Macromolecules 1988, *21*, 457-464

three parameters, κ, ζ, and e. Stress–strain experiments[19] show that κ may be estimated from the molecular constitution of the network and that ζ may be taken as zero in the first approximation. Thus, the coupling parameter e appearing in eq 23 is the only parameter that requires evaluation by experiments.

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Network Structure in Epoxies. 5. Deformation Mechanism in Epoxies

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ABSTRACT: Small-angle neutron scattering (SANS) was used to investigate the response of network molecules to large strain deformation. Partially deuteriated diglycidyl ether of bisphenol A (DGEBA) was cured with either tri- or diamines of different molecular weights. The change of the average distance between cross-links along the epoxy and the amine linkages can easily be detected from the shift in the positions of the scattering maxima. It was found that the average distance between cross-links remained almost unchanged along both the amine and the epoxy linkages as the bulk material underwent a large deformation. The above results are discussed and compared to the results from swollen networks that do show a substantial increase in average distance between cross-links.

Introduction

The conformational changes in molecules in cross-linked polymers have been a subject of extensive studies for decades. The cross-link density of the materials included in their work was low in most cases.[1-4] Small-angle neutron scattering (SANS) has proven to be a powerful technique for this type of study. The displacement of the cross-links in response to macroscopic deformation was found to be, in general, between what is predicted by the junction affine and the phantom network models.[5-10] Materials of high cross-link density such as most thermosetting polymers have not been included in this type of study. This work represents the first effort in applying SANS to study the deformation behavior of a commonly used thermosetting polymer/epoxy.

There are two additional characteristics of the networks in this work that differ from studies in the past. First, there is a difference in the chemical composition between the linkages, and second, there is low functionality of the cross-links. Usually, the linkages in epoxies are composed of two types of chains, one is the epoxy chain and the other is the amine chain. In the present case, the epoxy chain is basically the bisphenol A linkage and the amine one is made of the polypropylene oxide (PPO) linkage. The low functionality of the cross-links also make epoxies an interesting subject of study. Linear epoxies cured with either di- or triamines have a functionality of three. The amine ends that have reacted with two epoxide groups are the only cross-linking points for linear diamines. For triamine cured materials, in addition to the amine end cross-linking points, the junctions at the center of each amine constitutes anther cross-linking points. However, the functionality of this junction is also three.

For linear polymers, deformation results in a change of the overall shape of an average molecule. For example, the radius of gyration, R_g, will be distorted from that of a random coil. However the length of each repeat unit remains unchanged, and the change in the value of R_g is caused by the change in average step direction. For a highly cross-linked material, the molecular weight between cross-links is small enough to be considered as on statistical segment of the size commonly used to describe linear chain polymers. For the case of a cross-link functionality of three, it is possible that an average molecular network can accomodate the macroscopic deformation by some mechanism requiring less energy than altering the average distance between cross-links. With a functionality of three, the topological connectivity on a local scale can be considered as two dimensional. Consequently, a network could easily deform by unfolding without a dramatic change in the distance between cross-links.[11,12] The idea of network unfolding was originally proposed for cross-linked polymers with relatively low cross-linking density, i.e. high population of physical or spatial neighbors. This is not the case for epoxies. However, the low functionality of the cross-links may facilitate the unfolding process. According to Flory,[10] there are two types of neighbors for any given molecule in a cross-linked polymer, one is the topological or directly connected neighbors and the other is the spatial neighbors. On the basis of the argument of Bastide et al.,[11] the population of the topological neighbors increases as the second power of the functionality. Accordingly, the popularity of the spatial neighbors of a polymer of functionality of three will be rather high, hence facilitating a deformation mechanism such as unfolding.

It is noteworthy that the unfolding process was used to describe the swelling of loosely cross-linked polymers, while applied in the present context of deformation, certain clarifications may be necessary. The junction functionality of three is just one greater than the linear portion of the chains. In the deformation of epoxies what we propose as unfolding is that the cross-links and the linear part of the chains of the same topological neighbor move together as a whole. In other words, the macroscopic strain is accommodated by the inter-network displacement, i.e. by the relative displacement between chains of different topological neighbors.

This work provides an experimental basis for elucidating the deformation mechanisms in solid state for these high cross-link density and low functionality polymers. Besides deforming these materials in solid state, the change in the distance between cross-links upon swelling was also investigated. The difference in the molecular response to these two different deformation schemes will be delineated. A brief discussion of the scattering theory related to this problem will be given in the early part of the discussion. This theoretical discussion is intended to be illustrative since a quantitative description of the conformation of molecular networks is not yet available. The conclusions drawn from this work are based on the experimental findings and hence should not be obscured by the lack of complete understanding of the network structure in a fully cured epoxy.

Experimental Section

Specimen Preparation. As described in the previous publications,[13-15] DGEBA was chosen as the model epoxy monomer. To provide the neutron scattering contrast, all of the hydrogen atoms in the bisphenol A unit were replaced with deuterium. Detailed procedures for synthesizing the deuterium-labeled DGEBA can be found elsewhere.[13] Jeffamine [Tradename of Texco Chemical Co. Certain commercial materials and equipment are identified in this paper 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 that the materials or equipment identified are the best available for the purpose.] D-2000, D-400, D-230, and T-403 were used as the curing agents. The D-series amines are difunctional amines linked by polypropylene oxide (PPO), and the designation number refers to the approximate molecular weight of each species. The T-series amine is a three-branch triamine with a total molecular weight of about 400. The polydispersity of the polyether glycols, the precursor of these amines, is very low; consequently, these amines can be regarded as monodisperse.[13] The cure temperature was 95 °C for all the specimens to be reported herein. At this temperature, the cure reaction is dominated by the amine/epoxide reaction. Therefore, throughout this study, the molar ratio of the epoxide to amine was kept at 2:1 for the diamine cases and 3:1 for the triamine, the stoichiometric ratio.

The specimens included in this work are three single amino cured epoxies, i.e. the ones cured with D-2000, D-400, and T-403. In addition, one specimen containing a equimolar mixture of D-230 and D-2000 diamines is also included. It has been shown in previous publications[15,16] that the material composed of two diamines has an ordered network structure. Therefore, the deformation behavior of this type of material is expected to be different from the single diamine containing epoxies.

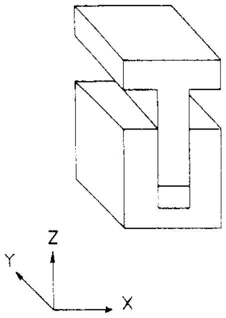

FIGURE 1

Figure 1. Device used to impose a pure shear deformation on all the samples. The compression direction is along the z axis; the samples flow along the y axis.

The epoxy monomer is heated in a 55 °C oven for 3 h to melt any crystalline material. After cooling, the epoxy was mixed with the amine followed by a 5-min degas cycle in a vacuum of 10^{-2} Torr. The cure temperature was 95 °C for all the specimens. The degree of cure was determined by using IR[17] to monitor the peak height of the 920 cm^{-1} band. The degree of cure for all the materials is about 95% as judged from the IR results. The cured epoxy specimens for the solid-state deformation study had a dimension of 12.7 × 20 × 1 mm.

Besides the deformation in solid state, solvent swelling was also conducted on the epoxies cured with D-2000 and D-400 to investigate the deformability of the chains. For this work, acetone was chosen as the swelling solvent because it contained the same ratio of atoms as the backbone of the amines used. As a result, the scattering contrast of the bulk material, which is derived from the deuteriated bisphenol A and the protonated PPO chains, remains unchanged upon swelling with acetone. The specimens for swelling study were of a disk shape, 1 mm thick and 10 mm diameter. The epoxy specimens were immersed in acetone at ambient temperature until the sample weight stayed constant, indicating swelling equilibrium.

Deformation Process. All of the materials except the one cured with the mixture of D-230 and D-2000 diamines are rather brittle in their glassy states and have low tear strength in their rubbery states. The fracture strain in a simple tensile mode for these materials was in the range of a few percent, a strain too small to impose enough change in the network structure. Therefore, pure shear was chosen to be the deformation mode. The specimens were deformed in bilateral compression with the device shown in Figure 1. The dimension in the x axis of the undeformed sample was identical with the width of the slot of the deformation device. Consequently, no deformation took place along this axis. Since there is no tensile stress acting on the specimen, the maximum strain obtained for most of the epoxies exceeded 20%. The strain is defined in the usual sense, i.e. the percentage of increase in length over the original sample length along the elongation direction which is designated as the y axis in Figure 1.

Even in the pure shear mode of deformation, the rupture of specimens during the deformation process still took place. For minimization of the occurrence of sample failure, all of the specimens were deformed in their glassy states to decrease the amount of stored elastic energy. Since the T_g of the epoxies cured with either T-403 or D-400 was higher than the ambient temperature, the deformation was carried out at room temperature. For these epoxies cured with either D-2000 alone or a mixture of D-2000 and D-230, the T_g is below room temperature. Consequently, the deformation was carried out at dry ice temperature.

Immediately after the deformation, the specimens were transferred to a pair of aluminum holders of the same configuration as the deformation device of Figure 1. The only differences are (1) the dimension along the z axis is much thinner for the aluminum holder and (2) these two pieces of aluminum holder can be held together securely with screws. After these screws were tightened, no relaxation of the sample strain was possible. The neutron scattering measurements were carried out on the portion of samples clamped in the aluminum holder. Within the measurement volume of the deformed sample the strain was very uniform. The transmission factor of the aluminum holder was determined to be 96%. All the neutron measurements were conducted at room temperature.

Neutron Scattering Measurements. All the scattering measurements were carried out by using the small-angle scattering (SANS) instrument at the NBS reactor. A wavelength used was 5 Å, and the q region covered was from 0.001 to 0.45 Å^{-1}. The incident beam was parallel to the z axis of the aluminum holder (along which the samples were compressed). The scattering data presented are the sector averages along the x and the y axes. A sector width of 20° along each direction was used for the data averaging.

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 were calculated in terms of the absolute scale by use of a silica standard, though reducing the scattering intensity to an absolute scale is not necessary since the focal point of the discussion will be on the position of the main peak.

Experimental Results

The maximum strain obtained on the D-2000 cured epoxy specimens was 35.5%. The scattered intensity of the samples before and after deformation are shown in parts a and b, respectively, of Figure 2. In a previous publication[14] it was demonstrated that the position of the first peak in the undeformed material reflects the average distance between two adjacent deuterated bisphenol A units along a PPO chain of 2000 molecular weight. After deformation, the position of this peak along the y axis seemed to shift to a somewhat lower q. However, the amount of shift was much less than the macroscopic strain. No change in the peak position was observed along the x axis; this is expected since no deformation was imposed along this direction. Besides the main peak position, deformation resulted in a rather pronounced change in the general shape of the scattering curve. For example, the zero angle intensity along the stretch direction (y axis) seemed to be lower than perpendicular to the stretch direction (x axis) in the deformed sample. Furthermore, the second scattering peak diminished in the deformed sample along both the x and y axes.

The maximum strain obtained on the D-400 cured epoxy was 23.6% The neutron scattering results are presented in parts a and b of Figure 3. No shift of the peak position could be detected along the y axis or the x axis. Once again, the zero angle scattering intensity along the stretch direction seemed to be lower than the direction perpendicular to the stretch direction where no deformation was allowed. Since the T_g of the D-400 cured epoxy is above the ambient temperature, both the deformation and the neutron measurements were conducted at a temperature below T_g. It is reasonable to question whether the chains inside the sample ever reached an equilibrium state in deformation. Therefore, the deformed sample, while constrained within the aluminum holder such that no relief in strain could occur, was annealed at 90 °C for 30 min. In a previous study, the T_g of this material was found to be 55 °C.[15] The neutron scattering result of this annealed sample is given in Figure 3c. The annealing above T_g had no effect on the scattering result.

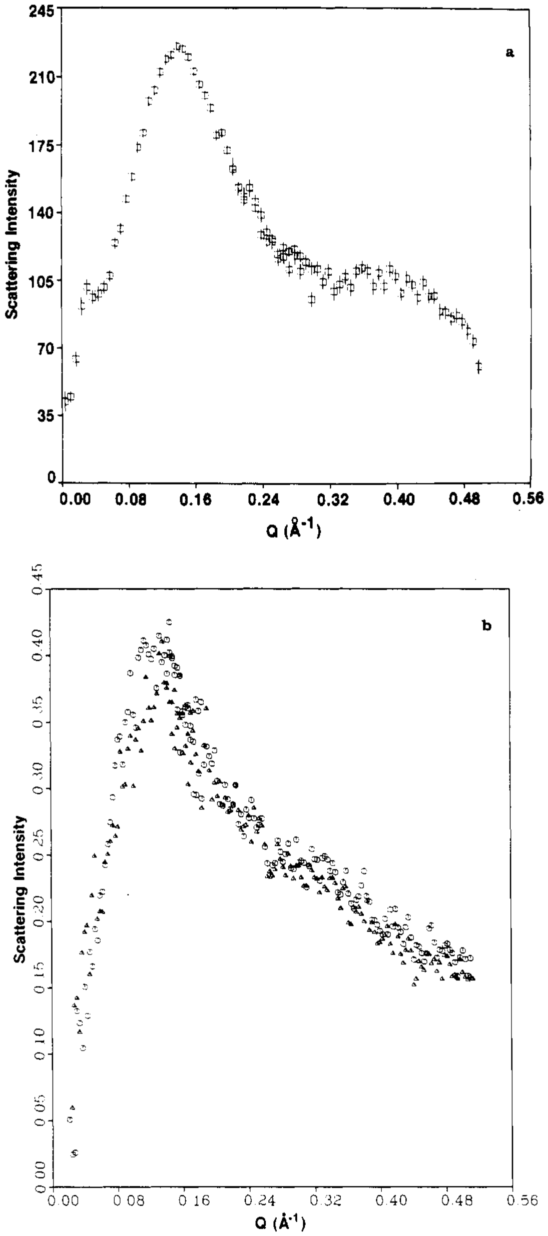

Figure 2. Neutron scattering results of deuteriated DGEBA epoxy cured with D-2000 amine: (a) before deformation, the scattering intensity is in arbitrary units; (b) after deformation with intensity on an absolute scale; ○, parallel to the stretch direction; △, perpendicular to the stretch direction.

For the T-403 cured samples, the maximum obtained strain was 21.6%. Just as for the case of the D-2000 cured epoxy, only a minor shift of the peak to a smaller q along the stretch direction, y axis, could be detected (parts a and b of Figure 4).

The maximum strain obtained on the epoxy specimens cured with a equal molar mixture of D-230 and D-2000 was 24.7%. As illustrated in previous publications,[15,16] epoxy of this composition forms a rather unusual network structure. A deformation of this magnitude resulted in a significant shift of the main peak to a smaller q along the stretch axis (parts a and b of Figure 5. Along the x axis, where no deformation occurred, no shift in the position of the main peak was observed. No shift in the position of the second peak at q = 0.34 Å^{-1} was observed for either x or y axes. The shift of the main peak to a lower q along the stretch axis was about 39% which was higher than the

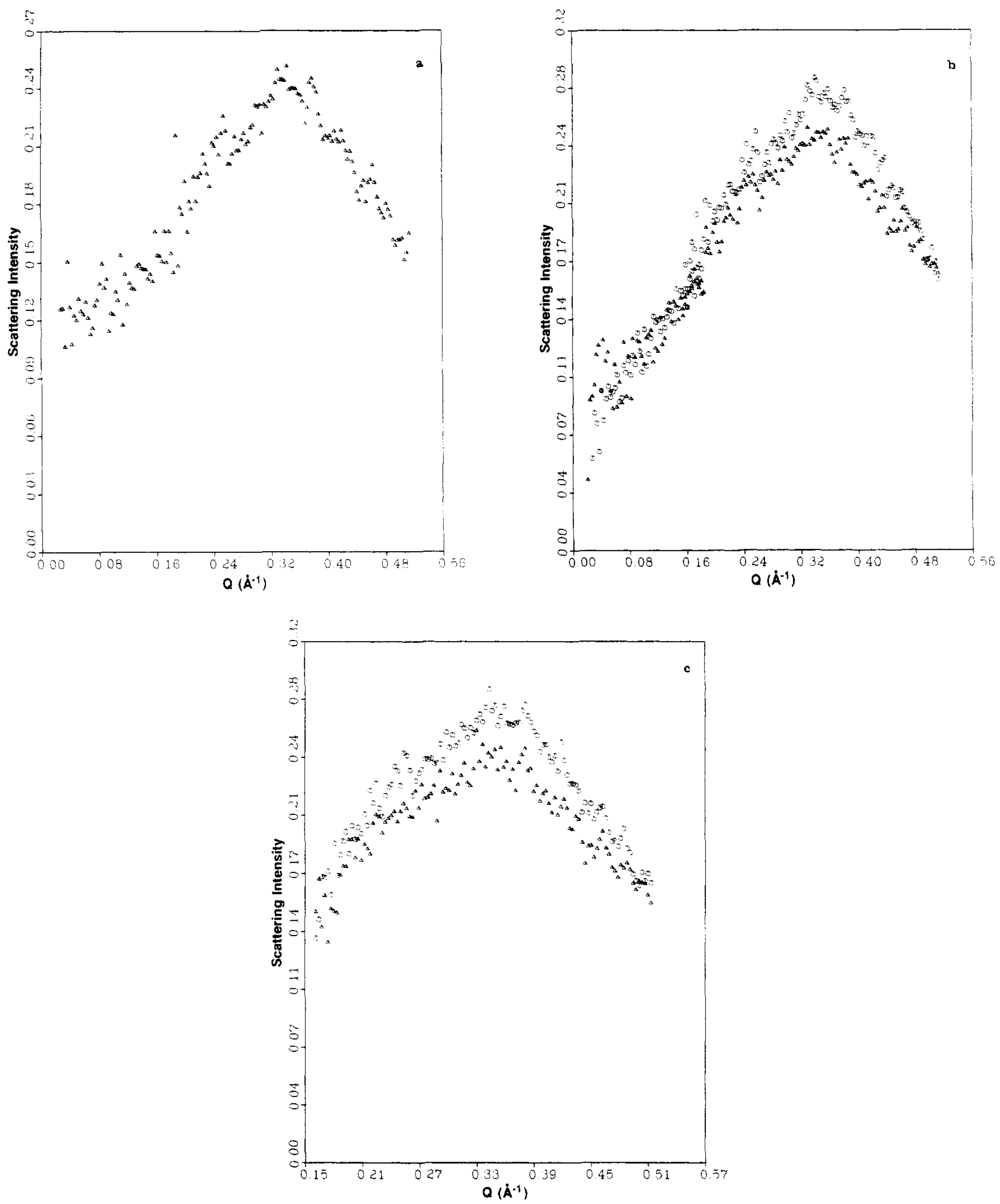

Figure 3. Neutron scattering results of deuteriated DGEBA epoxy cured with D-400 amine, the scattering intensity on an absolute scale: (a) before deformation; (b) after deformation; (c) annealed above the glass transition temperature after the deformation; ○, parallel to the stretch direction; △, perpendicular to the stretch direction.

value of the macroscopic strain imposed on the sample.

The epoxy specimen cured with the D-2000 amine was swollen in acetone at room temperature. The equilibrium swelling ratio, defined as the ratio of the volume of the swollen sample to that of the original one, was 2.549. The neutron scattering results before and after swelling are given in Figure 6. A significant shift in the main peak position was apparent. Assuming an affine model for the chain displacement due to swelling, the shift in the main peak position should be 26.8% which was rather close to the observed value of 27.0%. The other pronounced change in the scattering result due to swelling was the enhancement of the zero angle intensity. This was attributed to the heterogeneous nature of the network structure commonly observed in all the epoxies studied so far.[14] The second peak observed in the bulk sample was attributed partially to the intranetwork correlation of the bisphenol A units reacted to the same terminal amine. However this peak disappeared upon swelling. Consequently, whether the epoxy linkage became extended upon swelling remains an open question.

For the D-400 cured epoxy, the enhancement in the zero angle scattering intensity was so strong that the scattering peak of the swollen sample could no longer be detected. Therefore, the scattering results of the swollen D-400 epoxy are not discussed in this work.

The stretch ratio of all of the samples studied in this work and the percentage of the shift of the main peak from the original position are listed in Table I. The SANS result of the equimolar D-2000/D-230 sample is the only one possessing a second-order peak both before and after the deformation. This second-order originates from the

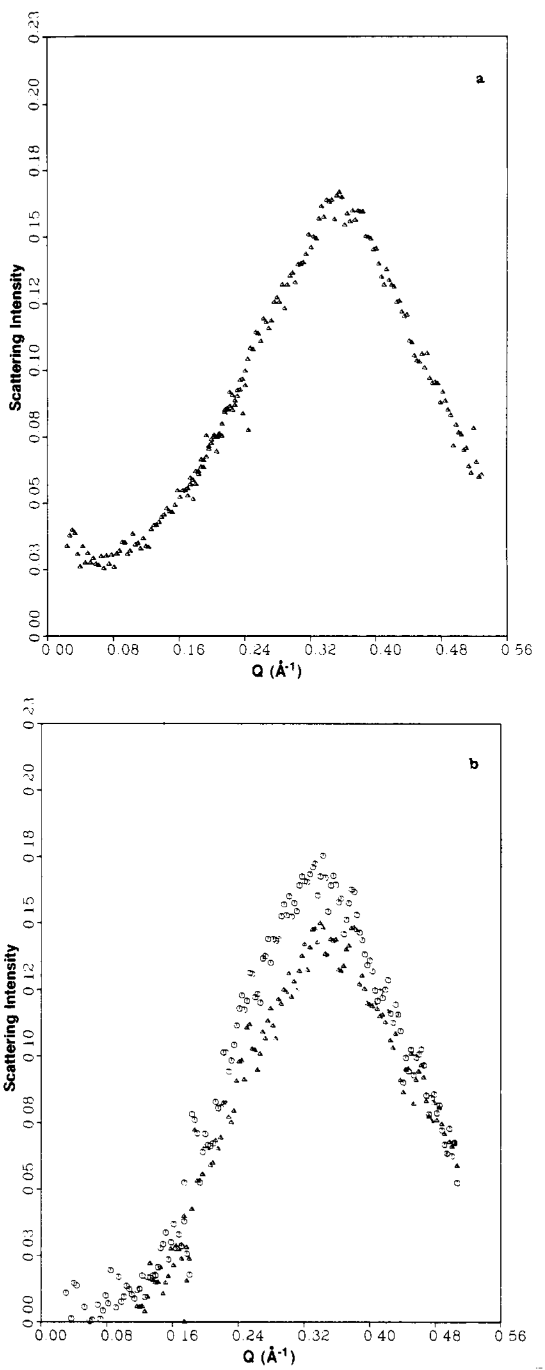

Figure 4. Neutron scattering results of deuteriated DGEBA epoxy cured with T-403 amine, the scattering intensity on an absolute scale: (a) before deformation; (b) after deformation; ○, parallel to the stretch direction; △, perpendicular to the stretch direction.

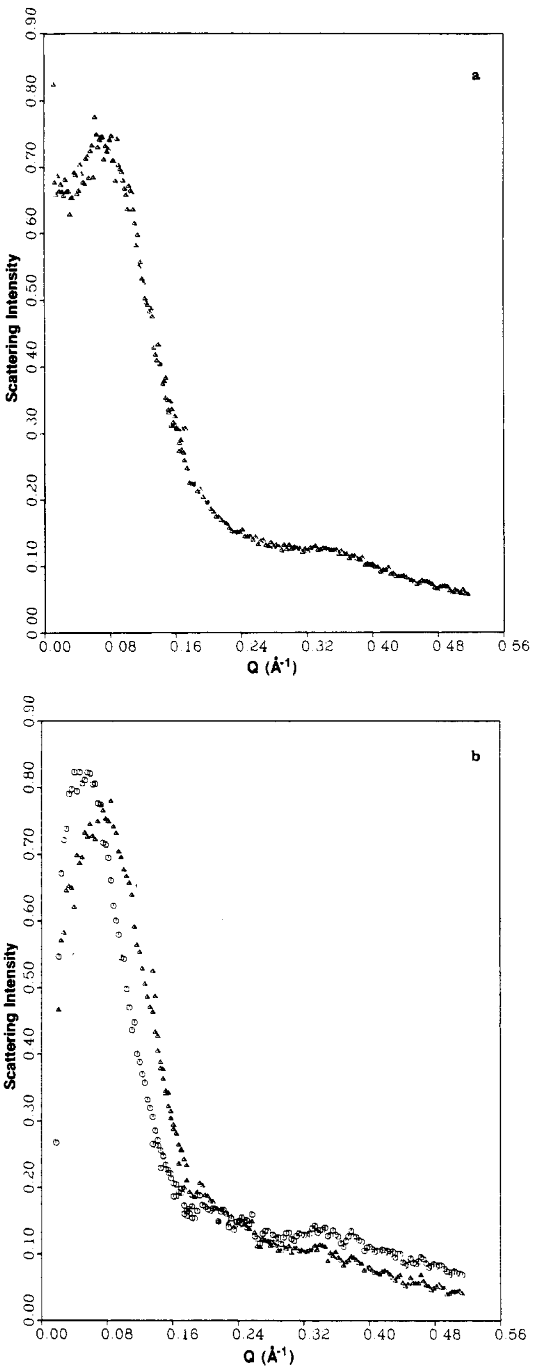

Figure 5. Neutron scattering results of deuteriated DGEBA epoxy cured with a mixture of D-2000 and D-230 amine of equal molar ratio with the intensity on an absolute scale: (a) before deformation; (b) after deformation; ○, parallel to the stretch direction; △, perpendicular to the stretch direction.

correlation distance of the deuteriated bisphenol A segments along the epoxy linkage. This second peak stays unchanged after deformation. Therefore, no deformation is attributed to the stretch of the epoxy linkages. The first peak is due to the correlation distance of the deuteriated blocks along the amine linkages; therefore, the decrease of the peak position to a smaller q value is attributed to the stretch along the amine chains. In the samples of D-2000 diamine the second peak loses its definition after deformation, no conclusion regarding the extent of deformation of the epoxy linkages can be obtained. Once again the shift of the first peak is listed under the amine column for the reason stated before. For the D-400 diamine sample since there is no shift in the peak position, neither the epoxy nor the amine linkages undergo any stretch. For the T-403 triamine sample, there is only one peak in the underformed state; the amount of shift caused by deformation is attributed to the amine chain since all the other cases suggests that the epoxy linkage does not deform. It is clear from the results of Table I that all the epoxies cured with amine of an uniform size have a similar deformation behavior; namely, the amount of chain stretch was smaller than the macroscopic strain.

Discussion

The scattering peak position is the only experimental result used to judge the average distance between the deuteriated segments of the topological neighbors throughout this work. It is therefore essential to understand the relation between the scattering peak position and

Table I
Summary of the Macroscopic Deformation Ratio and the Ratio Calculated from the SANS Peak Positions

compositn	macroscopic stretch ratio (%)	SANS results (%) along amine chain	SANS results (%) along epoxy chain	SANS peak position ($Å^{-1}$) before deformation along amine	SANS peak position ($Å^{-1}$) before deformation along EPOM
d-DGEBA (2) D-2000 (1)	35.5	9.0	...	0.13	0.37
d-DGEBA (2) D-400 (1)	23.6	0	0	0.35	
d-DGEBA (3) T-403 (1)	21.6	7.0	...	0.35	
d-DGEBA (4) D-2000 (1) D-230 (1)	24.7	39.0	0	0.09	0.35

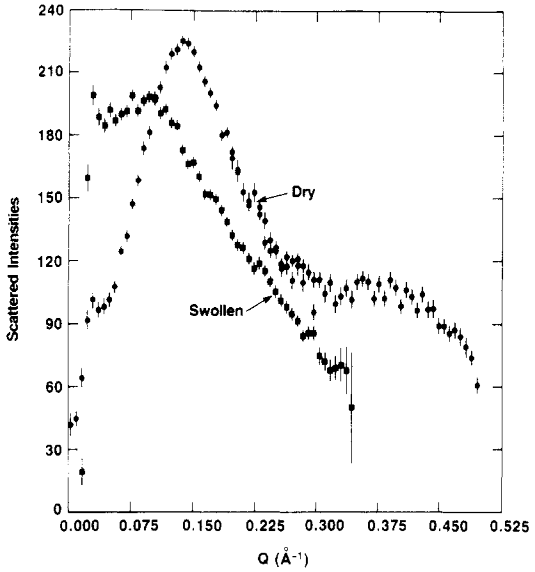

Figure 6. Neutron scattering results of deuteriated DGEBA cured with D-2000 amine with the intensity in arbitrary units: ○, before swelling; △, after swelling in acetone.

the average distance. As demonstrated in a previous publication,[14] the first peak at small q is derived from the correlation hole effect instead of from a Bragg reflection. The second peak, for example, the one at $q = 0.37$ $Å^{-1}$ of the D-2000 cured specimen, originates from a Bragg type of reflection. The one to one relationship between the average distance between the scattering centers and the Bragg peak position is well-established and will not be a concern in this work. However, the position of the primary peak was the one used to evaluate the possible change in the average distance between the scattering centers. It will be demonstrated that the peak position of correlation hole origin will also shift, in a similar fashion as the Bragg peak, with the change of the average distance.

To simplify the calculations without loss of generality, an A–B type diblock copolymer in bulk is chosen as the model. We further assume that the molecular weight of each block is monodisperse and equals N. A scattering peak due to the correlation hole can block interpreted quantitatively with the following equation

$$I(\mathbf{q})/\Delta b^2 = X_N(\mathbf{q})/2 - X_{2N}(\mathbf{q})/4 \qquad (1)$$

where $X_i(\mathbf{q})$ denotes the single chain form factor of molecular weight i. A Debye function for Gaussian chains is used for the present case. Δb^2 is the contrast factor between A and B blocks. In the above equation, $\mathbf{q}$ is in vector form instead of scalar form as presented in most cases. The above generalization from a scalar q to a vector can be justified as follows: the underlying principle in deriving eq 1 is the incompressibility of the material in real space. This relationship in Fourier space should hold true regardless of the direction and the magnitude of $\mathbf{q}$. An expression that is a precursor to eq 1 is given by de Gennes in terms of q.[18]

The expression for the scattering intensity for block copolymers in general can be used in lieu of the above equation. However a more comprehensive expression is considered to be unnecessary since one does not expect to have a quantitative comparison between the theoretical and the observed scattering results. This is due to the lack of the necessary information regarding the conformation of the topologocial neighbor. In a previous publication[14] attempts with limited success were made to derive a semiquantitative fit between the theoretical and the observed results for samples in the undeformed condition. Even for that case some simplifications have to be introduced regarding the network conformation. For the present case of deformed samples, the conclusion is based on the observed difference in the scattering behavior between sample subject to swelling and solid-state deformation. The theoretical part is intended to be for illustrative purpose only.

Now we deform this hypothetical diblock copolymer sample in a device shown in Figure 1, assuming an average chain undergoes certain amount of deformation and the vector $\mathbf{r}_{ij}$ connecting junctions i and j is related to its undeformed value through $\mathbf{r}_{ij} = |\lambda|(\mathbf{r}_{ij})_0$. $|\lambda|$ is a 3×3 matrix and denotes the magnitude of the strain. For the case of the junction affine model, $|\lambda|$ is just the strain tensor of the macroscopic sample; for the phantom network model, $|\gamma|$ is somewhat less than that of the macroscopic strain. Now the case in which $\mathbf{q}$ is parallel to the stretch axis (y axis) is examined. In the present case of epoxies, the number of segments between junctions is rather small. It seems reasonable to assume that the displacement of individual segments follows the same strain as the junctions (i.e. complete affine). With this premise the work by Benoit et al.[19] is applicable, the form factor of a distorted chain can be written as

$$X(q_\parallel) = 2/Y^2(\exp(-Y_\parallel) - 1 + Y_\parallel) \qquad (2)$$

where $Y_\parallel = q^2\langle R^2\rangle\lambda_\parallel{}^2/6$ and $\langle R^2\rangle$ is the mean square end to end distance of the undeformed sample. $\lambda_\parallel$ is the component of $|\lambda|$ in the stretch direction.

By substituting eq 2 into 1, it is apparent that the shift of the position of the scattering peak due to the correlation hole is proportional to the molecular deformation ratio along the respective axis. Qualitatively, this demonstrates that the shift of the scattering peak from the correlation hole follows the same rule as the Bragg peak; both change linearly with the molecular deformation ratio along the respective axis.

On the other extreme if one treats the chain between junctions in epoxies as a Guassian coil, certain deviation from what is expressed by eq 2 will result. The expression of the form factor of a deformed Gaussian coil can be found in the work by Pearson[20] and is rather complicated. Qualitatively, the amount of shift in the scattering maximum of a Gaussian coil after stretch is expected to be less than that of the complete affine model of eq 2. For either the junction affine or the phantom network model, they are expected to be applicable to the cases of high molecular weight between junctions. In this work on epoxies, the sample containing the longest chain is the one made of D-2000 diamine. However, the amount of shift in the scattering peak of this sample is equal to the cube root of the sample swelling ratio. This observation tends to suggest that the scattering result of the swollen D-2000 epoxy samples follows the complete affine scheme. Accordingly, one would expect that the solid-state deformation of the D-2000 samples and others containing shorter chains should all follow the chain affine model expressed by eq 2.

The physical meaning of the scattering peak position of swollen epoxies merits some discussion. According the work by Benoit et al.[21] that the peak position depends on the chain dimension only. The interaction parameters between the solvent and the polymer only serve to modulate the intensity of the scattering peak. This is the basis that the peak position is used to calculate the average distance between the deuterated bisphenol A units along either the amine or the epoxy chains.

All of the epoxy specimens included in this work are composed of two different linkages: the amine chain with PPO linkages and the epoxy one with a bisphenol A linkage. These two chains are different in their rigidity. The epoxy chain is considerably more rigid than the PPO chain. Certain modifications on the existing models of network deformation seem to be needed for the present case, since most of the rubber elasticity work was based on the case that all the linkages between cross-links are of the same chemical composition. Accordingly, it is not trivial to predict which chain, the rigid epoxy or the flexible amine, will first align in the stretch (y axis) direction under a finite strain.

The experimental results (Figure 2, parts a and b) for the D-2000 amine cured epoxy suggest that the amine chains were oriented along the stretch direction, since the scattering intensity of the first peak was higher in the stretch direction than that of the perpendicular one. The first peak registered the average distance between two deuteriated bisphenol A units connected by a diamine chain. However, the amount of elongation of the amine chain along the stretch direction is much smaller than the macroscopic strain as clearly demonstrated by the results in Table I. The second peak, which reflects the average distance between the deuteriated bisphenol A units along the epoxy chains, disappeared upon deformation. Consequently, there is no information to judge the amount of deformation along the epoxy chains.

As the diamine length decreases to 400 molecular weight, the average distance between the bisphenol A units is about the same along either the amine or the epoxy chains. Accordingly, only one scattering peak is observed for the D-400 cured epoxy. Upon deformation, the peak position stays unchanged. This suggests that neither the amine nor the epoxy chain gets stretched. However, the scattering intensity along the stretch direction is higher than that of the perpendicular one, indicating some realignment of the chains within the sample. The deformed sample also possesses some birefringence, again an indication that the molecules are aligned somewhat with respect to the stretch direction. However, such an alignment does not impose any distortion of the chain length as measured by neutron scattering.

To assure that the chains within the D-400 cured epoxy have reached their equilibrium state, the deformed sample was annealed at 90 °C for 30 min while constrained in its deformed state. The glass transition temperature of this material is 55 °C. The neutron scattering results (Figure 3c) of this deformed then annealed D-400 sample demonstrate that the annealing had no effect on the conformation of the deformed network chains. This result suggests that the molecular motion involved in the deformation of epoxies is independent of the temperature, whether it is above or below its glass transition temperature. However, this does not imply that the ultimate strain reachable is independent of the deformation temperature. It only suggests that the molecular displacements needed to accommodate the macroscopic strain seems to be independent of the deformation temperature.

The neutron scattering result of the undeformed T-403 cured epoxy sample (Figure 6a) also shows one peak, an indication that the average distance between the bisphenol A units is about the same along either the amine branches or along the epoxy chains. After deformation, the enhancement in the scattering intensity along the stretch direction is apparent. The deformed sample also has some birefringence indicating that the molecules were aligned with respect to the stretch direction. The shift of the peak position to a smaller q is small in comparison to the amount of strain. Therefore, the deformation mechanism of the T-403 cured sample seems similar to that of D-400 or D-2000 cured samples. The total functionality per amine monomer plays only very small role in its deformation behavior.

If one considers a diamine molecule as a point source of cross-linking, then the D-series diamines have a functionality of four and the T-403 triamine molecule has a functionality of six. However, the chain length between the amine ends is at least comparable to the length of an epoxy monomer. By disregarding the difference of the chemical composition and concentrating only on the connectivity of the network, the cross-links throughout this work have a functionality of three even for the epoxy cured with T-403 amine. This may be the reason that a similar deformation behavior is observed for both the D-series and the T-series cured epoxies.

As shown in the previous publications,[15,16] the epoxy cured with a mixture of D-230 and D-2000 diamines possesses a unique network structure. A certain amount of segregation takes place during the curing process, and the resultant network has a structure along the amine linkages analogous to an alternating block copolymer. More specifically, along the diamine linkages the long and the short diamines are linked in a regularly alternating fashion. The complete mechanism of such a network formation remains unknown. The reaction rate constant of the diamines depends on their molecular weight. The amines of the D-230 react faster than those of the D-2000.[16] It is conceivable that the curing of a mixture of D-230 and D-2000 diamines with epoxy can be considered as a two-step process. At first, the fast reacting D-230 diamines react with the epoxy monomers and form clusters which are rich in unreacted epoxy ends, because there are four moles of epoxy for every mole of D-230 diamine. The second step of reaction consists of the bridging of these clusters by the D-2000 amines. Consequently, these D-230 enriched clusters act as the cross-link points for the long D-2000 chains, and the functionality of this type of cross-link particles can be enormous. This difference in the effective functionality from the single amine-cured epoxies might account for the gross difference in the deformation behavior. The amount of the elongation along the amine direction exceeds the macroscopic strain slightly. The amine chain occupies only part of the specimen volume, and the other part of the volume is occupied by the epoxy chains which is too rigid to be stretched. The scattering intensity of the first peak is enhanced along the stretch direction, an indication of the alignment of the amine chains along the stretch axis. After the deformation, the second peak remains unchanged in its position as well as its intensity. Neither reorientation nor elongation takes place along the epoxy linkages. It is noteworthy that the network structure of the epoxy cured with a mixture of two amines has not been completely resolved so far, let alone the mechanism of the network formation process. The interpretation regarding the possible formation of D-230 gel particles is rather speculative. Nevertheless, the deformation result demonstrates once again the deformability of the amine chains and the rigidity of the epoxy linkages.

Another phenomenon commonly observed in most of the scattering results of the deformed samples was a decrease in the small-angle intensity in the stretch direction. Since there is no detailed molecular model available for the deformation process in epoxies or any highly cross-linked polymers, no interpretation can be attached to this finding.

In summary, the epoxies cured with di- or triamines with a narrow molecular weight distribution display an interesting deformation behavior; the flexible amine chains are preferentially aligned in the stretch direction without a significant increase in the length of the chains between the cross-links. The evidence supporting the chain alignment comes from the enhancement of the peak intensity in the stretch direction and the presence of the birefringence. For these samples containing the D-2000 diamine, the evidence of the alignment of the amine chain in the stretch direction is apparent; the changes in the intensity and the position of the scattering maximum all occurred at the q region corresponding to the average end to end distance of the amine chains. When the SANS results between the swollen sample and the solid-state deformed ones are compared the unfolding mechanism seems to operate in the later case; this is contrary to what the unfolding mechanism was originally proposed for. However, more data from other measuring techniques such as NMR are definitely needed before a definite model can be built.

All of the deformations were conducted at a temperature below the glass transition temperature of the samples. However, annealing above the glass transition temperature had no effect on the conformation of the chains in the deformed sample as judged by the scattering results.

The neutron scattering result of the swollen D-2000 cured epoxy clearly demonstrates the deformability of the flexible amine chains within the epoxy network. Furthermore, the scattering result of the cured epoxy sample made from mixed long and short amines suggest the importance of the topological connectivity on the deformation behavior for epoxies and possibly for other cross-linked polymers.

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Registry No. (DGEBA)(D-2000) (copolymer), 110302-44-8; (DGEBA)(T-403) (copolymer), 70548-69-5; neutron, 12586-31-1.

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On the Theory of Dynamic Screening in Macroparticle Solutions

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ABSTRACT: An analysis is presented of hydrodynamic screening in a suspension of mobile Brownian particles. It is shown that screening is a transient phenomenon which vanishes for stationary flows unless the particles interact so strongly that they form a rigid network of immobilized obstacles.

1. Introduction

In two earlier papers[1,2] we have analyzed the screening of hydrodynamic interactions in gels and porous media. The nonfluid parts of these systems were modeled as randomly distributed collections of interaction sites which scattered the flow of the solvent and thereby dissipated its energy. Because of the immobility of the matrix material the locations of the sites were permanently fixed.

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