Macromol. Symp. ***148**, 197–209 (1999)*

The effect of prepolymer composition of amino-hardened liquid crystalline epoxy resins on physical properties of cured thermoset

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SUMMARY: Diglycidyl terminated 4,4'-oxydiphenyl cured with an aromatic diamine exhibits liquid crystalline properties, even if the amount of hardener is used in defect with respect to the stoichiometric amount. Physical properties of the resin, hardened with different quantities of amine are presented and discussed. In particular the high values of fracture toughness of this class of thermoset has been explained on the basis of the biphasic nature of the crosslinked resin.The differences in mechanical properties are analyzed taking into account the different crosslink densities.

Introduction

This work is a part of a study to elucidate the correlation between physical properties and chemical structure in highly crosslinked liquid crystalline systems.

Epoxy resins are usually employed as glassy matrices for structural composites. Properties are strongly affected by nature of the reagents, as well as by curing cycles (i.e. amount of curing agent, heating rate, curing temperature, postcuring). Many studies in the past have been devoted to the relationship between properties and extent of hardening reaction, as a consequence of the relative amounts of curing agents [1,2]. No results have been presented on this aspect for liquid crystalline thermosets. For this class of materials, it has been established by us that curing reaction in many cases disturb the achievement of a liquid crystalline phase, due to the constrain imposed by crosslinking [3-6].Therefore it is interesting to verify how an

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CCC 1022-1360/99/$ 17.50+.50/0

excess or a defect of hardener could affect the liquid crystalline nature of the cured polymer, as well as properties.

Experimental

NA2 was synthesized according to the following procedure: p-aminoacetophenone (27 g, 0.20 mol) and 95% ethanol (100 ml) were charged in a 3 round neck flask, equipped with a condenser, N_2 sweep, and addition funnel. Hydrazine (0.22 mol, 35% water solution, 20 ml) was added dropwise. The solution was refluxed for two hours. 900 ml of water were added and the solution neutralized with glacial acetic acid. The product was filtered and recrystallized from 95% ethanol. M.p.=167^{o}C; yield= 41%. Product purity was checked by NMR, elemental analysis and DSC

4,4'-dihydroxydiphenyl was purchased from Aldrich and subsequently glycidyl terminated according to the following procedure: 20g 4,4'-dihydroxydiphenyl (0.107 mol) were charged in a 3 round neck flask, equipped with a condenser, N_2 sweep, and addition funnel, and dissolved in 65 mL 2-propanol, 18 mL water and 84,2 mL (1.07 mol) epichlorohydrine. 0.234 mol NaOH (20 wt.% aqueous solution) were added dropwise and the system was reacted at refux for 3 hours. The aqueous layer was removed and the organic layer was dried in roto-vap. The product was dissolved in boiling dioxane, the resulting solution was treated with $MgSO_4$, filtered and precipitated at 4°C. Yield=60%. Product purity was checked by NMR, elemental analysis, DSC and evaluation of the epoxy equivalent, by titration.

Curing was performed by mixing epoxy resins and curing agent in the proper ratio, then melting and pouring the mixture between two glass plates previously treated with a surfactant agent, Surfasil$^{@}$ Pierce. All samples were cured at the temperature reported for two hours and subsequently postcured at 200 °C. The compositions analyzed were the stoichiometric (reported as 1:1), the defect of amine (reported as 0.85:1), and the excess of amine (reported as 1.15:1) respectively.

Dynamic-mechanical thermal analysis was carried out at 1 Hz frequency and 0.012% strain by using a Polymer Laboratories Instr. MK II at a heating rate of 5°C/min. The analysis was performed using a three-point Dynamic-mechanical thermal analysis (DMTA); the dimensions of specimens were 13 x 10 x 3 mm. The storage modulus, E', the loss modulus E" and the loss factor, tan delta, were measured from 0 up to 250°C, temperature at which the material was always in the rubbery state. Impact measurements were obtained at room temperature by Charpy Pendulum Instr., ATS-FAR (25 J impact energy) on unnotched samples having the following dimensions: 60 x 10 x 1.4 mm.

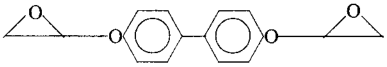
Scanning Electron Microscopy (SEM) analysis was performed using an Hitachi S2300 microscope. Samples were fractured in liquid nitrogen and sputtered with gold before observation.

Fourier Transfrom I-R spectra were collected by a Nicolet mod. 5PC, at a resolution of 4 cm^{-1}. Samples were mechanically ground to micron size powder and mixed with dried KBr (2 % wt.) in order to prepared FTIR window.

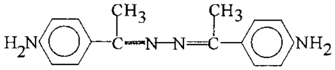
Optical Microscopy (OM) was performed by means of a Reichert-Jung microscope, mod. Polyvar. The resins were cured between two glass slides, coated with Surfasil release agent. The samples were subsequently fractured after notching the surface with a scalpel blade. Samples were observed in trasmitted mode without polarizers. Overall magnification was 100 X.

Results and Discussion

The glycidyl terminated monomers synthesized for this study were designed according to the following concept of liquid crystallinity in polymers. The polymers exhibiting liquid crystalline behaviour consist of polymer chains containing anisometric structural units which are incorporated into the polymer backbone. One of the most crucial parameter of rod-like units is their axial ratio which is the ratio of molecular length to its diameter. The theoretical critical value of axial ratio for phase separation from isotropic to nematic state in an array of cylindrical rods is 6.4 [7]. As a matter of fact, everything contributing to create rigidity in the backbone, contribute to stabilize the liquid crystalline phase. It has been reported that hydrogen bondings behave as promoter of liquid crystallinity in polymers, by increasing the thermal transition temperature ranges and, as a consequence, positively influencing processability [8-10]. Hydrogen bondings enhance stability of mesophase also in the case of thermoset [11]. The molecular rigidity is another important aspect of the molecular structure for polymer to be able to exhibit desirable properties such as low thermal expansion coefficients (CTE), high Tg, etc. The molecule should have a linear rod-like structure, without flexible linkages, such as ether, methylene, thioeter, sulfone. Ideally molecular architecture should include skeletons fused at para positions with 180 ° bond angles. Therefore the desired molecule should have axial ratio rigid rod central unit capped at both ends with crosslinking moieties. The simplest central rigid core described in the literature as a mesogenic unit for polymers is p,p'-dihydroxydiphenyl. It was glycidyl terminated and subsequently cured with a rigid curing agent. A rigid curing agent was preferred in order to get a liquid crystalline epoxy resins, even if some papers published by some of the authors have demonstrated that rigidity of the curing agent is not crucial for the obtainment of a liquid crystalline structure [6].



DIF



NA2

Fig. 1: Epoxy monomer (DIF) and curing agent (NA2)

As a first remark, all the prepared polymers show a nematic structure, as inferred from the X-ray diffraction patterns recorded on a flat film camera. On the basis of previous studies, the distinctive feature of the development of nematic structure for the thermoset systems compared to thermotropic polymers is that the liquid crystalline structure forms itself at different constant temperatures as a result of progressing reaction, while thermoplastics characteristically undergo through nematic- isotropic transformation at well defined single transition temperature [12]. We could therefore use the term *chemotropic* liquid crystal (as suggested by one of the referees) for this kind of systems, for whom the transition to a mesophase occurs as an effect of a chemical reaction. The thermosetting systems exhibit nematic-isotropic transitions in a relatively wide range of temperatures and their curing temperature can affect the morphology of nematic textures. For each thermoset there is a certain temperature, T_{ni}, above which the system always cures in isotropic state. If the system is cured in nematic state, its structure remains stable up to degradation temperature of the material. The mechanism of isotropic-nematic transition for a curing epoxy can be attributed to the development of weak interactions (including hydrogen bonding arising as an effect of the opening of the glycidyl group) which contribute to the stabilization of the nematic state. At a certain temperature, the mixture of epoxy resin and curing agent is isotropic. Upon reaction of primary reactive groups, the hydrogen bonds increase in number. At this point the system is not crosslinked and by heating to higher temperatures it can become isotropic again and when cooled it returns to the nematic state. Continuing cure in nematic state results in the development of linkages due to the reaction of secondary reactive groups which stabilize the nematic state further to the point that it can not be destroyed by heating. When systems are cured at temperature higher then a certain temperature T_{ni}, crosslinking takes place before the chain extension has been developed enough to stabilize the nematic structure and the system cures in the isotropic state. All these observation can be summarized in the following non-equilibrium phase diagram:

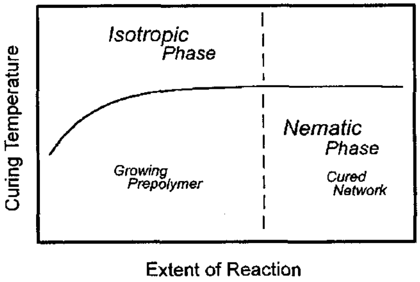


Fig. 2: Phase diagram of the curing cycle of the liquid crystalline epoxy resin

If all these considerations hold true it is clear why the liquid crystalline nature of the cured thermoset is not affected by the relative amount of curing agent. In fact, the first part of the reaction, that is critical for the achievement of the nematic structure, is independent of the amount of curing agent (at least in the range of composition investigated in this study).

Curing has been followed by evaluating heat release and peak maxima at the curing temperature. Figure 2 reports the isothermal cure at 160°C for the resin mixed with an excess and a defect of amine, respectively. In both cases the heat release occurs at very short times of the order of few minutes. Sample cured with the excess presents a maximum earlier then the sample cured with a defect of hardener.(Fig. 3)

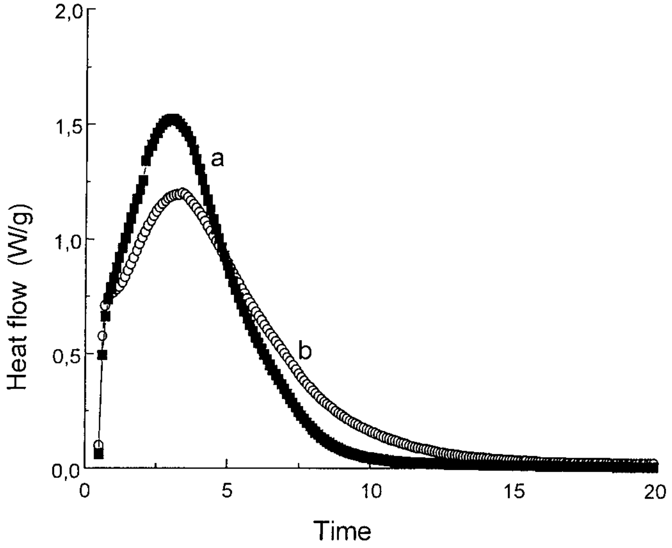


Fig. 3: Isothermal curing cycle at 160°C for epoxy resin cured with an excess of amine a), and with a defect of amine b)

This is obvious, if the probability of collision between different reagents is considered. Peak integral is practically the same (just larger in the case of the epoxy cured with an excess of amine). This trend indicates that the same extent of curing is reached by the resin in both cases.

Figure 4 shows the DMA spectra for the compositions investigated.

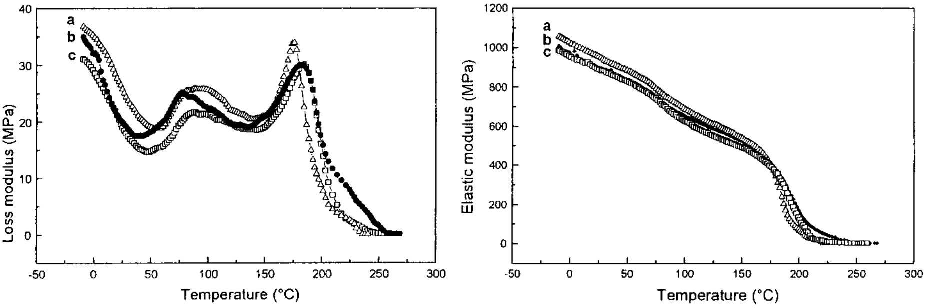
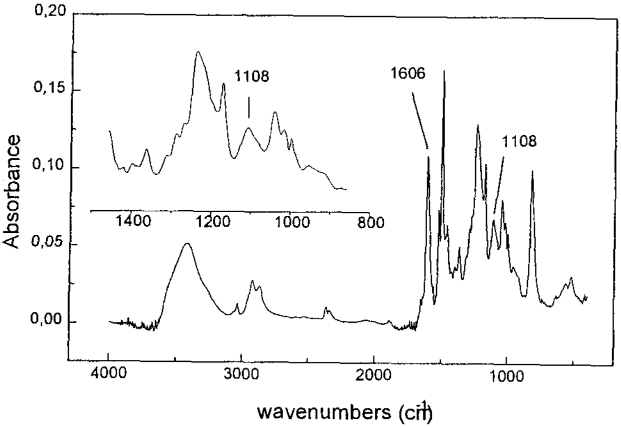


Fig. 4: DMA spectra for cured epoxy resin; a) stoichiometric amount of hardener, b) excess of hardener, c) defect of hardener

The form of the dynamic mechanical spectrum is substantially the same, independently from the amount of hardener and curing temperature (Fig.4). If the curve relative to E" is taken into account two peaks appear. The first peak is very broad and is centered around 90 °C. The second one is larger and centered at higher temperature. In correspondence to the first peak the value of E' is lightly reduced, while at the second peak E' is substantially reduced. According to our hypothesis the cured resin is constituted by two phases. Hardening of the resin has been carried out in several steps. As it has been said above, at first the mixture of epoxy monomer and amine is heated to melting. At this stage the blend of unreacted reagents is a single isotropic phase. After a certain time, depending on the curing temperature, the mixture turns to be liquid crystalline (this is clearly demonstrated by optical microscopy). The resin is still fluid and then hardens in a liquid crystalline structure. Due to the disturbing effect of crosslinks on the liquid crystalline order, it is reasonable to suppose that during the cure a certain degree of molecular orientation is not achieved: this affects the relative amounts of volumetric fractions of isotropic and nematic phases. In other words, it is possible that at the end of the curing cycle ordered domains having a liquid crystalline structure are embedded in an isotropic matrix, in which physical entanglements and extra crosslinks lock the chain in a more constrained structure. On the other hand in the ordered domains a less crosslinked structure is compatible with the liquid crystalline state. Therefore, we made the hypothesis that two glass transitions can be expected for such systems, the former occurring in the liquid crystalline portion, the latter in the more constrained, isotropic part. The first peak in the dynamic-mechanical spectrum of all the specimens can be attributed to the liquid crystalline part. This peak is broad because at this Tg the chains gain a relative mobility since they are constrained by their fractions cured in the isotropic state that is still glassy. At the second Tg, the resin behaves as a rubber above its glass transition. DSC analysis performed on some of these samples seems to confirmate the presence of two Tgs, but we are conscious that this technique is not really diagnostic in the case of thermosetting polymers. So the biphasic nature of these systems, suggested by DMA, is only a hypothesis not supported by direct experimental evidence at the moment. However FTIR carried out on samples, previously cured with defect and excess of amine, supports the hypothesis that homopolymerization reaction is present when the resin is reacted with an amount of curing agent less than stoichiometric. In fact Fig. 5 reports a typical FTIR spectrum performed on one of the resins investigated. The interest has been concentrated on the peak at 1108 cm^{-1}, ascribed to ether linkage bending, which is present in all the samples with different values of absorbances. This peak is an indication of the extent of the homopolymerization reaction, since the ether linkages form as an effect of the reaction between the unreacted glycidyl groups and the hydroxyl generated by the opening of the epoxy groups already reacted. By normalizing the values of the absorbance to an invariant band (the peak at 1600 cm^{-1}), and taking into account the different stoichiometries in the various cases, it was observed that the normalized value of the absorbance of ether peak is 0.15 in the case of resin cured with a defect of amine, while its value is 0.13 for the resin hardened with an excess of amine. This reduction of the order of 15 % is not too big, however it is indicative of a larger extent of homopolymerization reaction present in the case of the epoxy resin cured with a defect of amine.



Fig,5: FTIR spectrum for cured epoxy resin with a defect of curing agent

Table 1 reports data relative to physical characterization of the thermosets cured in different conditions

Table 1 Physical characterization of samples having different stoichiometries and cured in different conditions.

Stoichiom	T_{curing} °C	E_a (30°C) Mpa	E_a(100°C) MPa	Tg °C	CTE 10^{-6}/ °C	Density g / cm^3	Kq Mpa m $^{1/2}$
1/1	160	820	580	180	96	1.2521	14.1
1/1	120	580	450	174	101	1.2573	16.0
1.15/1	160	800	600	175	85	1.2512	17.6
1.15/1	120	700	520	169	126	1.2550	18.8
0.85/1	160	820	600	188	87	1.2524	11.9
0.85/1	120	860	600	191	96	1.2592	14.1

Stoichiom: relative amount of amine/epoxy resin as equivalent

T_{curing}: curing temperature

$E_{a\,(30°C)}$: flexural modulus at 30°C

$E_{a\,(100°C)}$: flexural modulus at 100°C

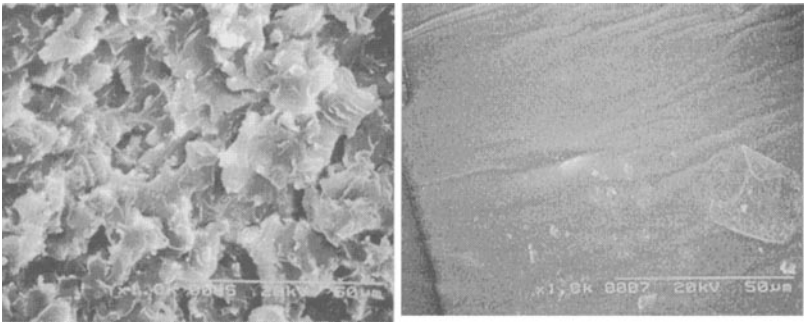
T_g: glass transition temperature

CTE: coefficient of thermal expansion as revealed by TMA at room temperature

Density: density as measured by flotation

K_q: resilience

The values of modulus and Tg's are higher for the compositions containing less amine. In order to explain this trend we should consider that in the case of a liquid crystalline thermoset, as previously supposed, crosslinks oppose to the formation of a mesophase. Once that the transition from the isotropic to the nematic state occurrs for the growing polymer, more crosslinks can disturb the proper geometry of rigid rods in a liquid crystalline array. A competition will hold among the forces driving the thermoset in an ordered structure and the chemical crosslinks. With a defect of amine, the sample completes its hardening cycle utilizing reaction of homopolymerization. This reaction involves etherification of the oxyrane ring with the OH previously generated by the reaction of the first hydrogen atom of the amine group with the glycidyl moiety. This reactions will force molecules in a more tight array creating several frozen stresses in the structure. Frozen stresses reduce fracture energy, so lowering toughness for the resin cured with a defect of amine. Entanglements contribute to enhance Tg's for the same class of compounds. Toughness comes higher for resins cured with an excess of amine, for which a lower crosslink density can be supposed. The relatively high values of fracture toughness for this class of liquid crystalline thermosets is worth being furtherly discussed. The fracture surfaces as revealed by electron microscopy shows that the nematic material has rough fracture surface (Fig.6a), while the fracture surface of a commercial isotropic epoxy resin (Epon 825$^{@}$) looks smooth, mirrorlike (Fig.6b).



a **b**

Fig. 6: SEM of the fracture surface of the cured epoxy resin: nematic material (a); isotropic material Epon 825$^{@}$ (b).

Different mechanism of crack propagation have been observed by others studying liquid crystalline epoxies [13]. Crack deflection, crack bifurcation, segmented cracking, crack bridging and possibly orientation/transformation toughening are found to operate in the liquid crystalline resin. In previous papers some of us presented results of fracture toughness for various liquid crystalline epoxies [14]. In these papers we reported that the liquid crystalline resin having overall isotropic properties, consists of anisotropic domains with properties, such as strength, different along and across their molecular orientations; this results in deviating crack propagation from straigth line. This suggests that inhomogeneity and localised anisotropy of nematic structure is the main reason for high values of fracture toughness for this novel class of thermosets.

In this paper we do not observe all of the mechanisms that Sue et al.[13] report in their paper because we supported our investigation only with polarized light optical microscopy and with SEM. Figure 7 reports the crack propagation as revealed by optical microscopy for one of the resins under investigation. As a comparison, on the same figure the picture of crack propagation of a conventional commercial resin is reported. The difference is straightforward. The level of magnification does not allow to verify if the crack propagates in the domains or in the regions among them. Probably the crack grows around the liquid crystalline domains in the border between the two phases because in this region it finds less resistance to propagate due also to the presence of defects and low molecular weight species. Sometimes it crosses the ordered domains depending probably on their relative orientation.

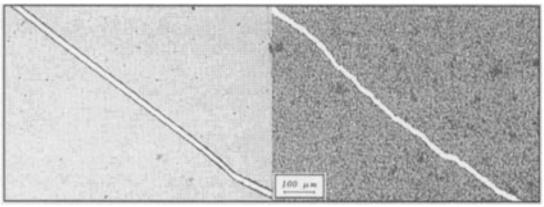


Fig.7: Fracture propagation through thin epoxy films. On the left: Epon 828$^{@}$; on the right: liquid crystalline epoxy resin cured with the stoichiometric amount of curing agent. Magnification = 100 X.

Figure 8 reports a schematic representation of fracture propagation in a liquid crystalline epoxy resin.

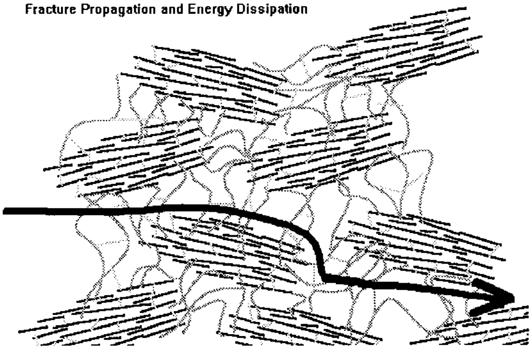


Fig. 8: Schematic representation of the fracture propagation in the cured epoxy resin

CTE values follow the same trend of Kq: they are lower for resins cured with a defect of amine. This parameter can be also interpreted on the basis of a more tight structure reached by the thermoset when cured with a defect of amine. Moreover, unlike the conventional flexible chain thermosets for which lower modulus is associated with increase of thermal expansion coefficient, in the case of these rod-like epoxies CTE does not increase compared to traditional high modulus thermoset materials. Therefore, the product of modulus and CTE is significantly lower for rod-like thermosets than in the case of traditional flexible chain thermosets. This makes liquid crystalline epoxy resins very attractive for low stress electronics packaging applications.

Conclusions

Epoxy terminated rigid-rod monomers can be cured in a liquid crystalline structure with lower and higher amounts of curing agents with respect to the stoichiometric values. Resulting properties are different as a consequence of the different crosslinking extent. The high values of fracture energies exhibited by the samples were explained on the basis of a liquid crystalline structure in which ordered domains are surrounded by boundary regions in which entanglements predominate. In particular, lower fracture energies exhibited by the resin cured with a defect of amine were explained on the basis of a constrained structure due to the competition between the arrangements of rigid rods in nematic domains and the constrains imposed to molecules by etherification reactions. DMA tests are similar for all the class of compounds, showing spectra containing two maxima for E". They were ascribed to a biphasic nature of the thermoset in which ordered domains are embedded in an isotropic matrix.

Acknowledgments

The financial support of MURST PRIN 97 is gratefully aknowledged

References

1. N. Hata and J. Kumanotani, *J. Appl. Polym. Sci.* **15**, 2371 (1971)
2. C. Carfagna, A. Apicella and L. Nicolais, *J. Appl. Polym. Sci.* **27**, 105 (1982)
3. C. Carfagna, E. Amendola and M. Giamberini, *Macromol. Chem. Phys.* **195**, 279 (1994)
4. B. Hirn, C. Carfagna and R. Lanzetta, *J. Mater. Chem.* **6**(9), 1473 (1996)
5. C. Carfagna, E. Amendola and M. Giamberini, *Prog. Polym. Sci.* **22**, 1607 (1997)

6. M. Giamberini, E. Amendola and C. Carfagna, *Mol. Cryst. Liq. Cryst*, **266**, 9 (1995)
7. P.J. Flory and G. Ronca *Mol. Cryst. Liq. Cryst*, **54** , 311 (1979)
8. L. J. Yu, *Liq. Cryst.* **14**, 1311 (1993)
9. L. J. Yu and J. S. Pan, *Liq. Cryst.* **14**, 829 (1993)
10. Mori, H. Takeshita, R. Nimura and M. Isobe, *Liq. Cryst.*, **14**, 821 (1993)
11. M. Giamberini, E. Amendola and C. Carfagna, *Macromol. Chem. Phys.* **198**, 3185 (1997)
12. C. Carfagna, E. Amendola and M. Giamberini in *Liquid Crystalline Polymers* Edited by C. Carfagna (Pergamon Press, Oxford, 1994), pp. 69-85
13. H.J. Sue, J.D. Earls and R.H. Hefner Jr., *J. Mater. Sci.* **32**, 4031 and ibid. 4039 (1997)
14. C. Carfagna, E. Amendola and M. Giamberini *Composite Structures*, **27**, 37 (1994)