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GPC analysis of polymer network formation

2. Bifunctional PPG prepolymer/crosslinker system

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Summary

Size distribution of polymer clusters in pre-gel state has been measured by means of gel permeation chromatography (GPC) for crosslinking system between bifunctional prepolymer and trifunctional crosslinker. Experimental chromatograms have been obtained at various degree of conversion, and compared with theoretical chromatograms predicted by the Flory-Stockmayer model. Experimental size distribution at low conversion is well described by the theory. On the other hand, experimental chromatograms at higher conversions show a long tail in lower elution volume region which is unexpected by the theory. This result suggests that clusters with relatively linear structure which is not predicted by the theory are formed. The formation of the clusters with fairly linear structure is estimated to originate from unequality in reactivity of sites in crosslinker which is due to steric hindrance by the reacted sites.

Introduction

Evolution of network structure during gelation process has been widely investigated by means of various analytical methods (1). As degree of conversion (p) approaches the value at gelation point (p_c), the average size of polymer clusters grows, and the broadening of size distribution of clusters occurs simultaneously. This phenomenon has been experimentally demonstrated by means of light, X-ray or neutron scattering (2-5) and gel permeation chromatography (GPC) (6,7). In our previous study (7), we investigated size distribution of clusters below p_c as a function of p by GPC. GPC measurements enable us to analyze not only average molecular weight of clusters but also the size distribution itself, which is the advantage of GPC over scattering experiments. Significant information about the mechanism of crosslinking reaction will be derived from measurements of size distribution of branched clusters. Size distribution obtained by GPC is governed by distribution for the mean-square radius of gyration ($<S^2>$) of molecules.

The Flory-Stockmayer model (8-10) (FS model) and percolation model (11-13) have been employed for theoretical interpretation of gelation process. Differences between the two theories, and the comparison of recent experimental results with the theoretical predictions are summarized in some references (1, 11-13). Experimental tests on both models have mainly been made on the basis of critical exponents for various physical quantities. Comparison of experimental size distribution of clusters in pre-gel state with theoretical one is a critical test on the theories, but there have been only a few studies (6,7) following this line. From the viewpoint of size distribution, it should be noted that FS model gives us an analytical solution for molecular weight distribution of clusters at a certain p, while percolation model with a finite-dimentional lattice does not. However, molecular weight distribution of clusters predicted by FS model can not be directly compared to size distribution obtained by GPC, because clusters with branched structure with identical molecular weight have various types of topological architecture, which means that molecular weight distribution is not equivalent to $<S^2>$ distribution. In order to obtain theoretical $<S^2>$ distribution based on FS model, we attempted to transform molecular weight distribution into $<S^2>$ distribution by computer simulation (14). By exhausive enumeration using iteration equations, all species in the clusters were counted one by one, and the weight fraction and $<S^2>$ for each cluster were calculated on the Gaussian chain statistics (14, 15).

In the previous study (7), we compared the experimental chromatograms at various p with the theoretical ones obtained by $<S^2>$ distribution on the basis of FS model. Crosslinking reaction between bifunctional siloxane monomer and multifunctional crosslinker was investigated. In this study, we have treated crosslinking reaction between bifunctional prepolymer and trifunctional crosslinker. This type of crosslinking has often been called "end-linking method". End-linking method has been employed for preparation of model polymer networks (in post-gel state), because molecular weight between crosslinks (M_c) is ideally identified with molecular weight of prepolymer (M_p) (16). Elastic modulus and degree of equilibrium swelling for end-linked model networks have been measured in fundamental studies on rubber elasticity (16). However, the identification of M_p with M_c has been considered to be a poor approximation due to deviation from ideal end-linking reaction (17,18). There have been some experimental results indicating $M_c \neq M_p$ (18-22), but the details of the mechanism for the deviation from ideal reaction are not fully elucidated. Analysis of size distribution for branched clusters in pre-gel state brings foundamental knowledge about end-linking reaction, which will be useful for preparing real model network. We have investigated the size distribution of clusters in end-linking system as a function of p by means of GPC, and have compared the experiemental chromatograms with the theoretical ones based on FS model. We have discussed some similarities in gelation process between end-linking system in this study and crosslinking system using low molecular weight spiece as a monomer in our previous study (7).

Experimental

Poly(oxypropyleneglycol) (PPG) ($HO(CH(CH_3)CH_2O)_nH$) (Asahi Glass Co.) purified by water-ethanol mixture was employed as a prepolymer. Number average molecular weight (M_n) of PPG is 3.15×10^3 which was determined by vapor pressure osmometry. The value of M_w/M_n was evaluated to be 1.18 by GPC. Here, M_w is the weight average molecular weight. Functionality of end groups in PPG was estimated to be 2.0 by titration. Triphenylmethane-4,4',4"-triyltriisocyanate (TTI) ($(C_6H_4NCO)_3CH$) (Sumitomo Bayer Urethane Co.) and 4,4'-diphenylmethanediisocyanate (MDI) ($(C_6H_4NCO)_2CH_2$) (Sumitomo Bayer Urethane Co.) were used as trifunctional and bifunctional crosslinker, respectively. Functionality of isocyanate groups in TTI and MDI was 2.7 and 2.0, respectively, which were determined by titration method.

Procedure of crosslinking reaction is as follows. PPG and TTI (or MDI) were mixed in benzene at stoichiometric ratio (i.e., molar ratio of PPG to TTI is 2.7/2, and that of PPG to MDI is 2/2.). PPG concentration in PPG/TTI and PPG/MDI system was 0.0156mol/l and 0.0135mol/l, respectively. Catalyst (1,8-diazabicyclo[5,4,0]undecene-7) for the crosslinking reaction was added to the solution. The mixture was kept at 30°C with stirring in an atmosphere of nitrogen for the crosslinking reaction. After a certain period, a portion of the solution was extracted from the reaction vessel, and then, an excess amount of methanol was added to the extracted solution for cessation of the reaction. The five solutions were extracted at different reaction periods to obtain the samples with different p. The solutions were dried under a reduced pressure to remove benzene and methanol. The residue was dissolved in tetrahydrofuran (THF) , which was used as a sample for GPC measurements.

Degree of conversion p for each sample was evaluated on the basis of the ratio of peak area of unreacted PPG to that of the total one in experimental chromatogram together with FS model. Assuming that a peak assigned to each cluster is given by a Gaussian curve, we separated the peak originating from unreacted PPG from the whole GPC curve. Weight fraction of unreacted PPG in the total one (w_0) was calculated from the area ratio of the peaks. The FS model gives the value of p, when w_0 is known. The details of determination of p are given in Appendix.

Chromatograms were obtained with a GPC HLC-802UR (Toyo Soda Co.) equipped with GMH4 and GMHXL columns. Polymer concentration of elute was detected by differential refractive index analysis. THF was used as the eluting solvent.

Results and discussion

Figure 1 shows experimental chromatograms at p=0.245, 0.355, 0.375, 0.415 and 0.515 together with the corresponding theoretical chromatograms for PPG/TTI system. The solid and dashed lines represent for the experimental and theoretical chromatograms, respectively. In order to obtain theoretical chromatogram at a given p, firstly, $<S^2>$

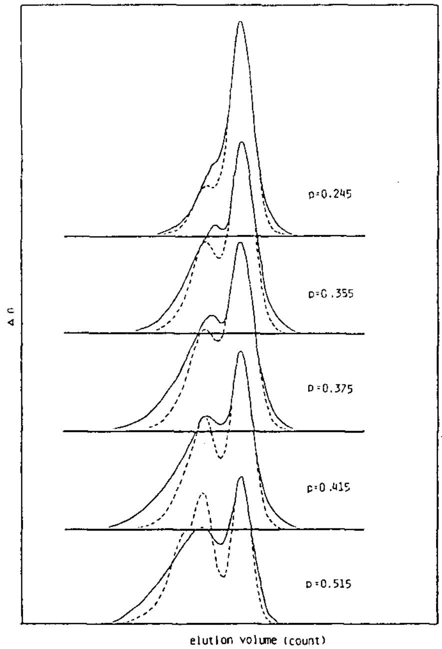

Figure 1. GPC chromatograms for PPG/TTI system. Solid and broken lines represent experimental and theoretical chromatograms, respectively.

distribution predicted by FS model was simulated on the basis of Gaussian statistics. The details of the simulation are described in ref. 7 and 14. In the simulation, the size ratio of prepolymer to crosslinker was approximated by the molecular weight ratio. Secondly, the obtained $<S^2>$ distribution was transformed into theoretical GPC trace. In this procedure, it was assumed that the shape of a peak for each cluster is given by a Gaussian curve. Half width of the peak for PPG at p=0 was used as that of each peak. The details of the transformation of $<S^2>$ distribution into GPC trace are given in the previous paper (7).

As can be seen in Figure 1, as crosslinking reaction proceeds (p increases), the height of the peak for unreacted PPG (the highest peak at p=0.245) decreases, while the peaks for clusters more than dimer newly appear and the size distribution becomes broader. It is seen that the separation between the peaks for unreacted PPG and dimer in the experimental curves is not as clear as in the calculated ones. This is attributed to a finite polydispersity of PPG used (M_w/M_n =1.18). However, the polydispersity of PPG used is considered to be small enough not to prevent quantitative comparison between experimental and theoretical chromatograms. The experimental chromatogram at p=0.245 are fairly well reproduced by the theoretical one. This means that the size distribution of clusters at lower conversion obeys the prediction of FS model.

On the other hand, discrepancy between experimental and theoretical ones becomes significant, as the crosslinking reaction proceeds. Especially, experimental curves at higher p show a longer tail in lower elution volume region (i.e., large $<S^2>$ region). This means that considerable number of clusters with larger size than predicted by FS model is formed in the system. The long tail in lower elution volume region as unexpected by the theory was also reported in bifunctional monomer and multifunctional crosslinker systems (7). The formation of theoretically unexpected large cluster is estimated to originate from unequality in reactivity of functional groups in TTI. When two of three isocyanate groups in TTI have already reacted with PPG, the reactivity of third one should be lower due to steric hindrance in comparison with in the case where both or either of other two groups have not yet reacted. Due to lower reactivity of the third isocyanate group in the crosslinker, the probability that clusters are linearly linked will become larger than expected by FS model assuming equal reactivity for all functional groups. Clusters with linear structure have larger $<S^2>$ than branched clusters, when the number of prepolymers in the cluster is the same. The long tail in lower elution volume region is due to the contribution of the clusters with rather linear (less branched) structure than predicted by the theory.

The results in Figure 1 also suggests that for an end-linking system in post-gel state, $M_c=M_p$ is a poor approximation, and M_c is larger than M_p due to chain-extention reaction caused by the steric hindrance. Recently, several researchers (19-22) have reported that the degree of equilibrium swelling of end-linked polymer networks (in post-gel state) show the minimum not at the stoichiometric ratio for functional groups in prepolymer and crosslinker ($r=1$, the definition of r is given in Appendix), but at $r>1$. This result means that model network with the least number of dangling chains (only one end of which is connected with network) is obtained under a condition of excess amount of crosslinker. (Dangling chains increase the degree of equilibrium swelling relative to the networks without dangling chains (19).) If $M_c=M_p$ holds, model network is obtained under $r=1$. It was reasonably estimated that the origin of the deviation from $r=1$ was attributed to chain-extention reaction resulting from steric hindrance around reactive sites in crosslinker (19-22). The size distribution with a longer tail in lower elution volume at higher p obtained in this study strongly supports this estimation.

Figure 2 indicates the chromatograms at five different values of p with the corresponding theoretical ones for PPG/MDI system. Since MDI is bifunctional, branching reaction does not occur, and only chain-extention reaction occurs in this system. It is found in Figure 2 that the peak of dimer in experiment is located in higher elution volume region than in theory, while any significant differences are not seen in lower elution volume region at $p\leq0.655$. The shift of peak for dimer is due to the formation of the ring structure where one end of a dimer reacts with the other end of itself. The FS model does not take formation of the ring structure into account. Polymer clusters with

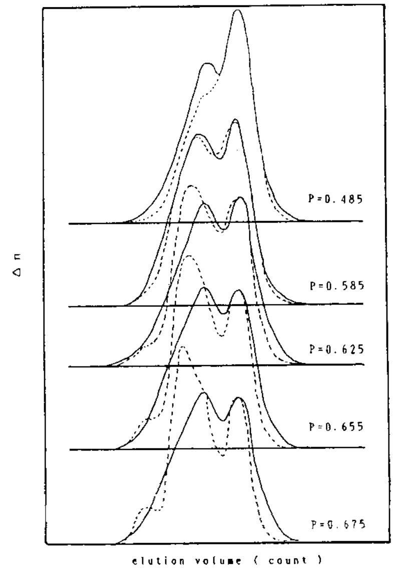

Figure 2. GPC chromatograms for PPG/MDI system. Solid and broken lines represent experimental and theoretical chromatograms, respectively.

cyclic structure have smaller $<S^2>$ than linear ones with the same molecular weight. It is also seen in the experimetal chromatogram at p=0.675 that the size distribution in larger $<S^2>$ region is shifted to lower $<S^2>$ region. This is also attributed to the formation of ring structure more than trimer. It is well-known that ring formation occurs to some extent at crosslinking in dilute systems. The system in Figure 2 (0.0135mol/l) seems to be the case. However, significant degree of ring formation is not observed in PPG/TTI system with almost the same concentration (0.0156mol/l), as seen in Figure 1. These results suggest that the system using bifunctional crosslinker might be more susceptible to ring formation than that employing trifunctional one.

Two features in comparison between experimental and theoretical chromatograms were commonly observed in crosslinking systems in the present and previous studies: (1)Size distribution of clusters at lower conversion is well described by FS model; (2)Experimental size distribution of clusters at higher conversion is broader than theoretical one because of the contribution of clusters with large size not expected by FS model. This implies that the above two features seems to be common for crosslinking systems prepared by use of bifunctional monomer and multifunctional crosslinker regardless of molecular weight of bifunctional monomer. The size distribution of clusters obeys the prediction by FS model, as long as the degree of conversion is so low that the reactivity of functional groups in crosslinker is not influenced by the steric hindrance. At higher conversion, steric hindrance becomes so significant that the reaction for the clusters to link linearly is preferable to branching reaction. The tendency of clusters to connect linearly should be unavoidable due to steric hindrance in the reacted crosslinker, as long as the crosslinker has no spacers linking functional groups with the core. If one employs a star-shaped crosslinker which has functional groups at the ends of long arms, the steric hindrance in reacted crosslinker will be diminished, and the experimental size distribution at higher conversion may be close to theoretical prediction by FS model.

Appendix

Relation between p and w_0 based on the Flory-Stockmayer model

Flory and Stockmayer (8-10) treated the crosslinking system between N pieces of f-functional crosslinker (Cf), L pieces of bifunctional crosslinker (C2) and S pieces of bifunctional monomer (P). Here, it is assumed that the reaction does not occur between Cf and C2. Stockmayer (8,9) derived the expression for the number of (n,l,s)-mer (m_{nls}) composed of n pieces of Cf, l pieces of C2 and s pieces of P in reaction bath at p as follows.

$$m_{nls} = \frac{A \; w_{nls} \; \xi^n \; \eta^l \; \zeta^s}{n! \; l! \; s!} \tag{1}$$

where $\xi = pr\rho(1-p)^{f-1}/f(1-rp)$, $\eta = pr(1-\rho)(1-p)/2(1-rp)$, $\zeta = p(1-rp)/2(1-p)$ and $A = fN(1-p)(1-rp)/pr\rho$. w_{nls} is the number of ways to form (n,l,s)-mers given by

$$w_{nls} = \frac{f^n 2^l 2^s (fn-n+l)!s!}{(fn-3n-l-s+3)!(s-n-l+1)!} \tag{2}$$

Here, r is the ratio of functional groups in crosslinker to those in monomer in preparation as

$$r = \frac{fN+2L}{2S} \tag{3}$$

and ρ is the ratio of functional groups in Cf to those in Cf and C2 as $\rho = fN/(fN+2L)$. Functionality of crosslinkers used in this study (TTI and MDI) was 2.7 and 2.0, respectively. In the case of PPG/TTI system, we defined the number ratio of C2 to Cf as 3/7 with f=3, considering that the functionality of TTI used is not exactly equal to 3. For PPG/MDI system, N=0 is used (i.e., the number of Cf is zero). The value of r is 1 from the experiemental condition in this study. The degree of conversion p is defined by the ratio of reacted functional groups in C1 and C2 to the total ones as follows.

$$p = \frac{N+L+S-M}{fN+2L} \tag{4}$$

where M is the total number of clusters in system.

We evaluated w_0 from the area ratio of the peak of unreacted PPG (i.e., (0,0,1)-mer) to the total one in experimetal GPC chromatograms. The value of p was determined from Eq. 1 with w_0 of (0,0,1)-mer.

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