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ABSTRACT

Local Structure of Network Resins

The objective of the project is to understand the local molecular organization in epoxy resin systems, and thus to establish a bridgehead in relating chemical composition to final properties.

The approach has been two-pronged. The local molecular structure of the cross-linked system has been modelled using advanced computer simulation systems which provide a prediction based on available chemical knowledge. A parallel experimental programme has been established in which wide angle X-Ray diffraction is measured from both oriented and unoriented samples. The experimental data are compared with diffraction patterns calculated from the computer generated molecular model.

The conformational flexibility has been calculated for a range of differently substituted varients of bis-phenyl A, and these units incorporated into simple models of the molecular network. The most important findings are that:

(1) The whole complex chemistry of the resin can be reduced to a simple model c onsisting of four rigid struts and six swivel points per cross link. This chemically justified physical model opens up the route by which it will be possible to simulate the architecture of complex 3D networks.

(2) Diffraction analysis has shown that there is segregation of the cross-linking points into closely spaced layers within the resin. The observed influence of the chemical details of the polymer chains on the segregation provides intriguing new signposts for molecular design.

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LOCAL STRUCTURE OF NETWORK RESINS

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NETWORK RESINS

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ABSTRACT

The aim of the work is to understand the local molecular structure in highly-crosslinked epoxy systems.

Molecular modelling results obtained earlier have been used to interpret data from wide-angle X-ray scattering experiments. This has shown the importance of chains of DGEBA units formed by secondary amine reaction in the later stages of curing. These chains are independent of the particular amine used (which forms a bridge between chains) and the local structure is mainly determined by the conformation and packing of the chains.

The chain packing is altered in systems formed from analogues of DGEBA in which the diphenyl linkage has a high dipole moment.

Curing specimens in a high magnetic field has little effect on the local structure.

INTRODUCTION

The aim of the work is to understand the local conformational structure in highly-crosslinked epoxies.

The results of molecular modelling were summarized in the Interim Scientific Report dated August 1988. This showed that the diphenyl linkages found in DGEBA and analogues adopted two main types of conformation: The butterfly (90°, 90°) or the twist (~40°, ~40°). The linkages which adopted the butterfly conformation were $-SO_2-$ and $-CH_2-$, and both have a large degree of conformational flexibility. The other linkages considered ($-O-$, $-S-$, $-CO-$, $-C(CH_3)_2-$ and $-C(CF_3)_2-$) all adopt a twist conformation.

Investigation of the link segment formed during amine-crosslinking of DGEBA showed that it has a low flexibility and can be approximated by a virtual bond, thus simplifying the description of the structure.

We now report results of wide-angle X-ray scattering (WAXS) investigations, particularly on the low-=angle peak which has previously been studied by Kumar & Adams [1]. The data show that the peak corresponds to a periodicity along chains of DGEBA units. These chains are formed by the reaction of secondary amines during the later stages of the curing process.

We also report some results of experiments on specimens of epoxy resin cured in a magnetic field.

WAXS RESULTS

Kumar and Adams have shown that the peak at $S \approx 0.4$ Å^{-1} is meridional, thus corresponding to a repeat of 18-20 Å along the length of orienting units.

We have confirmed these findings and shown that a weak peak also appears in this position when DGEBA is cured with aniline (a difunctional mono-amine which gives linear polymer chains [2] rather than a network structure).

Chemically identical chains are also formed during the later stages of network formation and we have termed them type II chains to distinguish them from the chains formed in the earlier stages (type I). For a tetrafunctional diamine (such as m PDA), the final network structure can be analysed into a unique system of type II chains crosslinked by diamine molecules.

Amines with functionality from 2 to 6 all give the low-angle peak on curing DGEBA, but the peak is most marked for a stoichiometric amount of m PDA (f = 4). (Fig. 1). There is a small but systematic trend for the peak to move to a lower angle as the functionality increases. Thus the periodicity increases slightly with functionality.

For aromatic diamines (f = 4), the periodicity decreases slightly as the size of the amine (van der Waals volume) increases. (Fig. 2).

We have confirmed Kumar and Adams' findings that the maximum intensity is given by the stoichiometric mixture (both epoxy-rich and amine-rich mixtures give lower intensity). This behaviour is similar to that for crosslink density and other properties (such as Tg and rubbery modulus) which depend on crosslink density. The periodicity decreases slightly as the amount of amine increases (Fig. 3).

WAXS FROM MODEL STRUCTURES

We gave concentrated on modelling structures of the linear type II chains which give rise to the low-angle WAXS peak for amine-cured DGEBA.

The virtual-bond structure for the repeat units allows considerable simplification in the analysis. To a good approximation, the chains consist of 9.5 Å bonds with fixed bond angles of 110° at the α-carbons and variable bond angles of 180° or 50° at the nitrogens (Fig. 4). Each bond has 4 equivalent rotation states (equal energy minima) thus giving a high degree of flexibility on a scale greater than 20Å.

Irregular chain conformations based on such a structure can give a WAXS peak at approximately $S = 0.4$ Å^{-1}.

There is no WAXS evidence for long sequences of regular conformation.

DISCUSSION

The presence of a low-angle peak indicates that type II chains are formed even for cured mixtures containing a large excess of amine (at least twice the stoichiometric ratio). This shows that curing is by a random reaction of amine with epoxy [3] rather by the 2-stage process proposed by Bell [4].

The different peak intensities found for different amines seem most likely to be due to changes in the chain packing. The small size of m pDA molecules may encourage nesting of DGEBA units and thereby enhance intensity.

Kumar and Adams [1] found that intensity decreased as the isopropylidene linkage (-C-(CH$_3$)$_2$-) in DGEBA was replaced by -CH$_2$-, -C(CF$_3$)$_2$- or -SO$_2$-. Thus the intensity decreases as the dipole moment of the linkage increases. This would imply changes in chain packing caused by dipole -dipole interactions.

CURING IN AS MAGNETIC FIELD

A number of groups in the Soviet Union have reported improved properties for epoxy resins cured in a magnetic field [5]. This has been attributed to changes in chemical structure including increased hydrogen bonding and cross-linking via ether linkages [6]. A small degree of molecular orientation has also been reported [7].

We have carried out similar experiments using DGEBA cured with triethylene tetramine at 55°C for 1 hour. However, we have not found any significant changes in the WAXS patterns from specimens cured in a magnetic field of ~1 Tesla. Nor is there any evidence, either from birefringence or WAXS, of molecular orientation in the specimens.

CONCLUSIONS

We conclude that the local structure is very similar in DGEBA cured with different aromatic amines, being mainly determined by packing of linear chains of DGEBA units (type II chains). The low-angle WAXS peak is due to periodicity of 18-20 Å along these chains.

The increased intensity of this peak, when mPDA is used, may be due to increased nesting of the DGEBA units encouraged by the small size of the mPDA molecules.

Analogues in which the diphenyl linkage has a high dipole moment give rise to a change in the mode of chain packing.

Curing specimens in a high magnetic field has little effect on the local structure.

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PUBLICATIONS

Three papers are being submitted for publication:

1. Conformational analysis of diphenyl linkages in "Computer Simulation of Polymers", ed. R.J. Roe (Prentice Hall) 1990.

2. Conformational analysis of amine-cured epoxy resins. Polymer (submitted).

3. WAXS investigation of local structure in epoxy networks. Polymer (to be submitted).

PRESENTATIONS

1.	Oral presentation:	"Local Structure of Network Resins"
	at the ACS symposium on Computer Simulation of Polymers, Miami
	Beach, September 1989. [Published in Polymer Preprints, Sept. 1989]

2.	Poster presentation: "Local Structure of Epoxy Networks"
	at the Polymer Physics Conference, Reading, U.K., September 1989.
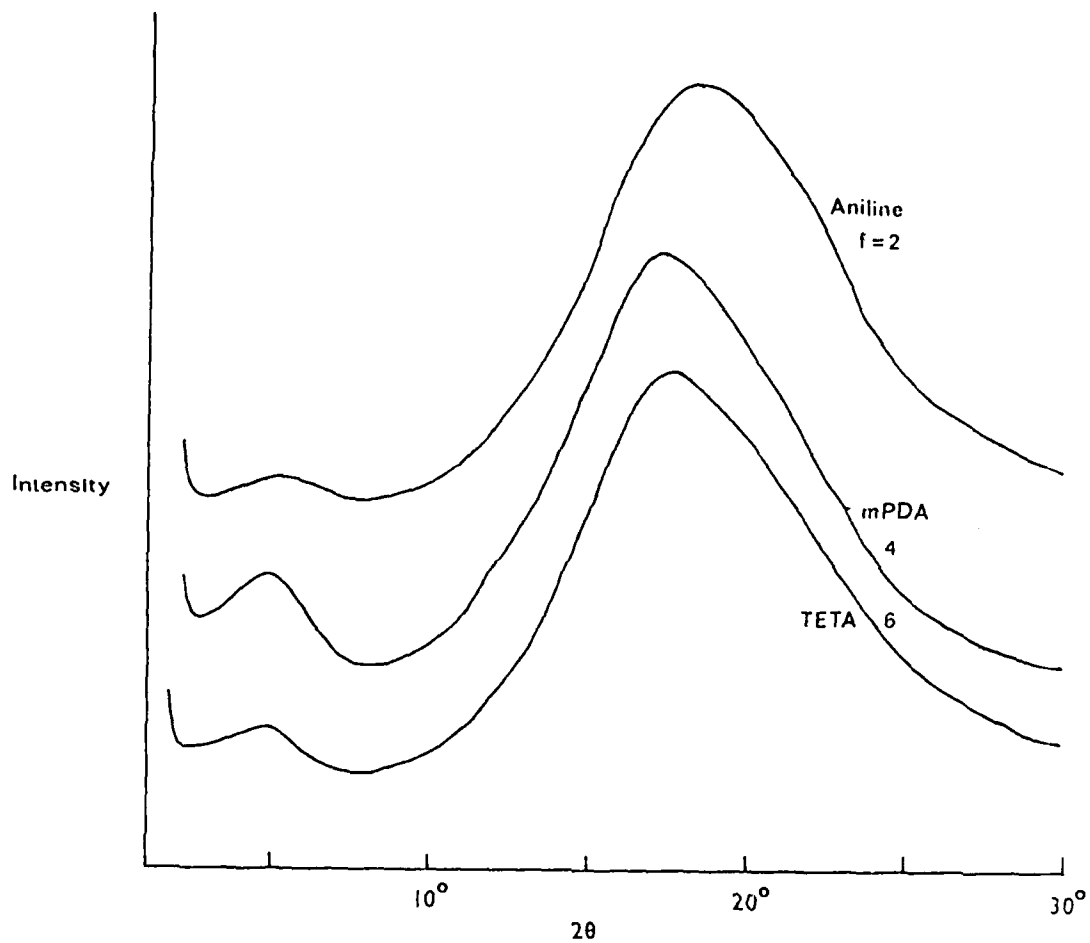
Figure 1   WAXS patterns for DGEBA cured with amines of
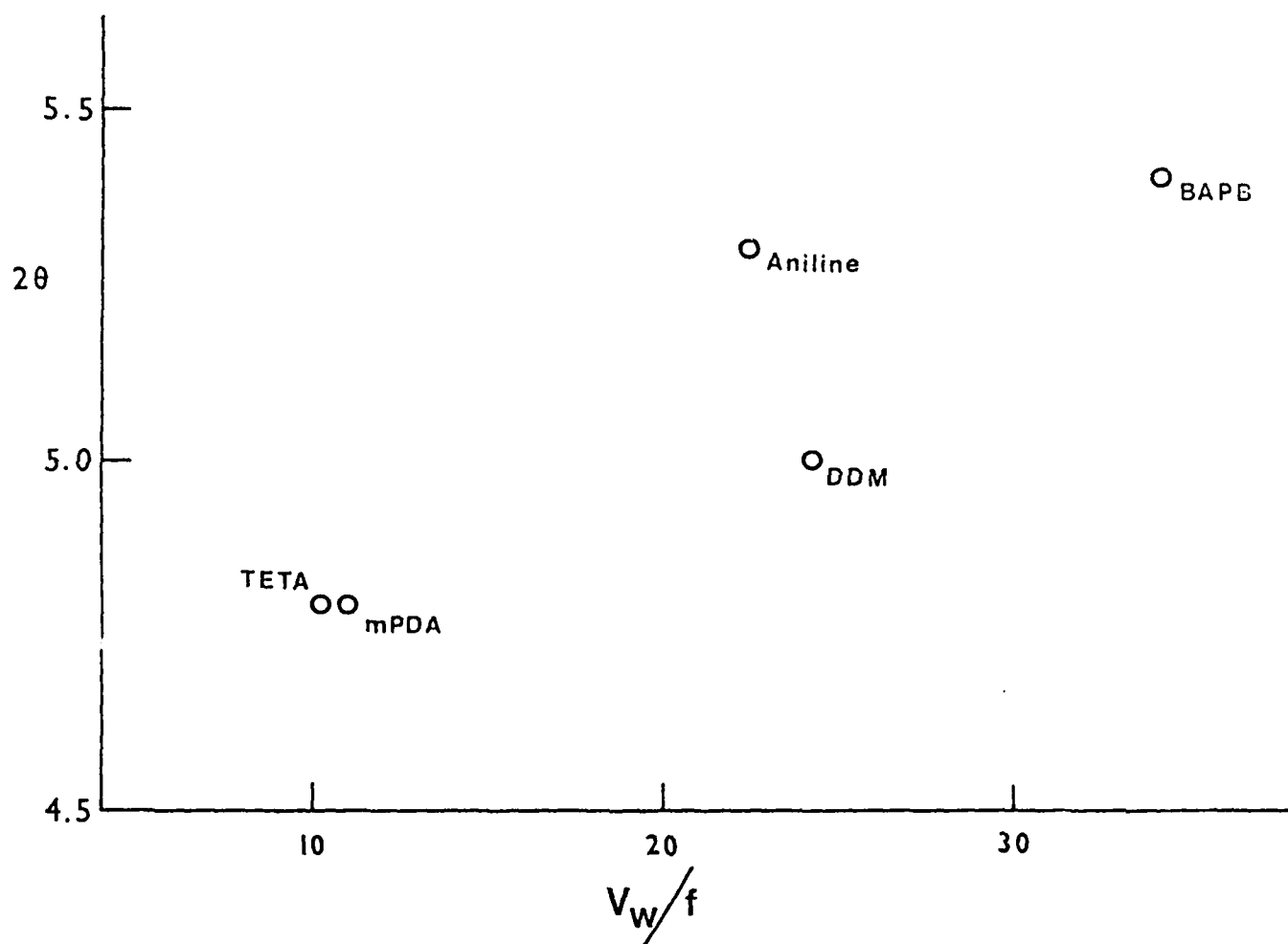   different functionalities (f).

Figure 2   Position of low-angle WAXS peak as a function of

size of amine molecules (van der Waals volume/f).
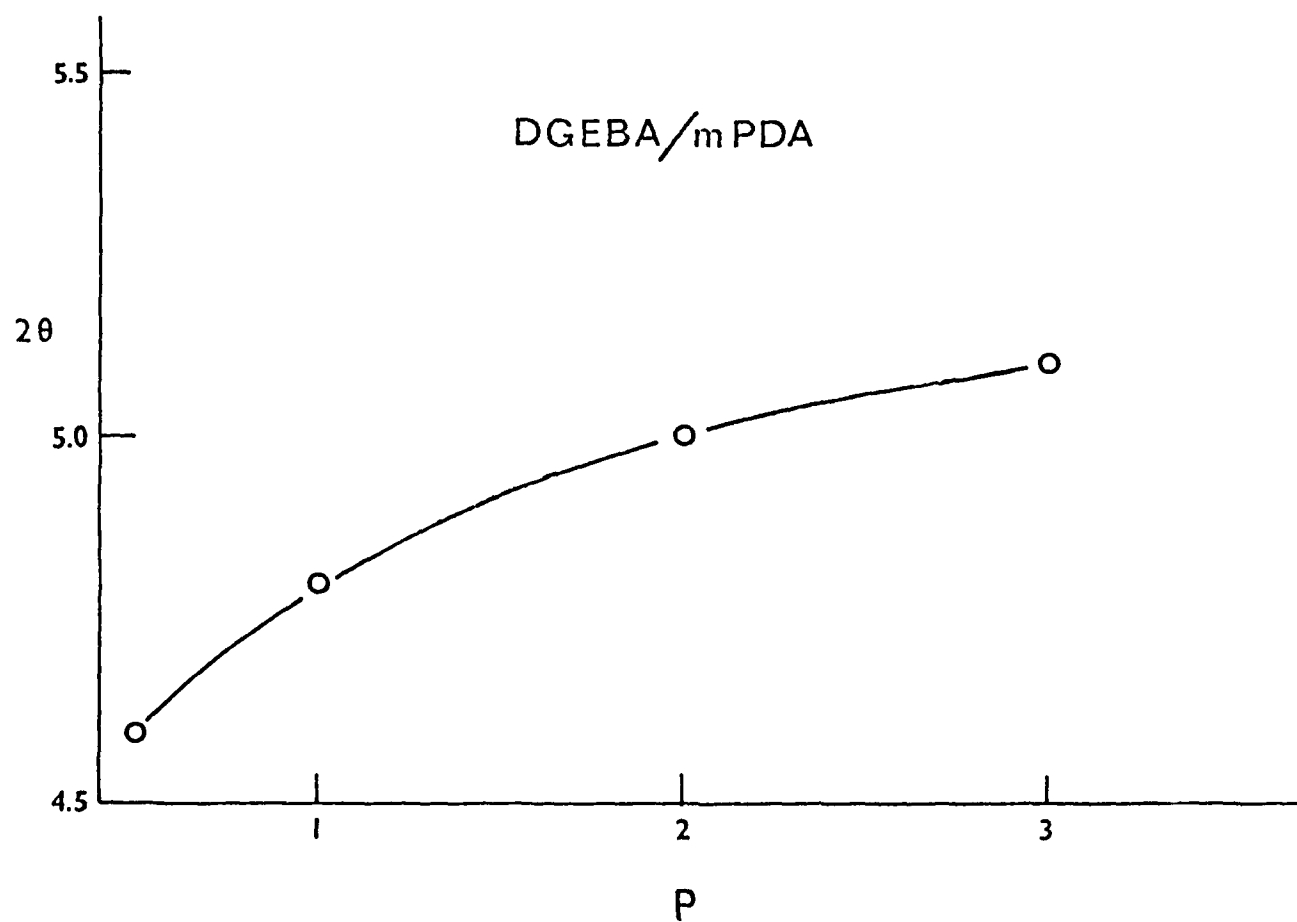
Figure 3   Position of low-angle WAXS peak as a function of
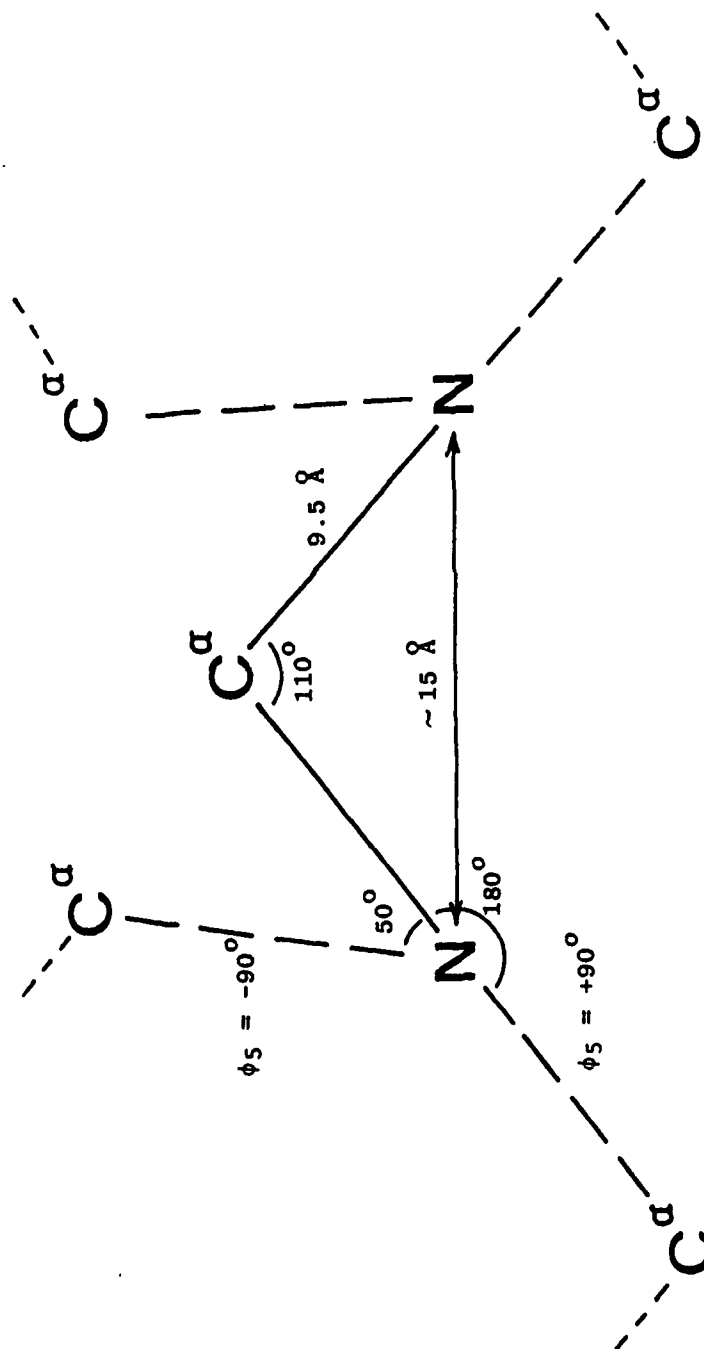
amine/epoxy ratio (P). P=1 for the stoichiometric mixture.

Figure 4   Structural unit of a chain of virtual bonds.