Polymer 42 (2001) 1507–1514

polymer

www.elsevier.nl/locate/polymer

Thermal and mechanical properties of liquid crystalline epoxy resins as a function of mesogen concentration

C. Farren, M. Akatsuka*, Y. Takezawa, Y. Itoh

Hitachi Research Laboratory, Hitachi Ltd 7-1-1, Omika-cho, Hitachi-shi, Ibaraki-ken 319-1292, Japan

Received 13 March 2000; received in revised form 12 June 2000; accepted 19 June 2000

Abstract

Liquid crystalline thermosets are known to exhibit a number of improved characteristics in comparison with traditional plastics. We now describe quantitatively how the thermal and mechanical properties of a number of liquid crystalline epoxy resins vary with polymer mesogen concentration, using biphenyl- and biphenol-based diepoxides with varying spacer lengths and a range of aromatic diamine curing agents. Although macroscopically isotropic, the degree of order at the microdomain level can be related to the network physical properties, and thus increasing mesogen content leads to increased intermolecular interactions between the polymer chains and hence reduced micro-Brownian motion and reduced free volume. These properties are manifested as increased elastic moduli at high temperatures, reduced thermal coefficients of expansion, increased decomposition onset temperatures and reduced solvent absorption. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Liquid crystal; Epoxy resin; Mesogen

1. Introduction

Although theories concerning the prediction of liquid crystalline behaviour in polymers came into existence almost 30 years ago [1], it was not until five years later that such systems were first prepared and reported by Bouligand et al. [2]. Following this a number of both main- and side-chain mesogen-containing networks were described [3], although it is only relatively recently that interest has peaked in this area. It is now well known that liquid crystalline thermosets often display a number of superior properties when compared to non-mesogenic references, and many groups have studied the synthesis and curing behaviour of such species [4–6]. Furthermore, both improved dynamic mechanical analysis (DMA) spectra at higher temperatures [7,8] and decreased thermal coefficients of expansion (TCE) [9,10] have been reported for epoxy resins containing a number of different mesogens such as biphenol [11], stilbene [12] and azine [13].

The current report examines how some of the physical properties of amine-cured liquid crystalline epoxy resins vary with the polymer mesogen concentration, using the biphenyl- and biphenol-based diepoxide monomers **1–6** described in Fig. 1.

2. Experimental

2.1. Materials

Diepoxy monomers **4–6** were used as obtained from Nippon Kayaku Co. Ltd (epoxy equivalents 173, 239 and 228 g/mol, respectively). Epoxides **2** and **3** were used as obtained from Yuka Shell Co. Ltd (epoxy equivalents 195 and 172 g/mol, respectively) and monomer **1** was obtained by fractional recrystallisation from mixture **3** (ethyl acetate) until a purity of over 95% was determined by chromatography and calorimetry measurements. 4,4′-diaminodiphenylmethane (DDM), 4,4′-diaminodiphenylsulphone (DDS) and 1,5-napthalene diamine (1,5-ND) were selected as curing agents, the structures of these being illustrated in Fig. 2. These diamines were analytical grade and used without further purification.

2.2. Network curing

The pre-weighed diepoxide monomer (approximately 10 g) was melted in an aluminium pan and subsequently kept to within 10°C of its melting point using a thermostatically controlled hotplate. Stoichiometric amounts (with one amine hydrogen atom corresponding to one epoxy group) of the diamine curing agent were added at this temperature, and the mixtures were magnetically stirred

---

* Corresponding author. Tel.: +81-294-52-5111; fax: +81-294-52-7632. *E-mail address:* makatsu@hrl.hitachi.co.jp (M. Akatsuka).

PII: S0032-3861(00)00499-7

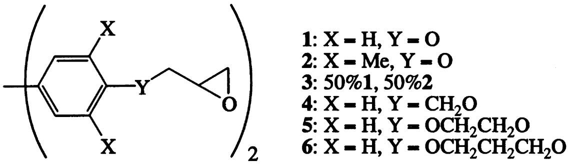

Fig. 1. Structures of epoxy monomers **1**–**6**.

until homogeneous (5–10 min). The liquid pre-polymers were then transferred to pre-warmed aluminium moulds in a vented oven at 150°C and cured for a period of four hours. Samples were isolated by allowing the polymer to return to room temperature and simply cutting away the mould.

2.3. Analytical measurements

Dynamic mechanical properties were determined between room temperature and 300°C from rectangular polymer samples of approximate dimensions $1 \times 3 \times 30\ \mathrm{mm}^3$ using a DVE-V4 non-resonance, forced vibration viscoelastometer (Rheology Co. Ltd). The measuring frequency was 10 Hz, the sample displacement was 3 μm and the heating rate was 2°C/min.

Optical microscopy was performed at room temperature using a Optiphot2-Pol polarising optical microscope (Nikon Co. Ltd) equipped with a H-III Polaroid camera (Nikon Co. Ltd).

Thermal coefficients of expansion were measured between room temperature and 250°C from the change in length of rectangular polymer samples of approximate dimensions $4 \times 4 \times 15\ \mathrm{mm}^3$ using a TA-1500 Thermal Analyzer (Sinku Riko Co. Ltd). The measuring frequency was approximately 0.01 Hz and the heating rate was 5°C/min.

Thermogravimetric analyses were performed between room temperature and 1000°C on powdered polymer samples with masses between 8 and 15 mg using a Hi-Res TGA 2950 Thermogravimetric Analyser (TA Instruments Ltd) at a heating rate of 10°C/min.

Solvent absorptions were calculated from the changes in mass during solvent exposure of cubic polymer samples with approximate dimensions $4 \times 4 \times 4\ \mathrm{mm}^3$ using a Sartorius 10 μg balance (Zeiss Co. Ltd).

The mesogen concentration of each network sample was approximately calculated on the basis of mass, with only the biphenyl/biphenol group being considered as contributing towards the mesogen content and the repeat unit consisting of two diepoxide molecules to one diamine. Thus, for example, a stoichiometric mixture of monomer **6** with DDM has two mesogenic biphenol groups in the repeat unit, at a mass of 184 g/mol each, and the total mass for the same repeat unit is 1018 g/mol. The mesogen concentration by mass can thus be calculated to be approx. 36%. A similar calculation for a mixture of **1** and 1,5-ND (again assuming that only the biphenol group contributes towards the mesogen content) gives a value of 49%, and the general formula used is written below.

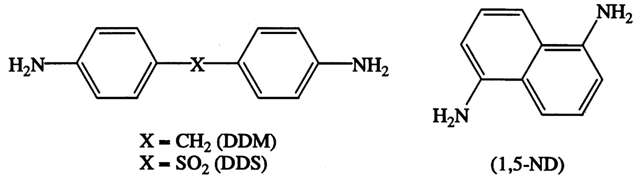

Fig. 2. Structures of diamine curing agents.

$$\text{(mesogen content)} = [\text{(total mass of mesogen groups)}/\text{(mass of whole repeat unit)}] \times 100\%$$

In cases where the mesogen unit is substituted, the mass of the substituents was not considered to increase the mesogen concentration and the only effect was one of increased repeat unit mass. However, substituted mesogens will induce a reduction in intermolecular interactions due to increased steric requirements, and this effect will be discussed later.

3. Results and discussion

3.1. Dynamic mechanical properties of liquid crystalline epoxy resins

The dynamic mechanical properties of the networks derived from monomers **1**–**6** and DDM are shown in Fig. 3. Monomers **4**, **5** and **6** have the longer alkyl spacers, and furthermore monomer **4** has a smaller mesogenic group (biphenyl as opposed to biphenol), and hence these three polymers have lower mesogen concentrations (35–38%) than those derived from monomers **1**–**3** (40–46%). Indeed, the DMA traces of the former three polymers display typical viscoelastic behaviour, similar to that observed in ordinary, non-liquid crystalline thermosetting resins [14]. The glass transition temperatures (T_g) are relatively low, and the elastic modulus decreases significantly during this relaxation to give a greatly reduced value in the rubbery region.

In contrast, the higher mesogen concentrations in the polymers derived from **1**–**3** give rise to higher T_g values, with much less severe drops in elastic modulus during this transition and hence large rubber elastic moduli. From this data it is clear that the micro-Brownian motion of the polymer network chains is increasingly strongly suppressed by both the increased number of inter-chain mesogen interactions and the reduced size of the flexible spacer groups. This effect seems to only become pronounced when the mesogen concentration reaches 40%, and indeed a closely packed arrangement of mesogens similar to that illustrated by Fig. 4 has been described previously by Ochi et al. [11] for monomers with short spacers cured with agents that contain adjacent active hydrogen atoms.

Furthermore, as the relative number of mesogen methyl

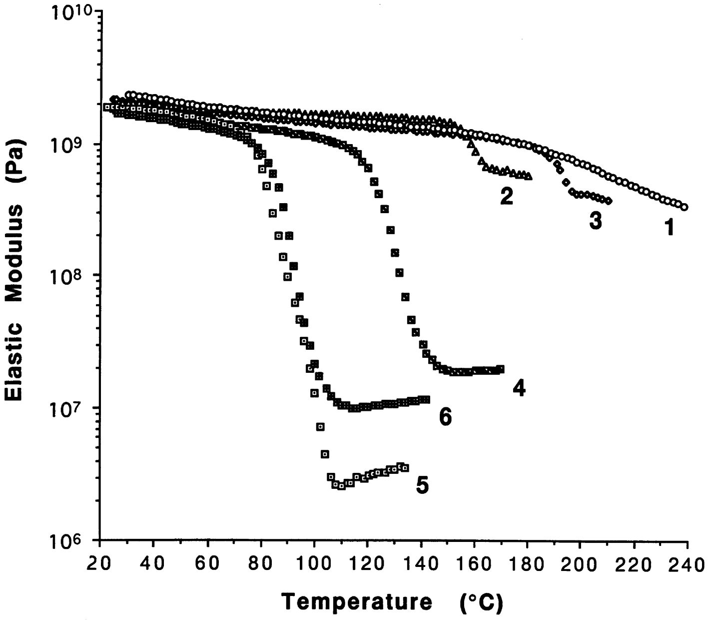

Fig. 3. DMA traces of DDM-cured polymers.

substituents decreases, in the order **2** > **3** > **1**, the polymers display consecutively higher temperature α-relaxations and more linear elastic modulus traces. Indeed, the sample derived from **1** and DDM displays no clear drop in elastic modulus, only a relatively smooth decrease between 200 and 240°C, and this is consistent with previous reports of this particular system [7]. The methyl substituted mesogens, whilst enforcing some degree of motion suppression and inducing a smaller drop in elastic modulus during the glass transition, are clearly still allowing a reduced level of micro-Brownian activity that is absent in the unsubstituted system. This is likely to be caused by the steric interactions of the methyl substituents preventing the close inter-chain approach of the mesogen groups, and thus for maximum chain suppression and hence the maximum increase in dynamic mechanical properties, the resin must have a high mesogen content and these mesogens must be unsubstituted.

We attempted to further investigate the minimum mesogen concentration at which polymer chain motion suppression would occur by the use of alternate curing agents, and indeed a similar trend can be observed in Fig. 5, which contains the DMA traces of monomers **1**–**6** cured with DDS. The larger, more massive curing agent reduces the mesogen concentration in all the networks when compared to the DDM-cured systems, but once again monomers **4**–**6** have the lower mesogen contents (34–36%) and give polymers that display typical viscoelastic behaviour as described previously. However, in this case the polymer derived from monomer **2** has a mesogen concentration of only 38%, and gives a similar DMA trace to the systems obtained from **4**–**6**, with a clear drop in elastic modulus at a relatively low temperature T_g.

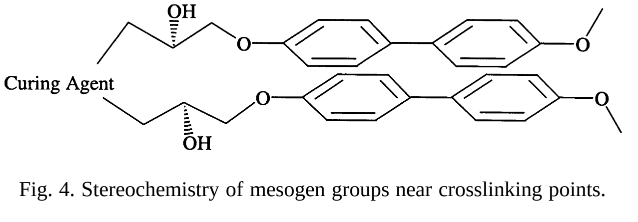

Fig. 4. Stereochemistry of mesogen groups near crosslinking points.

This again implies that there is a certain minimum mesogen concentration for suppression of thermal motion, at approx. 40% by mass, and below this point very little effect is seen. Indeed, only the networks derived from **1** and **3**, with mesogen concentrations of 44 and 41%, respectively, show any reduction of the polymer chain micro-Brownian motion and give rise to DMA spectra with higher temperature T_gs and smaller drops in elastic modulus during the α-relaxation, although the system derived from **3** and DDS seems to be a borderline case. To further illustrate this phenomenon we cured monomers **1**–**6** with 1,5-ND, and Fig. 6 shows the DMA spectra obtained. Once again, the polymers derived from **4**–**6**, with lower mesogen concentrations (37–39%), give typical thermosetting resin viscoelastic data. In clear contrast, the resins obtained from **1**–**3**, with higher concentrations of mesogen groups (43–49%), again show a strong suppression of polymer chain motion and the cut-off point for observing this effect again seems to occur at a mesogen content of around 40%. In fact the network synthesised from **1** and 1,5-ND, which has the highest mesogen concentration of all the polymers studied (49%), displayed an almost linear decrease in elastic modulus up to the onset of decomposition, the trace being more smooth than that of the polymer derived from **1** and DDM (46% mesogen concentration). No signs of a glass transition can

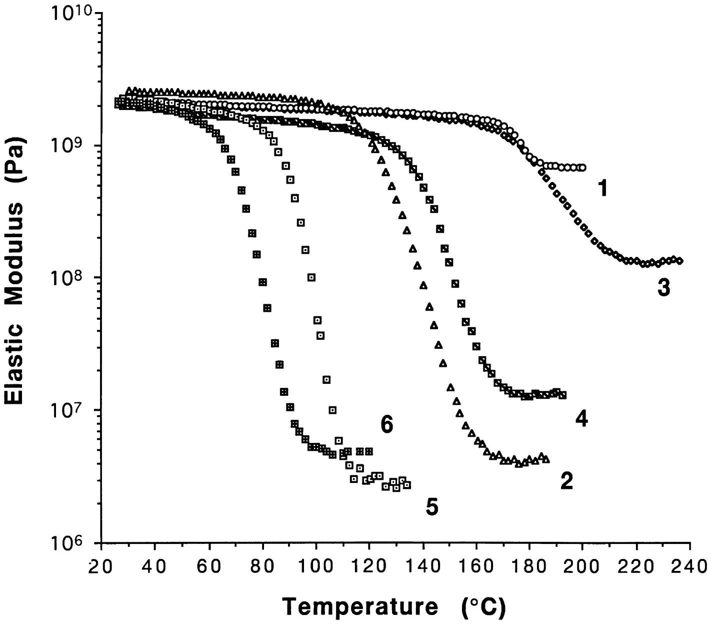

Fig. 5. DMA traces of DDS-cured polymers.

be detected in the 1,5-ND-cured polymer, and there is clearly an extremely strong suppression of the polymer micro-Brownian motion by both the higher density of intra-chain mesogen interactions and the small size and high rigidity of the diamine curing agent. The polymer chain suppression effect in these epoxy resin systems thus seems to be most strongly pronounced between 40 and 50% mesogen concentration by mass, below which value very little motion reduction is observed and above which value highly significant suppression is in evidence.

3.2. Optical properties of liquid crystalline epoxy resins

Polymer samples derived from monomers **1**–**6** displayed brightly coloured Schlieren textures with varying degrees of disclination density when viewed through crossed polarisers, as illustrated by the **1**/DDM system in Fig. 7. Although the bulk samples are isotropic, as no external field is applied during curing, the mesogen-containing thermosets clearly contain microdomains of relatively high molecular orientation that are of sufficient size to refract plane-polarised light

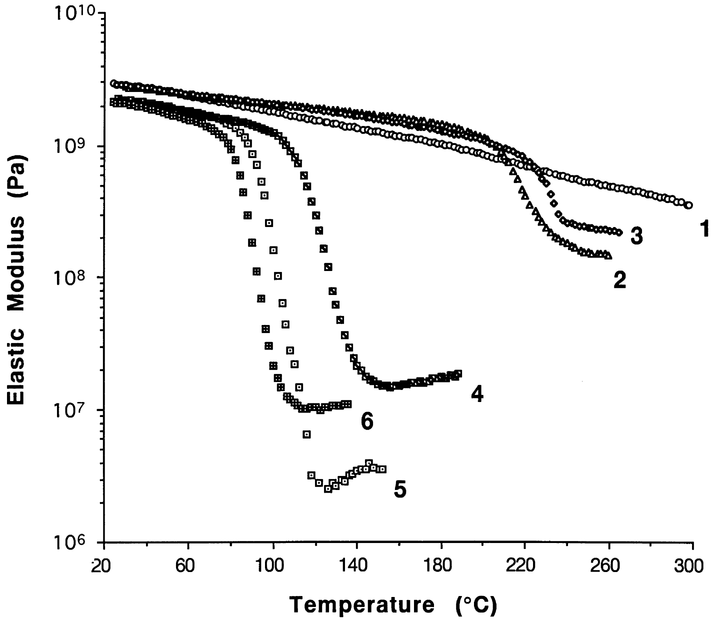

Fig. 6. DMA traces of 1,5-ND-cured polymers.

Fig. 7. Polymer **1**/DDM viewed through crossed polarisers.

and give rise to the observed texture. However, neither the nature of the liquid crystalline phases within the final networks nor the relative microdomain order parameters of the polymer samples could be determined solely from the POM data.

3.3. *Thermomechanical properties of liquid crystalline epoxy resins*

After confirming that the polymer chain micro-Brownian motion was increasingly suppressed with higher mesogen concentrations, we investigated the thermomechanical properties of the epoxy resins. Although some low thermal coefficients of expansion (TCE) have been reported for liquid crystalline epoxy resins, many of these concern either magnetically, electrically or mechanically oriented systems, in which the TCE parallel to the alignment is greatly reduced at the expense of the TCE perpendicular to the alignment, which is often correspondingly increased [10,15,16]. In comparison, the polymer systems in this report are macroscopically isotropic, and relatively few papers have discussed the benefits of liquid crystallinity on unaligned samples [17]. Fig. 8 contains the thermomechanical data obtained for the DDM, DDS and 1,5-ND-cured networks as related to the mesogen content of the sample.

For each curing agent there is a clear decrease in the polymer TCE as the mesogen concentration is increased, the most profound effect being detected for the DDS-cured networks. A bisphenol-A diglycidyl reference system was synthesised and cured using DDM under analogous conditions, giving an isotropic TCE value of 82×10^{-6}/K, and even the polymer networks with the lowest mesogen concentrations gave significant improvements over this value. It is theorised that the increasing suppression of the polymer micro-Brownian motion decreases the ability of the polymer to expand its free volume upon heating, and as a direct result the TCE is dramatically reduced. The smallest TCE value obtained (45×10^{-6}/K) is 55% that of the bisphenol-A reference sample, and although some reports of *oriented* polymers give TCE values parallel to the orientation that are closer to 20×10^{-6}/K [10], the above value is isotropic and thus applicable in all directions whilst the oriented samples have values of over 60×10^{-6}/K perpendicular to their orientation.

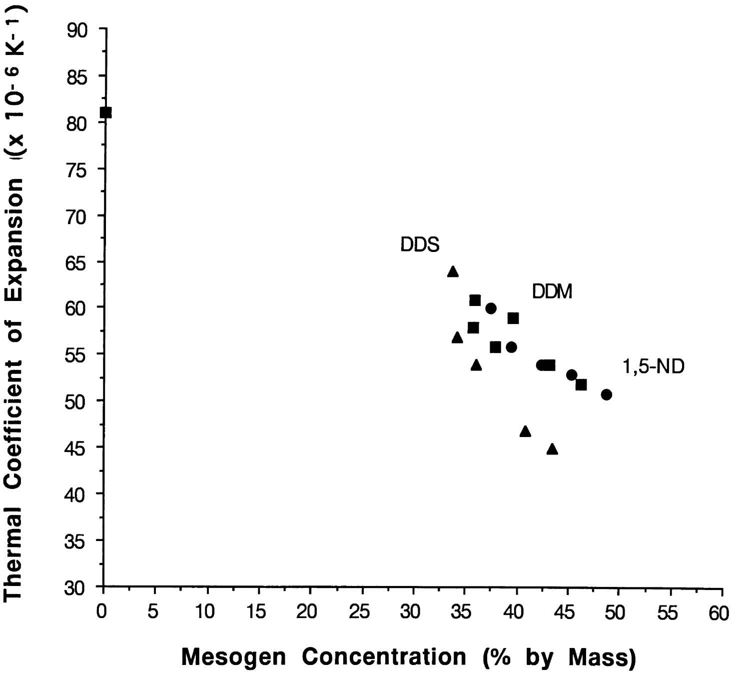

Fig. 8. TCE data of DDM, DDS and 1,5-ND-cured polymers.

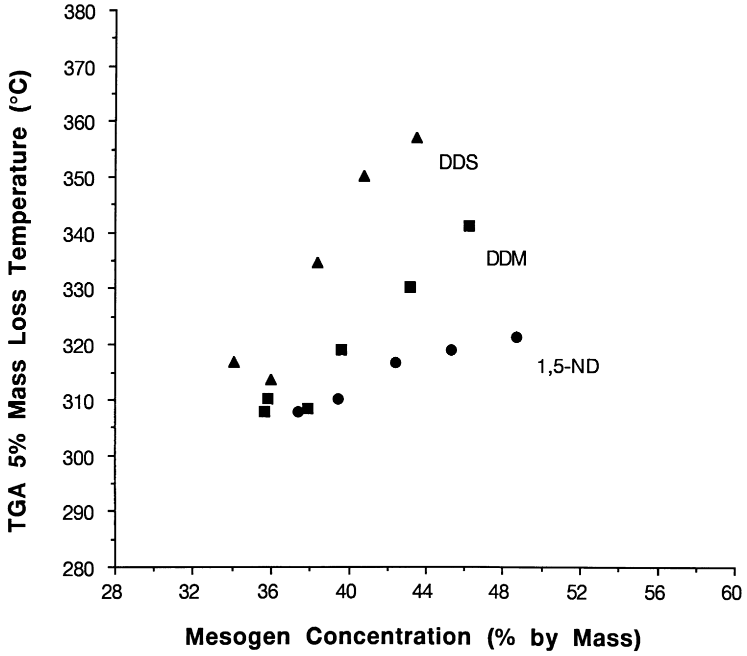

Fig. 9. TGA data of DDM, DDS and 1,5-ND-cured polymers.

3.4. Thermogravimetrical properties of liquid crystalline epoxy resins

Most typical epoxy resins undergo thermal decomposition at relatively low temperatures, usually losing up to 10% of their mass between 250 and 300°C in air [18], and the scant TGA data for liquid crystalline systems seem to corroborate this generalisation [13]. Indeed, the maximum recommended use temperature for most epoxy resins is between 80 and 110°C [19], and thus it would be advantageous if the temperature at which onset of decomposition occurs could be increased in line with the other physical properties for liquid crystalline polymers. Fig. 9 shows the temperature at which 5% of the sample's mass is lost, for each of the mesogenic epoxy resins under consideration.

There is a clear increase in the decomposition temperature with increasing mesogen concentration for

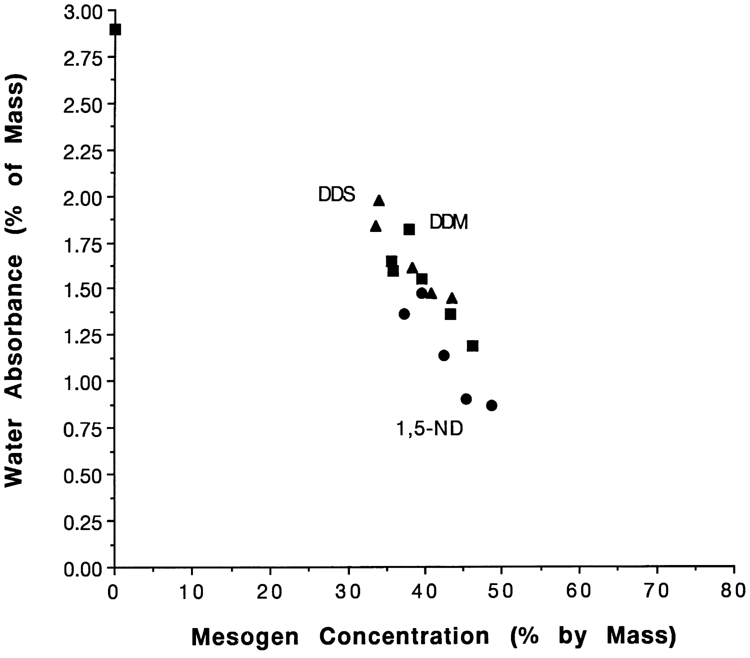

Fig. 10. Water absorption data of DDM, DDS and 1,5-ND-cured polymers.

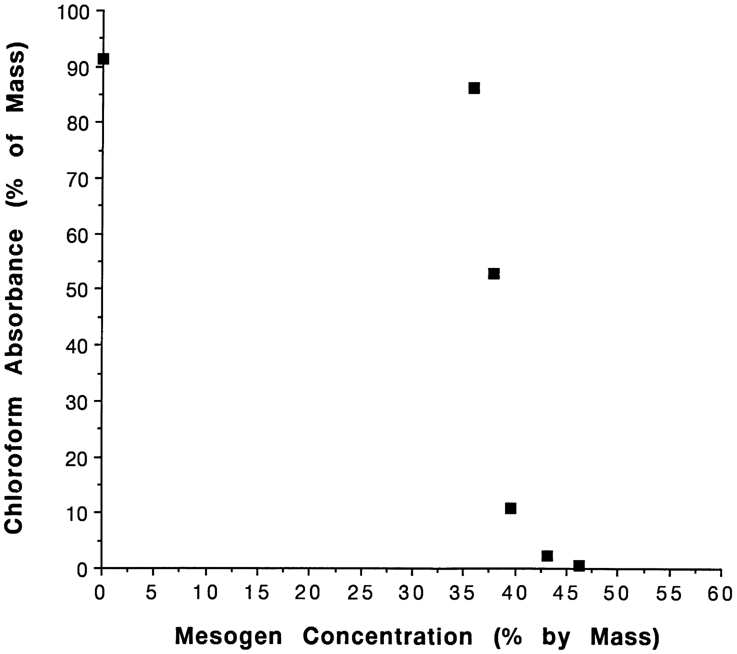

Fig. 11. Chloroform absorption data of DDM-cured polymers.

each of the curing agents used, the largest effect being induced by the use of DDS. Thermal decomposition generally occurs when the macromolecular chains gain sufficient energy to disrupt the backbone covalent bonds, and it is theorised that the increasing suppression of the polymer micro-Brownian motion by the intra-chain mesogen interactions reduces their vibrational energy and thus elevates the temperature at which such bond rupture will occur.

However, the decomposition process depends on the strengths of the bonds within the network functional groups, and thus the different curing agents give rise to different degrees of increased thermal stability. Indeed, 1,5-ND shows an improvement of less than 15°C, whilst DDS gives an elevation of over 50°C, although interestingly each of the curing agent series seems to have the largest change in thermal stability at or around the mesogen concentration of 40%, which is similar to the DMA data discussed previously.

3.5. Solvent absorption of liquid crystalline epoxy resins

Most epoxy resins exhibit relatively small degrees of solvent vapour absorption [20], and thus we performed accelerated absorption tests by exposing the polymer samples to the neat liquid solvents for a number of days. Fig. 10 shows the changes in mass during exposure to water (as a percentage gain over the initial mass) for each of the liquid crystalline polymers and also for non-mesogenic reference epoxy resins that were tested under analogous conditions.

The reference samples absorbed just over 2.9% of their mass in water during the two-week exposure period, whilst all of the liquid crystalline networks were much less susceptible to the solvent. Once again, the region of approximately 40% mesogen concentration by mass seems to contain the largest changes, and the samples with the lowest water absorption, derived from **1** and 1,5-ND, gained only 0.87% of their initial mass in water. This value is less than a third that of the references, and it was this polymer that displayed the greatest degree of micro-Brownian motion suppression during the DMA experiments. It is thus theorised that the shorter spacer groups and the mesogen-induced reduction in chain motion leads to a concomitant reduction in the polymer free volume, and that there is thus much less available space within the network matrix to accommodate solvent guest molecules. However, water does not wet most epoxy resins significantly, and the variance in solvent absorption is greatly magnified when organic species are used. Fig. 11 shows the same experiment for the DDM-cured polymer samples using chloroform as the exposure medium.

In this case the reference samples experienced severe swelling, absorbing almost 92% of their own mass again in solvent during the exposure period. The samples with lower mesogen concentrations fared little better, but as the mesogen content approached 40% the degree of absorption decreased rapidly, and the polymer derived from **1** and DDM (46% mesogen content) gained only 0.6% of its own mass in solvent. Clearly the reduction in free volume due to the shorter spacer groups and the increased inter-chain mesogen interactions makes a very large difference to the absorbance characteristics of these samples.

4. Conclusions

Variations in the thermal and mechanical properties of liquid crystalline epoxy resins were investigated as a function of mesogen concentration, calculated approximately on the basis of mass. Higher mesogen contents gave networks with increased glass transition temperatures and significantly larger elastic moduli in the rubbery region, and this is attributed to the suppression of the polymer chain micro-Brownian motion. The largest effects are observed as the mesogen concentration exceeds 40% by mass, but methylated mesogens had a less strong effect on the polymer chains, presumably due to the steric interactions of the substituent groups.

The suppression of thermal motion of the network chains by increasing mesogen concentration also led to a large decrease in the thermal coefficient of expansion and a moderate increase in the polymer decomposition temperature, with the largest changes again occurring as the mesogen content approached 40%. Furthermore the decrease in polymer free volume associated with chain motion suppression led to dramatically reduced solvent absorptions for both aqueous and organic media.

References

[1] de Gennes PG. Phys Lett 1969;A28:725.
[2] Bouligand Y, Cladis PE, Liebert L, Strzelecki L. Mol Cryst Liq Cryst 1974;25:233.
[3] Chapoy L, editor. Recent advances in liquid crystalline polymers. London: Elsevier, 1985.
[4] Gur'eva LL, Belov GP, Boiko GN, Kusch PP, Rozenberg BA. Polym Sci 1992;34A:593.
[5] Broer DJ, Lub J, Mol GN. Macromolecules 1993;26:1244.
[6] Carfagna C, Amendola E, Giamberini M. Liq Cryst 1993;13:571.
[7] Ochi M, Shimizu Y, Nakanishi Y, Murata Y. J Polym Sci, Part B: Polym Phys 1997;35:397.
[8] Ortiz C, Kim R, Ober CK, Kramer EJ. Macromolecules 1998;31:4074.
[9] Su WFA. J Polym Sci, Part A: Polym Chem 1993;31:3251.
[10] Barclay GG, McNamee SG, Ober CK, Papathomas KI, Wang DW. J Polym Sci, Part A: Polym Chem 1992;30:1845.
[11] Ochi M, Tsuyuno N, Sakaga K, Nakanishi Y, Murata Y. J Appl Polym Sci 1995;56:1161.
[12] Lin Q, Yee AF, Earls JD, Hefner RE, Sue H-J. Polymer 1994;35:2679.
[13] Giamberini M, Amendola E, Carfagna C. Makromol Chem Phys 1994;195:279.
[14] Potter WG. Epoxide resins. London: Iliffe Books, 1970.
[15] Benicewicz BC, Smith ME, Earls JD, Priester Jr. RD, Setz SM, Duran RS, Douglas EP. Macromolecules 1998;31:4730.
[16] Shiota A, Ober CK. Macromolecules 1997;30:4278.
[17] Lee JY, Jang J, Hwang SS, Hong SM, Kim KU. Polymer 1998;39:6121.
[18] Lee H, Neville K. Handbook of epoxy resins. New York: McGraw-Hill, 1967.
[19] Van Krevelen DW, Hoftyzer PJ. Properties of polymers. Amsterdam: Elsevier Science, 1976.
[20] Bruins PF, editor. Epoxy resin technology. New York: Interscience, 1968.