{32}[P]([A]/r_{31} + [B]/r_{32} + [P])}{r_{23}[B]([A]/r_{21} + [B] + [P]/r_{23})} \quad (20)$$

and

$$\frac{d(ps)}{db} = k_{ps}\frac{d(px)}{db} \quad (21)$$

Equations 20 and 21 combine to give

$$\frac{d(px)}{db} = \left(2\frac{d[P]}{d[B]} + 1 - k_{pp}\right) \Big/ (1 + k_{ps}) \quad (22)$$

A mass balance gives

$$da + db + d(px) + d(ps) + d(pp) = -(d[A] + d[B] + d[P]) = M^0\,dx \quad (23)$$

where M^0 is a constant given by the equation

$$M^0 = A^0 + B^0 + P^0 \quad (24)$$

A^0, B^0, and P^0 representing initial quantities and dx is some increment of conversion. The integral composition of the copolymer is calculated stepwise.[11] Let

$$u_j = (d[A]/d[B])_j$$

$$V_j = (d[P]/d[B])_j$$

$$U_0 = dA^0/dB^0$$

$$V_0 = dP^0/dB^0$$

and

$$P^0 = 0$$

then

$$(da)_j = M^0U_j\,dx/(U_j + V_j + 1) \quad (25)$$

$$(db)_j = M^0\,dx/[2(U_j + V_j + 1)] \quad (26)$$

$$[d(pp)]_j = M^0k_{pp}\,dx/[2(U_j + V_j + 1)] \quad (27)$$

$$[d(px)]_j = \frac{M^0(2V_j + 1 - k_{pp})\,dx/(1 + k_{ps})}{2(U_j + V_j + 1)} \quad (28)$$

$$[d(ps)]_j = k_{ps}\,[d(px)]_j \quad (29)$$

$$(d[A])_j = -M^0U_j\,dx/(U_j + V_j + 1) \quad (30)$$

$$(d[B])_j = -M^0\,dx/(U_j + V_j + 1) \quad (31)$$

and

$$(d[P])_j = -M^0V_j\,dx/(U_j + V_j + 1) \quad (32)$$

where $x = (j + 1)\,dx$. The integral compositions at the conversion x are

$$a = \sum_{j=0}^{n}(da)_j \quad (33)$$

$$b = \sum_{j=0}^{n}(db)_j \quad (34)$$

$$pp = \sum_{j=0}^{n}[d(pp)]_j \quad (35)$$

$$px = \sum_{j=0}^{n}[d(px)]_j \quad (36)$$

$$ps = \sum_{j=0}^{n}[d(ps)]_j \quad (37)$$

$$[A] = A^0 + \sum_{j=0}^{n}(d[A])_j \quad (38)$$

$$[B] = B^0 + \sum_{j=0}^{n}(d[B])_j \quad (39)$$

$$[P] = P^0 + \sum_{j=0}^{n}(d[P])_j \quad (40)$$

where

$$n = \frac{x}{dx} - 1$$

To use this kinetic model, values for the rate and cyclization constants must first be obtained. NMR data show the monomeric vinyls in the MMA–EGDMA system have an equal reactivity. Therefore, r_{12} and r_{21} will be set equal to 1 in this analysis. The reactivity of the pendant vinyl may be different due to influences from the polymer chain and steric hindrance and has not been determined prior to analysis with this model. The constant k_{pp} is equal to the y-intercept of the pendant vinyl conversion versus monomer conversion curve for each system. The slope of each of these curves is a result of corss-linking and secondary cyclization in combination with the reactivity of the pendant vinyl. If it is assumed that $r_{13} = r_{23} = 1/r_{31} = 1/r_{32} = r_3$, then there are two unknowns remaining, r_3 and k_{ps}.

Registry No. MMA, 80-62-6; EGDMA, 97-90-5.

References and Notes

(1) Flory, P. J. *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3091, 3097.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1947**, *69*, 30.
(3) Stockmayer, W. H. *J. Chem. Phys.* **1943**, *11*, 45.
(4) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
(5) Walling, C. *J. Am. Chem. Soc.* **1945**, *67*, 441.
(6) Gordon, M.; Roe, R.-J. *J. Polym. Sci.* **1956**, *21*, 27.
(7) Spurr, R. A.; Hanking, B. M.; Rowen, J. W. *J. Polym. Sci.* **1959**, *37*, 431.
(8) Holt, T.; Simpson, W. *Proc. R. Soc. London, A* **1956**, *238*, 154.
(9) Storey, B. T. *J. Polym. Sci.* **1965**, *A3* 265.
(10) Wesslau, H. *Angew. Makromol. Chem.* **1967**, *1*, 56.
(11) Malinksy, J.; Klaban, J.; Dusek, K. *J. Macromol. Sci.—Chem.* **1971**, *A5*, 1071.
(12) Mrkvickova-Vaculova, L.; Kratochvil, P. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2015.
(13) Ito, K.; Murase, Y.; Yamashita, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 87.
(14) Okasha, R.; Hild, G.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 975.
(15) Whitney, R. S.; Burchard, W. *Makrmol. Chem.* **1980**, *181*, 869.
(16) Dusek, K.; Galina, H.; Mikes, J. *Polym. Bull.* **1980**, *3*, 19.
(17) Hild, G.; Okasha, R. *Makromol. Chem.* **1985**, *186*, 93.
(18) Landin, D. T. Ph.D. Thesis, University of Minnesota, 1985.
(19) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975.
(20) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9* 199.
(21) Landin, D. T.; Macosko, C. W., manuscript in preparation.