Structural studies of epoxy resins, acetylene terminated resins and polycarbonate

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Wide angle X-ray scattering studies were performed in the Q range 2.1–35 nm^{-1} (Q is the scattering vector, $4\pi \sin\theta/\lambda$) on a number of cured epoxies, including diglycidyl ether of bisphenol A (DGEBA) cured with meta phenylene diamine (mPDA), and other epoxies in which the isopropylidene unit of DGEBA was replaced by $-SO_2-$, $-CH_2-$, and $-C(CF_3)_2-$ groups. WAXS studies were also done on acetylene terminated bisphenol (ATB) and on acetylene terminated sulphone (ATS). In DGEBA cured with mPDA, as well as in ATB, a scattering maximum was observed at $Q \approx 4\ \mathrm{nm}^{-1}$ (this maximum is referred to as a low angle peak in this paper). This peak was also present in the epoxy containing the $-CH_2-$ group between the phenyl rings. In ATS, as well as in epoxy containing the $-SO_2-$ group, this maximum was not observed. In epoxy containing the $-C(CF_3)_2-$ group the maximum was extremely weak, and an additional shoulder was present at $Q \approx 15.6\ \mathrm{nm}^{-1}$ in the main amorphous halo. The low angle maximum is also present in the polycarbonate of bisphenol A. On stretching the specimen, the intensity of the low angle peak in epoxy as well as in polycarbonate concentrates on the meridian. It was concluded that the low angle peak in polycarbonate, AT resin and epoxy has the same origin. Possible reasons for the occurrence of this peak are discussed. WAXS studies were also done on DGEBA cured with varying amounts of mPDA at two different curing conditions. For these samples, shifts were observed in the peak position of the main amorphous halo, which was found to have good correlation with the macroscopic density.

(Keywords: epoxy resin; acetylene terminated resin; polycarbonate; WAXS)

INTRODUCTION

In the X-ray scattering of a number of amorphous polymers, including polystyrene and poly(methylmethacrylate), a peak has been observed[1] at a scattering angle below the range of the main amorphous halo. The presence of such a scattering peak was also reported in cured epoxy resins[2] (diglycidyl ether of bisphenol A (DGEBA) cured with 4,4′-diaminodiphenylmethane (DDM) and with hexahydrophthalic anhydride (HHPA)), as well as in polycarbonate[3] of bisphenol A. A strong intensity peak (at $Q = 4\ \mathrm{nm}^{-1}$) has also been reported[4] in the small angle neutron scattering (SANS) study of deuterated DGEBA cured with low molecular weight di- and tri-functional amines. The intensity of this peak was shown to have diminished when the curing was done with higher molecular weight difunctional amine. It has been demonstrated that the scattering behaviour of amorphous polymers can give important structure information[5,6]. In this paper possible reasons for the occurrence of the low angle peak (Q in the range 3.4–4.6 nm^{-1}) in epoxy and in polycarbonate are discussed.

The curing conditions and the nature and amount of the curing agent can affect the intensity and the peak position of the maximum in the scattering curve. The peak position shift has been observed as a function of curing time in phenolic resins[7]. Generally one is tempted to use Bragg's equation for determining the d-spacing corresponding to the peak position in amorphous materials. However, the use of Bragg's equation can at best only give approximate values for the frequently occurring interatomic distances in amorphous materials[1,8,9]. Therefore, for amorphous halos it is not always possible to determine the exact value of inter- or intra-molecular distance from the peak position; however, from the shift in the peak positions in the same or similar specimens due to varying specimen treatments it is generally possible to infer the relative change in inter- or intra-molecular distances. For these reasons we will refrain from deducing the values of the spacings corresponding to the peak positions, and only their relative variations will be discussed.

The minimum energy conformations of DGEBA and the $-C(CF_3)_2-$ analogue of DGEBA are given in *Figures 1* and *2*, respectively. The positions of the two $-CF_3-$ groups are staggered, while the two $-CH_3-$ groups appear to be almost overlapping each other. The crystal structure of DGEBA was determined by Flippen-Anderson and Gilardi[10], who found the epoxide ring on one end of the molecule to be disordered.

EXPERIMENTAL

The X-ray scattering studies were performed on epoxy resins, acetylene terminated (AT) resins and polycarbonates. The chemical repeat units of all the samples and the curing agents are given in *Figure 3*. Curing conditions for various samples are listed below.

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Acetylene terminated sulphone[11] (ATS) was cured using the following cure cycle: 150°C, 45 min; 170°C, 45 min; 250°C, 4.5 h.

Acetylene terminated bisphenol[11] (ATB) was cured using the following cure cycle: 140°C, 15 h; 170°C, 5 h; 250°C, 4 h.

Diglycidyl ether of bisphenol A (DGEBA) was cured[12–15] with 7.5, 10, 14.5, 20 and 25 phr of mPDA (phr = parts per hundred of DGEBA) at the following cure conditions: standard cure, 2 h at 75°C, 2 h at 125°C; post-cure, standard cured samples cured at 175°C for 8 h in Argon.

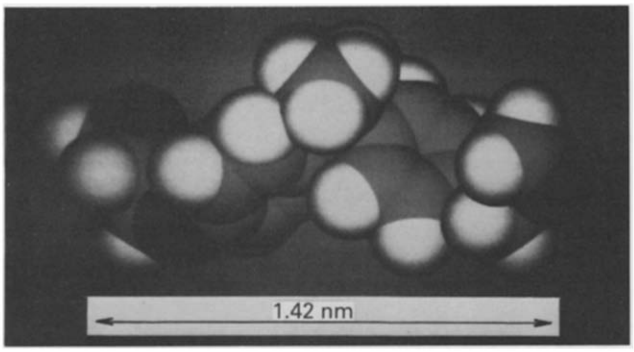

Figure 1 Minimum energy conformation of DGEBA molecule

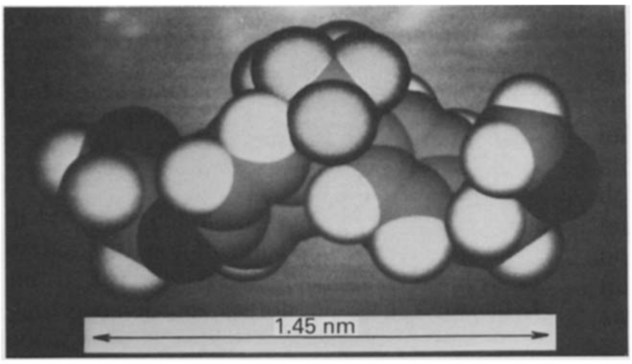

Figure 2 Minimum energy conformation of $-C(CF_3)_2-$ analogue of DGEBA molecule

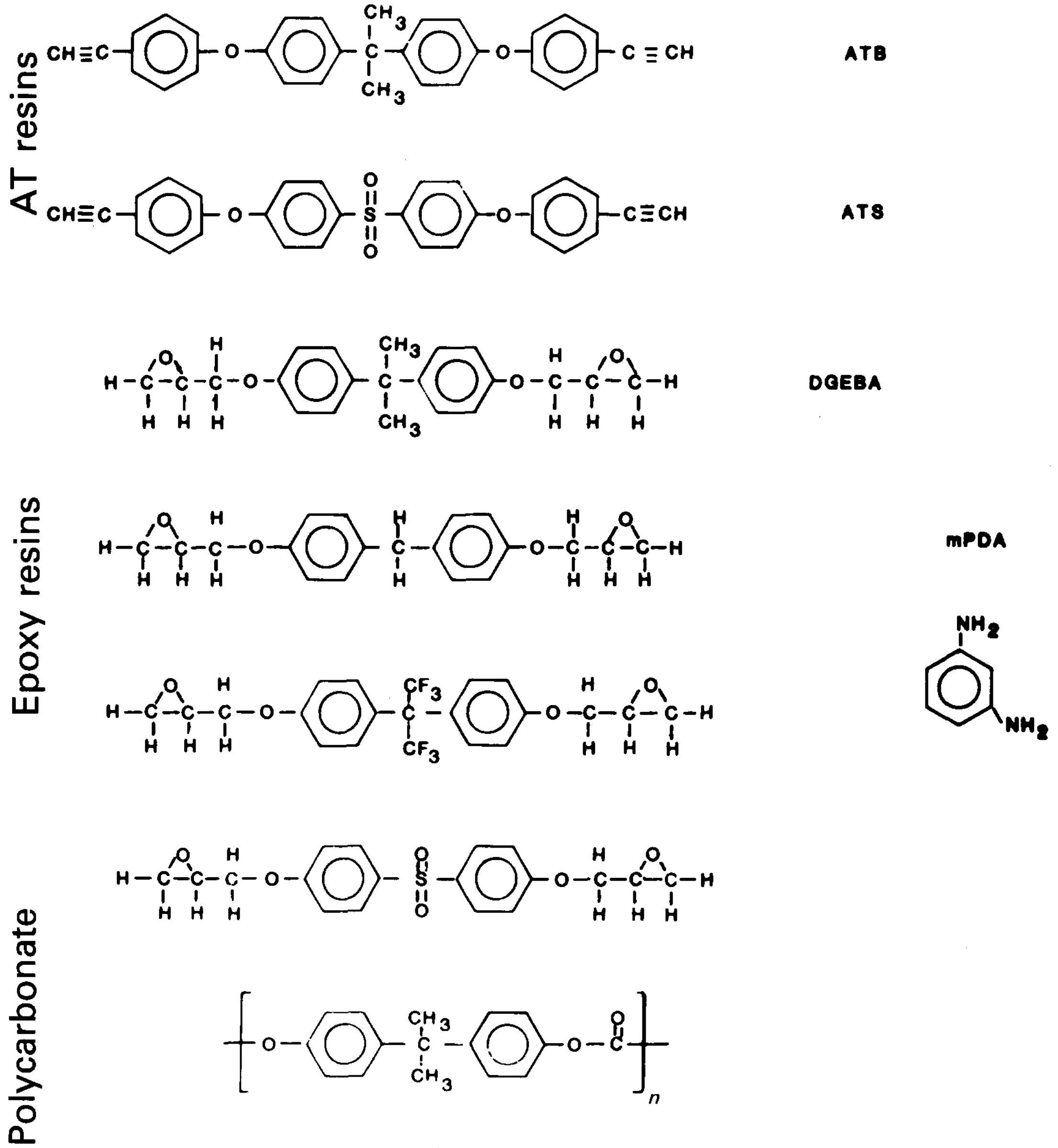

Figure 3 Repeat units of various specimens used in the present study

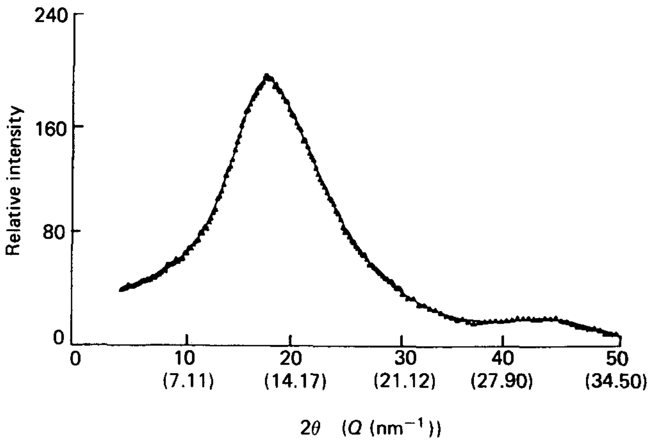

Figure 4 WAXS curve of ATS

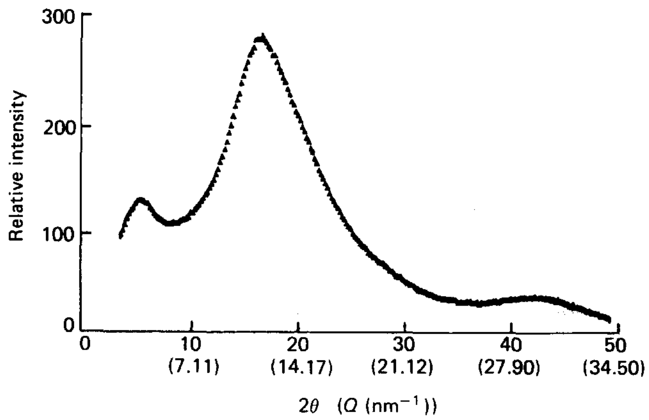

Figure 5 WAXS curve of ATB

$-CH_2-$ and $-C(CF_3)_2-$ analogues of DGEBA were standard cured (2 h at 75°C and 2 h at 125°C) with stoichiometric amounts of mPDA.

Diglycidyl ether of diphenyl sulphone (DGEDPS, $-SO_2-$ analogue of DGEBA) was also cured with the stoichiometric amount of mPDA. DGEDPS has a high melting point (about 155°C) and therefore mixing of mPDA at this temperature was not proper because of fast curing.

X-ray scattering studies were performed on a four-circle Picker diffractometer using CuKα radiation and a graphite crystal monochromator. Data was collected in the symmetrical-transmission geometry.

RESULTS

AT resins

The wide angle X-ray scattering (WAXS) curves of the cured ATS and ATB samples are given in *Figures 4* and *5* respectively. Within the given angular range for ATS two amorphous halos, approximately at Q values of 12.7 and 30 nm^{-1}, are observed. In ATB an extra peak is observed at $Q = 3.9$ nm^{-1}. The only difference in the chemical structure of ATB and ATS is that the isopropylidene group ($-C(CH_3)_2-$) in ATB is replaced by the sulphone group ($-SO_2-$) in ATS. Therefore it is natural to associate the 3.9 nm^{-1} peak with the isopropylidene group between the two phenyl rings. Further discussion on the nature of this peak will be deferred to a later section. On post-curing no significant difference in peak position or peak intensity was observed for ATB or for ATS. Curing conditions mentioned in the experimental section for the ATB and ATS specimens are the optimum cure conditions for the two specimens and it was ascertained that the WAXS differences in the two specimens do not occur due to differences in the curing conditions.

Epoxy resins

The typical WAXS curve of DGEBA cured with mPDA is given in *Figure 6*. This scattering curve apparently has three peaks at $Q = 3.7$, 12.9 and 30 nm^{-1} (the fitting of more than three peaks will be discussed later in the curve fitting section). The intermediate peak is typical of amorphous polymers and arises from intermolecular correlations.

DGEBA standard cured with 25 phr mPDA was stretched in a tensile tester at 90°C to a draw ratio of 1.6 and then the specimen was brought back to room temperature and allowed to relax. The WAXS curves of the stretched and unstretched specimens are given in *Figure 7*. The intensity of the small angle peak increases on the meridian and decreases on the equator. The intensity of the amorphous halo at 13 nm^{-1} decreases on the meridian and increases on the equator.

Since comparison of the scattering patterns of ATB and ATS suggests that the small angle peak is a manifestation of the presence of the isopropylidene group $-C(CH_3)_2-$ between the phenyl rings, we decided to investigate if in epoxy (DGEBA cured with mPDA) this peak arises due to the same cause. We selected materials in which $-C(CH_3)_2-$ is replaced by groups which would affect the position and/or intensity of the small angle peak. Therefore materials were obtained in which the $-C(CH_3)_2-$ group in DGEBA was replaced by $-CH_2-$, $-SO_2-$ and $-C(CF_3)_2-$ groups.

WAXS curves for $-CH_2-$, $-SO_2-$ and $-C(CF_3)_2-$ analogues of DGEBA cured with mPDA are given in *Figures 8*, *9* and *10*, respectively. From these figures note that a small angle peak of reduced intensity is present in the $-(CH_2)-$ analogue. The peak in the $-SO_2-$ analogue of epoxy is almost non-existent. The $-C(CF_3)_2-$ analogue shows signs of a very weak small angle peak and its main amorphous halo has a very pronounced shoulder at about 15.6 nm^{-1}.

Polycarbonate

We also did a limited WAXS study on polycarbonate (trade name Merlan of Mobay Chemical Co.) which indicated the presence of a small angle peak at 4.4 nm^{-1}.

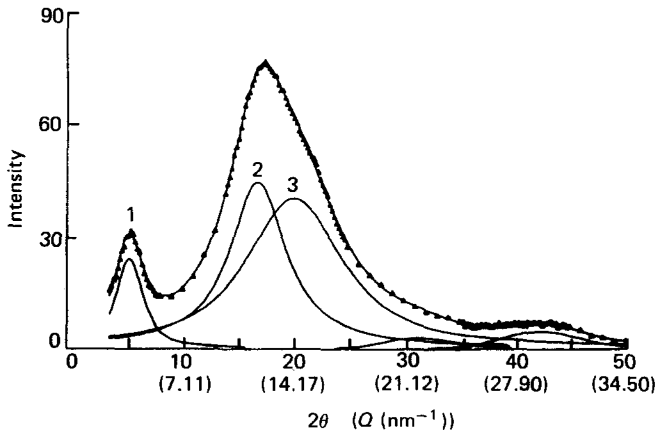

Figure 6 WAXS curve of DGEBA cured with 10 phr mPDA

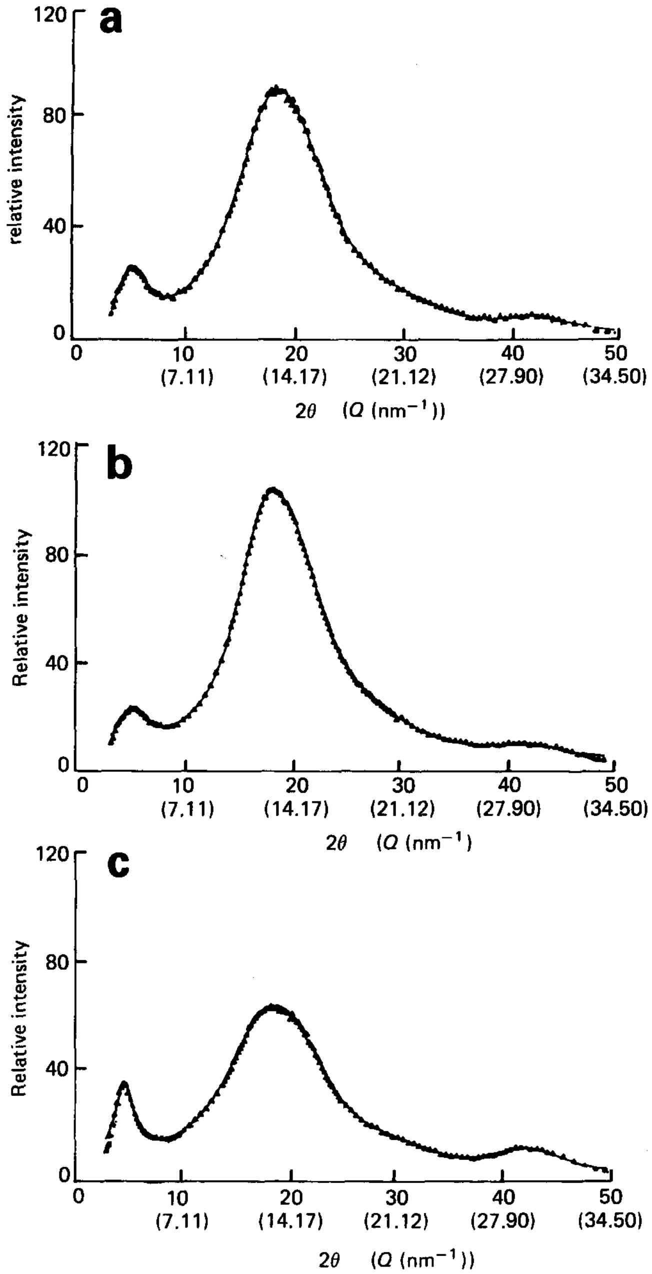

Figure 7 WAXS curve of DGEBA standard cured with 25 phr mPDA: (a) unstretched; (b), (c) stretched at 90°C to a draw ratio of 1.6; (b) equatorial; (c) meridional

Note, however, that in our WAXS scattering experiment the peak was not as intense and resolved as was observed by Turska *et al.*[3] On stretching the sample, the intensity of this small angle peak in polycarbonate (Merlan) increases on the meridian and decreases on the equator. Mitchell and Windle[19] have also studied the structure of polycarbonate.

Curve fitting

Detailed analysis of the amorphous scattering curves requires the use of a radial distribution function technique. However, useful information can be obtained from accurate determination of the peak positions and peak intensities, which in turn can be achieved by curve fitting. Initially we attempted to fit only three peaks in *Figure 6*. The fitting was done assuming the peaks to be Gaussian, Cauchy or a mixture of the two. It is emphasized that though the curves in all the figures are shown as a function of 2θ, the curve fitting was done as a function of scattering vector, Q. The DGEBA+mPDA scattering curves in the range 2.1–35 nm^{-1} could not be fitted by three peaks, and subsequently only two peaks were fitted in a limited Q range (up to 22.5 nm^{-1}) so that the peak positions and peak intensities of the first two intense peaks could be determined with accuracy. Although the two peaks in the limited Q range also did

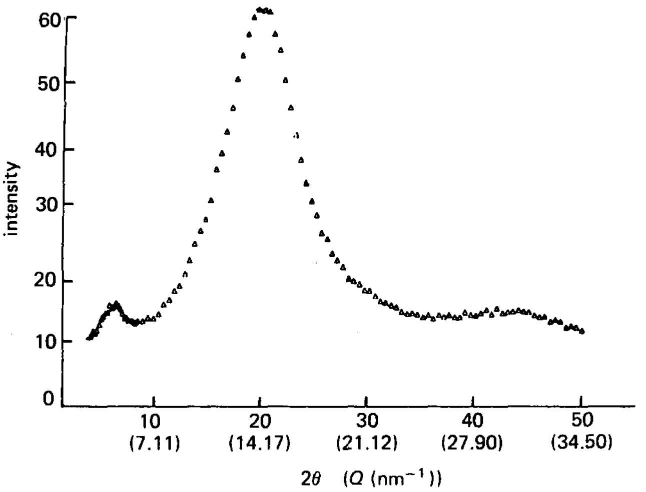

Figure 8 WAXS curve of $-CH_2-$ analogue of DGEBA standard cured with stoichiometric amount of mPDA

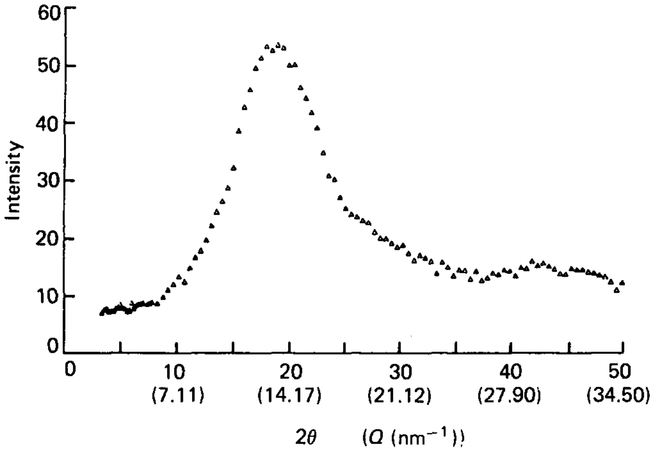

Figure 9 WAXS curve of $-SO_2-$analogue of DGEBA (DGEDPS) cured with stoichiometric amount of mPDA

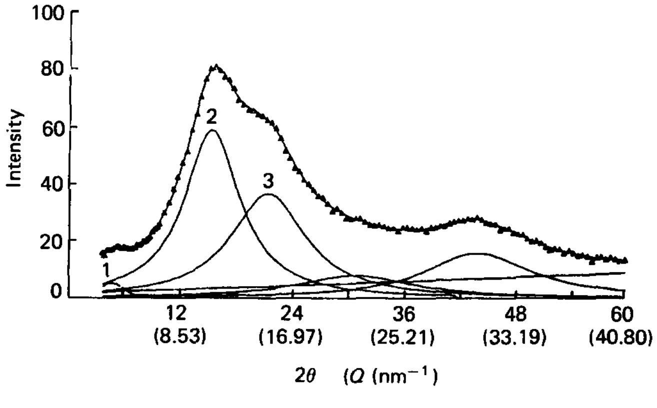

Figure 10 WAXS curve of $-C(CF_3)_2-$analogue of DGEBA cured with stoichiometric amount of mPDA

not fit satisfactorily, the peak positions and the peak intensities of both peaks could be better resolved. This avoids the problem of peak position shifts occurring due to overlapping peaks. Two-peak fitting parameters for the epoxy samples are given in *Table 1*. This table indicates the intensity and peak position variations as a function of the amount of mPDA and the cure condition. Discussion of intensity and peak position variation for the first peak will be deferred until the next section.

The peak position of the amorphous halo can be taken as a representation of the frequently occurring intermolecular distance. Macroscopic density also depends on molecular packing. Therefore the peak position of the amorphous halo is expected to have some correlation with the macroscopic density. The density values of the epoxy samples (DGEBA cured with mPDA) used in this study have been reported previously[12,13]. The correlation between peak position and (macroscopic density)$^{1/3}$ is shown in *Figure 11*. The one third power of the macroscopic density is plotted so that the length dimensions on both the axes are the same.

If the shoulder in *Figure 10* arises due to CF_3 groups, then scattering at similar angles is anticipated in *Figure 6*, arising from the CH_3 groups. The fact that the CH_3 group scattering is not distinguishable from the rest of the amorphous halo may be due in part to its lower electron density than its surroundings. To investigate the possibility of a shoulder similar to the one obtained in *Figure 10*, in DGEBA cured with mPDA, we attempted to fit an additional peak at the position at which the shoulder was anticipated.

Table 1 Parameters for two-peak curve fitting on DGEBA cured with different amounts of mPDA

	phr	I_1	A_1	Q_1 (nm^{-1})	I_2	A_2	Q_2 (nm^{-1})
Standard cure	7.5	1560	57	3.4	8120	1390	13.2
	10	1970	67	3.5	7840	1400	13.2
	14.5	2161	72	3.7	8610	1500	13.1
	20	1740	66	3.7	7890	1330	13.3
	25	1440		3.6	7520		13.4
Post-cure	7.5	1940	63	3.5	7840	1370	13.1
	10	2130	67	3.7	7480	1320	12.9
	14.5	2080	71	3.7	7940	1370	12.9
	20	1810	67	3.7	7560	1270	13.1
	25	1540	57	3.6	7360	1250	13.3

I = peak intensity, A = peak area, Q = peak position

During the curve fitting procedure it became obvious that in the Q range 2.1–35 nm^{-1} the curves could best be fitted by a minimum of four peaks at 3.7, 13, 22 and 31 nm^{-1}, and the fitting of a shoulder of the type in *Figure 10* requires five peaks. Therefore, in an attempt to fit five peaks, initially we allowed all the fitting parameters to vary. This revealed that for all the samples (DGEBA cured with mPDA) the positions of peak 2 and peak 3 (refer to *Figure 6* for peak numbers) did not change significantly; only their relative intensity was found to vary. Therefore these positions were fixed in the final fitting. The parameters of the first three peaks during such a five-peak fitting procedure are listed in *Table 2*. The typical five-peak fitting is shown in *Figure 6*. On post-curing, the intensity of peak 2 increases and that of peak 3 decreases, while for the same cure conditions the intensity of peak 2 was a maximum (and for peak 3 a minimum with the exception of the 20 phr standard cure specimen) for the specimen cured with the stoichiometric amount of mPDA.

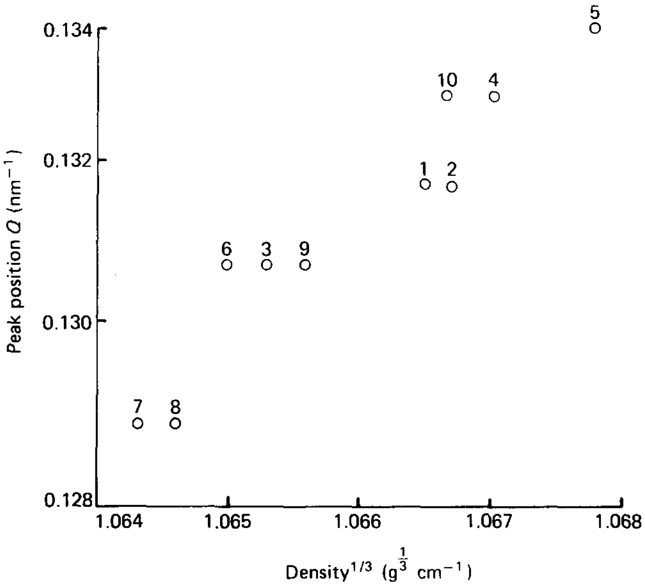

Figure 11 Peak position of the main amorphous halo of various specimens of DGEBA cured with mPDA, as a function of their macroscopic density: 1, 7.5 phr SC; 2, 10 phr SC; 3, 14.5 phr SC; 4, 20 phr SC; 5, 25 phr SC; 6, 7.5 phr PC; 7, 10 phr PC; 8, 14.5 phr PC; 9, 20 phr PC; 10, 25 phr PC

Table 2 Five-peak fitting parameters

	phr	Q_1 (nm^{-1})	I_1	HW_1	A_1	I_2	HW_2	A_2	I_3	HW_3	A_3
Standard cure	7.5	3.4	1780	0.041	95	3790	0.065	390	5280	0.094	780
	10	3.6	2330	0.037	134	4200	0.077	510	4460	0.112	700
	14.5	3.7	2570	0.034	139	5050	0.080	610	4380	0.112	710
	20	3.7	2050	0.039	127	4500	0.081	560	4250	0.099	586
	25	3.6	1670	0.043	110	4070	0.081	520	4320	0.087	528
Post-cure	7.5	3.6	2290	0.037	116	4060	0.069	440	4700	0.116	750
	10	3.7	2500	0.034	121	4700	0.077	570	3500	0.126	590
	14.5	3.8	2520	0.037	147	5150	0.084	640	3410	0.116	530
	20	3.7	2070	0.036	117	4418	0.080	540	4010	0.100	620
	25	3.7	1790	0.040	100	4140	0.080	520	4100	0.092	560

A = peak area, I = maximum peak intensity, HW = peak width at half maximum intensity
$Q_2 = 12.1\ nm^{-1}$, $Q_3 = 14.3\ nm^{-1}$

DISCUSSION

Small angle peak

The feature common to all the specimens (epoxy, AT resins and polycarbonate) in which a small angle peak of strong intensity has been observed is that they all have the isopropylidene unit between the two phenyl rings (with the exception of the $-CH_2-$ group between phenyl rings, which also gives a small angle peak). We believe that the origin of this peak in epoxy resins, AT resins and polycarbonates is the same and that it is a manifestation of the group between the two phenyl rings. Considering these observations and previously published results, any further understanding of this peak should at least satisfy the following known observations:

1. the presence[3] of the peak in polycarbonate of bisphenol A at 4.4 nm^{-1};
2. the presence of the peak in ATB and its absence in ATS (*Figures 4* and *5*);
3. the presence of the peak in DGEBA cured with mPDA, DDM[2] and HHPA[2], and in the $-CH_2-$ analogue of DGEBA cured with mPDA; and the variation in the peak position and intensity as a function of curing agent amount and cure condition (variations reported in *Table 2* for DGEBA cured with varying amounts of mPDA);
4. the absence or significantly reduced intensity of the peak in $-SO_2-$ and $-C(CF_3)_2-$ analogues of DGEBA cured with mPDA;
5. that on stretching the DGEBA cured with mPDA and in stretched polycarbonate of bisphenol A the intensity of the small angle peak concentrates on the meridian.

Factors giving rise to the above peak may be the chain flexibility and the intermolecular packing affected by the bulkiness and polarity of the various groups.

Chain flexibility

The flexibility of molecules having different units between the phenyl rings can be different. This question has been studied by Welsh *et al.*[16] for a number of chains having different groups, including $-C(CF_3)_2-$, $-SO_2-$ and $-CH_2-$, between the pyridylene rings. The energies for $-C(CF_3)_2-$, $-SO_2-$ and $-CH_2-$ groups between the pyridylene rings are 10, 16 and 19 kcal mol^{-1}, respectively, based on molecular mechanics computations. Since a lower energy barrier is easier to overcome, a chain with lower energy would be considered more flexible. Therefore the flexibility of these molecules would rank in the order pyr–$C(CF_3)_2$–pyr > pyr–SO_2–pyr > pyr–CH_2–pyr. If similar flexibility results are assumed for these groups between phenyl rings, then phenyl–CH_2–phenyl would be the most rigid of the three molecules. The rigidity in the chain may preserve some order for the intramolecular correlations between the two or more repeat units to be seen in the scattering. The molecules containing $-C(CF_3)_2-$ and $-SO_2-$ groups may be flexible enough that the intramolecular correlations are weakened, resulting in insignificant scattering.

Molecular packing

Besides flexibility, coulombic interactions between polar groups and the bulkiness of the side groups may contribute to a preferential packing arrangement which may be responsible for the small angle peak (or for the lack of it). A two-dimensional preferred packing arrangement of the DGEBA molecules is shown in *Figure 12*. In this model a number of isopropylidene groups form an elongated cluster (a four-group cluster is shown in *Figure 12*), the length of which is about the same as the observed spacing for the small angle peak. Such a cluster of $-C(CH_3)_2-$ groups, being of marginally lower electron density than its surroundings, can account for the observed small angle peak. A similar cluster model of $-C(CH_3)_2-$ groups can also be given for polycarbonate of bisphenol A. The possible arrangements leading to these packings were indicated by the space filling models.

For $-C(CF_3)_2-$ and $-SO_2-$ analogues of DGEBA, the question arises whether they cluster in similar manner to that proposed for the isopropylidene groups of DGEBA. If they cluster, then why is a significant intensity peak not observed in these two cases? If they do not cluster then why does isopropylidene cluster and not fluorinated isopropylidene and sulphone? Two possibilities exist: (1) $-SO_2-$ and $-C(CF_3)_2-$ are able to cluster, but their electron densities are not significantly different from their surroundings; (2) their clustering ability may be seriously hindered due to repulsions in the polar groups. The packing of $-SO_2-$ groups in clusters may be hindered due to repulsions of the negative oxygen atoms of the neighbouring sulphone groups. Similar arguments can be given for repulsions among the electronegative fluorines of neighbouring $-C(CF_3)_2-$ groups. Fluorine and oxygen are the most electronegative elements, their electronegativity being 3.98 and 3.44 respectively. The C–F

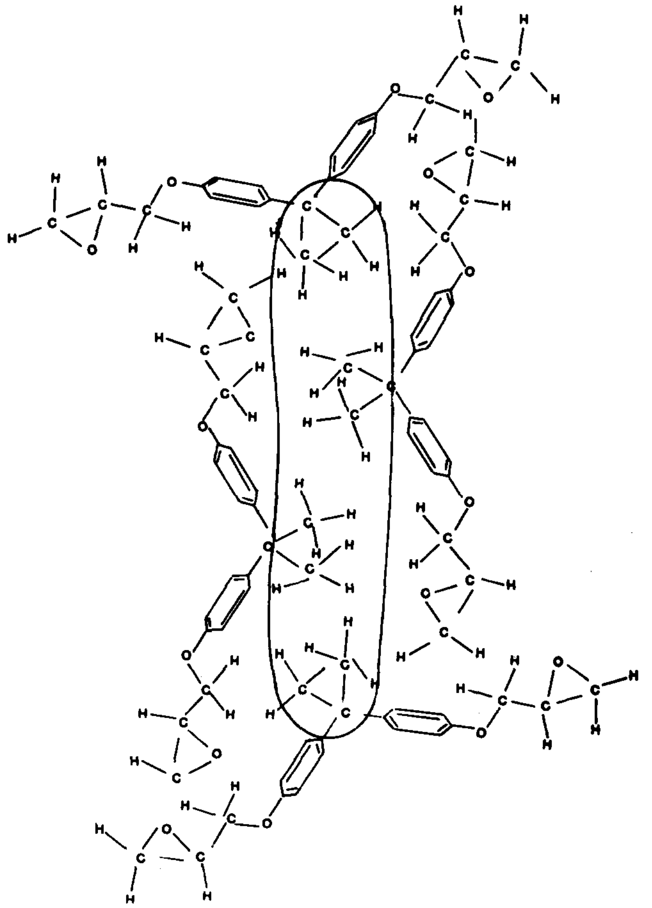

Figure 12 Two-dimensional representation of a model of DGEBA molecules (shown without crosslinking agent; bond angles and bond lengths not shown to scale)

Table 3 Small angle peak positions in various specimens

Specimen	Peak position Q (nm^{-1})	Reference
1 ATB	3.9	This work
2 DGEBA cured with mPDA	3.8	This work
3 $-CH_2-$ analogue of DGEBA cured with mPDA	4.2	This work
4 DGEBA cured with DDM	4.2	2
5 DGEBA cured with HHPA	4.6	2
6 DGEBA (d14) cured with D-400	4.0	4
7 DGEBA (d14) cured with T-403	4.0	4
8 Polycarbonate of bisphenol A	4.4	3

bond, with 44% ionic character[17], is the most ionic of the bonds of carbon with non-metallic elements. Likewise the S=O bond is strongly ionic. Therefore, because of electronegative repulsions, sulphone and fluorinated isopropylidene either are not able to cluster at all or there is no significant scattering because of the reduced electron density differences between the clusters and their surroundings.

The small angle peak positions of various specimens are listed in *Table 3*. The absolute values of peak positions obtained from scattering experiments in different laboratories cannot be compared because of differences in the background and incoherent scattering corrections. Also, the way in which peaks have been resolved can influence the peak position. However, data obtained in the same laboratory which has had the same data treatment procedures can be compared. Therefore the data of samples 1–3, 4 and 5, and 6 and 7 can be compared. Note that for the $-CH_2-$ analogue of DGEBA the peak is observed at a higher Q value than that for DGEBA itself. From the models it is evident that the length of the cluster in the $-CH_2-$ analogue of DGEBA is smaller than in DGEBA itself, which would explain the peak at higher Q in the $-CH_2-$ analogue.

According to Dusek *et al.*[2] a higher Q value of the peak position is obtained for a sample cured with HHPA than for a sample cured with DDM. If it is assumed that there is an equal probability of the adjoining DGEBA molecules in the cluster being crosslinked on the same nitrogen atom in DDM and being crosslinked on the second nitrogen, then it is expected that a significant number of DGEBA molecules participating in a cluster will be crosslinked on the opposite nitrogens. When the two molecules in a cluster are crosslinked on the opposite nitrogen atoms the length of the crosslinker will affect the length of the cluster and hence the peak position. Since the two crosslinking points of the DDM crosslinker are further apart than in HHPA, the specimen crosslinked with DDM would be expected to have a longer cluster and hence a smaller Q value for the peak position.

We also have to understand the variation of the peak position and intensity as a function of the amount of crosslinking agent (mPDA) and cure condition. It is observed (*Table 2*, peak 1) that for the stoichiometric amount (14.5) of mPDA the value of Q is a maximum and the intensity of the peak is highest both in standard and in post-cured samples. Samples having mPDA below the stoichiometric amount are deficient in the crosslinking agent and therefore some ends of the DGEBA chain would not have been crosslinked. The lack of crosslinking would mean a greater degree of freedom for the DGEBA molecule. It is anticipated that, due to the increased freedom of the uncrosslinked ends, the packing of the isopropylidene clusters may be somewhat loose, which will effectively increase the cluster length and decrease the Q value of the peak position. Increased numbers of uncrosslinked ends would also tend to reduce the total number of clusters per unit volume, which is reflected in the reduced peak intensity. Samples having the crosslinking agent (mPDA) in excess of the stoichiometric amount would have crosslinking points whose functionality is less than four. A reduced number of molecules attached to the mPDA will again increase the degree of freedom of the molecules. That is, the tetra-functional junction would be more restricted than the di- or tri-functional junction. The increased degree of freedom in the amine-rich samples makes the case analogous to that of amine-deficient samples.

Longer and flexible amines used for the neutron scattering studies[4] on the deuterated analogues are probably responsible for the absence of the 4.0 nm^{-1} X-ray peak. These amines may give different packing arrangements, leading to the SANS peak. To further answer these questions SANS experiments will also have to be done on deuterated DGEBA cured with mPDA.

The *Figure 12* type model is an idealized model and is qualitatively able to explain the X-ray scattering results on these systems. More rigorous quantitative analysis remains to be done to test this model further.

Structural inhomogeneity

The question of inhomogeneity in amorphous polymeric systems has long been a controversial one and still continues to be debated in the scientific literature. Two recent papers on this subject have been published which appear to give two opposing points of view[14,18]. From the electron microscopy investigation of the epoxies[14] it was concluded that all the epoxy samples studied were inhomogeneous at the level of several tens of nanometres. From the neutron scattering studies on DGEBA crosslinked with mPDA (of which the benzene ring was deuterated) it was concluded that the crosslinking agent (mPDA) does not have an inhomogeneous distribution at the several tens of nanometres level, and therefore could not explain the electron microscopy observations. Thus far the evidence of inhomogeneity in amorphous polymeric systems comes mostly from electron microscopy, with little or no support from the scattering data.

At this point we would like to reconsider the superchain model of polystyrene[6] and the model of crosslinked DGEBA given in *Figure 12*. In the superchain model of polystyrene it was proposed that the phenyl rings have an affinity for each other and are clustered in a tube. The current models of epoxies and polycarbonate suggest clusters of isopropylidene groups. The fact is that in order to be able to explain the scattering results we have to simulate models such as the ones described above, which are not homogeneous at the molecular level. The question which has so far not been addressed is the percentage of molecules in the material which are clustered as proposed. If it is assumed that only part of the chains are participating in the clusters and that the rest of the chains have a homogeneous distribution, then it is possible to conceive of regions dominated by the clusters of the type proposed in *Figure 12* and other regions in which no such clustering of the isopropylidene groups takes place. Though the electron density difference (which will give the X-ray scattering contrast) or the neutron scattering contrast between clusters and their surroundings is there, the overall density of the regions in which clusters are present may be quite close to the density of the unclustered regions. This would explain the absence of X-ray or neutron scattering reminiscent of a system which is inhomogeneous at the level of several tens of nanometres.

Evidence of inhomogeneity from electron microscopy best comes from plasma etched samples. If clustered and unclustered regions having similar overall density plasma etch differently, then this will explain the observation of inhomogeneity from the plasma etched surfaces in scanning electron microscopy and its absence on ultramicrotomed unetched sections as observed in transmission electron microscopy.

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