Macromolecules 1988, 21, 756-764

Epoxy Network Structure. 4. A Neutron Scattering Study of Epoxies Swollen in a Deuteriated Solvent

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Received May 26, 1987; Revised Manuscript Received September 18, 1987

ABSTRACT: The molecular network structure of epoxy specimens made from diglycidyl ether of bisphenol A and linear diamines of a poly(propylene oxide) chain was investigated using neutron scattering. Deuteriated acetone was used to swell these epoxies and to provide the scattering contrast. The molecular weight of the diamines was chosen to be the experimental variable in the present work. The swelling ratio as well as the scattering intensity of these epoxies in the small q (<0.18 Å^{-1}) region was found to increase with the average molecular weight of the diamines. For those specimens composed of two diamines of different molecular weight, the swelling ratio and the glass transition temperature were intermediate between those values of the single diamine containing specimens. For most cases, the scattering results on an absolute scale could be fitted quantitatively with an equation of Lorentzian form. The implications of this finding in terms of the homogeneity of the epoxy network are discussed. A scattering maximum was observed in the samples containing two diamines of different molecular weights at *an equal mole ratio*. This observation suggested the existence of a regular spacing between regions of different swelling ratio within an average molecular network. A semiquantitative equation based on a molecular network model with a regularly alternating block is chosen to account for this observed maximum.

Introduction

The question regarding the homogeneity of the molecular network in cross-linked polymers has been a long standing one. In this work, we try to address this problem with epoxies as an example. The scheme used to explore the homogeneity question is to swell the cross-linked polymers with solvents, followed by the determination of the distribution of the solvent molecules within the network.

Diglycidal ether of bisphenol A (DGEBA) was the epoxy monomer used and Jeffamine of different molecular weights was the curing agent. (Jeffamine is a tradename of Texaco Chemical Co. Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply necessarily the best available for the purpose.) Deuteriated acetone was used to swell the cured epoxies and to provide the scattering contrast. Neutron scattering was the technique for determining the distribution of the solvent molecules.

It was found that the neutron results from the most swollen epoxies could be fitted by an expression of Lorentzian form; an indication that no gross segregation existed between the polymer and the solvent. A quantitative relation between the scattering results and the homogeneity of the network is derived in the Theory section of this work. A comparison between the theory and the experimental results is given in the beginning of the Results and Discussion section.

The only swollen sample to show a scattering anomaly was the one cured with a mixture of long- and short-chain diamines at *an equal mole ratio*. A scattering maximum was observed. As reported in a previous publication,[1] the neutron scattering result of a partially deuteriated DGEBA cured with the two diamine mixture at an equal mole ratio exhibited a scattering peak located in a q region smaller than that of specimens cured with either of the two diamines alone. The magnitude of the scattering vector q is defined as $4\pi \sin \theta/\lambda$, where θ and λ have their ordinary meaning. Based on the above observation we proposed a tentative model regarding the disposition of the amine chains within an average network,[1] namely, that the short diamine and the lone ones were incorporated in the networks in a regularly alternating fashion as shown in Figure 1.

In this work we attempt to determine whether the type of regularly alternating network shown in Figure 1 can result in the anomalous scattering maximum in a swollen state. In the theoretical section a semiquantitative interpretation of this scattering maximum from swollen samples is given by using a theoretical framework developed elsewhere[2] for block copolymers in solution. In a qualitative sense, the scattering maximum is attributed to the difference in the excluded volume or the second virial coefficient between chains of different molecular weight. The short chains between cross-links have a greater excluded volume than the long ones. More explicitly, within an average network, the regions occupied by a short diamine chain have less deuteriated solvent than the regions with long-chain diamines. It is this difference in the local solvent concentration that gives rise to the scattering contrast.

The above notion regarding the solvent concentration is based on an intranetwork viewpoint; only the segments within the same network are taken into consideration. In reality, the local solvent content or swelling ratio is determined by the length of all the chains existing around the location under consideration. Within a small volume element, only a portion of these chains is chemically connected and the rest constitutes the physical neighbor.[3] We further assume that the physical neighbors of a short-chain amine can be either a long- or a short-chain diamines, the probability depends on the volume fraction of the respective species—a typical mean-field approximation. Therefore, the difference in the local swelling ratio between two regions which are occupied by a long-chain diamine and a short one must be smaller than that between the intrinsic swelling ratios of these epoxy specimens made

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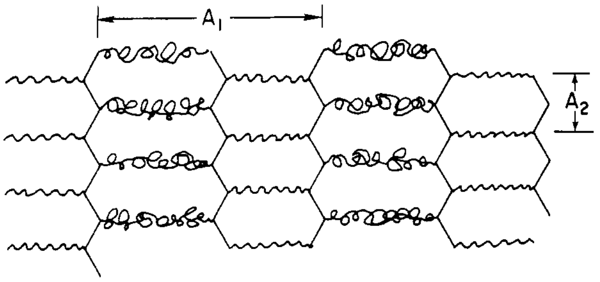

Figure 1. Schematic representation of an idealized epoxy network with regularly alternating short and long diamines: (∿) D-230 chains, (ꝏ) D-2000 chains, and (—) epoxy chains.

from a single diamine. In other words, the difference in the local swelling ratio is modulated by the internetwork contribution.

Qualitatively, an analogy can be drawn between the present case and diblock copolymers in bulk. Given that one of the blocks is deuteriated, the neutron scattering maximum is due to the intramolecular scattering contrast; the intermolecular contribution does not enhance the contrast since all the chains are packed at random. No interchain correlation except the incompressibility requirement exists as long as the interaction parameter between these two blocks is sufficiently small.[4] In the present case, for a given network the portion containing long diamine chains can be regarded as the deuteriated block since more deuteriated solvent is likely to exist in its vicinity after swelling. For a quantitative treatment, the difference in the swelling ratio is treated as a difference in terms of the excluded volume which is a function of the intrinsic swelling ratio and the interaction parameter χ between the polymer and the solvent.[5]

In order to measure the excluded volume between the chains of different length in the presence of a solvent, a theoretical expression is derived in this work to relate the macroscopic swelling ratio and the excluded volume. In addition, a series of swelling measurements were also conducted with epoxy specimens composed of both long- and short-chain diamines at various ratios.

The proposed model of a regularly alternating network for the epoxy cured with a mixture of long- and short-chain diamines at an equal mole ratio seems rather unusual. Since the molecular weight of the diamine is not expected to have any effect on the reactivity of the reacting end groups, one expects to see a randomly alternating network structure.

A conjecture based on a kinetic reason was proposed as the origin of this regular structure in a previous publication.[1] Experiments using infrared (IR) measurements on the curing rate of individual diamines with a stoichiometric amount of DGEBA were conducted. The results tend to provide partial support for the notion that this type of regular structure is caused by a difference in curing rate between these diamines of different chain length. These IR results will also be presented in this work.

To ensure that the epoxies cured with a mixture of diamines of different chain length are of one phase, i.e., do not contain domains of pure long- or short-chain diamines, the glass transition temperature T_g of these samples was measured by using different scanning calorimetry (DSC). The DSC results and the measurement procedure are also included in this work.

Throughout this work, the terms inter- and intranetwork are used frequently. Such terminology could be very confusing when referring to a highly cross-linked material like epoxy; every single atom within a sample may belong to a giant network. However, these terms intranetwork and internetwork are just equivalent to the topological neighbors and physical neighbors introduced by Flory[11] for cross-linked polymers.

Experimental Section

Neutron Scattering Measurement. All the scattering measurements were carried out by using the small-angle scattering (SANS) instrument at the NBS reactor. A wavelength of 5 Å was used and the q region covered was from 0.007 to 0.20 Å^{-1}. The contributions to the scattering intensity due to background and parasitic scattering were first removed followed by the removal of the incoherent component. The incoherent component was determined from that of a solvent mixture of the same atomic composition as the epoxy specimen. Thickness and transmission corrections were also implemented for each scattering result. All of the scattering results were obtained in terms of the absolute scale. A silica standard was used for the calibration. This silica standard was calibrated against both a water and a vanadium specimen.

Specimens for Neutron Measurements. Two types of epoxy specimens were studied; one contained a single diamine and the other contained a mixture of two diamines. In all the specimens the epoxy and the diamine were mixed at their respective stoichiometric ratios and cured at 95 °C for at least 24 h. The single diamine specimens were cured with either D-2000 or D-230 Jeffamines, and the dual diamine ones were D-2000/D-230 at 75/25, 50/50, and 25/75 mol ratios. The designation number of these diamines denotes the molecular weight of each species. All these diamines were connected with linear polypropylene (PPO) chains. More details about the structure of the diamines can be found in a previous publication.[8] In general, these diamines have rather narrow molecular weight distribution; GPC results indicate that the polydispersity is below 1.1 for these materials. The number-average molecular weights for D-2000, D-400, and D-230 diamines are 1994, 390, and 225, respectively. DER332 was used as the protonated DGEBA monomer. This epoxy was recrystallized once for purification purpose and the crystal was melted at 60 °C a few hours prior to the curing process. The epoxide equivalent molecular weight of the recrystallized materials is 178.

All specimens were cured in Teflon molds with a specimen thickness of 1.0 mm. Deuteriated acetone was the swelling agent and the temperature for the swelling process was set at 50 °C to avoid cracking the specimens. The time for the swelling to reach its equilibrium was found to be a week for the D-230 specimens which was the most highly cross-linked, hence the one with the lowest diffusion coefficient. Accordingly, all the neutron measurements were taken on the specimens after at least 1 week of immersion in deuteriated acetone.

Infrared (IR) Measurements. Since one explanation that has been proposed for the alternating network involved kinetic arguments, it is of interest to examine the reactions of these systems. In particular, the effect of the diamine molecular weight on reaction rate was studied by using IR. Immediately after mixing DGEBA with the stoichiometric amount of the diamine at room temperature, the mixture was placed between a pair of KBr disks. These disks were then placed in to a IR cell maintained at the curing temperature (95 °C) throughout the whole measurement. A Perkin-Elmer 1420 IR spectrophotometer was used and more than 20 spectra were recorded automatically throughout a run of 24 h. The magnitude of epoxide absorption band at 920 cm^{-1} was monitored as a function of the curing time, and the absorption band at 1600 cm^{-1} was used to normalize all the spectra to eliminate the effect of thickness change during curing. The degree of cure (DC) was calculated from the amount of the decrease in the 920 cm^{-1} peak height in comparison with the height of the peak of the uncured specimen.

For a semiquantitative comparison between the reaction rates for these diamines of different molecular weight, only the data in the early stage of the cure are analyzed. The substitution effect within the amino might cause some difference in the reaction rate between the primary and the secondary amines. Without getting into the details of the reaction kinetics, the IR data will be analyzed merely to extract the rate constant of the primary amine by using the following relation:

$$\mathrm{d}[\mathrm{E}]/\mathrm{d}t = -k[\mathrm{E}][\mathrm{A}] \qquad (1)$$

where [E] and [A] denote the epoxide and the primary amine concentrations respectively, k is the rate constant, and t is time. The above relation holds true only in the vicinity of $t = 0$ as the concentration of the secondary amine is negligibly small. The values for [E] and [A] are about equal in this early stage since the initial concentrations are stoichiometric and an exclusive amine–epoxide reaction is assumed. By definition, DC equals $([E_0] - [E])/[E_0]$. The solution of the above equation is $DC/(1 - DC) = k[E_0]t$, where $[E_0]$ denotes the epoxide concentration before curing. All the IR results are used to determine the reaction rate constant k for three diamines of different molecular weight used herein.

Differential Scanning Calorimetric Measurements (DSC). In order to examine any segregation that might occur between the D-2000 and D-230 portions of the molecular network inside the dual diamine specimens, the glass transition temperature (T_g) was determined by using the DSC test. The scanning rate used was 40 °C/min over a temperature range 170–400 K.

Swelling Ratio Measurement. The equilibrium swelling ratio of all the neutron scattering samples and a few additional dual diamine ones at certain intermediate compositions was determined. The weight of the specimens before and after swelling was measured and the swelling ratio in terms of volume was then calculated on the basis of the density of acetone and of the individual epoxy samples. The density of acetone was taken as 0.87 g/cm^3 and the density for the epoxy sample of different compositions was determined by measuring the sample weight while immersed in water. Protonated acetone was used throughout the swelling ratio test.

Theory

Scattering Intensity of Swollen Networks. For a swollen network or a semidilute polymer solution the change in free energy per unit volume due to concentration fluctuation $\delta\Phi/\Phi$ can be approximated as

$$F = \tfrac{1}{2}E(\delta\Phi/\Phi)^2 + \tfrac{1}{2}L(\nabla\delta\Phi/\Phi)^2 \qquad (2)$$

where Φ is the local polymer volume fraction, E is the second derivative of F with respect to Φ, and the physical meaning of L can be found in the work by Cahn and Hilliard.[6] According to de Gennes[4] the above expression can be rewritten in a Fourier space as

$$I(q) = T/(E + Lq^2) \qquad (3)$$

This is a typical Lorentzian form for the scattering intensity and T is a proportional constant relating the concentration fluctuation and the scattering intensity.

In a network at swelling equilibrium an expression for E can easily be derived by using a mean-field result of Flory[7]

$$(F/KT)_{\text{site}} = (1 - \Phi)\ln(1 - \Phi) + \chi\Phi(1 - \Phi) + 3Q\Phi^{1/3}/M^{4/3}a^3 \qquad (4)$$

where the third term accounts for the elastic energy contribution to the free energy, Q is a constant, M is the molecular weight of a blob, and a is the linear dimension of a solvent molecule. The value of M is believed to be less than the average value between chemical cross-links because the cross-linking process of the epoxies takes place in bulk instead of in dilute solution. Numerous physical cross-links seem to be inevitable in this materials. However, the magnitudes of Q, M, and a have no consequence on the value of E since these quantities will be eliminated in the final expression by introducing the condition of swelling equilibrium: $\partial(F/\Phi)/\partial\Phi = 0$.

After replacing $\ln(1 - \Phi)$ by an expansion series and carrying out a simple manipulation, the second derivative of F with respect to Φ at swelling equilibrium has the following expression:

$$\partial^2F/\partial\Phi^2 = 1/(1 - \Phi) - \tfrac{1}{6} - 5\chi/3 \qquad (5)$$

It is well-known that the scattering intensity at its $q = 0$ limit is equal to the inverse of the second derivative shown in eq 5. This is also consistent with the relation shown in eq 3 since the quantity E is proportional to the second derivative of F. Accordingly, eq 3 can be rewritten as

$$[I(q)/\Delta b^2]^{-1} = [1/(1 - \Phi) - \tfrac{1}{6} - 5\chi/3](1 + \xi^2q^2) \qquad (6)$$

where ξ^2 is defined as L/E and is the square of the correlation length of the concentration fluctuation.[5] Δb^2 is the square of the difference in the scattering length between the deuteriated solvent and the protonated polymer.

The above equation is derived on the basis of a mean-field approximation that the disposition of the chains within the solution is homogeneous. In a highly cross-linked system such as epoxies, additional heterogeneities arise from at least the following two sources: (1) the possible uneven distribution of chemical cross-links throughout the specimens; (2) the enhancement in the polymer segment density around the chemical cross-link points in a swollen material. As long as the size scale of these heterogeneities is close to the correlation length ξ, eq 6 can still be written as

$$[I(q)/\Delta b^2]^{-1} = [1/(1 - \Phi) - 2\chi'](1 + \xi^2q^2) \qquad (6a)$$

where χ' can be regarded as a curve-fitting parameter to account for the additional scattering intensity due to these heterogeneities in addition to the concentration fluctuation of a homogeneous polymer solution. As a result, the value of χ' can be greater than $5(\chi + 0.1)/6$ and the difference can be regarded, to some extent, as an index of the network heterogeneity.

For polymer networks swollen in solvent, the equilibrium swelling ratio $1/\Phi$ is related to the molecular weight through eq 4. More explicitly,

$$1/\Phi = Q^{-0.6}(1 - 2\chi)^{-0.6}M^{-0.8}a^{-1.8} \qquad (7)$$

The above relation was first derived by Flory,[7] also known as the C^* theory.[4]

The quantity $1/(1 - \Phi) - 2\chi'$ of eq 6a can also be regarded as the excluded volume between the chains of molecular weight M within semidilute solutions mentioned in the recent work by Benoit and Benmouna.[5] In an epoxy network composed of two diamines of different sizes but the same chemical composition as shown in Figure 1, three excluded-volume parameters can be defined; they are v_{11}, v_{22}, and v_{12}. Let the indices 1 and 2 refer to the long- and the short-chain diamines, respectively; thus v_{12} denotes the excluded volume between a long and a short chains, v_{11} is that between two long chains, and so forth. For v_{11} and v_{22}, the following expression is apparent:[4]

$$v_{ii} = v_s[1/(1 - \Phi_i) - 2\chi'] \qquad (8)$$

where Φ_i is the equilibrium volume fraction of the epoxy containing the diamine type i only, and v_s is the molar volume of the solvent. As to the magnitude of v_{12}, no theoretical development is yet available. Therefore, some results of swelling experiments will be used in the later part of this work to provide an empirical relation for v_{12} in terms of the other two excluded volumes and the macroscopic swelling ratio of the dual diamine containing samples. With the definition of the excluded-volume parameters v_{ij} given in the above paragraphs, we now proceed to treat the scattering problem of a swollen network of regularly alternating blocks. The relation among the swelling ratio and v_{ij}'s will be treated thereafter.

In the following section the relation between the scattering intensity and the excluded volume will be presented

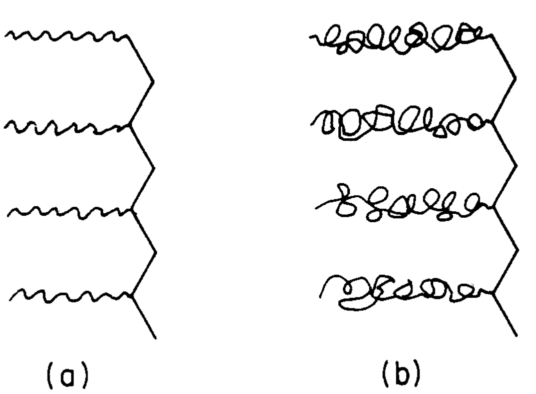

Figure 2. Idealized network was divided into two building blocks: (a) containing the short (〰) D-230 chains, (b) containing the long (➰) D-2000 chains.

for the deuteriated solvent swollen epoxy whose basic structural entity is the network shown in Figure 1. Even the chemical composition of the long- and the short-chain portions of the network is the same; one can still treat this problem as if the network is made of two different species 1 and 2. In other words the present problem can be considered as equivalent to diblock copolymers in solution. The expression for the scattering intensity for such a case has already been solved elsewhere.[2] By letting the scattering cross sections of both blocks be identical, one has the following expression for the scattering intensity:

$$I(q)/\Delta b^2 = [X_{11}(q) + X_{22}(q) + 2X_{12}(q) + (v_{11} + v_{22} - 2v_{12})(X_{11}(q)X_{22}(q) - X_{12}^2(q))]/[1 + v_{11}X_{11}(q) + v_{22}X_{22}(q) + 2v_{12}X_{12}(q) + (v_{11}v_{22} - v_{12}^2)(X_{11}(q)X_{22}(q) - X_{12}^2(q))] \quad (9)$$

where $X_{11}(q)$ denotes the Fourier transform of the intranetwork correlation function between the part of network made of long chain amines. The other two $X_{ij}(q)$s have a similar meaning. For the present case, the portions 1 and 2 of an average network are given in Figure 2, all the epoxy linkages are evenly divided into these two portions. Equation 9 clearly demonstrates that the total scattering intensity consists of two parts: (1) the one from the whole network as expressed by $X_{11}(q) + X_{22}(q) + 2X_{12}(q)$; (2) the one caused by the difference in the excluded volume as expressed by these terms preceded by either $v_{11}v_{22} - v_{12}^2$ or $v_{11} + v_{22} - 2v_{12}$. The contrast factor Δb^2 of eq 9 accounts for the difference in the scattering cross sections between the deuteriated solvent and the epoxy network.

The details involved in the calculation of these three X_{ij}s are almost identical with what was reported elsewhere.[8] The only difference is the definition of the unit cell and the corresponding lattice. These two structural entities are needed to specify the contour length of the network as described in a previous work.[8] Figure 3 demonstrates the unit cell and the lattice for the calculation of $X_{11}(q)$. The average over the molecular weight and the chain orientation of this correlation function can be written as

$$X_{11}(q) = \langle f_1(q)^2\rangle + \langle f_1(q)\rangle^2\langle \sum\sum \exp(-qr_{ij})\rangle \quad (10)$$

where $f_1(q)$ denotes the form factor of segment 1 of Figure 3a about its center of mass. The term with a double summation stands for the Fourier transform of the lattice of Figure 3b. The distance r_{ij} between the origin and the ij node is related to the contour length l_{ij} through a Porod–Kratky approximation as described elsewhere.[8] The so-called contour length l_{ij} is defined as $(i^2A_1^2 + j^2A_2^2)^{1/2}$. The lattice for the calculation of $X_{12}(q)$ is also the same as given elsewhere[8] and will not be repeated here.

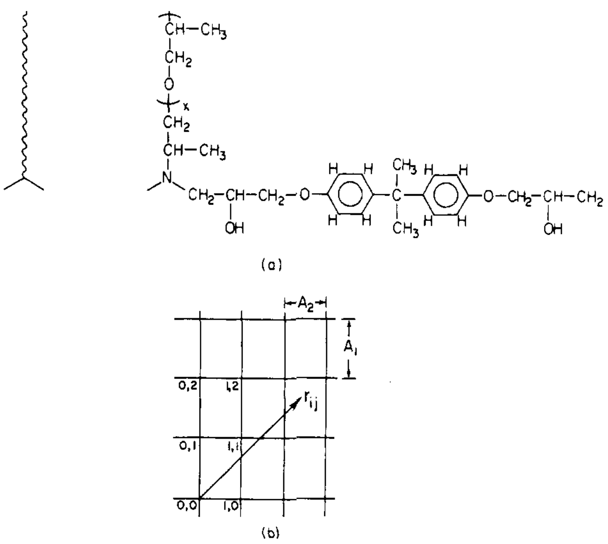

Figure 3. Each of the two building blocks was subdivided into unit cells shown in (a) and also shown was the corresponding chemical structure; $x = 3.4$ for D-230 blocks and $x = 33$ for D-2000 blocks. (b) The corresponding unit lattice.

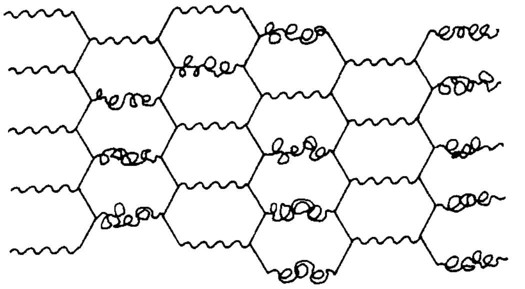

Figure 4. Certain randomization was introduced into the idealize network of Figure 1 by interchanging the two types of amines.

The alternating sequence of the long and the short amines shown in Figure 1 is highly idealized. A more realistic case is presented in Figure 4 where a certain extent of randomization is allowed. Both the long- and the short-chain unit cells thus contain a certain fraction of short- and long-chain amines, respectively. Accordingly, such randomization results in a broadening of the unit cell molecular weight; along a diamine chain direction there may be a short-chain diamine replacing a long one and vice versa. For such a case the calculation of the molecular average of the scattering function, eq 10, is even more difficult since the shape factor of the unit cell as well as the unit lattice spacing becomes molecular weight dependent. Consequently, we restrict our calculation only to the case of the idealized network in this work.

As for the form factor of the unit cell, a linear Gaussian chain approximation will still be used for the individual segment even though the chain length is rather small. The explicit forms are given as follows:

$$\langle f_1(q)^2\rangle = \langle n_1^2\rangle P_{n_1}(q) \quad (11)$$

and

$$\langle f_1(q)\rangle = \frac{12}{q^2l^2}\left(1 - \exp\left(-\frac{\langle n_1\rangle q^2l^2}{12}\right)\right) \quad (12)$$

$\langle n_1\rangle$ is the average molecular weight of unit cell of type 1 and $P_n(q)$ is the normalized Debye function of a chain with size n_1. The expressions for the unit cell of type 2 are identical with those given above. With such gross approximations used, the resultant theoretical curves can only be regarded as semiquantitative at best. The quantity

l of the above equations is the Kuhn length of the linkages constituting the epoxy network. Since the network is composed of several species of different chemical compositions, the following approximation is introduced. A Kuhn length of 5.8 Å for the PPO chain,[9] the main constituting linkage of the diamines, was used as the average one for the whole network.

The Relationship between the Swelling Ratio and v_{ij}. It is desireable to have an empirical expression for the excluded volume parameter v_{12} between chains of different length. This knowledge regarding v_{12} is essential before one can calculate the scattering intensity using eq 9. By taking the molecular weight of the solvent as unity the $q = 0$ limit of eq 6a has the following expression:

$$[I(q=0)/\Delta b^2]^{-1} = 1/(1 - \Phi) - 2\chi' \tag{13}$$

We now examine the above $q = 0$ limit from a different viewpoint; namely, we taken the $q = 0$ limit of eq 9. To do so, the $q = 0$ limits of $X_{11}(q)$, $X_{22}(q)$, and $X_{12}(q)$ need to be examined first. According to the definitions of these $X_{ij}(q)$s (eq 10), one has the following expressions for these limits:

$$X_{11}(q=0) = \Phi x_1 N n_1 \tag{14}$$

$$X_{22}(q=0) = \Phi x_2 N n_2 \tag{15}$$

and

$$X_{12}(q=0) = \Phi x_1 N n_2 = \Phi x_2 N n_1 \tag{16}$$

N denotes the number of the unit cells within a network and will drop out later, therefore it is just a dummy variable. x_i denotes the fraction of type i chains in the network. After substituting the above three equations into eq 9 and letting the zero q limit of the resultant equation be equal to that of eq 13, one has the following relation for the case of large N:

$$1/(1 - \Phi) - 2\chi' = x_1^2 v_{11} + x_2^2 v_{22} + 2x_1 x_2 v_{12} \tag{17}$$

The above expression is consistent with the definition of v_{11} and v_{22}; by letting either x_1 or x_2 be zero, eq 17 reduces to eq 8. By recalling the definition of v_{11} and v_{22} given in eq 8, eq 9 can be rewritten as

$$1/(1 - \Phi) = x_1^2/(1 - \Phi_1) + x_2^2/(1 - \Phi_2) + 2x_1 x_2 v_{12} \tag{17a}$$

where Φ_1 and Φ_2 are the equilibrium polymer content in the swollen specimens containing only D-2000 or D-230 diamine, respectively. On the basis of the above equation, one can obtain an empirical relation among v_{12}, v_{11}, and v_{22} by measuring the swelling ratio $1/\Phi$ at various values of x_1 or x_2.

Results and Discussion

Scattering Intensity of Swollen Epoxies. Figure 5 shows the neutron scattering results in absolute scale for the epoxies composed of D-2000, D-230, and mixtures of the above two amine at three different ratios. As shown in this figure, all these curves can be fitted with a Lorentzian function given in eq 6a except the one made from equal mole fraction of the D-2000 and D-230 diamines; a broad and weak peak is present in a q region around 0.03 Å^{-1}. For the D-230 specimen, some excess intensity in the q region less than 0.01 Å^{-1} cannot be accounted for by using eq 6a. This excess intensity could be caused by some heterogeneities of a large size above 600 Å such as impurities. Since the D-230 specimen is the weakest scatterer among all the samples due to its low swelling ratio, the excess intensity may also arise from other causes, e.g., insufficient background substraction.

Table I
Epoxide–Amine Reaction Rate Constant Measured with IR at 95 °C

	$[E_0]k$, s^{-1}	k (arbitrary unit)
D-2000	1.85×10^{-4}	1.0
D-400	9.11×10^{-3}	1.99
D-230	1.97×10^{-3}	3.63

Table II
Summary of the SANS Results of the Acetone-d_6 Swollen Epoxies[a]

comp, DGEBA +	polym cont (Φ)	$1/(1 - \Phi) - 2\chi'$	correlation length (ξ), Å	heterogeneity param (χ')
D-230	0.706	0.422	9.0	0.53
D-230 + D-2000	0.526	1.267	11.3	0.66
D-230 + D-2000	0.472	1.760	12.3	0.66
D-230 + D-2000	0.435	2.252	9.3	0.66
D-2000	0.392	2.582	11.0	0.63

[a] Parameters are from the fit with the equation $I(q)/\Delta b^2 = (1/(1 - \Phi) - 2\chi')^{-1}(1 + \xi^2 q^2)^{-1}$.

The resultant parameters of the fitting between the experimental results and eq 6a are given in Table II. The correlation length ξ of all the specimens regardless of the composition is about 10 Å. This value is rather close to that reported by others on highly cross-linked polystyrene gel.[10] Therefore, this value of the correlation length of 10 Å may reflect the size of a solvent-depleted domain around each cross-link.

The magnitude of the scattering intensity for all the specimens increases with the solvent content as predicted by eq 6a. However, a χ' greater than 0.5 is needed for each case to accommodate the observed intensity. It is noteworthy to recall the physical meaning of χ'; χ' reflects the state of segregation of the network chain from the solvent molecules. As explained in the previous section, there are two obvious causes for an enhancement of the value of χ' above that of the traditional interaction parameter defined for the enthalpy of mixing. They are (a) solvent depletion around the cross-links and (b) heterogeneous distribution of the cross-links. By recognizing the difference between χ' and the Flory–Huggins interaction parameter χ, one should not be disturbed by the high observed values of χ'.

In the following sections, the scattering result for the swollen network made from equal mole fraction of D-230 and D-2000 diamine will be the focal point of discussion. However, the IR results of the curing kinetics will be discussed first to examine the possible cause of the block network formation. Furthermore, the DSC result will also be examined to ensure that no gross segregation occurs in the sample containing the diamines of two different sizes or molecular weights. Gross segregation means that the sample is composed of domains made of pure long- or short-chain diamines. This type of segregation has often be observed in phase segregated block copolymers, and it is exemplified by the existence of dual T_g's seen in DSC results.

IR Results of the Curing Kinetics. The values of DC for D-2000, D-400, and D-230 diamines cured with a stoichiometric amount of DGEBA at 95 °C were obtained. On the basis of eq 1 the values of DC/(1 − DC) are plotted against the cure time in seconds (Figure 6). The values of $k[E_0]$ are obtained from the initial slope of these curves on Figure 6. The results are given in Table I. These values for $[E_0]$, the initial concentration of epoxide, of these three DGEBA/diamine mixtures can be calculated based on values of 340, 225, 390, and 1994 for the molecular weight of DGEBA D-230, D-400, and D-2000, respectively. For

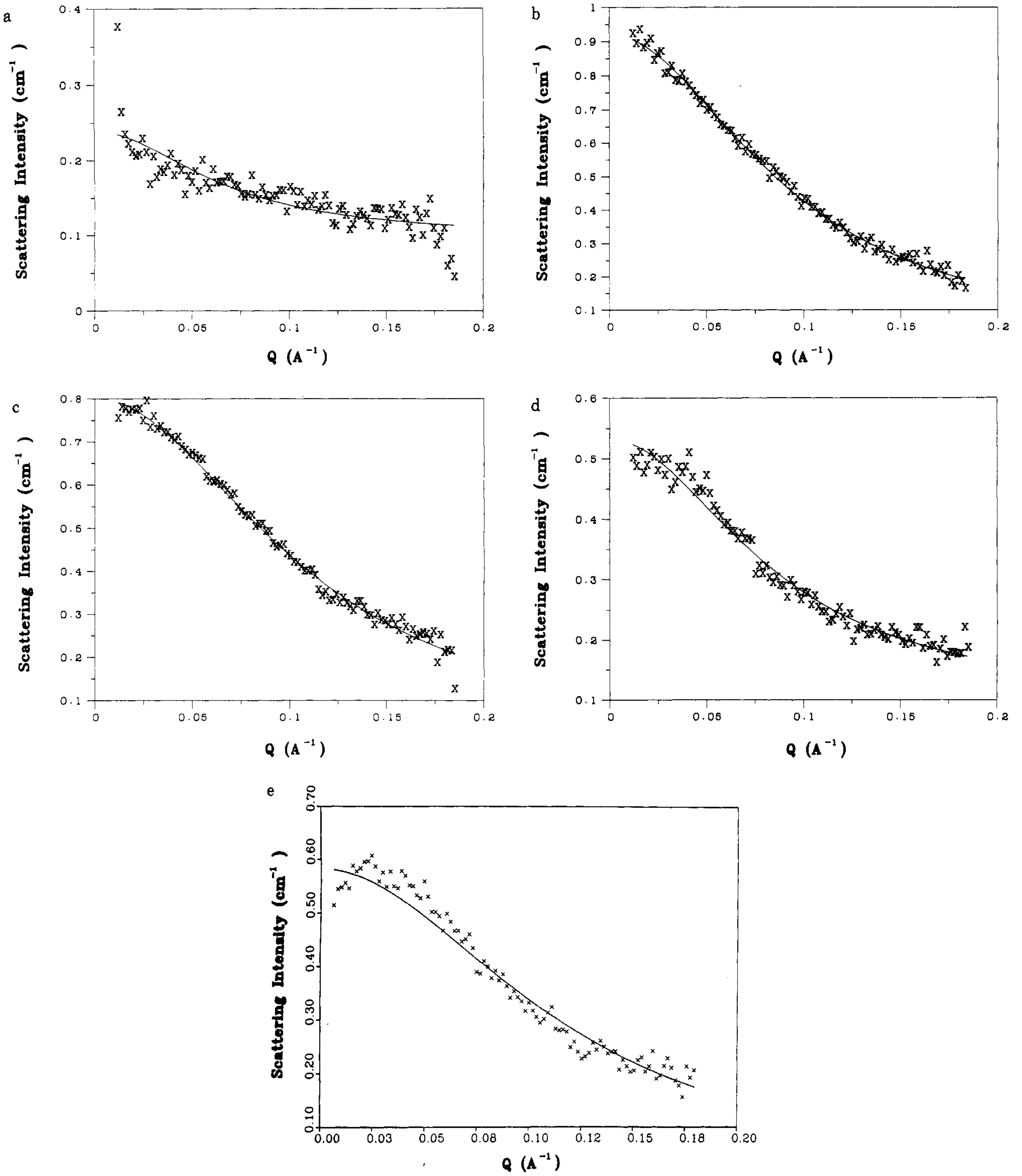

Figure 5. (a) Neutron scattering results of epoxy swollen in acetone-d_6. The epoxy was composed of DGEBA (2 mol) and D-230 diamine (1 mol) cured at 95 °C to its completion. The ordinate is the scattering intensity in the absolute scale (cm^{-1}). (b) Same as (a) except for D-2000 diamine. (c) Same as (a) except for the composition DGEBA (8 mol), D-2000 (3 mol), and D-230 (1 mol). (d) Same as (a) except for the composition DGEBA (8 mol), D-2000 (1 mol), and D-230 (3 mol). (e) Same as (a) except for the composition DGEBA (4 mol), D-2000 (1 mol), and D-230 (1 mol).

the present work only the relative values of k with respect to that for D-2000 diamine are calculated and the result is given in Table I.

A significant dependence of the rate constant k on the diamine molecular weight is obvious from Table I. However, the origin of this dependence is not clear. One possible cause is the conformation of the amine chains within the epoxy–amine mixture; the short diamine chain could be in a more expanded form compared with the long one. The long one could be in the form of a partially collapsed coil due to a finite value of the interaction parameter between the PPO chain and the DGEBA molecule, while it is more difficult for the short one to collapse simply due to its low molecular weight. The above reasoning is highly speculative, and the generality of this finding needs to be investigated with other epoxy–amine systems. The reaction rate constant k referred herein is for the primary amine. As for the rate constant for the secondary amine, the current IR data are not accurate enough for a thorough kinetics study.

A possible process for the formation of the type of network shown in Figure 1 or 4a can then be constructed

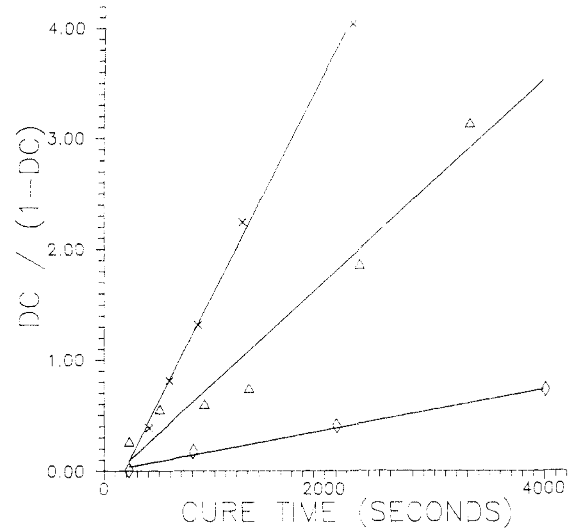

Figure 6. IR results of the curing of DGEBA (2 mol) with diamines (1 mol) at 95 °C. The ordinate is DC/(1 - DC) where DC (degree of cure) is defined as the ratio between these amounts of reacted epoxide ([E$_0$] - [E]) to the original epoxide content [E$_0$]. The abscissa is the cure time in seconds: (◇) D-2000; (△) D-400; (×) D-230.

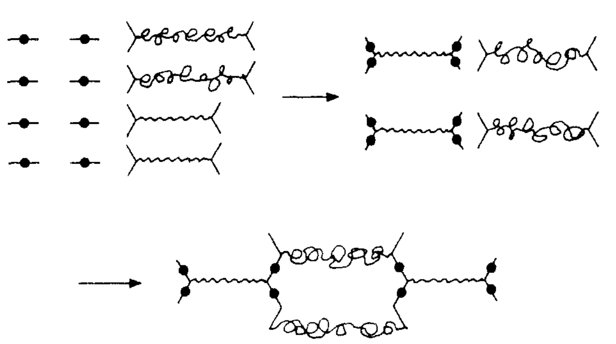

Figure 7. Possible explanation based on the curing kinetics for the formation of the idealization network structure of Figure 1. All the epoxy was reacted first with the short amines followed by the reaction with the longer ones: (-●-) epoxy monomer, (〰) D-230 diamine, and (➰) D-2000 diamine.

based on the kinetic data of Table I for the sample of equal mole of D-2000 and D-230 diamines. Figure 7 demonstrates such a mechanism in a simplified version. Due to its high reaction rate, half of the epoxide ends reacts with the D-230 amines as the first phase of cure until all the D-230 monomers are consumed. This is followed by the second step of the cure; the D-2000 amines react and connect all the D-230 and epoxy complexes. The implicit assumption of the process shown in Figure 8 is that the reaction rate of the second epoxide group is slower than that of the first one; once one end of a epoxy monomer is connected with an amine end, the reaction rate of the other end gets retarded. Such an additional assumption is required for the formation of a regular alternating block structure. Without such an assumption the gross difference in the reaction rate of the amines of different molecular weight will still result in a random structure. At present time no experimental evidence is available to substantiate the above assumption regarding the reaction rate of the epoxy monomers.

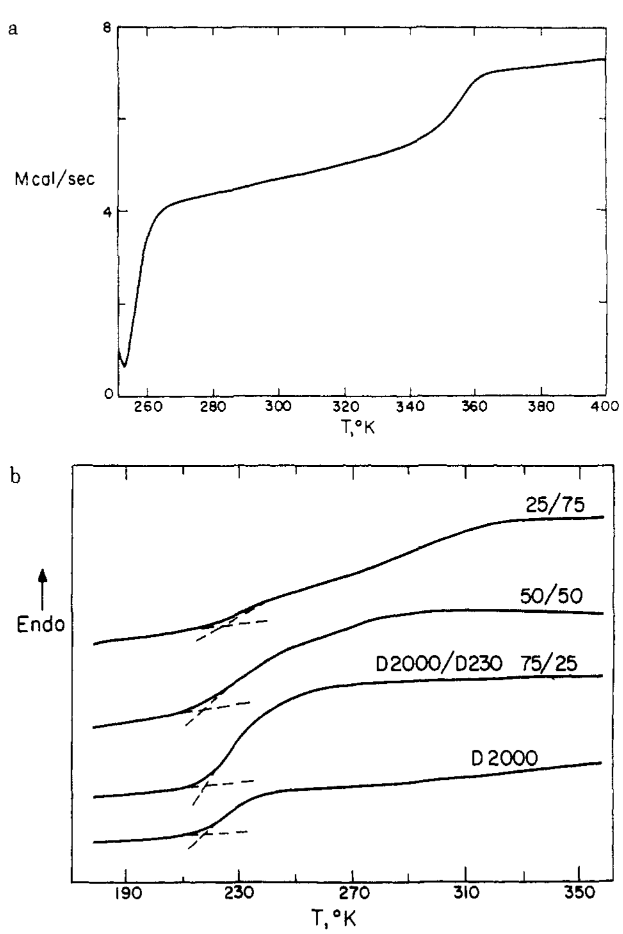

Figure 8. (a) DSC results of epoxy composed of DGEBA (2 mol) and D-230 (1 mol) cured at 95 °C to completion. Scan rate was 40 °C/min. (b) Same as (a) except for the amine compositions as denoted on the individual curves.

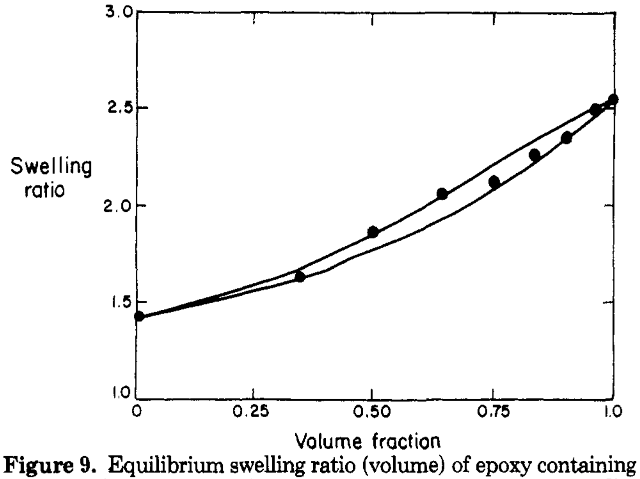

Figure 9. Equilibrium swelling ratio (volume) of epoxy containing D-230 and D-2000 diamines at various ratios in acetone. The abscissa is the volume fraction between these two diamines. The data at the origin are for the 100% D-230 diamine specimen, and the right-most data are for the D-2000 specimen. The dotted lines are the fit for $v_{12} = v_{11}^{t} v_{22}^{1-t}$ with $t = 0.33$ for the upper curve and $t = 0.15$ for the lower one.

Differential Scanning Calorimetric Measurement Results. To determine the compatibility of the diamine molecules of different size within the fully cured epoxies, DSC measurements were conducted on these specimens. The result for a fully cured epoxy made of D-230 amine alone is given in Figure 8a; the glass transition temperature, T_g, was found to be 85 °C. For the epoxies containing a certain amount of D-2000 amine, the DSC results are given in Figure 8b. It is evident from these results that no gross segregation occurs between these two diamines chains, otherwise one would detect two distinct transitions which are about 125 °C apart. Instead, a gradual transition is observed and the incipient temperature coincides with the T_g of the epoxy containing only D-2000 amine.

Swelling Ratio and Its Dependence on the Diamine Chain Length. The swelling ratios of epoxies containing the stoichiometric amount of diamine are given in Figure 9. Acetone was used as the swelling agent and the diamines were the mixtures of D-2000 and D-230 of various ratios. A nonlinear relation exists between the swelling ratio and the diamine composition reported as a volume fraction. Based on eq 17a, the results of Figure 9 are analyzed to provide an empirical relation for v_{12}. By letting

$$v_{12} = v_{11}{}^{t} v_{22}{}^{1-t} \qquad (18)$$

the experimental results could be fitted by eq 17a with the parameter t of eq 18 between 0.33 and 0.15. The fitting results are also shown in Figure 9.

The index 1 of the above equation is assigned to the long D-2000 chains and index 2 to the D-230 ones, the value of v_{22} is thus greater than that of v_{11}. This is because the swelling ratio of the epoxy cured with short chain diamine is lower than that of D-2000. The fact that t is less than 0.5 indicates that the short chains inside a cross-linked material affects the swelling ratio to an extent greater than its volume fraction. Such a result is rather consistent with an intuitive one, namely, the presence of a few short chains inside a network can impose a significant constraint on the swelling of the whole specimen. This empirical relation for v_{12} (eq 18) will be used in eq 9 to calculate the scattering intensity for the epoxy cured with a diamine mixture of equal mole of D-2000 and D-230.

Scattering Intensity of Acetone-d_6 Swollen Epoxy Containing Equal Moles of D-2000 and D-230 Diamines. The scattering result of the deuteriated acetone swollen epoxy specimen containing equal moles of D-2000 and D-230 diamines was given in Figure 5e. This scattering curve differs from the others on the same graph by the presence of a broad maximum at $q = 0.03$ Å^{-1}. The unit cell dimension along the amine chain in the bulk was estimated from the peak position observed in the bulk sample with partially deuteriated DGEBA,[1] and the value was around 0.07 Å^{-1}. This value corresponded to a distance of 90 Å. The swelling ratio of this material was found to be 2.12 as given in Table II. Assuming an affine deformation for the cross-links upon swelling, this results in a value of 115 Å for the value of A_1 in eq 10. The second peak position of 0.35 Å^{-1} observed in the bulk sample made from the partially deuteriated DGEBA[1] reflects a distance of 18 Å which was taken as the mean value of the unit cell along the epoxy linkages. After swelling this value increases to 23 Å, which was taken as A_2. The value of P, the persistence length as defined elsewhere,[8] was set to be 300 Å as before.

The values of Φ_1 and Φ_2, the equilibrium polymer content in the swollen epoxies containing D-2000 and D-230 diamines, respectively, are needed to calculate v_{11},v_{22} and v_{12} by using eq 8 and 18. As given in Table II, 0.39 and 0.71 are assigned for Φ_1 and Φ_2, respectively.

The scattering contrast factor Δb^2 of eq 6 is calculated based on the average scattering cross section of the epoxy and that of the deuteriated acetone. Given that the density of the epoxy of this composition is 1.09 and 0.96 for deuteriated acetone, the calculated value for Δb^2 per mole volume of acetone is 0.353 cm^{-1}.

By substitution of all the above values in eq 6 and letting χ' be a curve-fitting parameter, the results are shown in Figure 10. A broad maximum is the common feature for all these curves regardless of the value of χ'. This observation indicates that the difference in the excluded volume between the linkages of different length can indeed result in a scattering maximum as long as these linkages are arranged in a regularly alternating sequence. Furthermore, by comparing the peak heights for the calculated results with the observed one (Figure 5e), it seems that the appropriate value for χ' is about 0.5–0.55. This value is also found to be close to the results for the homogeneous network swollen in acetone-d_6 (Table II).

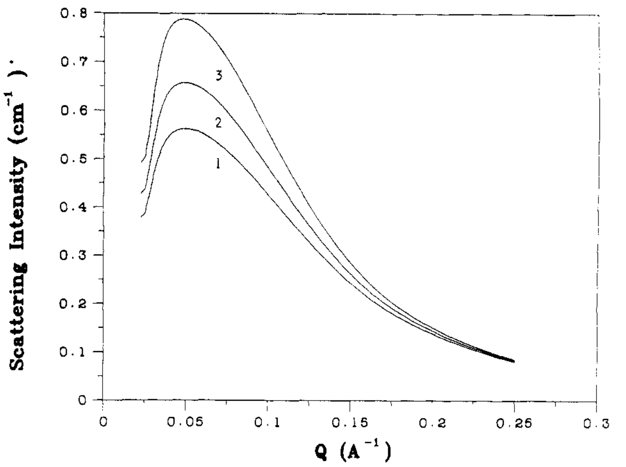

Figure 10. Theoretical neutron scattering curves for epoxy swollen in acetone-d_6. The epoxy is made from DGEBA (4 mol), D-230 (1 mol), and D-2000 (1 mol). These three curves (1, 2, 3) were calculated by using eq 9 with $\chi' = 0.5$, 0.55, and 0.6, respectively.

There are some obvious discrepancies between the calculated results and the observed data, the severe ones are the position and the sharpness of the maximum. The experimental one is located at $q = 0.03$ Å^{-1} where the calculated one is at 0.05 Å^{-1}, furthermore the calculated maxima are well defined while the experimental one is not pronounced at all. These difference may originate from the fact that a highly regularly alternating block structure is assumed in this model. The major obstacle in taking some randomization of the connection sequence into consideration comes from the molecular weight dependence of the term $v_{11}v_{22} - v_{12}{}^2$ in eq 9.

The values used for all three v_{ij}s are the ones for the monodispersed molecular weight, no provision is built into eq 9 for the case that the D-2000 or D-230 chains substitute for each other within unit cells at certain location with a finite probability as shown in Figure 4. In reality, such a randomization seems to be an inevitable consequence for the amine and epoxy reaction discussed herein. It also seems reasonable to believe that the difference in the local swelling ratio or local acetone-d_6 content gets enhanced over the ideal case of Figure 1 for the following case. Between the regions where several long amine chains are connected and where several short ones are connected, the scattering contrast as well as the periodicity must be enhanced. In other words, the scattering is dominated by those parts of a network where a string of, instead of one, long or short diamine chains occurs. This will also move the scattering maximum to lower q corresponding to a longer periodicity which encompasses several D-2000 and D-230 diamines instead of one D-2000 and one D-230 chain as in the ideal case. Even with the presence of some gross discrepancies between the calculated and the observed ones, this work still demonstrates, for the first time, that a scattering maximum can arise from the intranetwork correlation among chains of different length. The current model of regular alternating blocks, although it yields a scattering maximum at a q region somewhat higher than the observed one, does result in a scattering maximum of a right magnitude.

Conclusions

The possible cause of the formation of an epoxy network with a regularly alternating long and short diamine chains is explored. The IR results indicate that the rate constant for the epoxy and primary amine reaction depends on the diamine molecular weight. The rate constant increases as the molecular weight of the diamines decreases. However, the molecular weight dependence of the rate constant by itself can only provide a partial explanation for the formation of the observed structure. The DSC results indicate that the samples containing two diamines of different molecular weight are single-phase materials.

The scattering results of the acetone-d_6 swollen epoxies can be quantitatively fitted with one Lorentzian function, and the correlation length is about 10 Å regardless of the diamine size. However, the high value of χ' needed to fit the data again indicates the heterogeneous nature of the gel structure; the χ' obtained is found to be greater than 0.5. Once again, χ' shall not be regarded simply as the interaction parameter between acetone-d_6 and the epoxy network chains. Rather, it is an index denoting the extent of heterogeneity of solvent distribution throughout the specimen. The heterogeneity of the network in terms of the spatial distribution of the cross-links can result in a high χ' value as observed.

The broad scattering maximum observed in the acetone-d_6 swollen epoxy containing an equal mole of D-2000 and D-230 diamines can be interpreted with a regularly alternating block structure in an intranetwork sense. Within an average network the D-230 and D-2000, diamine chains were situated in a regularly alternating fashion. A semiquantitative explanation is provided by using the excluded-volume concept to account for the scattering maximum observed. However, the theoretical work is derived for a highly regular structure, the possible randomization of the regular alternating sequence is not included in this current treatment. Consequently, the fit between the calculated and the observed results is only marginal.

Acknowledgment. We are grateful to C. J. Glinka and J. Gotaas for their help in the neutron measurements. Two of the authors (Yang and Stein) would like to thank CUMIRP for its financial support of this work.

Registry No. (D-230)(DER 332) (copolymer), 112320-38-4; neutron, 12586-31-1.

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Free Energy Change in Hydrophobic Interactions Involving a Polyelectrolyte and Ruthenium Tris(bipyridine). A Pulsed Laser Study

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ABSTRACT: Comparison between the effects of inert salts on the distribution of $Ru(bpy)_3^{2+}$ ions around three negative polyelectrolyes, poly(styrenesulfonate) (PSS), poly(vinyl sulfate) (PVS), and poly(acrylate) (PAA), is reported. Much higher ion concentrations are required in order to remove $Ru(bpy)_3^{2+}$ from PSS, as compared to removal from a PVS or PAA. Attributing the difference between these systems to the effect of hydrophobic interactions in the PSS enables the calculation of the free energy change involved in the formation of $Ru(bpy)_3^{2+}$–PSS. The results show a definite distinction between $Ru(bpy)_3^{2+}$ "inside" and "outside" the polymer, with no exchange during the lifetime of the excited state of the ruthenium tris(bipyridine), $Ru(bpy)_3^{2+*}$. The $Ru(bpy)_3^{2+}$ ions are located more deeply "inside" the PSS as compared with the PVS.

Introduction

Thermodynamic properties of hydrophobic bonds have been quantitatively treated in biological systems for many years. Thus, Klots, Walker, and Pivan[1] investigated the binding of organic ions by proteins and separated the electrostatic interactions from the hydrophobic interactions between the aromatic rings. The additional affinity due to the hydrophobic interactions was estimated in this system as 0.52 kcal. Nemethy and Scheraga[2] calculated standard free energies for interactions between two side chains of proteins as ranging between −0.2 and 1.5 kcal/mol. Several aromatic ammonium salts were reported to interact with anionic polyelectrolytes and with a neutral polymer by hydrophobic interactions.[3-6] The thermodynamics of hydrophobic interactions in biological systems has been lately discussed in detail by Ben-Naim.[7] Paramauro, Pelizzetti, and Diekmann[8] investigated the separation of electrostatic and nonelectrostatic environmental effects in redox reactions involving osmium coordination compounds observed in micelle solutions. Hydrophobic interactions between hydrophobic segments of polyelectrolytes and photosensitizers, electron donors, and electron acceptors have been extensively investigated lately. Weber[9] and Morishima et al.[10-14] employed charged co-

0024-9297/88/2221-0764$01.50/0