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Anisotropic liquid crystalline epoxy thermoset

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The processing of an anisotropic liquid crystalline thermoset formed by *p*-bis(2,3-epoxypropoxy)-α-methylstilbene (DOMS) and 1-methyl-2,4-diaminobenzene (DAT) with uniformly oriented mesomorphic molecules, and consequently strongly birefringent, is described. The unidirectional alignment of the molecules was achieved during the curing process by external factors such as surface–liquid crystal interactions and/or an applied electric field. The control over the molecular orientation enabled us to produce well oriented highly anisotropic and birefringent epoxy thin films. In this paper, we discuss the formation process and the properties of the anisotropic epoxy network.

1. Introduction

Much attention has been focused on liquid crystal networks during the last few years due to their great potential for use as optical switches, waveguides, non-linear optical materials and advanced composites. The occurrence of liquid crystalline networks has been recognised since 1974 and the concept was used to describe the ensemble of rigid and elongated molecules, bonded as pendant side-groups to the flexible cross-linked chemical backbone and structured in a liquid crystalline phase. Depending on the cross-link density, i.e. the average length between two contiguous cross-links along the molecular backbone, the materials may exhibit reversible transitions from the liquid crystalline to the isotropic state.

Loosely cross-linked structures exhibiting liquid crystalline behaviour were theoretically investigated a long time ago [1–3]. The rubber elasticity theory applied to this material predicted unusual behaviour indicating abrupt changes in the dimension of samples subjected to increasing loading conditions, with the discontinuity being related to the orientation of nematic domains in the bulk material. However, the experimental confirmation of this theory has failed up to now due to the mismatch between the theoretically stated ideal conditions and the properties of the liquid crystalline networks synthesized so far. The possibility for introducing the liquid crystalline moieties into the main chain had also been exploited, fulfilling the requirement of end-capping the elongated molecules with two or more chemical groups suitable for further reaction.

A wide variety of chemical reactions is available to produce tridimensional networks such as, for example, the use of double bonds in chain reactions or the reactions of silanes, imides, epoxides, isocyanates, esters, ethers etc.

The physical properties of conventional cross-linked networks are greatly affected by the flexibility of the chemical units and the cross-link density. If the cross-linking density is low, the resulting physical properties will be governed by the toughness and ductility of the materials, but the elastic modulus and dimensional stability will be poor. On the other hand, by increasing the cross-link density, the benefits gained in terms of elastic modulus and stability of the materials will invariably be coupled with an increased brittleness of the material. Investigations on fracture mechanics have suggested the addition of rubber particles acting as crack stoppers as a practical means of absorbing the deformation energy and increasing the material toughness. Nevertheless, the costs of the resulting manufacturing processes are quite high.

It has been shown [4] that the energy absorbed during fracture, K_q, is sensibly increased if an epoxy resin is cross-linked while in the nematic state. Simultaneously, there is no decrease of elastic modulus

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such as that associated with the presence of plasticisers or rubber particles in the resin. Several approaches have been followed in order to produce a liquid crystalline thermoset.

In our previous investigations [5], it was demonstrated that the use of a bifunctional epoxy molecule with a stiff and elongated structure is the main factor in determining the features of the resulting liquid crystalline network. The cross-links were introduced by reacting the epoxy groups with both polyfunctional amines or dicarboxylic acids. The choice of the cross-linking agents has to match several requirements. The temperature range and kinetics of the curing reactions have to be controlled in order to achieve a full development of the liquid crystalline phase. Moreover, the stiffness and cross-linking density of the resulting network are greatly affected by the choice of the suitable cross-linking agent.

It has also been reported that the pure epoxy compounds used do not necessarily exhibit a liquid crystalline phase. In fact, the lack of long and flexible tails attached to the rigid core generates high melting temperatures for these compounds, thus hindering formation of the liquid crystalline phase. However, during the curing process, as the reaction proceeds and produces longer molecules, the liquid crystalline phase does appear at an early stage.

For completely cured systems, the liquid crystalline order of the molecules is stabilized over a temperature range depending on the overall molecular mobility, which, in turn, is mainly affected by the choice of the cross-linking agent. On the other hand, if the cross-link density is quite poor, then the transition from liquid crystalline to isotropic state can be observed as the temperature increases.

The overall orientation of the elongated mesogenic units is dependent on the curing temperature and external factors such as electromagnetic fields or surface–liquid crystal interactions. If the epoxy resin is cured in bulk in the absence of external fields, then a random distribution of the liquid crystalline domains is achieved. The overall degree of order measured for such a sample is zero and the mechanical properties are isotropic. Nevertheless, the low viscosity of the epoxy/curing agent mixture during the early stages of the reaction allows the molecules to be unidirectionally oriented before the formation of chemical cross-links hinders the molecular realignment process and finally freezes the structure. This procedure can be used for the production of highly aligned samples with a stable molecular orientation over a wide temperature range.

In the literature, there are reports that liquid crystalline epoxy networks could be aligned either by applying a magnetic field or by stretching them mechanically [6, 7]. The first method is applied during the curing process, whereas the second is used to align networks with a low cross-link density above the glass transition temperature. However, while the first method is not very efficient for the preparation of uniform liquid crystalline networks, the alignment achieved by the second method is thermally unstable and can even totally disappear on heating.

The most effective way to achieve a uniform molecular alignment in liquid crystal materials seems to be through liquid crystal–surface interactions which can be combined with an applied electric field or with unidirectional shear flow. In this paper we report the processing of uniformly aligned epoxy thermosets where the liquid crystal–surface interactions are of major importance in the achievement of such an alignment.

2. Materials preparation and characterization

The chemical structures of *p*-bis(2,3-epoxypropoxy)-α-methylstilbene (DOMS) and 1-methyl-2,4-diaminobenzene (DAT) employed in the formulation of the mixtures used to obtain the thermosets are illustrated in figure 1. The synthesis of the epoxy compound has already been reported in literature by the authors [8].

DOMS was purified chromatographically on a column packed with silica gel (Aldrich 130–270 mesh) and eluted with chloroform at room temperature. The presence of the DOMS in the eluted solution was detected by thin layer chromatography using a UV lamp as detector. The DAT used was a commercial grade (Aldrich) that was distilled under reduced pressure at 170°C.

The model compound *p*-bis(1-hexoxy)-α-methylstilbene, referred to as MS6, is also sketched in figure 1. This was synthesized according to the following procedure: *p*-bis(hydroxy)-α-methylstilbene (4·0 g), the stoichiometric amount of 1-bromohexane and a 10% excess of potassium carbonate were heated at reflux in 18 ml of *N*,*N*-dimethylformamide for 150 min. The solution was then poured into distilled water and acidified with sulphuric acid. The solid obtained was filtered off and recrystallized from ethanol.

The epoxy terminated compound and the tetrafunctional amine were mixed in the molar stoichiometric ratio of 2/1. The mixture was prepared by dissolving the epoxy compound and the amine in chloroform at room temperature. The solvent was subsequently evaporated at room temperature and the residue finely ground. The sample was then desiccated under vacuum.

The temperatures and enthalpies of phase transitions were investigated by means of a TAI-DuPont differential scanning calorimeter (DSC) (model 2910). Both isothermal and dynamic scans at $10^{\circ}\mathrm{C\,min^{-1}}$ were run using nitrogen as the purge gas. The optical rotatory power of DOMS was measured at 25°C by a Perkin

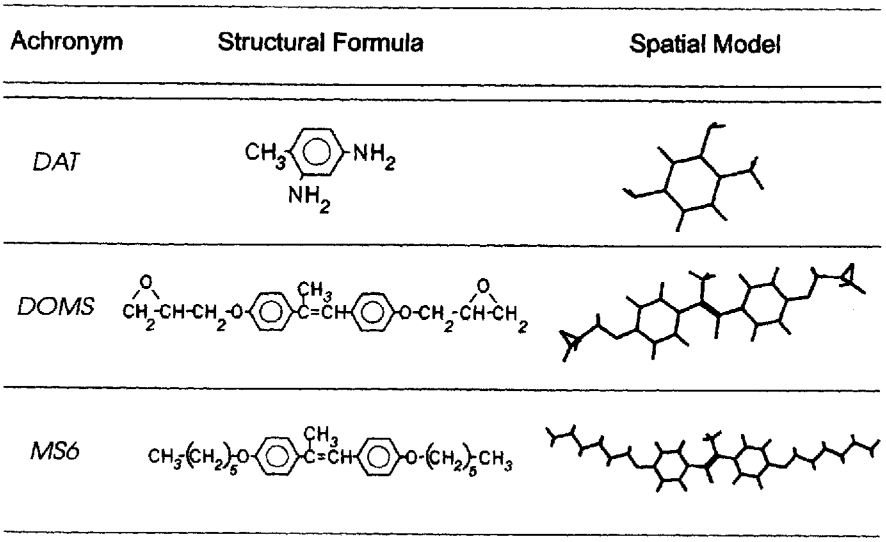


Figure 1. Structural formulae and computer simulated spatial conformations of 1-methyl-2,4-diaminobenzene (DAT), *p*-bis (2,3-epoxypropoxy)-α-methylstilbene (DOMS), and *p*-bis (1-hexyloxy)-α-methylstilbene (MS6).

Elmer polarimeter (model 141). Chloroform was used as solvent.

Conventional sandwich cells, consisting of two parallel glass plates with the inner surfaces covered by ITO (Indium–Tin Oxide) transparent conductive layers, were used. The cell gap was fixed by Mylar spacers. A thin film of polyimide was deposited on top of the ITO layer. The polyimide solution was spin-coated onto the glass substrates and the solvent evaporated at 180°C for 1 hour. After complete removal of the solvent, the polymer layer was rubbed unidirectionally in order to achieve a planar alignment of the molecules in the liquid crystal phase. The epoxy/curing agent mixture was introduced into the cell in the isotropic phase. In order to stabilize the planar alignment of the DOMS/DAT mixture (since the dielectric anisotropy of the material is negative) an electric field was applied. The electric field was however found to affect strongly the kinetics of the curing process. In addition, to improve the planar alignment of the liquid crystal molecules in thicker cells, a unidirectional mechanical shear of the glass plates was applied. In order to obtain a homeotropic alignment, ITO glass plates covered by a thin polysiloxane film were used.

Investigations on the process of formation and alignment of the epoxy network were carried out using a Reichert–Jung Polyvar microscope. The experimental cell was mounted in a Mettler FP 52 hot stage and the temperature controlled to within a 0·1°C accuracy in the isothermal mode or in 10°C min^{-1} heating and cooling scans.

3. Results and discussion

In the molecular structure of DOMS, two epoxy groups are symmetrically situated with respect to the rigid core, each of them possessing an asymmetric carbon atom. The synthetic procedure involves stages of opening and closing of the oxirane ring linked to the rigid block. Since the D- and L- configurations of the asymmetric carbon atom are equally probable, a racemic mixture is attained. The measurement of the optical rotatory power of the DOMS in chloroform solution indeed confirmed the absence of any optical activity of the compound, since $[\alpha]_D^{25} = 0{\cdot}00$.

The characterization of the phases exhibited by DOMS was accomplished by means of DSC and optical microscopy. Using the DSC method, the epoxy compound, recrystallized from ethanol, melts to the isotropic liquid at 131·0°C with a transition enthalpy of 48·67 kJ mol^{-1}. During cooling from the isotropic melt, the monotropic liquid crystalline phase appears at 115·0°C with a transition enthalpy of 0·94 kJ mol^{-1}.

The purification of the DOMS increased the stability of the liquid crystalline phase, and the absence of acidic impurities that catalyze the addition reaction of the amine onto the epoxy group strongly influenced the curing kinetics. The thermal characteristics of purified DOMS are shown in figure 2. The DSC thermogram on heating shows a transition centred at 133·2°C, transition enthalpy 50·76 kJ mol^{-1}, (*a*) which is associated with the melting of the sample to the isotropic state. In order to detect the transition from the liquid crystalline to the isotropic state, the sample was quenched to 90°C. During the subsequent heating (*b*), the transition associated with the isotropization of the sample was observed at 111·1°C, with a transition enthalpy of 1·12 kJ mol^{-1}.

The identification of the liquid crystalline phases of DOMS was carried out by means of optical microscopy, but the transition temperatures detected by optical microscopy during heating and cooling scans of the hot stage were slightly different from those detected by DSC

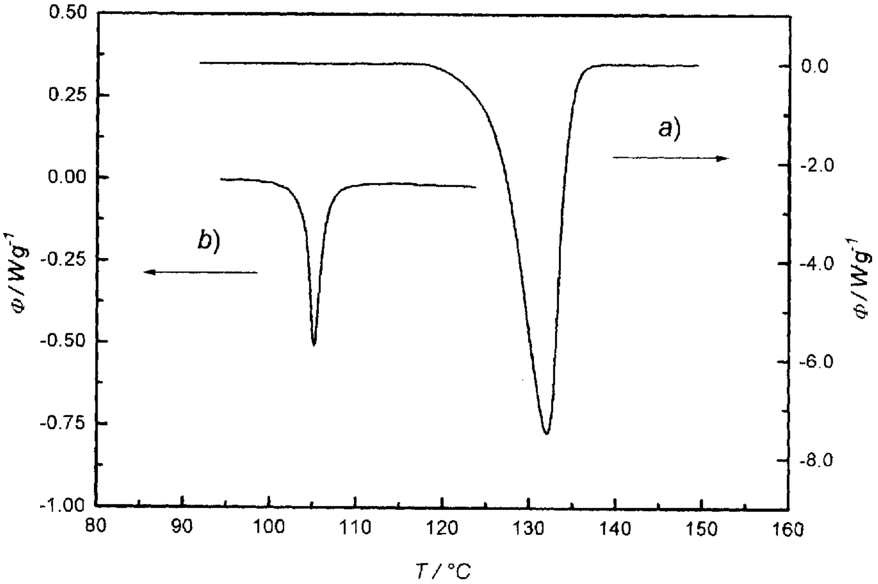


Figure 2. DSC traces of DOMS at 10°C min^{-1} heating rate using an N_2 flow as the purge gas: (*a*) first heating; (*b*) second heating.

due to differences in sample geometries and instrumental sensitivities.

Optical observation during cooling indicated that the liquid crystalline phase exhibited by DOMS confined between untreated glass substrates was nematic, with a strong tendency to homeotropic orientation, i.e. with molecules aligned perpendicularly to the glass plates. The birefringent border between the isotropic phase and the homeotropically aligned molecules of DOMS, observed near to the nematic–isotropic transition, can be attributed to a surface-induced alignment transition [9]. These observations will be reported elsewhere.

The reason for the homeotropic alignment of the DOMS molecules must be related to the chemical composition of the glass substrates used to support the sample. The glass surface is rich in hydroxylic groups that can easily form hydrogen bonds with polar molecules such as the epoxy groups at both ends of the DOMS molecules. These interactions could anchor the epoxy molecules on the surface, but only one end of the molecule may be subjected to this restraint, because to anchor both ends onto the surface (which means a planar alignment) might result in strong geometrical constraints because it is likely that the epoxy group lies out of the plane.

The effect of surface treatments on the molecular orientation and phase transition temperatures of DOMS was studied using two types of aligning film. Planar alignment was achieved by a unidirectionally rubbed polyimide film, whereas the homeotropic alignment was obtained by means of a polysiloxane film.

The sample with a polyimide aligning film, after melting of the DOMS, was cooled down and the transition from isotropic to nematic was detected. As the temperature was further decreased, the nematic phase adopted a uniform planar alignment with the director essentially parallel to the rubbing direction as one might expect. The presence of the polyimide coating widened the temperature range over which the nematic phase is stable and suppressed the tendency for the epoxy molecules to orient themselves perpendicular to the glass surface. In fact, the polyimide surface is not rich in hydroxylic groups, and the hydrogen bonds between the polymeric surface and the epoxy end groups are weaker and less likely to be formed than in the case of uncoated glass. The rubbing of the polyimide film results in a local heating and stretching of the film which partially aligns the polymer molecules unidirectionally [10]. In addition, the rubbing process also creates microscopic groves on the polyimide surface. Thus, the liquid crystal molecules in contact with the unidirectionally rubbed polyimide surface adopt a uniform planar alignment with a preferred direction along the rubbing direction.

In order to investigate the role of the epoxy groups in the alignment of DOMS, the model compound referred to as MS6 was synthesized and characterized. As can be seen from figure 1, the chemical structures of DOMS and MS6 are quite similar with the epoxy end groups replaced in MS6 by 6 carbon atom aliphatic tails.

The DSC plot of MS6 (figure 3) revealed a melting transition at 90·4°C and a clearing point at 92·7°C. In order to resolve the DSC trace and split it into the contribution from melting as well as that from isotropization, the sample was quenched before the next heating ramp for the detection of the clearing point transition. The optical characterization of the phases exhibited by MS6, carried out during heating and cooling ramps at 10°C min^{-1}, showed a crystal-to-crystal transition

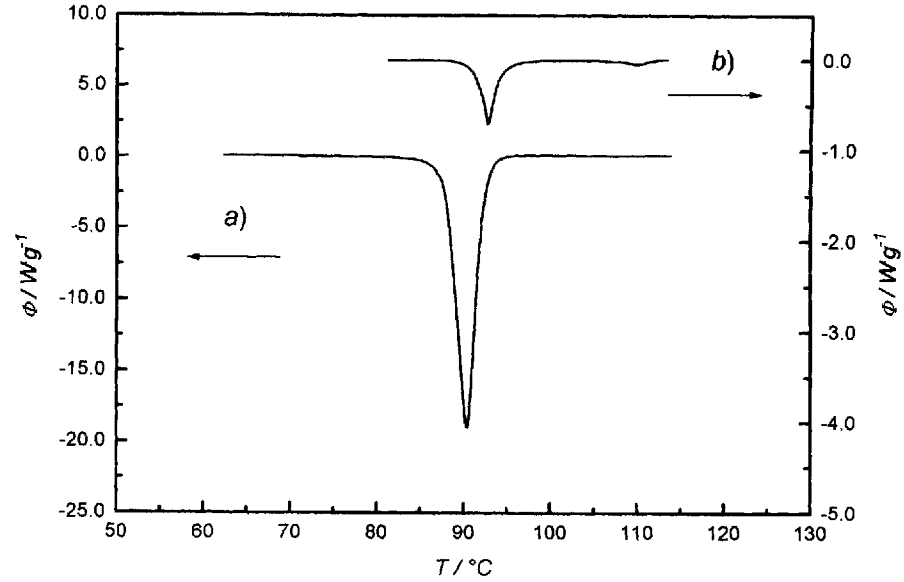


Figure 3. DSC traces of MS6 at 10°C min^{-1} heating rate using an N_2 flow as the purge gas: (*a*) first heating; (b) second heating.

followed by melting to the nematic phase, and finally the occurrence of isotropization.

In contrast to the epoxy DOMS, the liquid crystalline model compound has no tendency to give homeotropic alignment in cells with untreated glass substrates. This observation supports the assumption that the homeotropic alignment of DOMS is due to the hydrogen bonds between the epoxy groups and the glass surface and is not at all an intrinsic property of the rigid core of the molecule.

The reactivity of epoxy compounds towards quite a large number of chemicals is well known, but only a few reactions are likely to proceed in good yield and without by-products making them suitable to produce high molecular weight networks. A tetra-functional amine was used in our work to cure the epoxy system. The use of a rigid aromatic amine instead of a more flexible aliphatic amine was preferred in order to slow down the curing process and allow the development of the nematic phase before the crosslinking process was accomplished. The degree of crosslinking achieved at the end of the curing reaction was very high, and the nematic order was completely preserved in the network in which the molecules were chemically bonded together.

The mixture composed of the epoxy compound and the tetra-functional amine was cured in the molten state. Figure 4 shows typical DSC isothermal traces of DOMS/DAT mixtures heated in the temperature range between 150 and 190°C. Several features of these thermograms should be pointed out and associated with

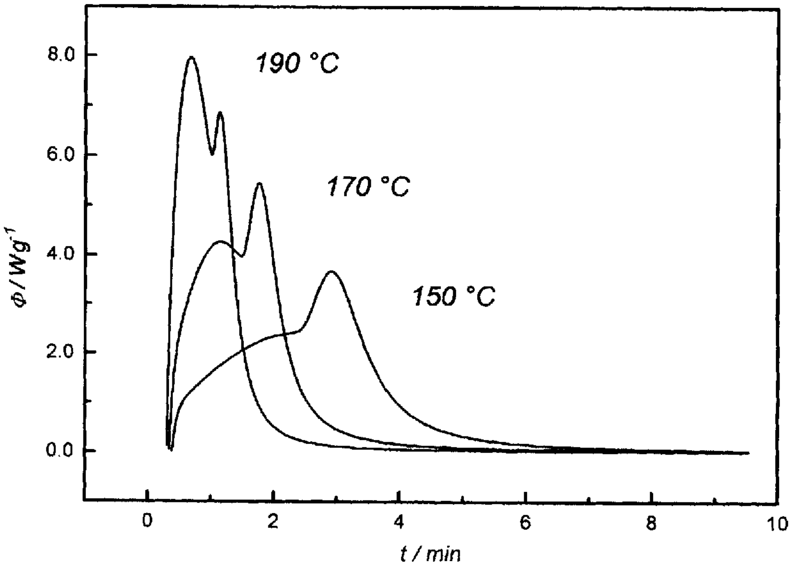


Figure 4. DSC traces of DOMS/DAT mixtures in the isothermal mode using an N_2 flow as the purge gas. Curing temperatures of 150, 170, and 190°C.

microscopic observations. The presence of two peaks during the isothermal cure is one peculiarity that we have observed during the curing reaction of many liquid crystalline thermosets. It is related to the phase transition that occurs in the isothermal condition as the reaction proceeds from the reactants to the infinite molecular weight network. In order to start the curing reaction, the solid epoxy and amino compounds have to be melted. At this stage, the epoxy/curing agent mixture is in the isotropic state, and the fractional conversion is virtually zero. As the reaction starts and proceeds further, the fractional conversion and the average molecular weight of the epoxy resin increase. It has been reported that the reaction of the primary amino group with the epoxy compound is favoured with respect to the reaction of the secondary amino group that is produced, with the ratio of the kinetic constants of the primary and secondary amine reactions, k_1/k_2 lying in the range 2 to 4 [11, 12]. The main reason for this behaviour is the increased steric hindrance caused by the addition of the first epoxy group to the nitrogen atom that is now shielded from attack in the further reaction. This accounts for the formation of linear or slightly branched oligomers. The aspect ratio of the molecules increases and eventually reaches the limit beyond which the liquid crystalline phase is stabilized by intermolecular forces. As a result of the formation of oligomers, the initially isotropic state transforms into a nematic phase. The appearance of the birefringent nematic phase was observed by polarizing microscopy. In figure 5, the structures of oligomers constituted from two DOMS molecules and one DAT molecule are schematically illustrated. The molecular structures proposed in figure 5 are only estimates of some of the possible spatial conformers with minimum energy. Nevertheless, they are in agreement with the molecular concept of the nematic phase.

As the curing reaction proceeds further, the formation of the nematic phase accelerates the reaction and a second peak appears in the DSC curve. This behaviour has not been reported previously for reactions of conventional epoxy systems. As the temperature increases, the kinetics are affected as well. The second peak in the DSC curve decreases and eventually disappears. In fact at high temperatures, the nematic phase is destabilized by Brownian motions, and the critical molecular aspect ratio for the formation of the nematic phase cannot be reached.

Despite the complexity of the proposed curing mechanism [13], the reaction kinetics can be evaluated and the overall heat flow curve can be resolved into two contributions associated with the reaction of the primary and secondary amino groups. The authors found that the ratio between the kinetic constants is only 0·2 [14]. This unusual result is related to the increased reactivity of the mixture when it is in the nematic state, possibly due to the reduced viscosity of the medium and/or to increased ordering of the molecules that makes the reaction easier. Microscopic analysis was in agreement with this model. The curing process is illustrated with the sequence of photographs given in figure 6. After melting the sample at 130°C, the sequence was recorded at 80°C.

The average molecular weight increased during the curing process from that of the starting monomers up to that of the infinite network. When the aspect ratio reached the threshold value, depending on the temperature, the liquid crystalline phase formed. Due to surface–liquid crystal interactions, the molecules in the nematic phase became uniformly oriented, and thus a strongly birefringent monodomain was finally observed. The low curing temperature resulted in slow kinetics which allowed the molecules to align themselves along

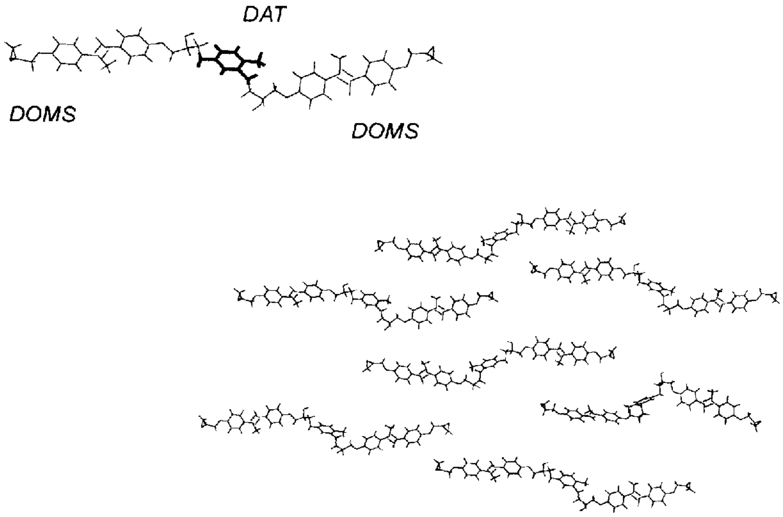
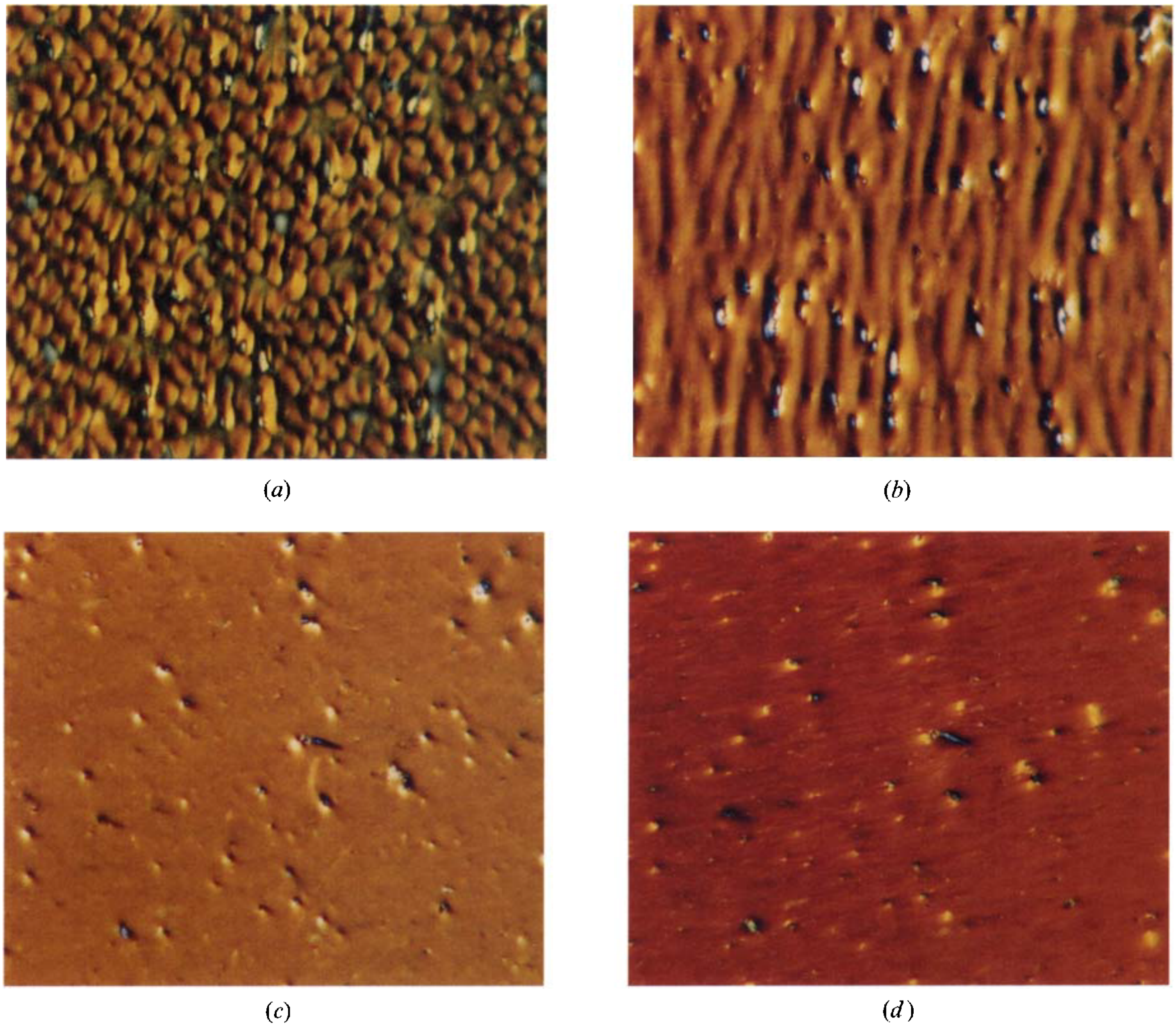


Figure 5. Molecular structures of oligomers formed by two DOMS molecules and one DAT molecule. Computer simulated spatial conformations.



(a) (b)

(c) (d)

Figure 6. Sequence of optical micrographs of a DOMS/DAT mixture supported between glass substrates spincoated with polyimide and unidirectionally rubbed. The pictures illustrate the curing process and correspond to the time sequence (*a*) to (*d*) recorded at 80°C.

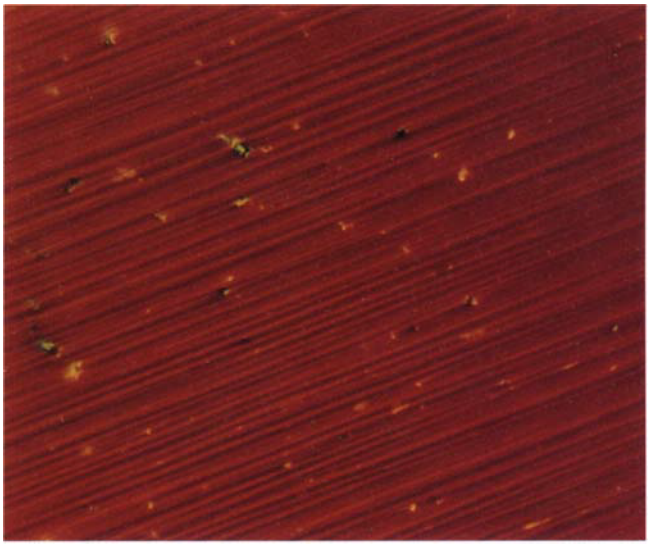


Figure 7. Optical micrograph of a DOMS/DAT thin film cured at 80°C and subsequently postcured at 160°C.

the rubbing direction of the polyimide film. A fast increase in the viscosity in fact hinders the molecules from adopting a uniform alignment. The reason seems to be related to the rigidity of the cross-linking agent as well as to the high cross-link density of the epoxy network. In figure 7, the aligned texture of a sample completely cured at 80°C and subsequently postcured at 160°C is shown. As can be seen, the final texture of the epoxy is not completely uniform, since a number of defects are present. The reaction of the secondary amine and the development of cross-links create distortions of the molecular order in the nematic phase, thus developing the system of defects. The structures of a cross-linked oligomer, i.e. the spatial conformations of DAT molecules with the four hydrogen atoms reacted with the corresponding number of epoxy groups, are proposed in figure 8. The tendency towards parallel alignment of the rigid mesogenic moieties is still retained, but the spatial constraints constituted by the formation of the chemical bonds necessarily compromise the former defect free nematic texture. The uniformity of the epoxy thermoset can probably be increased by a proper choice of curing agent.

In order to obtain a cross-linked film with homeotropic orientation of the molecules, a polysiloxane aligning layer was used. In fact, unlike pure DOMS, the molecules in the nematic phase of the reacting mixture develop a random orientation of liquid crystalline domains when supported between untreated glass surfaces. The homeotropic alignment was preserved after the curing process, like the planar one. In figure 9, the conoscopic image of the sample is given for a sample obtained using a polysiloxane aligning film, revealing the homeotropic order in the cured epoxy network.

The nematic order of the epoxy molecules frozen by the development of the tridimensional network, either in the planar or in the homeotropic alignment, is very stable even at high temperatures. Observations performed by optical microscopy showed that the orientation is maintained on heating the sample up to thermal decomposition of the epoxy resin, i.e. at temperatures higher than 250°C.

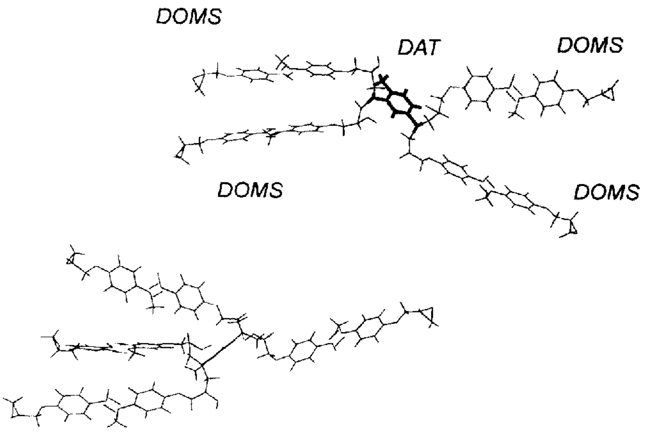


Figure 8. Molecular structures of oligomers formed by four DOMS molecules and one DAT molecule. Computer simulated spatial conformations.

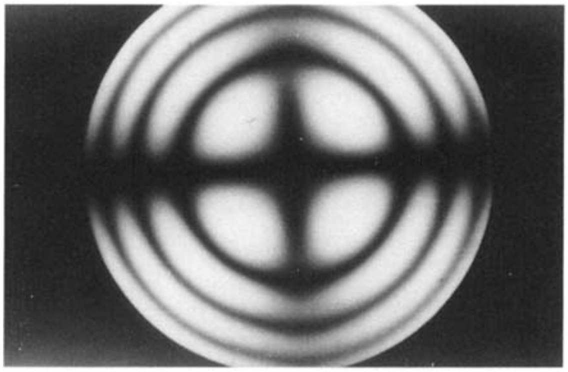


Figure 9. Conoscopic image of a DOMS/DAT thermoset with homeotropically oriented molecules supported between glass substrates covered by a polysiloxane film as aligning layer.

4. Conclusions

Surface–liquid crystal interactions are of great importance in the achievement of uniform alignment in liquid crystal devices. These interactions were used also to align the molecules of an epoxy thermoset during the curing process. Thermosets with planar or homeotropic alignment of the molecules were prepared. In addition to the surface–liquid crystal interactions, an electric field and/or unidirectional mechanical shear flow were used to improve the planar alignment of the molecules in thicker cells. It was found that the uniform alignment of the epoxy molecules in highly cross-linked thermosets was preserved to a great extent after the curing process was completed. Thus, the thermosets formed with highly anisotropic properties and, in particular, they were strongly birefringent. The uniform molecular alignment was thermally and mechanically stable; only the decomposition process at high temperatures can destroy it. A number of possible applications of such anisotropic epoxy networks in the field of linear and non-linear optics is feasible.

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References

[1] Landau, L., 1937, *Phys. Z., Sowietunion*, **11**, 26.

[2] de Gennes, P. G., 1971, *Mol. Cryst.*, **12**, 193.

[3] de Gennes, P. G., 1982, *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum and R. B. Meyer, (Academic Press).

[4] Carfagna, C., Amendola, E., and Giamberini, M., 1994, *Liquid Cristalline Polymers*, edited by C. Carfagna (Pergamon Press).

[5] Giamberini, M., Amendola, E., and Carfagna, C., 1995, *Mol. Cryst. liq. Cryst.* **266**, 9.

[6] Barclay, G. G., Ober, C. K., Papathomas, K. I., and Wang, D. W., 1992, *J. Polym. Sci., Part A*, **30**, 1831.

[7] Barclay, G. G., McNamee, S. G., Ober, C. K., Papathomas, K. I., and Wang, D. W., 1992, *J. Polym. Sci., A*, **30**, 1845.

[8] Carfagna, C., Amendola, E., and Giamberini, M., 1994, *Compos. Struct.*, **27**, 37.

[9] Komitov, L., Lagerwall, S. T., Sparavigna, A., Stebler, B., and Strigazzi, A., 1992, *Mol. Cryst. liq. Cryst.*, **223**, 197.

[10] Kim, Y. B., Olin, H., Park, S. Y., Choi, J. W., Komitov, L., Matuszczyk, M., and Lagerwall, S. T., 1992, *Appl. Phys. Lett.*, **66**, 2218.

[11] Barton, J. M., 1985, *The Application of Differential Scanning Calorimetry (DSC) to the Study of Epoxy Resin Curing Reactions* in *Advances in Polymer Science* (Springer-Verlag).

[12] Rozemberg, B. A., 1986, *Kinetics, Thermodynamics and Mechanism of Reactions of Epoxy Oligomers with Amines* in *Advances in Polymer Science* (Springer-Verlag).

[13] Smith, I. T., 1961, *Polymer*, **2**, 95.

[14] Amendola, E., Carfagna, C., Giamberini, M., and Pisaniello, G., 1995, *Macromol. Chem. Phys.*, **196**, 1577.