Epoxy Network Structure. 3. Neutron-Scattering Study of Epoxies Containing Monomers of Different Molecular Weight

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ABSTRACT: Neutron-scattering studies of partially deuterated epoxies were performed on specimens containing mixtures of amines of the same chemical repeat unit but with different molecular weights. The epoxy monomer used was a partially deuterated diglycidyl ether of bisphenol A (DGEBA), and the diamines were linear diamines of poly(propylene oxide) chains. A pronounced scattering maximum was observed in specimens cured with a mixture of diamines at a q region smaller than what observed in specimens made from any of the constituent amines alone. A molecular network model with regularly alternating blocks was the obvious choice to accommodate the scattering results. Each unit consists of two amines and two DGEBA monomers. The term "alternating" refers to the connection between the long-chain and the short-chain blocks. An analytic solution of linear Gaussian chains and rigid rods was obtained to illustrate the effect of polymer structure on the position of the scattering maximum.

Introduction

In order to elucidate the effect of the molecular weight distribution between cross-links on the physical properties of epoxies, diamines with the same composition but different molecular weight were blended and cured with a partially deuterated diglycidyl ether of bisphenol A (DGEBA). All the monomers are liquids of quite low viscosity at room temperature. Therefore, it is reasonable to assume that a homogeneous mixture can be achieved readily for the blends of these diamines and the epoxy monomer. Consequently, one will expect the distribution of the diamines of different molecular weights to be random throughout the cured specimens.

However, a set of neutron-scattering experiments has been conducted on these epoxy specimens, and the results strongly suggest that there is not a random structure. The amines of different molecular weight do not randomly position themselves within the molecular network. The experimental findings will be described first followed by a qualitative argument supporting the nonrandom arrangement of the diamines. An analytic solution for the scattering intensities of regularly alternating multiple-block copolymers of linear chains will be derived in the following section. The solutions will be given both for a flexible Gaussian chain and for a rigid-rod approximation. The analytic results of random multiple-block copolymers will also be provided in comparison with the results of regular block copolymers. Such a comparison is intended to provide indirect evidence supporting the notion of regular block structure in epoxies.

It is noteworthy that the block copolymers described in the previous paragraph have a more complex connecting sequence than the case of only one diamine. The case described here is an alternating $-A_1-B-A_2-B-A_1-B-A_2-B-$ type, where A_1 and A_2 are diamines of an identical chemical composition but different molecular weights.

Experimental Section

Specimen Preparation. As in the previous papers,[1,2] DGEBA was chosen as the model epoxy monomer in this work. To provide the neutron-scattering contrast, all the hydrogen atoms in the bisphenol A unit were replaced with deuterium. Detailed procedures for synthesizing the deuterium-labeled DGEBA can be found elsewhere.[1] Jeffamines[8] D-2000, D-400, and D-230 were used as the curing agents. The D-series amines are difunctional amines linked by poly(propylene oxide) (PPO), and the designation number refers to the approximate molecular weight of each species. The polydispersity of the poly(ether glycol) diamines is very low; consequently, these diamines can be approximated as being monodisperse.[1] The maximum cure temperature was below 110 °C for all of the specimens studied. Within this temperature range, the cure reaction is dominated by the amine/epoxide reaction. Therefore, the molar ratio of diepoxide to diamine was kept at 2:1, the stoichiometric ratio, throughout this study.

Table I
Curing Conditions, Glass Transition Temperature, and Degree of Cure of the Epoxies

curing agent	curing conditions	T_g, °C	degree of cure, %
D-230	110 °C/24 h	91.4	95.8
D-400	95 °C/24 h	52.0	95.8
D-2000	95 °C/72 h	<23	94.0
D-2000 + D-400	95 °C/48 h	<23	95.0
D-2000 + D-230	110 °C/48 h	<23	95.2

The specimens included in this work were three single-diamine-cured epoxies, and two additional specimens each contained a mixture of diamines. The single diamines used were D-2000, D-400, and D-230, and the diamine mixtures were D-2000/D-400 and D-2000/D230, both at 1:1 molar ratio. The glass transition temperatures (T_g) of all the fully cured materials were measured by using a rheogoniometer, and the results are given in Table I. The cure temperature was set at 20 °C above the T_g value for each respective composition. The epoxy monomer was heated in a 55 °C oven for 3 h to melt any possible crystalline phase. After cooling, the epoxy was mixed with the diamine, followed by a 5-min degas cycle in a vacuum of 10^{-2} torr. The amount of cure time required to achieve 95% cure was found to be composition dependent; the curing conditions of these materials necessary for a 95% cure are also included in Table I. The degree of cure was determined by using IR techniques[3] to monitor the peak height of the 920-cm^{-1} band. The cured epoxy specimens were all of disk shape, 1 mm in thickness and 20 mm in diameter.

Neutron-Scattering Measurements. All of the scattering measurements were carried out by using the small-angle neutron-scattering (SANS) instrument of the NBS reactor. A wavelength of 5 Å was used, and the q region covered was from 0.007 to 0.54 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 chemical composition as the epoxy specimen. Thickness and transmission corrections were also implemented for each scattering result. Some of the results are presented in terms of the absolute scale; for these cases a silica standard was ussd for the calibration.

For the work to be disscussed in this paper, reducing the scattering intensity to its absolute scale was not necessary since the focal point of the discussion is on the position of the main peak. However, in the forthcoming papers, an analytic solution will be provided for the scattering intensity in the absolute scale

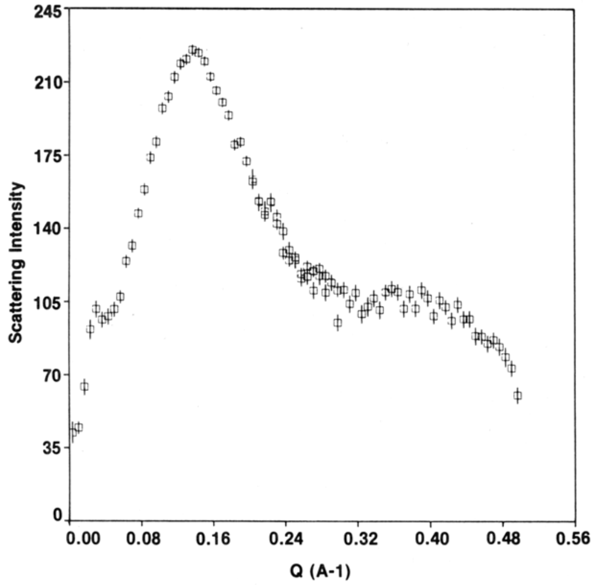

Figure 1. Circularly averaged neutron-scattering intensities of epoxy network made with D-2000 diamine.

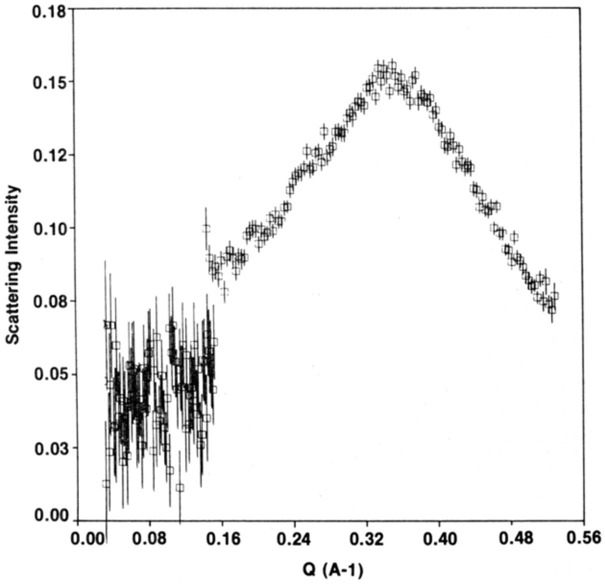

Figure 2. Circularly averaged neutron-scattering intensities of epoxy network made with D-400 diamine.

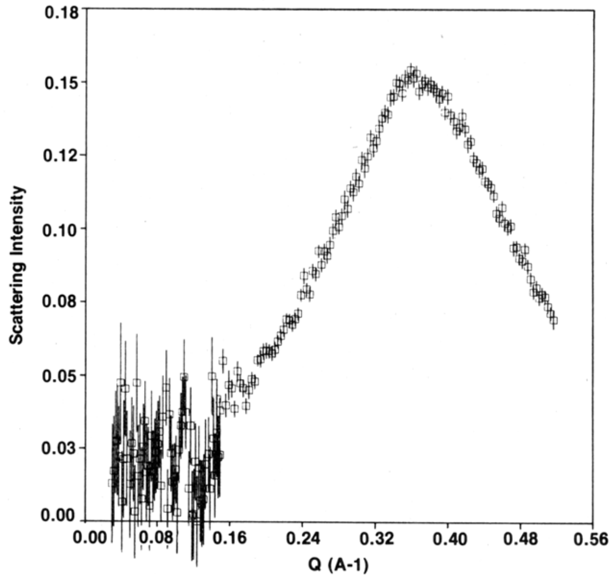

Figure 3. Circularly averaged neutron-scattering intensities of epoxy network made with D-230 diamine.

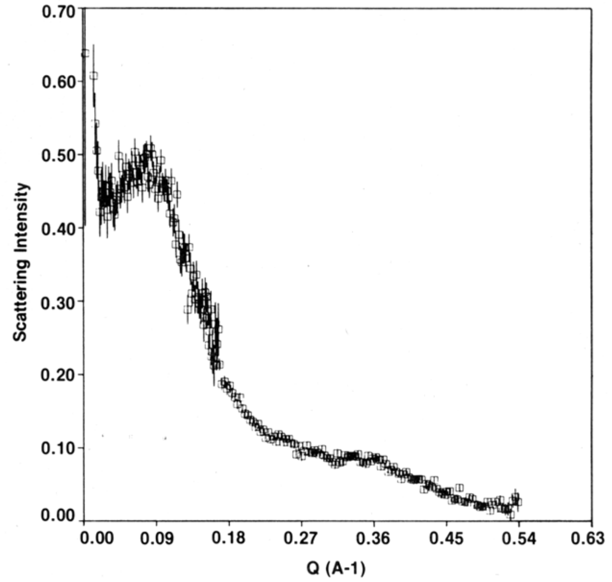

Figure 4. Circularly averaged neutron-scattering intensities of epoxy network made with D-2000 and D-400 diamines in a 1:1 molar ratio.

in order to determine quantitatively the amount of heterogeneities within these epoxies.

Experimental Results

The scattering results of these three single-diamine-cured epoxy specimens are shown in Figures 1–3. Pronounced scattering maxima are located at $q = 0.13$ and 0.4 $Å^{-1}$ for the D-2000-containing sample as previously reported.[2] For the D-400-containing sample, the peak is located at 0.35 $Å^{-1}$, and for the D-230 specimen the peak position is just slightly above that of the D-400 specimen.

The materials containing mixtures of diamines give rise to pronounced maxima as shown in Figures 4 and 5. The specimen made from DGEBA, D-2000, and D-400 of 4:1:1 molar ratio is designated D2K4H411. The one composed of DGEBA, D-2000, and D-230 of 4:1:1 molar ratio is designated D2K2H411. For both of these materials, the main peak is located at 0.09 $Å^{-1}$, and the second maximum is around 0.35 $Å^{-1}$. The position of the main peak of these two blends is much lower than that of the single-diamine specimens. It is this position of the main peaks of both D2K4H411 and D2K2H411 that raises the question of the arrangement of the diamines within the epoxy molecular network. The main peak is attributed to the correlation among the deuterated segments along the amine linkages: the higher the amine molecular weight, the lower the q where the peak located. As to the peak at $q = 0.35$ $Å^{-1}$, the correlation among the deuterated segments along the epoxy linkages is the main contributing factor. Consequently, the disposition of the amines of two different molecular weights has no bearing on the second peak; hence its existence will not be investigated in this paper.

Discussion

There is little doubt that the D-2000 diamine can be mixed homogeneously with either the D-400 or D-230 diamines since the compositions of these diamines are almost identical. Consequently, it is a natural tendency to assume that these diamines incorporate themselves into the molecular network in a random fashion. According to previous work in the scattering of block copolymers,[4,5] such a randomization will result in (a) an enhancement in the zero-angle scattering intensity and (b) the disappearance

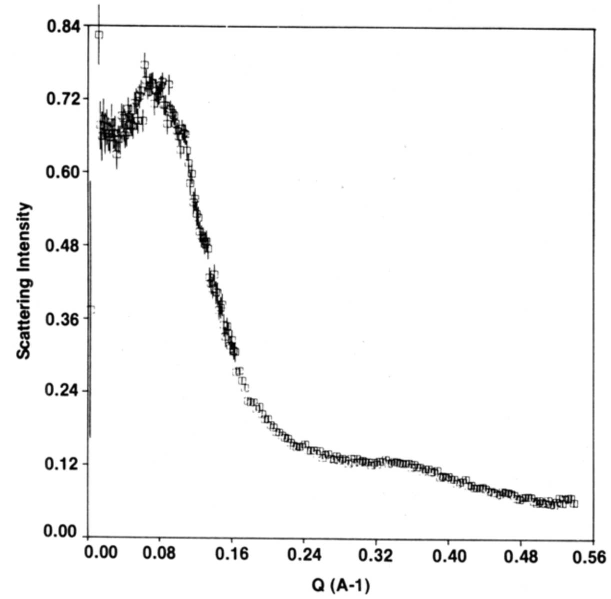

Figure 5. Circularly averaged neutron-scattering intensities of epoxy network made with D-2000 and D-230 diamines in a 1:1 molar ratio.

or shift of the main peak to the region between 0.35 and 0.13 Å^{-1}. One would expect to locate the peak, if it exists, somewhere between the main peak positions of two epoxy networks each made from one of the diamines. The results of Figures 4 and 5 clearly show that this is not the case; the main peak position is much lower than that of any of the single-diamine epoxies.

A parallelism will be drawn between the network structure of epoxies and block copolymers. There is a basic difference between these two structures; the former is topologically two- or three-dimensional, while the latter is topologically one-dimensional. Despite this difference, one still expects that the scattering behavior of block copolymers will provide a useful guide to the understanding of certain aspects of the network structure. The scattering function of a linear multiple-block copolymer will be derived in the next section. From the results of the multiple-block copolymers one can learn, in a qualitative sense, the effect of the arrangement of the two diamines of different molecular weights on the position of the main peak. In the analogy between the epoxy network and the multiple-block copolymers –A–B–A–B–A–B–, the deuterated bisphenol A is regarded as block B and the diamines are the A block. In the case of single-diamine epoxies, block A is considered as monodisperse; in the case of the epoxy containing two diamines, block A is then made of two sizes, A_1 and A_2. The present study treats only the cases where these two diamines have an equal molar ratio. This corresponds to the block copolymers composed of equal numbers of units A_1 and A_2. The disposition of A_1 and A_2 within the copolymer is, therefore, the focal point of discussion in terms of its effect on the main scattering-peak position. The main thrust of the calculations in the following sections is to demonstrate that the long periodicity depicted by the scattering results is $A_1 + A_2 + 2B$ for the case of regularly alternating block copolymers.

Before we derive the equation for the scattering of a multiple-block copolymer in bulk, it is instructive to examine the scattering of an individual rodlike block molecule of infinite molecular weight (Figure 6). In the case illustrated in figure 6b the disposition of A_1 and A_2 along the rod is completely random. To derive the expression of scattering, one can follow the scheme of Hosemann.[6] To simplify the problem further without losing the essence of the main objective, the size of block B is reduced to a point. The scattering expression can be written as

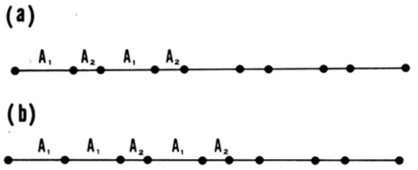

Figure 6. Arrangement of block A_1 and block A_2 along a linear chain: (a) regularly alternating; (b) random.

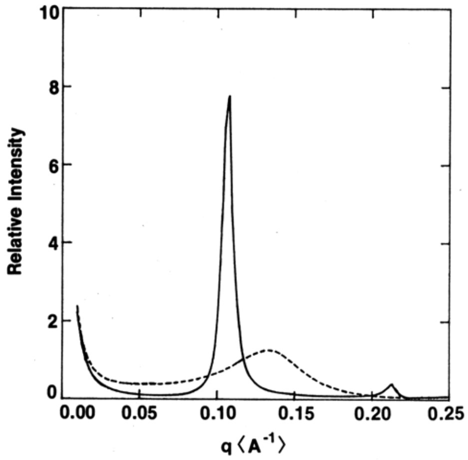

Figure 7. Scattering intensities of rigid-rod molecules with A_1 = 43 Å, A_2 = 16 Å, and ρ = 0.9: (solid line) alternating blocks; (dotted line) random blocks.

$$I(q) = 1 + \sum_{n=1}^{\infty} [(\phi_1 H(q,A_1) + \phi_2 H(q,A_2))^n + (\phi_1 H^*(q,A_1) + \phi_2 H^*(q,A_2))^n] \quad (1)$$

where ϕ_1 and ϕ_2 are the molar fraction of diamines 1 and 2, respectively, $H(q,A_1)$ stands for the Fourier transform of the position distribution function of a point connected to the origin by an A_1 chain and is approximated as ρe^{-qA_1}, and $H^*(q,A_1)$ is the conjugate of $H(q,A_1)$ accounting for block A on the left-hand side of the origin. The origin can be chosen at random since the length of the rod is infinite. ρ accounts for the fluctuation of block A around the equilibrium positions as defined by Hosemann. The value of ρ approahes unity for the case of little delocalization around the mean position. In the present case the value of both ϕ_1 and ϕ_2 is 0.5; the expression for scattering can then be reduced to

$$I(q) = [1 - 0.5\rho^2(1 + \cos q(A_1 - A_2))]/[1 + 0.5\rho^2(1 + \cos q(A_1 - A_2)) - \rho(\cos qA_1 + \cos qA_2)] \quad (2)$$

For the case of Figure 6a, the regularly alternating block, the following expression is apparent for the scattering intensity:

$$I(q) = 1 + H(q,A_1)(1 + H(q,A_2))\left(\sum_{n=0}^{\infty} (H(q,A_1)H(q,A_2))^n\right) + H^*(q,A_1)(1 + H^*(q,A_2))\left(\sum_{n=0}^{\infty} (H^*(q,A_1)H^*(q,A_2))^n\right) \quad (3)$$

After a simple manipulation, eq 3 can be reduced to

$$I(q) = 1 + [(\rho - \rho^3)(\cos qA_1 + \cos qA_2) + 2\rho^2 \cos (q(A_1 + A_2)) - 2\rho^4]/[1 + \rho^4 - 2\rho^2 \cos (q(A_1 + A_2))] \quad (4)$$

From the results reported elsewhere[2] the value of A_1, the length of the D-2000 linkage, is about 43 Å; A_2, the length

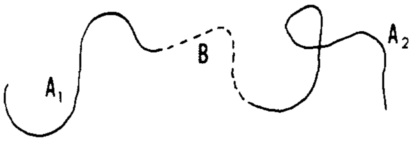

Figure 8. Representation of a triblock Gaussian chain with blocks A_1, B, and A_2.

of the D-400 and D-230 diamines, is about 21 Å. By substituting these values into eq 2 and 4 and letting ρ be 0.9, one obtains Figure 7. As expected, the first peak position in the regularly alternating block reflects the long periodicity of $A_1 + A_2$. In addition to being broader, the first peak position of a random block chain is between those of rods with a uniform block size A_1 or A_2. The peak positions of a rod with a uniform periodicity A follow the simple relation $qA = 2\pi n$.

Hereafter, the question of the scattering behavior of flexible Gaussian chains with a chemical sequence identical with those shown in Figure 6 will be addressed. We will determine whether the relationship between the peak position and the chemical sequence in rigid rods will also be preserved in the case of flexible coils. An analytic expression for bulk materials made of chains with either regularly alternating blocks or completely random ones will be derived. To begin the derivation, the correlation function of an individual triblock chain (Figure 8) will be obtained. The molecular weight of each block is n_{11}, n_{12}, and n_2 for A_1, A_2, and B, respectively. Following the lead of diblock copolymers,[4] the correlation function between blocks A_1 and A_2 can be written as

$$2X_{a_1a_2}(q) = G_{a_1ba_2}(q) - G_{a_1}(q) - G_{a_2}(q) - 2X_{a_1b}(q) - 2X_{a_2b}(q) \quad (5)$$

$G_{a_1ba_2}(q)$ stands for the Debye function of a molecular weight $n_{11} + n_{12} + n_2$, and all the rest of $G_2(q)$ in eq 5 have the same meaning. The Debye function $G_{a_1ba_2}(q)$ is related to the normalized single-chain correlation function $P_{a_1ba_2}(q)$ through a simple relationship

$$G_{a_1ba_2}(q) = (n_{11} + n_2 + n_{12})^2 P_{a_1ba_2}(q) \quad (6)$$

X_{a_1b} in eq 5 is the correlation function between two connected blocks A_1 and B, and the expression has been derived by others[4] as follows:

$$X_{a_1b}(q) = \frac{1 - \exp\left(-\dfrac{n_{11}q^2b^2}{6}\right)}{\dfrac{q^2b^2}{6}} \; \frac{1 - \exp\left(-\dfrac{n_2q^2b^2}{6}\right)}{\dfrac{q^2b^2}{6}} \quad (7)$$

b is the length of the repeat unit and is assumed to be equal for both blocks A and B. For simplification, the quantity $(qb)^2/6$ will be designated as t. After substituting eq 6 and the expression for the Debye function into eq 5, one obtains

$$X_{a_1a_2}(q) = \left(\frac{1 - e^{-n_{11}t}}{t}\right) e^{-n_2t} \left(\frac{1 - e^{-n_{12}t}}{t}\right) \quad (8)$$

Equations 5 and 8 are the basic building blocks to construct the scattering curve for the multiple-block-copolymer problem with the chemical connecting sequence presented in Figure 6. The repeat unit of the chain shown in Figure 6a is defined as $-A_1-B-A_2-B-$, and that for the chain of Figure 6b is $-A-B-$, where A can be either A_1 or A_2 with equal probability. The scattering intensity of a bulk sample made of block copolymers can be written as

$$I(q) = \frac{X_{aa}(q)X_{bb}(q) - X_{ab}^2(q)}{X_{aa}(q) + X_{bb}(q) + 2X_{ab}(q)} \quad (9)$$

The above equation has been derived by others[6] using the requirement of incompressibility. The terms $X_{aa}(q)$, $X_{bb}(q)$, and $X_{ab}(q)$ for the case shown in Figure 6a, i.e., a regularly alternating block copolymer, will be derived first. The number of repeat units is given as N; hence the molecular weight of the whole chain is $N(n_{11} + 2n_2 + n_{12})$. By the use of eq 8 the correlation among all the blocks A_1 and A_2 of Figure 6a can be summed to obtain the following expression for $X_{aa}(q)$

$$\begin{aligned} X_{aa}(q) = {} & Nn_{11}^2P_{a_1}(q) + Nn_{12}^2P_{a_2}(q) + \\ & 2\left(N - 1 - \frac{e^{-nt} - e^{-Nnt}}{1 - e^{-nt}}\right)\left(\frac{e^{-(n-n_{11})t}}{1 - e^{-nt}}\left(\frac{1 - e^{-n_{11}t}}{t}\right)^2 + \right. \\ & \left. \frac{e^{-(n-n_{12})t}}{1 - e^{-nt}}\left(\frac{1 - e^{-n_{12}t}}{t}\right)^2\right) + 2\frac{e^{-n_2t}}{1 - e^{nt}} \times \\ & \frac{(1 - e^{-n_{11}t})(1 - e^{-n_{12}t})}{t^2}\left(2N - 1 - \frac{2e^{-nt} - e^{-Nnt} - e^{-(N+1)nt}}{1 - e^{-nt}}\right) \end{aligned} \quad (10)$$

where n is the molecular weight of a repeat block and is equal to $n_{11} + 2n_2 + n_{12}$. By summing the correlation among all the block B units, one obtains the following relation for $X_{bb}(q)$:

$$\begin{aligned} X_{bb}(q) = {} & 2n_2^2\left(\frac{1 - e^{-n_2t}}{t}\right)^2\left(N - \right. \\ & \left. \frac{e^{-nt} - e^{-(N+1)nt}}{1 - e^{-nt}}\right)\left(\frac{e^{-n_{12}t}}{1 - e^{-nt}}\right) + 2n_2^2\left(\frac{1 - e^{-n_2t}}{t}\right)^2\left(N - \right. \\ & \left. 1 - \frac{e^{-nt} - e^{-Nnt}}{1 - e^{-nt}}\right)\left(\frac{2e^{-(n-n_2)t} + e^{-n_{11}t}}{1 - e^{-nt}}\right) + 2Nn_2^2P_{\mathrm{b}}(q) \end{aligned} \quad (11)$$

The cross term $X_{ab}(q)$ can be easily obtained through the relation

$$2X_{ab}(q) = (Nn)^2P_{Nn}(q) - X_{aa}(q) - X_{bb}(q) \quad (12)$$

where $P_{Nn}(q)$ is the normalized single-chain correlation function for the entire chain with a molecular weight of Nn. With eq 10–12 now available, one has all the necessary relationships to examine the scattering behavior of bulk material composed of regularly alternating block chains.

As to the randomly alternating chain of Figure 6b, the same approach used in the foregoing section will be applied to derive $X_{aa}(q)$ and $X_{bb}(q)$. The cross term $X_{ab}(q)$ will be obtained by again using eq 12, and eq 7 will also be used for the scattering intensity. The only difference in the derivation of this random block case vs. the regular one is a molecular weight average will be taken over eq 8. This average can be fractionated into three parts as follows:

$$\langle X_{a_1a_2}(q)\rangle = \left\langle\frac{1 - e^{-n_{11}t}}{t}\right\rangle \langle e^{-n_2t}\rangle \left\langle\frac{1 - e^{-n_{12}t}}{t}\right\rangle \quad (13)$$

This can be done because these three terms are independent in terms of the value of n. Within the present context n_{11}, n_{12}, and n_2 are generalized to be the molecular weight of any three connected blocks regardless of their chemical compositions. The average of eq 13 is carried out with 0.5 molar fraction of D-2000 diamine and 0.5 molar fraction of the short-chain diamine, either D-400 or D-230.

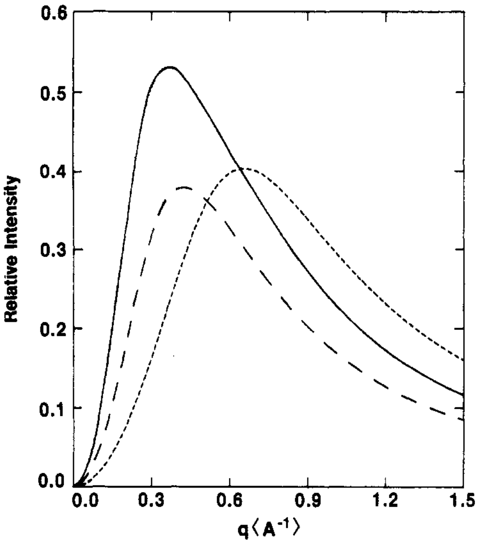

Figure 9. Scattering intensities of Gaussian chains with $N = 500$, $b = 2.7$ Å, and $n_2 = 5.7$ Å: (solid line) alternating blocks with $n_{11} = 33$ Å and $n_{12} = 6.6$ Å; (dashed line) $n_{11} = n_{12} = 33$ Å; (dotted line) $n_{11} = n_{12} = 6.6$ Å.

After summing all of the correlations of the A blocks shown in Figure 6b, one has

$$X_{aa}(q) = N(n_{11}{}^2P_{a_1}(q) + n_{12}{}^2P_{a_2}(q)) + \left(\frac{2 - e^{-n_{11}t} - e^{-n_{12}t}}{t}\right)^2\left(\left(\frac{e^{-n_2t}}{1 - e^{-(n_{11}+n_2)t}}\right)\left(2N - \frac{1 - e^{-2N(n_{11}+n_2)t}}{1 - e^{-(n_{11}+n_2)t}}\right) + \left(\frac{e^{-n_2t}}{1 - e^{-(n_{12}+n_2)t}}\right)\left(2N - \frac{1 - e^{-2N(n_{12}+n_2)t}}{1 - e^{-(n_{12}+n_2)t}}\right)\right) \quad (14)$$

The summation of the correlation among all the B blocks yields

$$X_{bb}(q) = 2Nn_2{}^2P_b(q) + \left(\frac{1 - e^{-n_2t}}{t}\right)^2\left(\left(\frac{e^{-n_{11}t}}{1 - e^{-(n_{11}+n_2)t}}\right)\left(2N - \frac{1 - e^{-2N(n_{11}+n_2)t}}{1 - e^{-(n_{11}+n_2)t}}\right) + \left(\frac{e^{-n_{12}t}}{1 - e^{-(n_{12}+n_2)t}}\right)\left(2N - \frac{1 - e^{2N(n_{12}+n_2)t}}{1 - e^{-(n_{12}+n_2)t}}\right)\right) \quad (15)$$

Equations 12, 14, and 15 are the basis for calculation of the relationship between the scattering behavior and the chemical connection of the randomly alternating block case.

To illustrate the effect of the chemical connecting sequence on the scattering peak position, a set of scattering curves is constructed based on the equations just derived. The values of n_{11}, n_{12}, and n_2 are chosen to be 33.0, 6.6, and 5.7, respectively, to approximate the degree of polymerization of the D-2000 and D-400 diamines and the deuterated DGEBA. The molecular weight of a propylene oxide unit, C_3H_6O, is taken as unity. The value of b, the length of a repeat unit, is chosn to be 2.7 Å^2 to approximate the length of a PPO linkage. For linear chains the value of b should be assigned as the Kuhn length. Its value is considerably greater than 2.7 Å as judged from the Kuhn length of the poly(ethylene oxide) chains.[7] However, the above value was chosen in a previous publication[2] to account for the fact that the segment density distribution was depleted somewhat near the cross-links. This value of b, when applied to linear chains, seems too low to yield a main peak at the correct position in q space. However, the major thrust of this work is to compare the relative peak positions of alternating block copolymers with respect to the simple block copolymers. To match the peak positions between the observed and the calculated ones is not the main concern of this work.

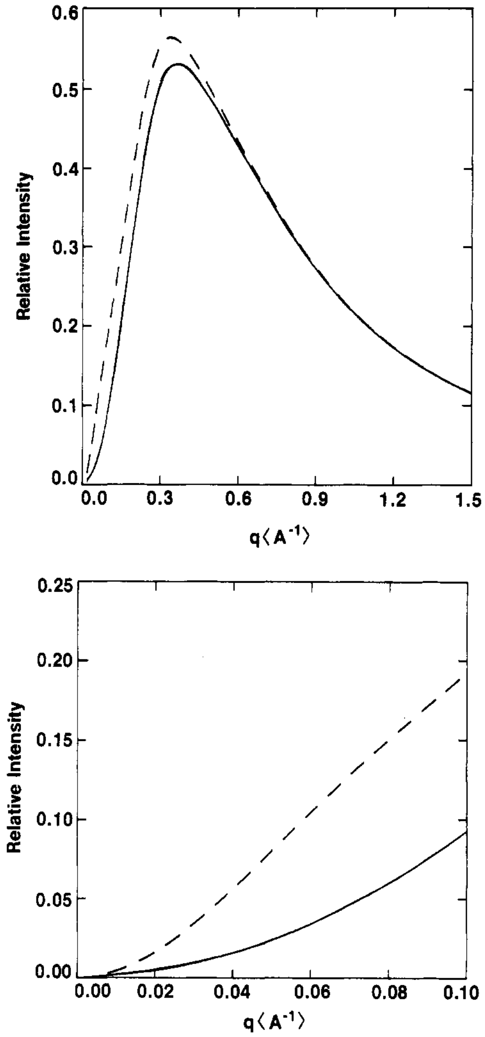

Figure 10. (a) Scattering intensities of Gaussian chains off an alternating block structure with $n_{11} = 33$ Å, $n_{12} = 6.6$ Å, $n_2 = 5.7$ Å, and $b = 2.7$ Å: (solid line) $N = 500$; (dashed line) $N = 5$. (b) Low q region of part a.

Using these equations for the regularly alternating block chains and letting N be 500, one obtains curve A on Figure 9. To calculate the case of an ($-A_{11}-B-$) chain, one has $n_{11} = n_{12} = 33$, and the result is shown as curve B. Curve C is based on $n_{11} = n_{12} = 6.6$ to calculate the ($-A_{12}-B-$) chain. The above results clearly demonstrate that even in a Gaussian chain the sequence of regularly alternating blocks results in a scattering peak located at q smaller than those from a simple ($-A_{11}-B-$) or ($-A_{12}-B-$) type chain.

The other interesting feature demonstrated by the curves of Figure 9 is the slope of the intensity near $q = 0.0$; it is about zero for these three multiple-block chains. This near-zero slope is believed to be a common characteristic of multiple-block chains of large N. A decrease in N, the number of repeat blocks, will increase the value of this initial slope. The above notion is clearly illustrated in Figure 10. In Figure 10a, a curve obtained with $N = 5$ is plotted together with curve A of Figure 9. The only difference in the parameters used to construct these two curves is a decrease in N from 500 to 5. It is shown that the peak position is not affected by the value of N. In Figure 10b the initial slope for the case $N = 5$ is clearly greater than that for $N = 500$. It is also interesting to reexamine the experimentally observed scattering curves

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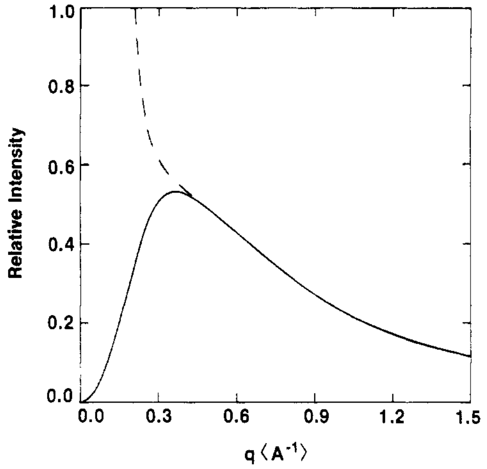

Figure 11. Scattering intensities of Gaussian chains with N = 500, b = 2.7 Å, n_{11} = 33 Å, n_{12} = 6.6 Å, and n_2 = 5.7 Å: (solid line) alternating blocks; (dashed line) random blocks.

of the single-diamine-cured epoxies, i.e., Figures 2 and 3 for D-400- and D-230-cured epoxies, respectively. The initial slope, after neglecting a few data points around the beam stop, is rather close to what is depicted with the fact that the molecular weight of an average epoxy network approaches infinity. The approximation scheme reported earlier by Wu and Bauer[2] also provided a scattering curve with zero slope near q = 0.

Substituting eq 12, 14, and 15 into eq 9 and using the same values for n_{11}, n_{12}, n_2, and b as before in the regular block case gives the resultant curve in Figure 11. No scattering peak can be observed in such a randomly alternating case. This finding is consistent with the diblock results reported earlier by others[4] for the case of high polydispersity.

In summation, the results of both the rigid-rod and the flexible-coil calculations suggest that the network structure of the mixed-diamine-cured epoxies (D-2000/D-400 and D-2000/D-230) could be of the $(-A_1-B-A_2-B-)$ type along the amine linkages. The second peaks at q = 0.35 of both D2K2H411 and D2K4H411 compositions are originated from the correlation of the labeled segments along the epoxy linkages; hence their position is not expected to depend on the arrangement of the amines within the network.

The origination of this regular chemical sequence is rather puzzling. An explanation based on curing kinetics is currently under investigation. If the newtork structure of the epoxies studied herein is indeed kinetics-controlled, the existence of the regularly alternating block will likely be sensitive to the curing conditions.

Conclusions

A pronounced scattering peak has been observed for the epoxies cured with the diamine mixtures containing two diamines with the same repeat unit but different molecular weights. The peak is located at a q value smaller than those observed in any of the single-diamine-cured epoxies. This observation suggests that the two diamines and the epoxy monomer form a regularly alternating lattice. The chemical periodicity of this lattice contains two epoxy monomers, one long-chain diamine and one short-chain diamine.

The linear-chain analogue of the lattice proposed above is of the $(-A_1-B-A_2-B-)_N$ type. The scattering intensity of this regularly alternating chain has been calculated on the basis of a single rigid rod as well as a Gaussian chain. The theoretical results indicate that such an alternating block arrangement will result in a main peak located at a q smaller than that from either $(-A_1-B-)_{2N}$ or $(-A_2-B-)_{2N}$ chains.

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^{39}K and ^{87}Rb NMR Study of Chemical Shift Effects in ι- and κ-Carrageenan Gels

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ABSTRACT: ^{39}K and ^{87}Rb NMR spectra of specific ion forms of ι- and κ-carrageenans in the presence of excess counterions are reported. Chemical shift effects are observed which are attributed to the effects of specific site binding. The effects of temperature, anion type, and urea on the spectra of the potassium form are reported, and it is concluded that the results are consistent with a model in which the primary mechanism for gelation is a change in the solvent property rather than ion binding.

Introduction

The role of metal cations in the gelation of carrageenans has been the subject of considerable interest.[1–5] NMR studies[4,5] have demonstrated that K^+, Rb^+, and Cs^+ can interact strongly with κ-carrageenan and that K^+ and Rb^+ show similar interactions with ι-carrageenan.[3] In the case of Cs^+ interacting with the κ form, strong chemical shift effects were observed,[5] which were interpreted in terms of specific site binding. We now report on a similar study of chemical shift effects using ^{39}K and ^{87}Rb NMR.

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