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Network structure of bimodal epoxies—a small angle X-ray scattering study

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

Small angle X-ray scattering measurements were performed on epoxies to determine their network structure. To provide the necessary scattering contrast the epoxy monomer used was a partially brominated diglycidyl ether of bisphenol A and the cross-linking agents were linear, low polydispersity, amine terminated poly(propylene oxide)s. Samples with both single and bimodal molecular weight distributions of cross-linking agent were prepared. A pronounced scattering maximum was observed in all networks and it can be interpreted in terms of correlation holes. Networks cured with a mixture of two cross-linking agents with different molecular weights, i.e. bimodal networks, exhibited scattering maxima at significantly lower scattering vector (q) than was observed for any single amine networks. In model bimodal epoxy graft copolymers with nearly identical chemical structure as the networks the shift to low q was barely perceptible. Experimental results from both epoxies and model graft copolymers are compared to a model calculation in order to establish a methodology to reduce molecular structure information from X-ray results. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: X-ray scattering; Small angle neutron scattering; Epoxy

1. Introduction

The evaluation of structure in highly cross-linked polymer networks using small angle neutron scattering (SANS) methods has been the subject of a series of investigations spanning the last decade [1–6]. In each of these studies the thermosetting epoxies were chosen as the model networks because of the simplicity of their crosslinking chemistry and the availability of the monodispersed monomers. Diglycidyl ether of bisphenol A (DGEBA) cured with difunctional diamine terminated polypropylene oxide (PPO) cross-linking agents was used as the model system. DGEBA was partially deuterated to provide scattering contrast for neutron measurements. Emphasis has been on identifying heterogeneity in the network structure in general, and specifically in evaluating the effects of the molecular weight distribution between cross-links on the structure and physical properties of epoxy networks.

In all of the previous SANS experiments a pronounced maximum was observed in the scattering from partially deuterated epoxy networks. The characteristic dimension of the networks, which manifests itself as a scattering maximum, has been correlated with the physical distance between epoxy linkages separated by a diamine chain in networks formed from d-DGEBA with a nearly monodispersed cross-linking agent [2]. However, a structural anomaly was observed in a network formed from reaction of epoxy with a mixture of diamines having two different molecular weights. The characteristic dimension of this ‘bimodal’ network was found to be larger than the characteristic dimension of single diamine networks formed from either of the component diamines [3]. In addition, the response of the bimodal network to mechanical deformation was found to differ from the response of single diamine networks [5]. Bimodal networks deformed almost affinely with the macroscopic dimension while the single diamine

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networks hardly underwent any changes. This sort of observations has been interpreted by the existence of super-structures in bimodal networks. For example, one model proposes ordering of long and short molecular weight diamine blocks along a linear path through the network [3] and a second, semi-quantitative treatments suggests correlation between sections of the network having a high density of a single diamine molecular weight [5]. Limited success has been achieved in qualitatively addressing the structure of bimodal networks through these theoretical models.

The purpose of this investigation was to confirm and to further examine structural changes occurring in epoxy networks resulting from mixing the cross-linking agents of different molecular weights. To this end, small angle X-ray scattering (SAXS) has been employed to evaluate the structure of brominated DGEBA/difunctional diamine terminated PPO networks. Formulations prepared include single diamine networks having different PPO molecular weights, dual diamine or bimodal networks prepared using a given molecular weight pair mixed over a range of concentration ratios, and most significantly, model copolymers prepared from a single monoamine and monoamine pairs mixed in various compositions. The anomalous scattering maximum observed by SANS has been reproduced consistently in the X-ray scattering from bimodal brominated epoxy networks. This feature has been found to vary in position and intensity depending on the molecular weight and composition of the blend of diamines used to form the network. Experimental scattering results are compared with theoretical predictions based on a comb shape copolymer calculation [7].

2. Experimental section

2.1. Materials

Brominated DGEBA, (DER 542) epoxy resin obtained from Dow Chemical Co. was chosen as the model epoxy monomer for use in this work[2]. Bromine atoms, substituted for the hydrogen in the ortho positions on the aromatic rings of the epoxy monomer, provide X-ray contrast between DGEBA and the cross-linking agent. The cross-linking agents employed were Jeffamines D-400, D-2000 and D-4000, supplied by Texaco Chemical Co.[2]. The D-series Jeffamines are difunctional amines linked by poly(propylene oxide); the designation number refers to the approximate molecular weight of each species. Model graft copolymers were formulated using Br-DGEBA and monofunctional amine terminated PPOs, M-2000 and M-600 (designation number represents again the approximate molecular weight). Networks were prepared by mixing PPO diamines with stoichiometric amounts of Br-DGEBA followed by degassing at 70°C in a vacuum oven. A few drops of the de-gassed mixtures were then sandwiched between two pieces of polyimide film separated by 1 μm thick Teflon spacers, and then cured at 120°C for two days. Copolymer samples were prepared by mixing PPO monoamines with stoichiometric amounts of Br-DGEBA at 130°C, sandwiching the mixtures between polyimide sheets, and curing at 110°C for three days. At these temperatures the cure reaction is dominated by the amine/epoxide reaction. All samples were fully cured at under the conditions employed.

The specimens prepared for this study included three single amine networks, a series of twelve network formulations using a pair of diamines mixed over a range of molar ratios, and model copolymers with both single and bimodal distributions of PPO grafting molecular weights. The single diamines used were D-400, D-2000, and D-4000. The bimodal networks were D-400/D-2000 mixtures in molar ratios of 8/1, 5/1, 3.5/1, 2/1, 1.5/1, 1.22/1, 1/1, 1/1.22, 1/1.5, 1/2, 1/3.5, 1/5, and 1/8. Model copolymers were prepared using M-600/M-2000 mixtures in molar ratios of 0/1, 1/0, and 1/1.

2.2. Small angle X-ray scattering measurements

X-ray scattering measurements were carried out at the 10 m SAXS facility at the National Institute of Standards and Technology [8]. The X-ray source used was a rotating copper anode operated at 47 kV and 180 mA with a wavelength of 1.54 Å selected with a graphite monochromator. The instrument uses pinhole collimation. Two dimensional data were taken over the range of scattering vector, q, ($q = 4\pi/\lambda \sin\theta$) from 0.02 to 0.26 Å^{-1} and were subsequently reduced to one dimensional (1D) intensity via circular averaging. Data in the $q = 0.25$–$0.5\ \text{Å}^{-1}$ range were obtained using a 1D detector. All data were corrected for dark currents and empty cell scattering. Sample thickness and transmission corrections were also implemented for each scattering result. A polyethylene standard was used for converting intensity data into absolute units. All Data presented are scaled by a factor $\vartheta_{\mathrm{Ep}}(1 - \vartheta_{\mathrm{Ep}})$, where ϑ_{Ep} is the volume fraction of Br-DGEBA in the sample, in order to normalize the dependence of scattering intensity on the composition of the network.

2.3. Thermal analysis

Differential scanning calorimetry was used to determine the glass transition behavior of epoxy networks curing using D-400/D-2000 diamine mixtures. The experiments were performed using a Perkin–Elmer instrument over a programmed temperature range of 213–423 K at a scanning rate of 30 K/min.

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[2] Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

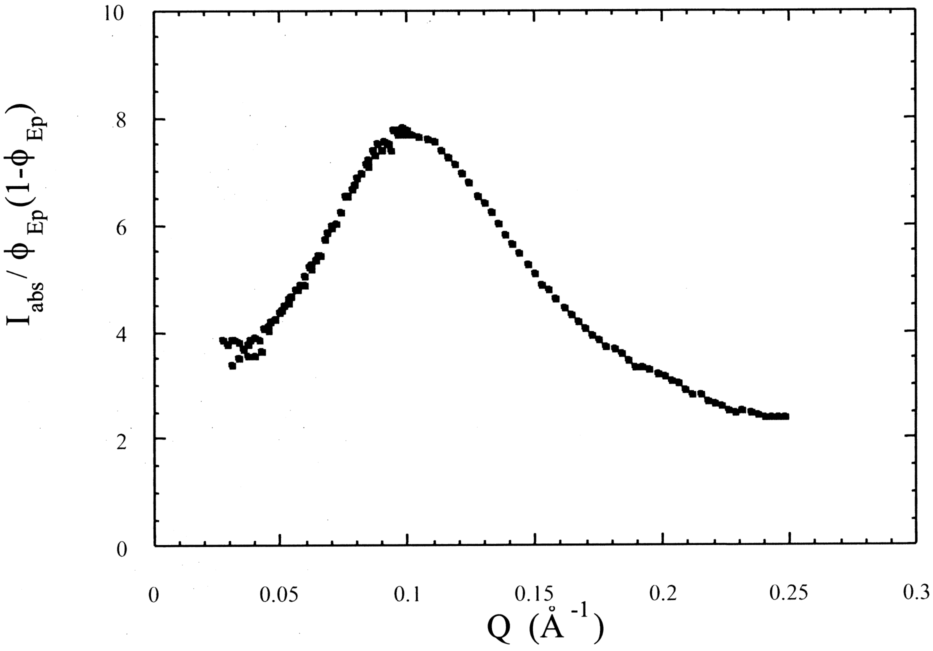

Fig. 1. X-ray scattering intensity versus scattering vector for an epoxy network made from Br-DGEBA and D-4000 diamine.

3. Results and discussion

The scattering intensity versus scattering vector curves for single amine networks are shown in Figs. 1 and 2. Pronounced scattering maxima are located at approximately 0.32, 0.15 and 0.10 Å^{-1} for the D-400, D-2000, and D-4000 networks, respectively. These peaks are in essentially the same position as those measured from deuterated DGEBA/D-series networks [3,5]. The scattering peak apparent in Fig. 1 can be attributed to the intra-network correlation among brominated epoxy segments separated by amine linkages, in analogy with the correlation between deuterated epoxy

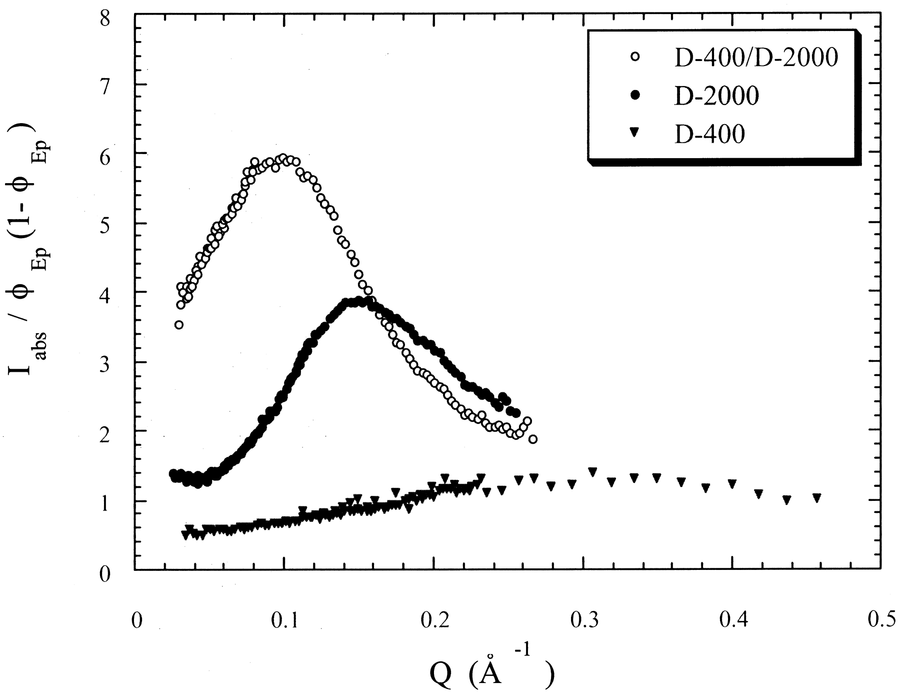

Fig. 2. X-ray scattering intensity versus scattering vector from epoxy networks: (○) Br-DGEBA//D-400/D-2000, 4//1/1; (●) Br-DGEBA//D-2000, 2//1; (▼) Br-DGEBA//D-400, 2//1.

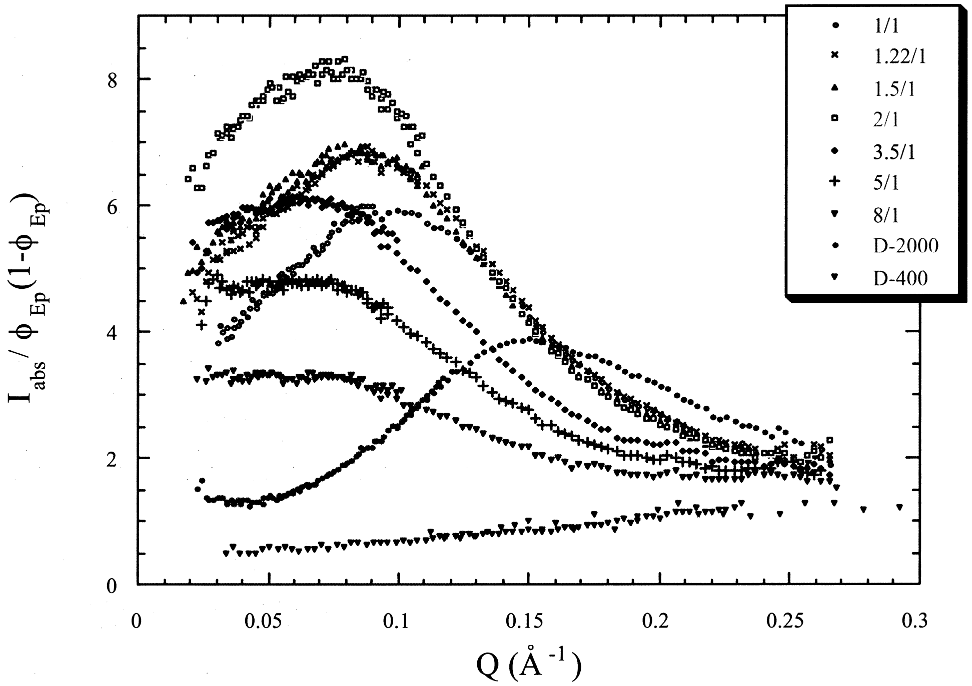

Fig. 3. X-ray scattering intensity versus scattering vector from epoxy networks. Br-DGEBA//D-400/D-2000 diamine cross-linking agent mixtures. D-400 rich mixtures. D-400/D-2000 ratios as indicated.

segments separated by amine linkages which was experimentally observed and theoretically verified previously [1–3].

Bimodal epoxy networks also show pronounced scattering maxima (Figs. 2–5). The scattering from the D-400/D-2000 1/1 bimodal network is compared to the scattering from D-400 and D-2000 single amine networks in Fig. 2. The main peak from the bimodal network occurs at

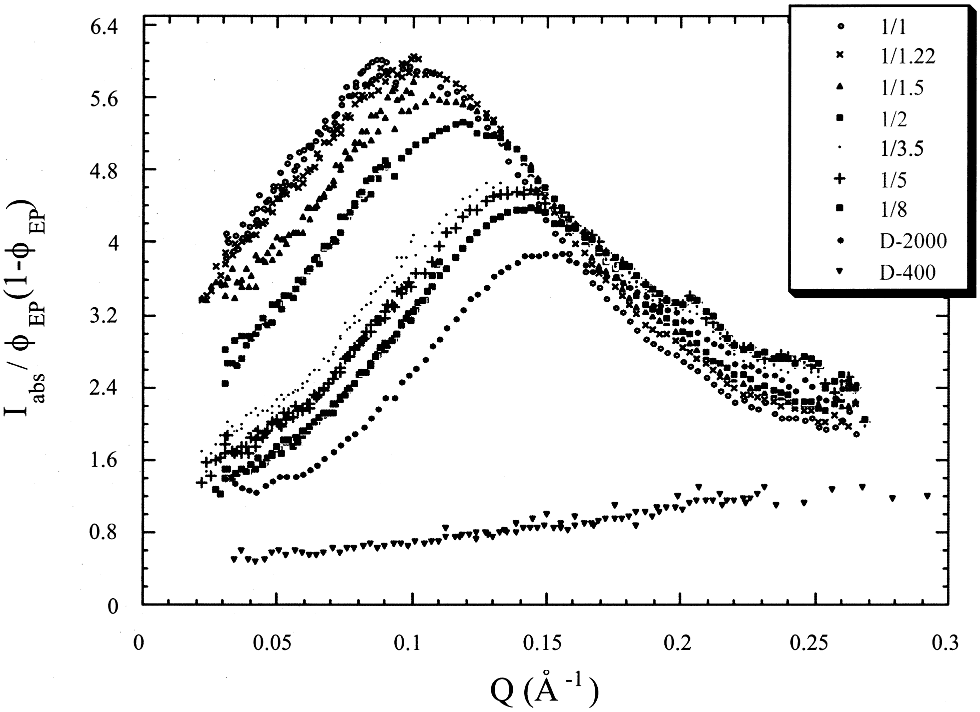

Fig. 4. X-ray scattering intensity versus scattering vector from epoxy networks. Br-DGEBA//D-400/D-2000 diamine cross-linking agent mixtures. D-2000 rich mixtures. D-400/D-2000 ratios as indicated.

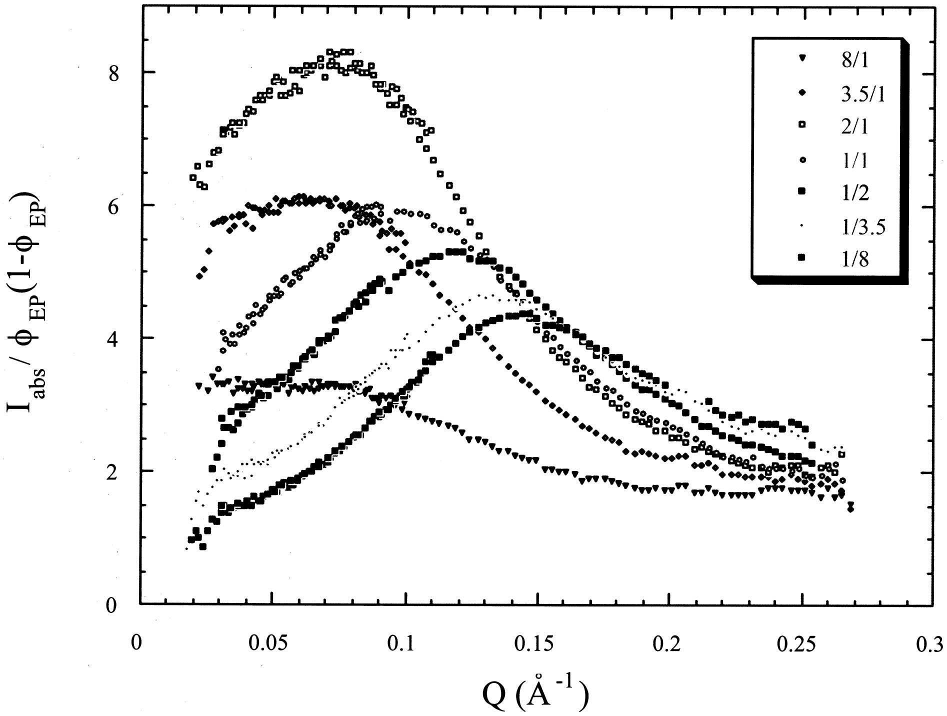

Fig. 5. X-ray scattering intensity versus scattering vector from epoxy networks. Br-DGEBA//D-400/D-2000 diamine cross-linking agent mixtures. D-400/D-2000 ratios as indicated.

much lower q than the main scattering peak from either of the single amine networks formulated using the component diamines. This result confirms the earlier indications of peak shifting in bimodal networks observed in a deuterated DGEBA/D-series epoxy network [3]. In addition to a shift in position, the contrast normalized intensity $I_{abs}/2(\vartheta_{Ep}(1-\vartheta_{Ep}))$ of the main scattering peak from the D-400/D-2000 network exceeds the intensity of the scattering peak from both the D-400 and the D-2000 networks.

The shift of the main scattering peak in the bimodal networks to lower q relative to the single amine specimens raises questions about the arrangement of the different amines in the network. (Previous studies suggested ordering of long and short chain diamines [3]). For this reason, additional information about the development of bimodal epoxy network structure was sought by investigating of the structure of a specific bimodal network system, D-400/D-2000, as a function of the compositions of the diamine

Table 1
Scattering characteristics of Br-DGEBA//D-400/D-2000 bimodal networks

Mole ratio: D-400/D-2000	Peak position, q_{peak}(Å^{-1})	Peak intensity, I_{peak} (cm^{-1})	Normalized peak intensity, $I_{peak}/(\vartheta_{Ep}(1-\vartheta_{Ep}))$ (cm^{-1})
1/0	0.32	0.29	1.2
0/1	0.15	0.78	3.8
1/1	0.10	1.4	5.8
1.22/1	0.085	1.6	6.7
1.5/1	0.082	1.7	7.0
2/1	0.075	2.0	8.0
3.5/1	0.065	1.5	6.1 (diffuse)
5/1	0.060	1.2	4.8 (diffuse)
8/1	0.055	0.83	3.3 (diffuse)
1/1.22	0.11	1.4	5.9
1/1.5	0.11	1.3	5.5
1/2	0.12	1.2	5.3
1/3.5	0.14	0.98	4.7
1/5	0.14	0.95	4.5
1/8	0.15	0.89	4.5

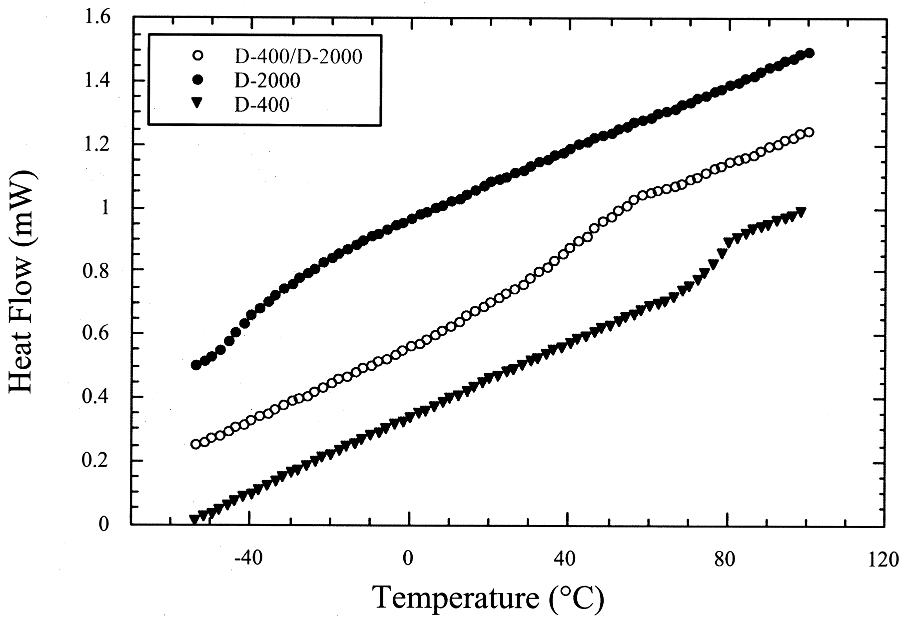

Fig. 6. DSC traces from Br-DGEBA/ diamine networks: (○) Br-DGEBA//D-400/D-2000, 4//1/1; (●) Br-DGEBA//D-2000, 2//1; (▼) Br-DGEBA//D-400, 2//1.

cross-linking agent mixtures. It is important to note that the stoichiometric molar ratio of epoxy to amine, 2:1, is maintained throughout this series of formulations, and only the ratio of the number of amine groups contributed by D-400 chains relative to the number of amine groups contributed by the D-2000 chains is changed. The results of the composition study, shown in Figs. 3–5, clearly demonstrate that the main scattering peak from bimodal networks prepared in any D-400/D-2000 mole ratio is positioned below the main scattering peak from either D-400 single diamine network or the D-2000 single diamine network. The position and intensity of the scattering peak in the bimodal networks is clearly a function of composition of the diamine mixture (Table 1 and Figs. 3–5). Peak intensity reaches a maximum near the middle of the concentration range on the D-400 rich side, where the molar ratio of amine groups contributed by D-400 to amine groups contributed by D-2000 equals 2/1. The peak position appears to shift continuously towards lower q as the concentration of D-400 in the network increases (Fig. 3) although it becomes difficult to identify a peak position once the ratio of D-400 to D-2000 exceeds 3.5/1 as the zero angle scattering intensities also increase.

The D-series diamines are expected to mix homogeneously regardless of molecular weight due to the nearly identical chemical compositions of the molecules. Therefore, it is also expected that the two diamines used to formulate any given bimodal network will incorporate themselves randomly into the epoxy network. However, the appearance of a highly reproducible, anomalous scattering peak at low q in all bimodal networks suggests the formation of a structure having a larger correlation length than that corresponding to the spacing between amine linkages, as observed in single amine networks. This suggestion of longer range correlations raises questions about the arrangement of diamines within bimodal networks; what sort of structure may lead to an increase in the correlation length of bimodal networks relative to single diamine networks?

One possibility is a macroscopic segregation within the network of Br-DGEBA//D-400 linkages and Br-DGEBA//D-2000 linkages. This possibility was investigated using differential scanning calorimetry, which would be expected to show evidence of a single glass transition temperature for a chemically homogeneous network, and two glass transition temperatures for a segregated network. The results for D-400/D-2000 bimodal networks, illustrated in Fig. 6, show evidence of a single, broad glass transition occurring over the region spanning the glass transition temperatures of D-400 and D-2000. This behavior indicates that segregation has not occurred over a macroscopic length scale in the bimodal network. The SAXS results may also be examined in terms of the structural heterogeneity in the bimodal networks. Power law behavior in the high q region with a limiting power law exponent of $n = -4$ is a signature of scattering from phase separated systems with sharp interfaces [9]. For those networks in which the maximum occurs at low enough q such that power law behavior may be observed, the characteristic exponent is from $n = -1.3$ to $n = -1.5$ which is considerably lower than would be expected for a phase separated system.

In the absence of phase segregation, one may look to intra-network structure to account for the observed behavior. This approach was taken in previous work by Wu and Bauer [3], and an ordered, linear, alternating copolymer of the type $(A_1{-}B{-}A_2{-}B)_N$ was chosen as a model system where A_1 represents diamine 1, A_2 represents diamine 2, and B represents the epoxy linkage. The scattering from such a

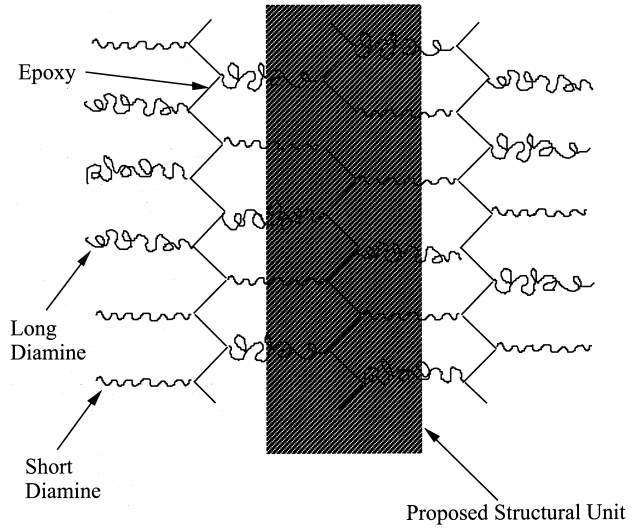

Fig. 7. Schematic representation of a bimodal network, illustrating the repeat unit chosen as the building block of the network for modeling.

model system was calculated for comparison with that from single amine chains $(A_1–B)_N$ or $(A_2–B)_N$. The comparison between such a model system and a network structure is based on the observation that as one maps out the monomers in the network along the (A–B–A–B–…) paths, many $(A_1–B–A_2–B–…)$ paths will be encountered. Thus, the theoretical prediction for the scattering from an $(A_1–B–A_2–B)_N$ model structure was derived, and the following points have been demonstrated; 1) the primary scattering feature of such a structure is a single peak occurring at lower q than that resulting from either an $(A_1–B)_N$ structure or an $(A_2–B)_N$ structure; 2) the scattering maxima corresponding to the individual A_1–B and A_2–B structures are absent. These results agree qualitatively with the scattering behavior of bimodal epoxy networks, as observed currently and previously [3], and are the motivating factor for examining the scattering from bimodal networks over a range of composition.

While the previous calculations based on $A_1–B–A_2–B–…$, a regularly alternating structures, provided encouraging results, they are difficult to compare to the scattering from bimodal networks in which the ratio of A_1 to A_2 monomers is greatly different from unity. This difficulty can be circumvented by modeling the networks in an alternative manner. In addition to mapping along the A_i–B paths, the monomer positions in an A_i/B network can also be fully mapped along $(B'–B'–B'–…)$ paths, in which B' represents a B monomer having an A_i graft (Fig. 7). Such a comb-shaped, B' molecule is taken as the basic building block or the structural unit for the networks. Exact replicas of the idealized comb-shaped or graft molecules were synthesized from epoxy mixed with mono-functional amines. This allows a direct comparison of the scattering from these copolymers to our calculation, and to the scattering from nearly chemically identical networks. Though the theoretical calculations will be compared to network scattering, they are strictly derived for bulk systems in which comb-shaped or graft copolymers are packed randomly. The connectivity among the graft copolymer chains to form a network has not been included in the model calculation. In principal, the connectivity inherent in real networks could significantly affect the scattering.

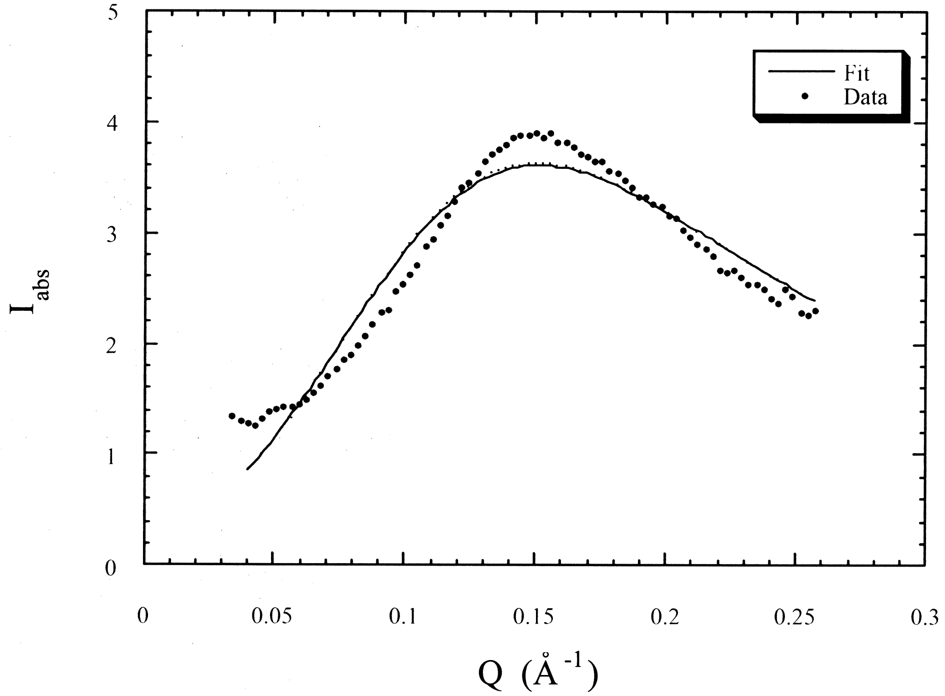

Fig. 8. Comparison between experimental scattering (●) from the Br-DGEBA//D-2000 network and the best numerical fit to the data (·).

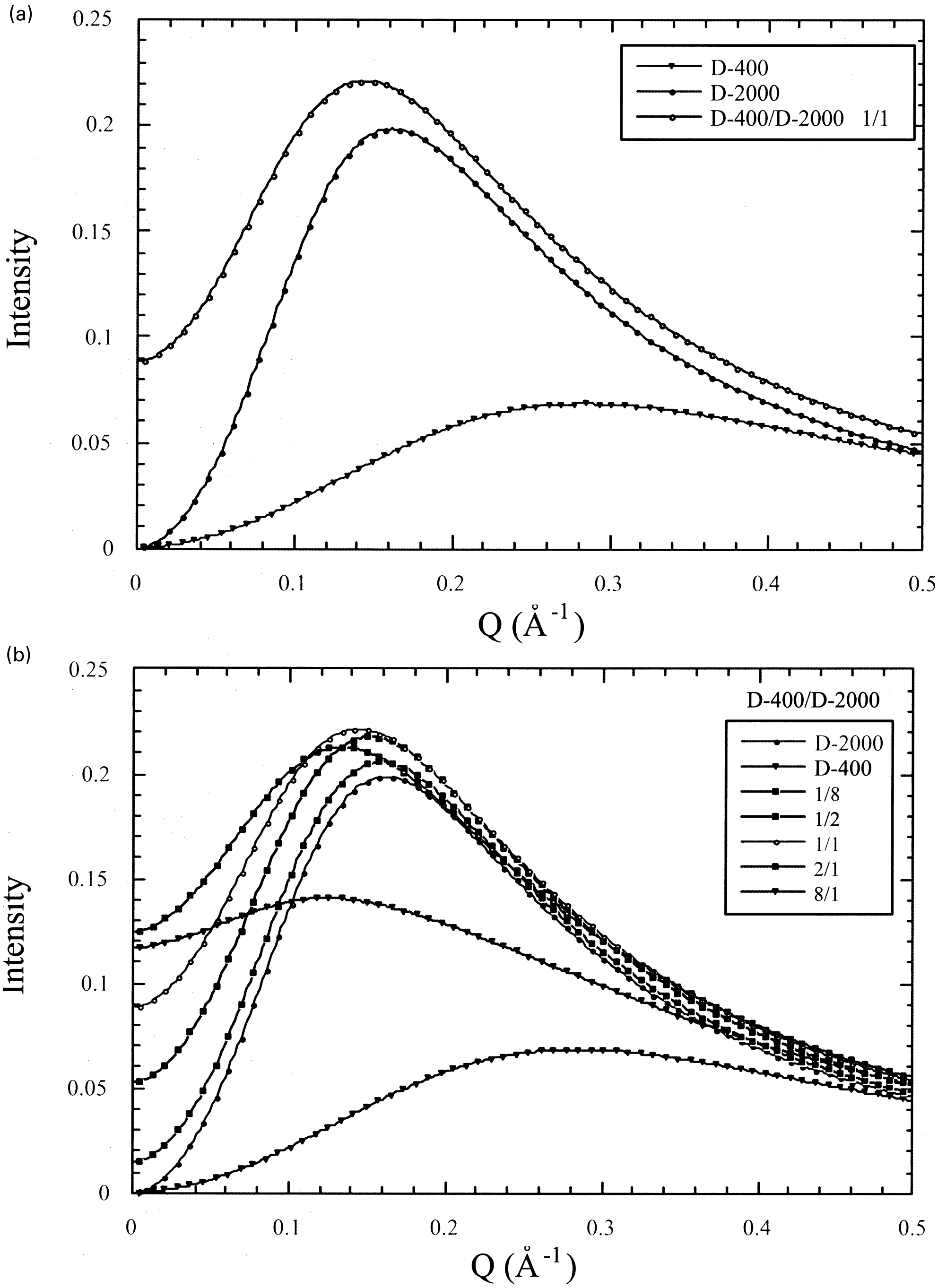

Fig. 9. Simulated scattering from epoxy networks based on the copolymer scattering model with $l = 6.44$ Å: (a) D-400 and D-2000 single amine networks and the 1/1 D-400/D-2000 bimodal network; (b) D-400/D-2000 bimodal networks (mixtures as indicated).

The theoretical framework for the calculation of scattering from bimodal comb-shaped molecules is outlined below. Random phase approximation scheme was used and the form factors for the comb-shaped copolymers were calculated using the expressions given by Benoit and Hadziioannou [7]. For the bimodal networks a random placement of the long diamine chains and the short diamine chains is assumed and the resultant scattered intensity, $I(q)$, from an $(\mathrm{A{-}B})_N$ multiblock copolymer is given by:

$$I(q) = \Delta b^2 \frac{P_\mathrm{A}(q)P_\mathrm{B}(q) - P_\mathrm{AB}(q)^2}{P_\mathrm{A}(q) + P_\mathrm{B}(q) + 2P_\mathrm{AB}(q)}, \tag{1}$$

where Δb^2 is the difference in scattering length density between a and b monomer units, and P_A, P_B, and P_AB are intra-chain structure factors corresponding to all A–A, B–B, and A–B correlations along a given comb or

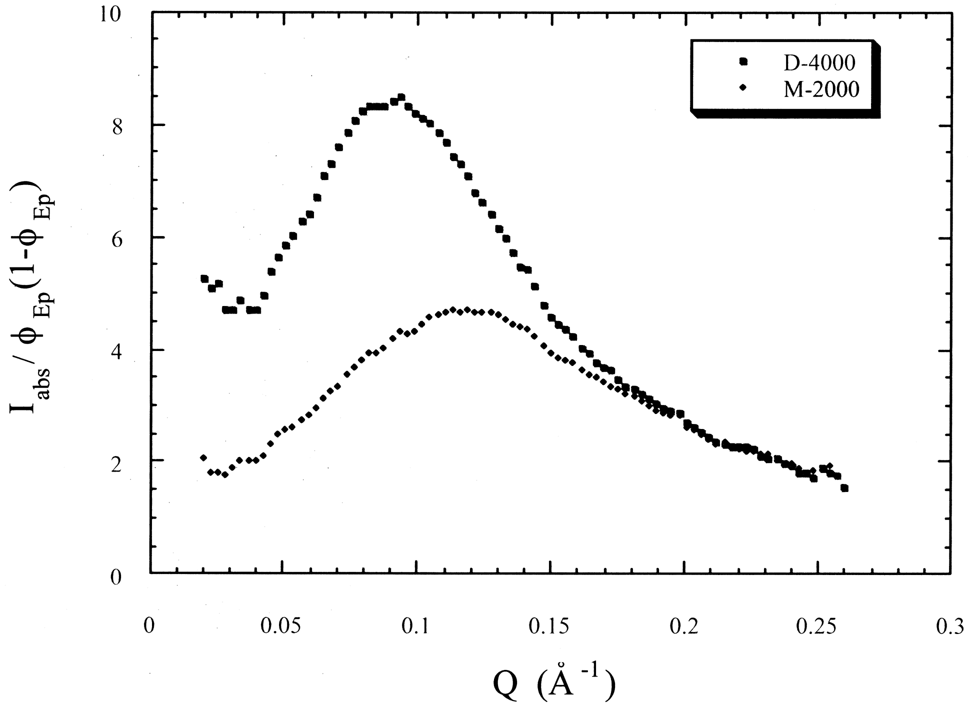

Fig. 10. X-ray scattering intensity versus scattering vector from the Br-DGEBA//D-4000 network (■) and the Br-DGEBA//M-2000 copolymer (◆).

graft molecule, respectively. Throughout this work the molecular weight of a PPO repeat or monomer unit was taken as unity. The thermodynamic interaction parameter between A and B units (χ_{AB}) is assumed to be zero. The structure factors $P_{i,}$ for a block copolymer having a comb shaped or graft architecture are:

$$P_A(q) = u\left[\frac{P_a(q)}{n_a} + \frac{2A_a^2(q)X_b}{Nn_a}\left(\frac{N}{1-x_b} - \frac{1-x_b^N}{(1-x_b)^2}\right)\right], \tag{2a}$$

$$P_B(q) = v\left[\frac{P_b(q)}{n_b} + \frac{2A_b^2(q)}{Nn_b}\left(\frac{N}{1-x_b} - \frac{1-x_b^N}{(1-x_b)^2}\right)\right], \tag{2b}$$

$$P_{AB}(q) = \frac{u}{Nn_a}A_a(q)A_b(q) \times\left[\frac{1-x_b^N}{(1-x_b)} + \frac{2}{1-x_b}\left(N - \frac{1-x_b^N}{1-x_b}\right)\right], \tag{2c}$$

where N is the total number of (A–B) repeat units, n_b is the number of monomers per B block, n_a is the average number of monomers per A block defined as ($f_{a1}n_{a1} + f_{a2}n_{a2}$) where f_{ai} is the number fraction of a_i blocks, u the volume fraction of a monomers, v the total volume fraction of b monomers identical to ϑ_{Ep} (used to normalize the scattering intensities in Figs. 1–5, 10, 11), and x_i, A_i and $P_{a,b}$ are defined in the following equations for polymer chains approximated as Gaussian coils:

$$P_a(q) = n_{a1}^2 f_{a1} P_{a1}(q) + n_{a2}^2 f_{a2} P_{a2}(q), \tag{3a}$$

$$P_{ai}(q) = \frac{2}{q^2 r_{ai}^2}(1 - A_{ai}(q)),$$

$$P_b(q) = n_b^2\left[\frac{2}{q^2 r_b^2}\left(1 - \frac{A_b(q)}{n_b}\right)\right], \tag{3b}$$

$$A_a(q) = n_{a1} f_{a1} A_{a1}(q) + n_{a1} f_{a2} A_{a2}(q),$$

$$A_{ai}(q) = \frac{1}{q^2 r_{ai}^2}(1 - x_{ai}), \tag{4a}$$

$$A_b(q) = n_b\left[\frac{1}{q^2 r_b^2}(1 - x_b)\right], \tag{4b}$$

$$x_{ai}(q) = (1 + \epsilon q^2 r_{ai}^2)^{-1/\epsilon}, \tag{5a}$$

$$x_b(q) = (1 + \eta q^2 r_b^2)^{-1/\eta}, \tag{5b}$$

$$\left(\frac{M_w}{M_n}\right)_A = 1 + \epsilon, \tag{6a}$$

$$\left(\frac{M_w}{M_n}\right)_B = 1 + \eta, \tag{6b}$$

where $r_i = ((1/6)\ n_i)^{0.5}\ l_i$ is the radius of gyration of block i with n_i monomer units of step length l_i. Eqs. (1)–(3b) may be used to calculate the scattering for a

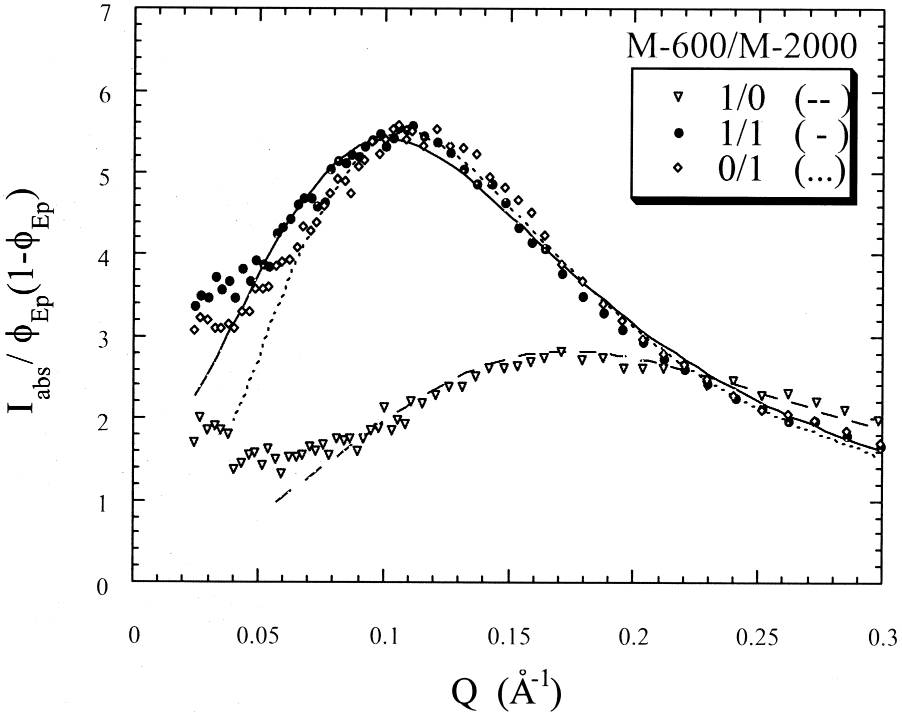

Fig. 11. The experimental results and their best fits of Br-DGEBA//M-600/M-2000 copolymer series. M-600/M-2000 ratios as indicated.

comb copolymer if the parameters N, n, l_i, ϵ and η are known, or to fit one or more of these parameters by matching the calculation with experimental scattering data.

The expressions (1)–(6b) have been employed to fit the experimental data from both single diamine and bimodal networks using a non-linear least squares numerical routine. The fitted parameters include an arbitrary intensity scaling factor and a single monomer step length l. While it is recognized that the epoxy segments should be stiffer than the PPO segments and therefore l_{Epoxy} should be larger than l_{PPO}, it is not possible to fit these variables separately using the current analysis due to close coupling of these two variables. Consequently a single fitted parameter l was used for both A and B units and this provides a simplistic average of characteristic lengths of all the chains in the network.

A comparison between the theoretical fit and the experimental data from the Br-DGEBA//D-2000 network is shown in Fig. 8. The peak position is fit reasonably well, though the shape of the peak and the low q intensity do not match well between experiment and the best fit to the comb copolymer scattering prediction. The fitted values of l (D-400: 6.3Å, D-2000: 6.6 Å, D-4000: 8.5Å) are similar to what may be expected for the Kuhn length of PPO [10]. Fitted curves for the bimodal networks have been generated in the same manner, the agreement between experiment and the model is only marginal. In addition, an acceptable fit of the peak positions in bimodal networks can be achieved only when the characteristic length, l, of the bimodal network is allowed to substantially exceed that of the single amine networks. The maximum l value occurs in the network where the weight fraction of D-400 and D-2000 chains are roughly equal (Table 2). If this result were valid it would imply that the PPO chains assume a stretched configuration in bimodal networks relative to single amine networks. However, previous evidence gathered from swelling studies has shown that the swelling ratios of bimodal networks lie between those of the corresponding single diamine networks [4], indicating that there is not significant perturbation of chain conformations in bimodal networks relative to single amine networks. The scaling factor, I_s, for normalizing the scattering intensities between the calculated and the experimental results, varies widely from case to case, but is significantly greater than the expected value of $\Delta b^2 = 0.22\ \mathrm{cm}^{-1}$ Eq. (1). This suggests that the interaction parameter, χ_{AB}, between the brominated epoxy and the diamines is greater than zero. Alternatively, this observation can be interpreted in terms of an inter-chain segregation between (A1–B) units and (A2–B) units. All calculations conducted so far have been based on a simplified model with $\chi_{\mathrm{AB}} = 0$.

Without resorting to the unrealistic notion that the value of characteristic length l depends on bimodal or unimodal compositions, (1)–(6b) with a fixed $l = 6.44$ Å (the average from the D-400 and D-2000 fits) are used in the following calculations to evaluate the effect of a bimodal cross-linker molecular weight distribution on the scattering from Br-DGEBA//D-400/D-2000. The calculated results (Figs. 9a and 9b) show very little similarities with experimental trends; such as a shifting of the scattering peak in bimodal networks to lower q than for single amine networks across

Table 2
Fitting Parameters. Characteristic length, l_{fit}, and scaling factor, I_s

Amine pair (I/II)	Mole fraction I	Weight fraction I	Peak position q_{peak} (Å^{-1})	l_{fit} (Å)	I_s
D-400/D-2000 (1/0)	1.00	1.00	0.32	6.27	0.67
D-400/D-2000 (0/1)	0.00	0.00	0.15	6.61	3.88
D-400/D-2000 (8/1)	0.89	0.62	0.085	11.2	6.32
D-400/D-2000 (3.5/1)	0.78	0.41	0.075	12.9	8.38
D-400/D-2000 (2/1)	0.67	0.29	0.065	13.1	1.97
D-400/D-2000 (1/1)	0.50	0.17	0.10	10.1	6.26
D-400/D-2000 (1/2)	0.33	0.09	0.12	8.62	1.09
D-400/D-2000 (1/3.5)	0.22	0.05	0.14	7.30	4.25
D-400/D-2000 (1/8)	0.11	0.02	0.15	6.82	4.18
M-600/M-2000 (1/0)	1.00	1.00	0.17	6.83	0.87
M-600/M-2000 (0/1)	0.00	0.00	0.12	7.65	0.74
M-600/M-2000 (1/1)	0.50	0.23	0.12	7.91	0.85

the entire composition spectrum and broadening of the maxima corresponding to highly D-400 rich formulations. The only exception is the enhancement in zero angle scattering intensity, this enhancement is easily predictable once the building block of networks or linear chains is changed from a monodisperse structure unit to a mixture of two units of different molecular weight. Thus, it is concluded that the ‘‘bimodal comb or graft copolymer model’’ formulated above does not adequately describe the scattering from bimodal networks.

Owing to the failure of applying the aforementioned model to bimodal networks, it becomes interesting to examine whether it ever works for bimodal comb copolymer systems. To investigate this point, measurements on copolymers made from Br-DGEBA and monoamine terminated PPO were conducted. Before one makes a comparison between the model calculation and the experimental data, the scattering curves from a Br-DGEBA//M-2000 copolymer and a Br-DGEBA//D-4000 network are compared in Fig. 10. If the scheme outlined in Fig. 7 holds true, i.e. if the scattering of a network can be simulated by a randomly packing of comb-like chains, one expects the scattering intensities from the D-4000 and the M-2000 samples to be identical. Clearly, there is a difference between the scattering from the two systems— the network peak is sharper and occurs at lower q than the peak in the model copolymer scattering. The enhanced peak intensity indicates the existence of inter-chain correlations in the networks and these correlations have not been included in the current calculation based on randomly packing. One possible remedy to this deficiency is to introduce a positive interaction parameter between the amine chains and the epoxy chains as discussed before.

Bimodal comb copolymers were synthesized in addition to single monoamine chains, and the scattering results from these molecules (Fig. 11) can be fitted reasonably well using the theoretical model described before. The differences between the single amine copolymer scattering and the bimodal copolymer scattering are clearly less dramatic than the parallel comparison in scattering between networks; there is virtually no shift in the peak position observed in the bimodal copolymer scattering relative to the scattering from the corresponding single monoamine copolymers. Fitting of the data with the equations outlined above results in predictions of nearly identical characteristic length for bimodal copolymers and single monoamine copolymers, in contrast to the widely varying characteristic lengths predicted for bimodal versus single amine networks (Table 2). These results indicate that the model developed herein works well for graft copolymers even it failed badly for networks.

4. Conclusions

The small angle X-ray scattering behaviors from single amine epoxy networks, bimodal epoxy networks, and model epoxy graft copolymers have been examined. Prominent scattering peaks have been observed in all the materials. The scattering from a model graft copolymer with uniform graft molecular weight was found to be significantly different from that of a network comprised of identical chains. The network scattering exhibits a sharper maximum at lower q than that from the model graft copolymer. This observation indicates that the molecular structure of networks can not be adequately described by a randomly packing of equivalent graft chains. Inter-network correlations, which have not been included in our model calculation, are likely the cause of these differences. A theoretical framework based on randomly packing comb-shaped or graft copolymers work well for all the model graft copolymers including the bimodal graft copolymer. The scattering from bimodal graft copolymer did not exhibit the anomalous shift of peak to lower q, such a shift was conspicuous in the scattering from bimodal networks as compared to the corresponding single amine networks. This shift of the scattering maxima to lower q in bimodal networks has been highly reproducible, occurring in networks over a wide range of compositions. This observed shift in peak position indicates the existences of longer correlation distances in bimodal networks. Both thermal analysis and limiting power law behavior of the X-ray scattering data preclude phase segregation in the bimodal epoxy networks studied so far. The molecular structure responsible for this long correlation length remains elusive.

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