

# WAXS investigation of local structure in epoxy networks\*

R. Lovell and A. H. Windle†

Department of Materials Science and Metallurgy, University of Cambridge,  
Pembroke Street, Cambridge CB2 3QZ, UK

(Received 11 October 1989; revised 21 November 1989; accepted 23 November 1989)

The wide-angle X-ray scattering peak which appears near  $s=0.4 \text{ \AA}^{-1}$  on curing diglycidyl ether of bisphenol-A (DGEBA) is investigated as a function of different amine curing agents and stoichiometry. Its development during the curing process is also observed. The intensity and position of the peak correlate with the presence and spacing of crosslinks (nitrogen atoms) in flexible chains of DGEBA units which form by secondary-amine reaction during the later stages of curing. Although the chains have high flexibility, the spacing between the nitrogen atoms is fixed at about 15 Å. Such chains are components of all amine-cured DGEBA.

(Keywords: epoxy resin; wide-angle X-ray scattering; conformation; modelling; network structure)

## INTRODUCTION

The physical structure of highly crosslinked network polymers such as cured epoxy resins is not well characterized at the molecular level. In contrast, the chemical reactions leading to network formation have been quite fully investigated<sup>1,2</sup>.

We have already presented conformational modelling of structures present in aromatic-amine cured diglycidyl ether of bisphenol-A (DGEBA)<sup>3,4</sup>:



In this paper we aim to interpret experimental evidence, especially wide-angle X-ray scattering (WAXS) data, on the local conformation and packing of the network chains.

Although a number of workers have made WAXS measurements on various cured epoxy systems<sup>5,6</sup>, there are few specific structural conclusions. There is general agreement that such materials are non-crystalline, giving WAXS peaks similar to those found for uncured (liquid) DGEBA. (However, there are claims from the Soviet Union that (i) epoxy cured in a constant magnetic field of 0.012 Tesla shows crystalline WAXS peaks<sup>7</sup> and (ii) single crystals of epoxy polymer are found which give a crystalline electron diffraction pattern<sup>8</sup>.)

The main change on curing DGEBA is the appearance of a comparatively low angle WAXS peak at  $s \approx 0.4 \text{ \AA}^{-1}$  (where  $s = 4\pi \sin \theta_B / \lambda$ ). By applying a modified Bragg formula<sup>9</sup> ( $d = K/s$  where  $K = 7.5\text{--}8.0$ ), this peak can be seen to correspond to a repeat distance of 18–20 Å. Measurements on a drawn tensile specimen by Kumar and Adams<sup>6</sup> have shown that the low-angle peak is meridional (i.e. it intensifies when the scattering vector is parallel to the extension direction) so that the periodicity must be along orienting units which are most likely to be polymer chains.

Kumar and Adams further found that the intensity of the peak is very sensitive to the nature of the diphenyl linkages in DGEBA. Specimens prepared from analogues of DGEBA in which the isopropylidene,  $-\text{C}(\text{CH}_3)_2-$ , was replaced with  $-\text{C}(\text{CF}_3)_2-$  gave a much weaker peak while for  $-\text{SO}_2-$  the peak was absent altogether.

In the present paper we report WAXS data for DGEBA cured with a number of different aromatic amines including aniline, diamino diphenyl methane (DDM), *meta*-phenylene diamine (mPDA) and 1,3-bis(3-amino-phenoxy) benzene (BAPB). Kumar and Adams found that the intensity and position of the low angle peak varied with the ratio of amine to epoxy in the mixture and we have extended the range used. The mixtures are characterized by the ratio of amino hydrogen to epoxy ( $P = [\text{NH}]/[\text{EP}]$ ). For the stoichiometric mixture of two DGEBA molecules to one diamine molecule,  $P = 1$ .

## NETWORK FORMATION

The structures formed during curing (particularly of non-stoichiometric mixtures) are influenced by the relative rates of the various possible reactions. We review the evidence and discuss the structural implications, mainly as they apply to diepoxide/diamine mixtures such as DGEBA/mPDA.

### Polymerization reactions

Figure 1 shows the chemical reactions between an aromatic primary amine and an epoxy resin such as DGEBA. Reactions A and B are the most important but reaction C also occurs, particularly in epoxy-rich mixtures ( $P < 1$ ).

*Reactivity of diepoxides.* Although it is generally agreed that the two epoxy groups in the DGEBA molecule react independently of each other (ref. 1, p. 133), there seems to have been little experimental verification of this. If the second epoxy group were to react more slowly than the

\* Presented at Polymer Physics Group Conference 'Physical Aspects of Polymer Science', Reading, 13–15 September 1989

† To whom correspondence should be addressed

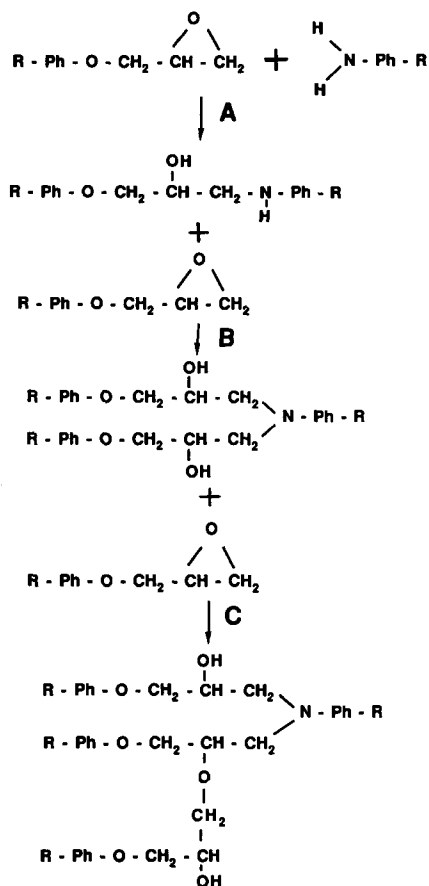


Figure 1 Main reactions in the amine curing of epoxy resins

first<sup>10</sup>, then epoxy-rich mixtures would react to form only small (finite) networks.

**Reactivity of aromatic amines.** There is still disagreement as to the relative rates of reactions A and B<sup>11,12</sup>. Evidence has been presented<sup>13</sup> showing that the primary amine reaction (A) is much faster than the secondary amine reaction (B), which would lead to a mixture of linear oligomers that only slowly reacted to form branched molecules and networks (i.e. a two-stage reaction<sup>14</sup> would take place).

Assuming that the epoxy groups react independently, then the average number of DGEBA units in the linear oligomers formed by reaction A with a diamine is  $2/(2-P)$  (see Appendix). Thus the average length for  $P=1$  would be two DGEBA units and only for  $P>1.7$  would long chains form as a result of reaction A.

The main evidence in favour of the two-stage process is the infra-red measurements of Schiering *et al.*<sup>15</sup> which failed to find any primary amine remaining even in the least reacted mixtures of DGEBA/mPDA. Bell's chemical analysis of the reaction of DGEBA/DDM also gives results closer to those expected from a two-stage reaction<sup>14</sup>.

However, chemical analyses (particularly on model reactions such as PGE/aniline<sup>16</sup> or DGEBA/aniline<sup>17</sup>) generally show approximately equal rates for reactions A and B (i.e. a random process). Kinetics experiments<sup>11,18</sup> also support a random reaction.

The different structural implications of the random or two-stage reactions only appear for amine-rich mixtures with  $P>1.5$ . For these conditions, the random reaction

predicts highly branched structures whereas the two-stage reaction predicts mainly linear chains<sup>14</sup>.

In the above discussion we have assumed that the two amino groups in a diamine react independently. However, there is some evidence<sup>19</sup> that in DGEBA/DDM ( $P=1$ ) the second amino group reacts more slowly than the first, presumably as a consequence of the reduced mobility of the bound group.

**Etherification reaction.** Although the main reactions in amine-curing of epoxies are between epoxy and amino groups, there is evidence<sup>20</sup> that in the later stages of curing the epoxies can react with hydroxyls formed in the earlier stages thus forming ether linkages (reaction C, Figure 1). This is particularly true for epoxy-rich mixtures ( $P<1$ ) cured above 100°C (ref. 2, p. 54).

For DGEBA/mPDA cured at 125°C, Schiering *et al.*<sup>15</sup> made infra-red (i.r.) measurements of epoxy and amine consumption (both are almost totally consumed for  $P=1$ ) which show that no etherification occurs for  $P=1$ . (If etherification occurred, then unreacted amine would be expected to remain when all epoxy was consumed.) However, for  $P<1$ , far more epoxy seems to react than expected for the amount of amine used (the fraction of epoxy remaining should not fall below  $1-P$ ). The most likely explanation is that etherification is occurring once the amine is exhausted.

#### Connectivity and topology

Modelling of network formation has generally concentrated on the processes leading to gelation<sup>21,22</sup> and comparisons have been made with experimental measurements such as sol fraction or molecular weight distribution in the sol as a function of the extent of reaction<sup>23</sup>. Such modelling has also been used to predict post-gelation properties such as rubber modulus and crosslink density but in general these have been for quite lightly crosslinked networks.

**Amine functionality.** If etherification reactions are excluded, then the functionality ( $f$ ) of DGEBA is 2, whereas the functionality of an amine molecule is equal to the number of hydrogens on its amino groups. Thus diamines such as mPDA, DDM and BAPB all have  $f=4$  and will be able to form branched structures and networks. Monoamines such as aniline have  $f=2$  and can only form linear polymers. This has been confirmed by a number of workers<sup>24,25</sup>. In contrast, a polyamine such as triethylene tetramine (TETA  $f=6$ ) will give a highly crosslinked structure.

**Junction statistics.** For amines with  $f=4$  or more, various types of branch points (junctions) can occur, dependent on the value of  $P$  and on the extent of the reaction ( $\alpha$ ), where  $\alpha=1$  corresponds to fully reacted mixtures. When  $f=4$ , the fully reacted ('4-arm') junction will only predominate for  $\alpha/P$  greater than about 0.8. Sung *et al.*<sup>19</sup> have measured the populations of the various junctions in DGEBA/DDS ( $P=1$ ) as a function of  $\alpha$ , and found that they agree with the predictions of a random reaction. Topolkarayev *et al.*<sup>26</sup> have performed computer modelling which has shown the dependence of junction statistics on  $P$ . As expected, the amount of '4-arm' junctions was greatest for  $P=1$ . The dependence on  $P$  was very similar to that for the glass transition temperature ( $T_g$ ) and the rubber modulus.

**Ring statistics.** Although it seems certain that fully cured stoichiometric mixtures consist of highly branched and crosslinked structures, there has been little progress in quantifying these structures. Most theories of gelation ignore the formation of rings by intramolecular reaction. However, since the number of branches increases much more rapidly than the volume available to them, ring formation must predominate in the later stages of curing (ref. 27, p. 179), though the rings formed might be quite large (e.g. containing about 20 DGEBA units).

For models of simple inorganic networks, such as amorphous silica, the order on a larger scale than the local coordination has been described by ring statistics (ref. 27, p. 66). However, such statistics have not as yet proved accessible to experimental investigations even for simple systems.

For DGEBA cured with a stoichiometric amount of diamine, the smallest rings are likely to be of such an average size (6 or more DGEBA units giving typical dimensions of 30 Å with perhaps 8 or 10 chains passing through each ring), and with such a wide distribution of sizes, that the structures are not sufficiently discrete or monodisperse to give small-angle scattering.

Although such rings may be important in determining mechanical properties, branched structures consisting of a small number of DGEBA units will be the component of local structure most accessible to WAXS, owing to their smaller size and more limited range of conformations.

Some models of epoxy networks<sup>26,28</sup> are characterized by quite small rings but this is due to the two-dimensional nature of the models which leads to much smaller rings than would be typical in three dimensions.

#### Simplified network structure—crosslinked chains

Analysing a highly crosslinked network in terms of molecular chains seems very arbitrary, since even on a local scale there are many possible ways of decomposing the structure into chains. However, in fully cured DGEBA/diamine networks (with no etherification reactions) two types of chemically regular catenation can be

recognized (see Figure 2). In type I chains (formed by reaction A) the DGEBA units are connected through the diamine, whereas in type II chains (formed by reaction B) the DGEBA units are connected through the nitrogen atoms.

In fact, type II chains will be present in all primary amine-cured DGEBA and could account for common features. Moreover, all the DGEBA units in the network can be linked into a unique system of type II chains. So, for small-molecule diamines (such as mPDA for which the nitrogen-to-nitrogen distance is  $\sim 4.8$  Å), we can visualize the network structure as a mass of type II chains joined by short 'amine' bridges at intervals of 15–20 Å along these chains (Figure 2c).

Since type I chains are formed by the reaction of primary amino groups, they will be formed early in the curing process and only in later stages will type II chains form as a result of the reaction of secondary amino groups. (For monoamines however, only type II chains are formed.)

The concentration of type I chains is relatively independent of the amine-epoxy ratio (for  $P=0.5-2$ ), whereas that of type II chains is strongly dependent on  $P$  with a maximum for the stoichiometric mixture ( $P=1$ ), (see Appendix). Moreover, for  $P>1$  the amount of type II chains depends on the amine reactivity. The nearer to a two-stage reaction, the fewer type II chains are formed. For a pure two-stage reaction, no type II chains will be formed for  $P\geq 2$ .

#### Chain packing

Even in fully crosslinked epoxy networks, most chain segments which are in contact are only spatial neighbours rather than topological neighbours<sup>29</sup> (directly bonded to each other). Hence the chain packing is unlikely to be very different from that in amorphous linear polymers. However, branching and network formation do have some effect as shown by the packing density (ratio of van der Waals volume to total volume). Cured epoxies have packing densities 2–3% greater than for typical linear polymers<sup>30,31</sup>. The value varies slightly as crosslink density is varied (either by using non-stoichiometric mixtures<sup>31</sup> or by varying the average amine functionality using DDM/aniline mixtures<sup>32</sup>).

#### WAXS DATA

##### Experimental

The epoxy resin used throughout was Epikote 828 (Shell Chemicals UK Ltd) which is mainly DGEBA with some higher oligomers also present ( $k\approx 0.11$ , epoxy molar mass = 182–194). The hardeners used are shown in Figure 3. Aniline, mPDA and DDM were supplied by Aldrich Chemical Co. Ltd (UK), BAPB by Frinton Laboratories Inc. (Vineland, New Jersey, USA) and TETA (Araldite HY 951) by Ciba-Geigy Plastics (UK).

The resin and hardeners were used in the as-received condition to prepare cured specimens 1–2 mm thick. mPDA, DDM and BAPB are all solid at room temperature and so they were heated to just above their melting points before being mixed with the Epikote 828 which was at the same temperature. Aniline and TETA were mixed at room temperature. The curing took place in an air oven at temperatures of 70°C or greater and times from a few hours to a few days. A standard schedule of

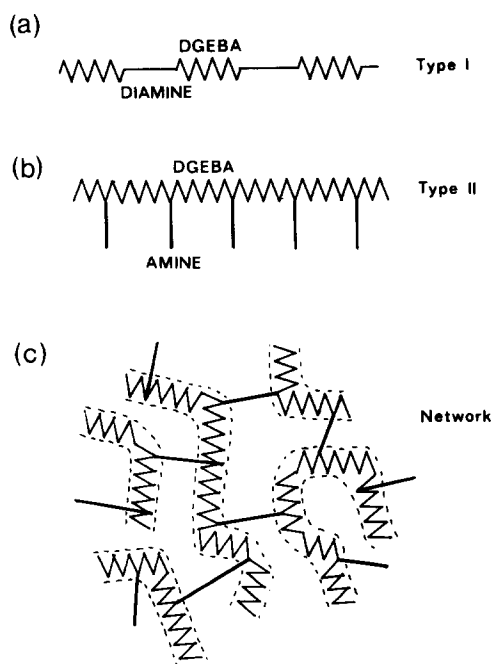


Figure 2 Chemically regular chains formed in amine-cured DGEBA

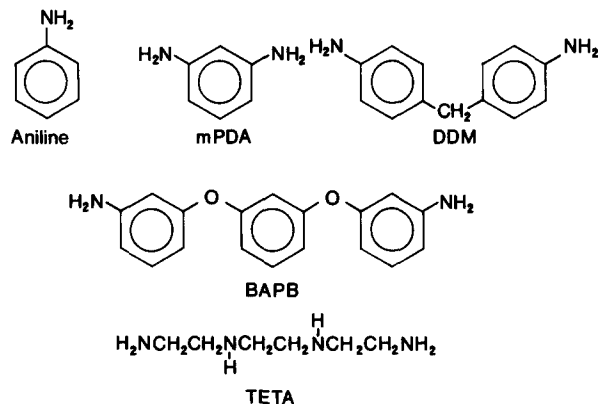


Figure 3 Amine hardeners used

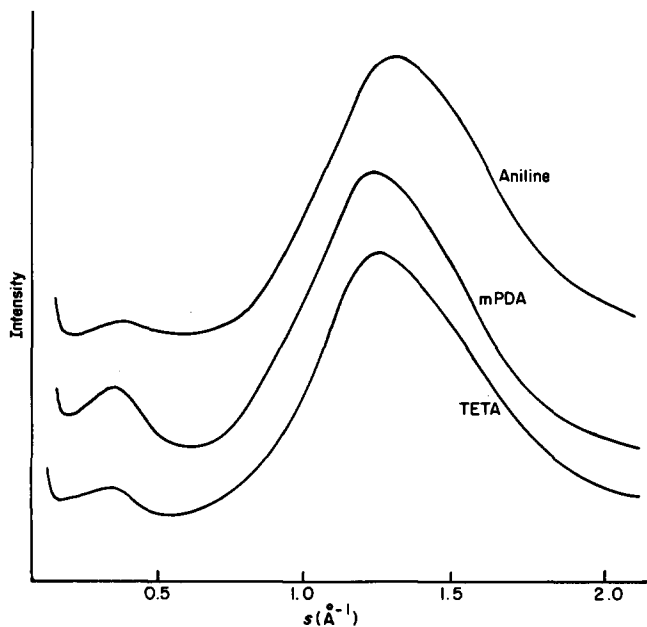


Figure 4 Diffractometer scans for DGEBA cured with stoichiometric amounts of different amines

2 h at 70°C followed by 2 h at 125°C was used for most mixtures<sup>33</sup>. However, DGEBA/aniline needed 6 days at 70°C to be fully cured.

The WAXS data was mostly obtained using a modified Philips horizontal diffractometer in the symmetrical transmission mode, with slit collimation. The diffractometer was equipped with a focussing graphite monochromator in the incident beam with copper K $\alpha$  radiation. The scattered intensity was measured using a gas-filled proportional counter and associated electronics.

WAXS data on uncured (liquid) DGEBA and on mixtures during curing were obtained on a Siemens  $\theta$ - $\theta$  vertical diffractometer equipped with a heating stage.

Diffractometer traces for DGEBA cured with stoichiometric amounts of different amines are shown in Figure 4. The main features are quite similar even though the amine functionality ranges from 2 (aniline) to 6 (TETA), so that the structures range from a linear polymer to a highly crosslinked network polymer. However, there is a systematic trend in the position of the low-angle peak (Figure 5). The peak moves to a higher  $s$  (shorter spacing) as the 'bulk' of the amine molecules increases. We have characterized the bulk by using  $V_w/f$ , where  $V_w$  is the van der Waals volume ( $\text{cm}^3 \text{mol}^{-1}$ ) and  $f$  is the functionality as before. Of the five amines used here, mPDA

gave the most intense low angle peak and aniline gave the least intense.

Results for non-stoichiometric mixtures of DGEBA/mPDA are shown in Figures 6 and 7. The low-angle peak moves to higher  $s$  as the amine/epoxy ratio ( $P$ ) increases from 0.5 to 3. In contrast with the present results, Kumar and Adams<sup>6</sup> found that the low-angle peak was at the highest  $s$  ( $=0.37 \text{ \AA}^{-1}$ ) for  $P=1$  and moved to lower  $s$  for non-stoichiometric mixtures ( $0.5 < P < 1.7$ ). However,

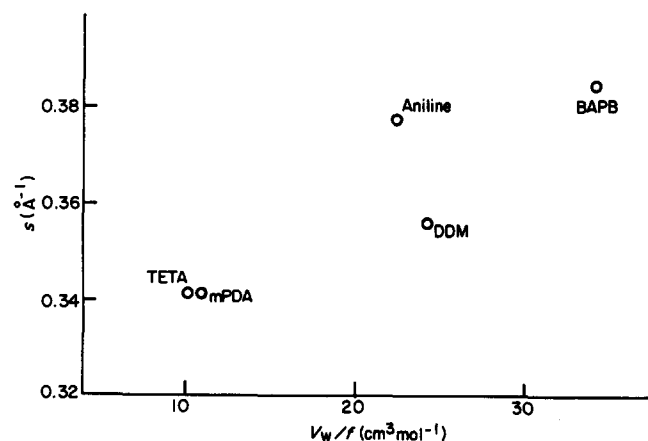


Figure 5 Position of low-angle peak as a function of amine 'bulk'. This is characterized by van der Waals volume ( $\text{cm}^3 \text{mol}^{-1}$ ) divided by functionality

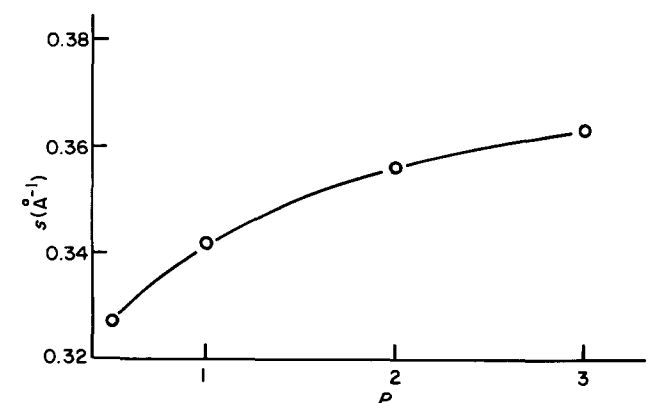


Figure 6 Position of low-angle peak as a function of amine/epoxy ratio ( $P$ ) for DGEBA cured with mPDA

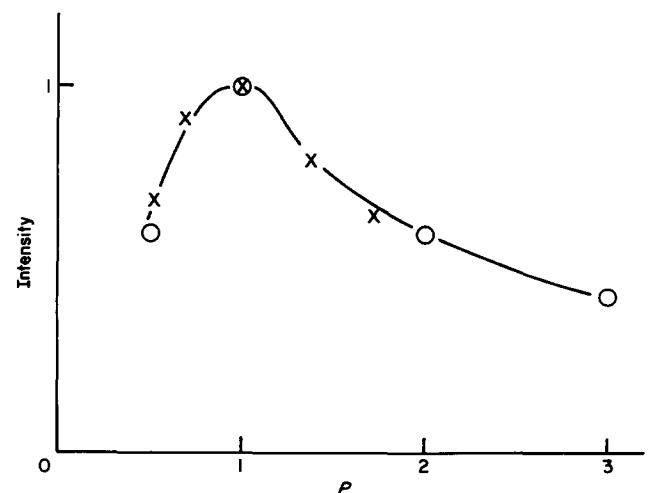


Figure 7 Intensity of low-angle peak as a function of amine/epoxy ratio for DGEBA cured with mPDA.  $\times$ , data from Kumar and Adams<sup>6</sup> normalized to the value at  $P=1$

the intensity of the peak is a maximum for the stoichiometric mixture ( $P=1$ ). This intensity variation is similar to that found by Kumar and Adams<sup>6</sup> whose data are also shown in Figure 7. Moreover, the form of plots (both for standard and postcured specimens) are similar to those for  $T_g$  (refs 33 and 34). Since  $T_g$  is a function of the crosslink density<sup>26</sup>, this points to the intensity of the low-angle peak also increasing with crosslink density. However, the further crosslinking in post-cured epoxy-rich ( $P < 1$ ) specimens almost certainly occurs by an etherification reaction<sup>15</sup>, and thus the low-angle peak would not be evidence of a specific form of crosslink.

Extrusion of a DGEBA/mPDA ( $P=1$ ) specimen in a channel die at 125°C led to some molecular orientation. We have confirmed Kumar and Adams's<sup>6</sup> finding that the low-angle peak is meridional, whereas the main peak ( $s=1.3 \text{ \AA}^{-1}$ ) is equatorial (intensifies perpendicular to the extension direction).

The development of the low angle peak during curing was followed for a specimen of DGEBA/mPDA ( $P=1$ ). Figure 8 shows how the intensity increased over 2.5 h at 70°C, followed by a rapid increase when the temperature was raised to 125°C.

Diffusion of acetone into cured DGEBA/mPDA ( $P=1$ ) has a surprisingly small effect on the WAXS. At room temperature, the diffusion follows a Case II process with sharp fronts, and, for a specimen originally 1.5 mm thick, it took about 120 days before the fronts met and the specimen became uniformly swollen. Although nearly 20% of the weight of the fully swollen specimen was acetone, the low-angle peak was still clearly visible (Figure 9). In contrast, Wu *et al.*<sup>10</sup> found that epoxies swollen with deuterated acetone gave very different small angle neutron scattering.

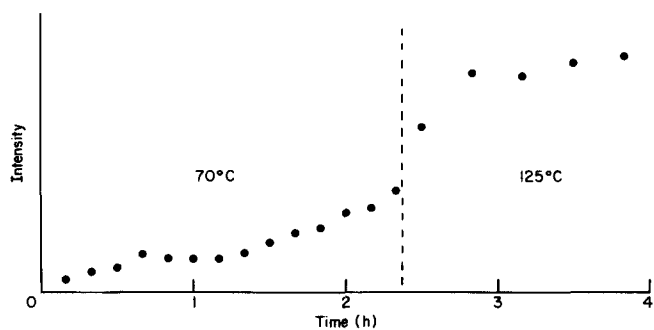


Figure 8 Development of low-angle peak during curing of DGEBA/mPDA ( $P=1$ ), for 2.5 h at 70°C followed by 1.5 h at 125°C. The intensity at  $0.36 \text{ \AA}^{-1}$  is plotted after correcting for the background

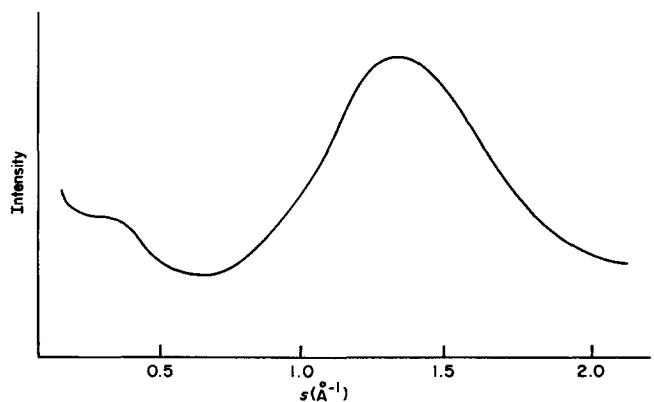


Figure 9 Diffractometer scan for cured specimen of DGEBA/mPDA ( $P=1$ ) swollen in acetone for 120 days at room temperature

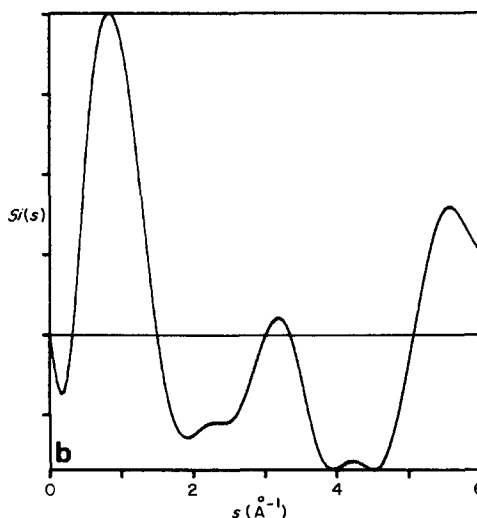
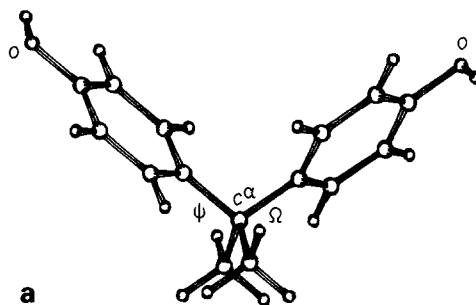


Figure 10 (a) Molecule of bisphenol-A. (b) Calculated scattering from bisphenol-A molecule

## MODELLING WAXS

The modelling will concentrate on the simple network-forming system DGEBA/mPDA and on the analogous linear-chain system DGEBA/aniline. However, the effects of using other amines and analogues of DGEBA will also be considered.

The scattering from models was calculated as the  $s$ -weighted reduced scattering<sup>35</sup>,  $si(s)$ , where

$$i(s) = \sum \sum (f_j(s)f_k(s) \sin sr_{jk})/sr_{jk}$$

where  $f_j$  is the scattering factor of atom  $j$  and  $r_{jk}$  is the separation of atoms  $j$  and  $k$ .

All the calculated scattering has been corrected for the small size of the models using the method of Mitchell<sup>36</sup> in which the atoms were taken to be spheres of radius 1.7 Å.

### Basic scattering units

The cured systems contain a number of rigid structures of which the largest are bisphenol-A (BPA) units (Figure 10a). These have a single minimum energy conformation<sup>3</sup> (though with some freedom for coordinated rotation of the phenylenes).

About 55% of the electrons in DGEBA/mPDA ( $P=1$ ) are contained in the BPA units which thus make an important contribution to the X-ray scattering. The scattering calculated for a BPA molecule is shown in Figure 10b. It was taken to have an idealized conformation (with phenylene rotation angles:  $\Psi = \Omega = 60^\circ$ ) which is within the calculated low energy region<sup>3,37</sup>. However, rotation of the phenylenes between  $\Psi = 30^\circ$  and  $60^\circ$  has little effect on the calculated scattering. The

pattern shows peaks near 5.5 and 3.2 Å<sup>-1</sup>, corresponding to first and second nearest neighbour bond distances. The main peak near 0.7 Å represents the average dimension of the molecule.

Density considerations

Since the low-angle peak corresponds to a distance of 18–20 Å, any structure to account for it must be on a larger scale than a single BPA unit (maximum dimension about 9 Å). Therefore we consider the minimum spacings between units (both BPA and amine) in uniform mixtures of the correct density.

Minimum spacings are maximized for a random isotropic structure by considering the centres of the units to be distributed as the centres of randomly close packed spheres.

With this assumption, the closest approach distance is given by:

$$d \approx 1.10V^{1/3}$$

where *V* is volume per unit. [Regular packings change the factor 1.10 to 1.0 (for simple cubic) or 1.12 (for face centred cubic or hexagonal close packing).]

As shown in Table 1, none of these spacings is greater than 12 Å. Larger spacings could be obtained by considering structures which are locally anisotropic. This would agree with the meridional nature of the low-angle peak and the fact that neither its intensity nor position is changed by orientation.

Predominant chain type

The modelling so far has not taken account of the polymeric nature of the structure. Yet we know that the low-angle peak only appears on curing, that it is meridional in oriented samples, and that network structures are not essential for its appearance (as shown by the aniline-cured material). It is reasonable to conclude that the peak represents a periodicity along a chain molecule, albeit a poorly ordered one. The next step is to decide whether the peak can be identified with either type I or type II chains. Some useful evidence is provided by the study of the influence of different sizes of diamine molecule on the peak position. In Figure 5 the amine is characterized by its van der Waals volume, but it is apparent from the structures of the aromatic members of the amine series drawn in Figure 3, that increasing size will also increase the mean spacing between the amine groups. Now, in type I chains the distance between the amine groups will add to the repeat length along the chain, and thus one would expect that the peak would move to lower angles with increasing amine size, and that the movements would be substantial. The fact that the opposite behaviour is observed indicates that the peak cannot be identified with type I chains.

Of course at first sight, the repeat along type II chains should be independent of the spacing between the amine groups on the curing molecule, as in this case it is only

Table 1 Spacing of various chemical units in DGEBA/mPDA (P=1). The units are assumed to be randomly distributed

Structure	Spacing (Å)
Bisphenol-A unit	9.0
mPDA unit	11.3
Nitrogen atoms (not on same phenyl)	10.4

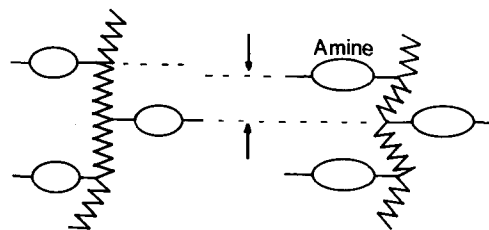


Figure 11 Schematic diagram showing how bulkier crosslinking groups may cause the type II DGEBA chains to shorten in order to pack more effectively

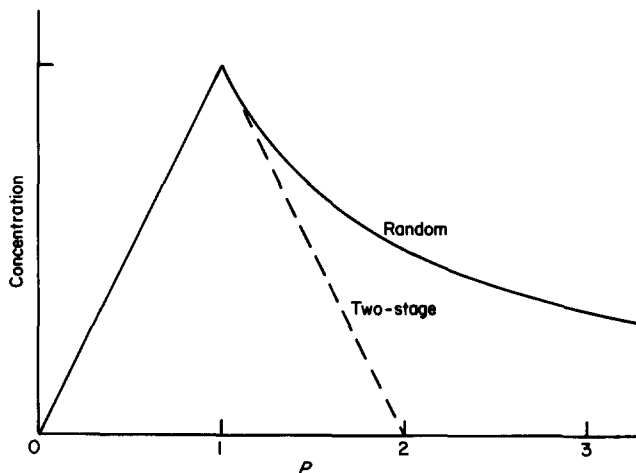


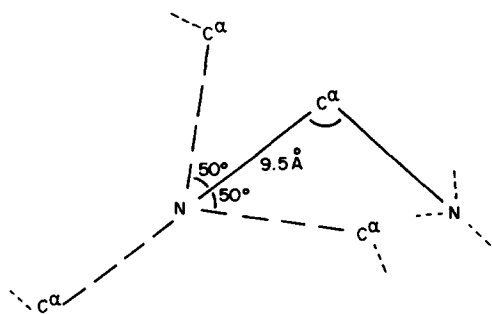
Figure 12 Dependence of concentration of type II chains on amine/epoxy ratio (P)

the nitrogen atoms which contribute to the repeat along the chain. It is thus necessary to explain why the chain repeat actually decreases by about 10% as the size of the diamine molecule increases along the series from mPDA to BAPB. If the repeat corresponds to that along the type II chain between the successive crosslinking points (Figure 2c), then increasingly bulky crosslinking groups will tend to force apart the DGEBA chain segments between these points. The segments will compensate for this potential disruption to their packing by conformational adjustments which will shorten their length in order to increase their lateral cross-section. Figure 11 is a schematic representation of this argument.

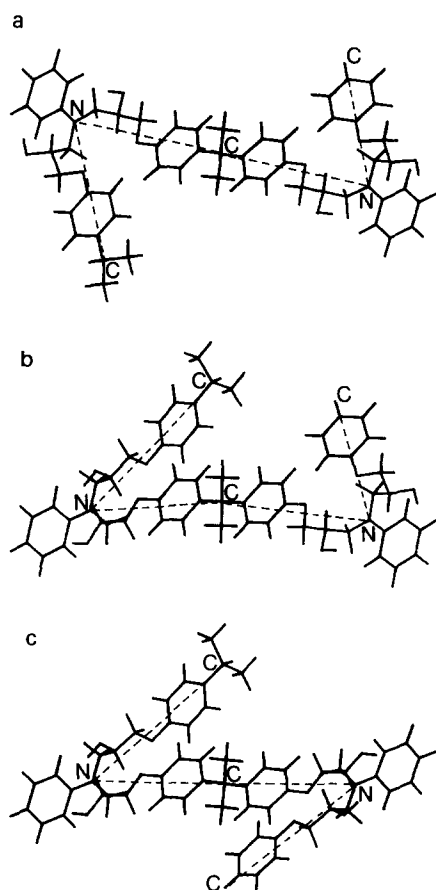
Further evidence that type II chains are responsible for the low-angle scattering peak comes from the dependence of their concentration on amine/epoxy ratio (P). This shows a maximum at P=1 which is similar to the behaviour of the intensity of the low-angle peak (Figures 7 and 12).

The weight of the diffraction evidence thus supports the conclusion derived above from the initial consideration of network formation that type II chains are a characteristic feature of all amine-cured DGEBA (both linear polymers and networks). Furthermore, it is these chains which are responsible for the diffraction peak which develops on curing, and these chains which orient parallel to the extension axis on deformation.

Virtual bond chains. Conformational analysis of the asymmetric unit of type II chains has shown that it can be approximated by a virtual bond about 9.5 Å long<sup>4</sup>. Hence we can consider a simplified structure consisting of chains of virtual bonds. The simplified chain structure is shown in Figure 13. It consists of rigid 'V-shaped' units



**Figure 13** Structural unit of a chain of virtual bonds, showing the two possible angles ( $50^\circ$  and  $180^\circ$ ) between virtual bonds at the nitrogen atoms<sup>4</sup>

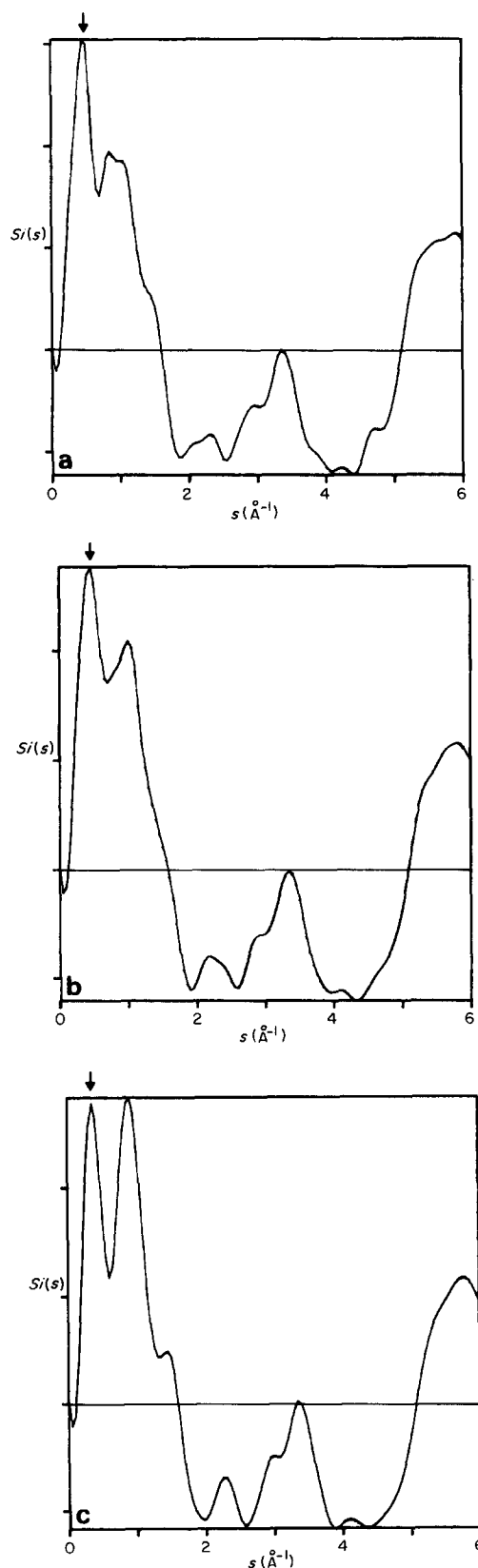


**Figure 14** Lengths of type II chain containing two chemical repeat units. ---, Virtual bonds between  $\alpha$ -carbons and nitrogens. The three different conformations have rotations about the virtual bonds of (a)  $0, 0^\circ$ , (b)  $0, 180^\circ$  and (c)  $180, 180^\circ$

joined at the nitrogen atoms. The angle between virtual bonds meeting at the  $\alpha$ -carbons is fixed at  $110^\circ$  but the angle at the nitrogens can be either  $180^\circ$  or  $50^\circ$ . This leads to two values for the spacing between neighbouring  $\alpha$ -carbons of 19 or 8 Å; but a fixed distance between neighbouring nitrogens of 15 Å.

The two conformations at the nitrogen are of very similar energies. However, it was found that the 'acute angle' ( $50^\circ$ ) structures gave better agreement with the WAXS data than do the 'straight' ( $180^\circ$ ) structures. As discussed earlier<sup>4</sup>, each virtual bond has two rotation states ( $0^\circ$  and  $180^\circ$ ), so that a bond pair forming the 'V-shaped' unit has three distinct conformations of similar energy: ( $0, 0^\circ$ ), ( $0, 180^\circ$ ) and ( $180, 180^\circ$ ). Of these, the ( $0, 180^\circ$ ) is likely to predominate, since there are two

ways for it to occur, ( $0, 180^\circ$  and  $180, 0^\circ$ ). However, all three 'acute angle' structures (shown in Figure 14) can give a low angle peak in approximately the correct position (Figure 15). The other features in the calculated scattering are similar to those found for bisphenol-A and have the same origin.



**Figure 15** Scattering calculated for the three structures in Figure 14: (a)  $0, 0^\circ$ , (b)  $0, 180^\circ$  and (c)  $180, 180^\circ$ . The peak near  $0.4 \text{ \AA}^{-1}$  is marked in each case

We therefore conclude that the acute angle structures predominate in amine-cured DGEBA but the type II chains of DGEBA units are highly disordered, due to different rotations about the virtual bonds.

#### Networks and packing

The main difference in the WAXS pattern for DGEBA/mPDA networks is the increased intensity of the low-angle peak as compared with that for DGEBA/aniline. Crosslinking may lead to increased nesting of the DGEBA units which could cause the increased intensity. Similar nesting of BPA units has been suggested for amorphous polycarbonate<sup>38,39</sup>.

Chain packing may also be responsible for the different intensities found in cured analogues of DGEBA in which the  $-(CH_3)_2-$  is replaced by more polar linkages<sup>6</sup>. There is a strong negative correlation between dipole moment of the linkage and the intensity of the low angle peak, so that the sulphone linkage which has the highest moment does not give a peak at all. Such a correlation will arise if the packing changes as the moment increases.

#### CONCLUSIONS

The diffuse diffraction maximum which appears at  $s \approx 0.4 \text{ \AA}^{-1}$  on curing DGEBA with amines is identified with chain pathways through the network which consist of DGEBA units connected through single nitrogen atoms. The complete amine molecule itself is not incorporated in these (type II) chains.

In oriented specimens, these chains are seen to align with the extension axis.

The conformation of the type II chains which is consistent with the position of the  $0.4 \text{ \AA}^{-1}$  peak involves an acute ( $50^\circ$ ) rather than a linear ( $180^\circ$ ) angle between the virtual bonds which meet at the nitrogen atoms. It has not been possible at this stage to distinguish between the likely rotational states about the virtual bonds.

Variations in position of the peak with changes in the size and concentration of the amine molecules can be understood in terms of the influence of these on the packing of the type II chains.

The prominence of the type II chains would favour a random reaction of the amine rather than a two-stage reaction in which the first hydrogen of an amino group reacts much more rapidly than the second.

#### ACKNOWLEDGEMENTS

We are grateful to the Air Force Office of Scientific Research, Air Force Systems Command, USAF, who sponsored the research under grant number AFOSR 87-0220. Thanks are also due to Dr G. C. Stevens of CERL who first drew our attention to this interesting problem.

#### REFERENCES

- 1 Rozenberg, B. A. *Adv. Polym. Sci.* 1986, **75**, 113
- 2 Oleinik, E. F. *Adv. Polym. Sci.* 1986, **80**, 49
- 3 Anwer, A., Lovell, R. and Windle, A. H. in 'Computer Simulation of Polymers' (Ed. R. J. Roe), Prentice-Hall, New York, 1990
- 4 Lovell, R. and Windle, A. H. *Polymer* submitted
- 5 Dusek, K., Plestil, J., Lednický, F. and Lunak, S. *Polymer* 1978, **19**, 393
- 6 Kumar, S. and Adams, W. W. *Polymer* 1987, **28**, 1497

- 7 Man'ko, T. A., Kvasha, A. N., Solov'ev, A. V., Scheneva, V. B. and Ermolaev, I. M. *Mech. Comp. Mater. (USA)* 1984, **20**, 402
- 8 Molchanov, Yu. M. and Korkhov, V. P. *Mekh. Komp. Mater.* 1988, **5**, 834
- 9 Klug, H. P. and Alexander, L. E. 'X-ray Diffraction Procedures', Wiley, New York, 1974, p. 847
- 10 Wu, W.-L., Hunston, D. L., Yang, H. and Stein, R. S. *Macromolecules* 1988, **21**, 756
- 11 Buist, G. J., Magger, A. J., Jones, J. R., Barton, J. M. and Wright, W. W. *Polym. Commun.* 1988, **29**, 5
- 12 Johncock, P. J. *Polym. Sci., Polym. Chem. Edn.* 1989, **27**, 647
- 13 Gross, A., Kollak, H. and Brockmann, H. *Int. J. Adhes. Adhes.* 1988, **8**, 225
- 14 Bell, J. P. *J. Polym. Sci. A2* 1970, **8**, 417
- 15 Schiering, D. W., Katon, J. E., Drzal, L. T. and Gupta, V. B. *J. Appl. Polym. Sci.* 1987, **34**, 2367
- 16 Charlesworth, J. M. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 731
- 17 Grenier-Loustalot, M-F., Grenier, P., Horny, P. and Chenard, J-Y. *Br. Polym. J.* 1988, **20**, 463
- 18 Charlesworth, J. M. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 621
- 19 Sung, C. S. P., Pyun, E. and Sun, H-L. *Macromolecules* 1986, **19**, 2922
- 20 Grenier-Loustalot, M-F. and Grenier, P. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 4011
- 21 Dusek, K. *Adv. Polym. Sci.* 1986, **78**, 1
- 22 Macosko, C. W. and Miller, D. R. *Macromolecules* 1976, **9**, 199
- 23 Dusek, K. *Makromol. Chem. Macromol. Symp.* 1987, **7**, 37
- 24 Hörhold, H.-H., Klee, J. and Flammersheim, H.-J. *Makromol. Chem., Rapid Commun.* 1981, **2**, 113
- 25 Klee, J., Hörhold, H.-H. and Schütz, H. *Acta Polym.* 1987, **38**, 293
- 26 Topolkarayev, V. A., Oshmyan, V. G., Berlin, A. A., Nisichenko, V. P., Zelenetskii, A. N., Prut, E. V. and Yenikolopyan, N. S. *Polym. Sci. USSR* 1979, **21**, 1663
- 27 Zallan, R. 'The Physics of Amorphous Solids', Wiley, New York, 1983
- 28 Morgan, R. J., Kong, F.-M. and Walkup, C. M. *Polymer* 1984, **25**, 375
- 29 Flory, P. J. *Br. Polym. J.* 1985, **17**, 96
- 30 Chepel', L. M., Topolkarayev, V. A., Zelenetskii, A. N., Prut, E. V., Trofimova, G. M., Novikov, D. D. and Berlin, A. A. *Polym. Sci. USSR* 1982, **24**, 1873
- 31 Bellenger, V., Dhaoui, W. and Verdu, J. *J. Appl. Polym. Sci.* 1987, **33**, 2647
- 32 Bellenger, V., Verdu, J. and Morel, E. *J. Mater. Sci.* 1989, **24**, 69
- 33 Gupta, V. B., Drzal, L. T., Lee, C. Y-C. and Rich, M. J. *J. Macromol. Sci. Phys.* 1985, **B23**, 435
- 34 Salamatina, O. B., Akopyan, Ye. L., Rudnev, S. N., Vladimirov, L. V., Oshmyan, V. G., Oleinik, E. F. and Yenikolopyan, N. S. *Polym. Sci. USSR* 1983, **25**, 209
- 35 Mitchell, G. R. in 'Order in the Amorphous "State" of Polymers' (Eds S. E. Keinath, R. L. Miller and J. K. Rieke) Plenum, New York, 1987, Ch. 1, pp. 1-31
- 36 Mitchell, G. R. *Acta Cryst.* 1981, **A37**, 488
- 37 Laskowski, B. C., Yoon, D. Y., McLean, D. and Jaffe, R. L. *Macromolecules* 1988, **21**, 1629
- 38 Mitchell, G. R. and Windle, A. H. *Colloid Polym. Sci.* 1985, **263**, 280
- 39 Cervinka, L., Fischer, E. W., Hahn, K., Jiang, B-Z., Hellmann, G. P. and Kuhn, K.-J. *Polymer* 1987, **28**, 1287

#### APPENDIX

##### Linear type I oligomers formed by reaction A

A mixture of DGEBA/diamine contains: 2N DGEBA molecules (i.e. 4N epoxy groups) and PN diamine molecules (i.e. 2PN primary amino groups).

For the two-stage reaction with  $P \leq 2$ , all primary amino groups react before any secondary so that (4N - 2PN) epoxy groups remain unreacted after the first stage. These unreacted groups form the chain ends (two per chain), so that the number of chains is (2N - PN). Hence the average number of DGEBA units per chain



is  $2N/(2N - PN) = 2/(2 - P)$ . This average includes the completely unreacted DGEBA molecules which will predominate for low values of  $P$ .

*Type II chains in fully reacted mixtures*

The DGEBA units in type II chains are linked via tertiary amino groups. Hence the concentration of type II chains is proportional to the concentration of tertiary amine. For fully reacted mixtures, there are two regimes:

(a)  $P \leq 1$ . All amino groups are tertiary, so that the concentration of type II is proportional to  $P$ ; (b)  $P \geq 1$ . For the random reaction, the concentration of tertiary amine (and hence of type II) is proportional to  $1/P$ . For the two-stage reaction, the concentration of tertiary amine (and type II) is proportional to  $2 - P$ , and hence no type II chains will be formed for  $P \geq 2$ .

The dependence of the concentration of type II on  $P$  is shown in *Figure 12*.