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Phase Separation and Morphology of PDLC Based on Poly(Ethyl 2-Cyanoacrylate)

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Phase Separation and Morphology of PDLC Based on Poly(Ethyl 2-Cyanoacrylate)

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The paper deals with polymer/liquid crystal composites prepared by polymerization induced phase separation of homogeneous mixtures of ethyl α-cyanoacrylate (ECA) and nematic E7. DSC analysis of the polymerization reaction indicates that the monomer conversion is unaffected by the presence of E7 which acts only as a diluent. Thermal characterization of the composite films PECA/E7 reveals a partial solubility of E7 in the polymer matrix (about 20%), a degradation of the LC purity, an anomalous variation of the specific heat increment of E7 at Tg and of the isotropization enthalpy with the E7 content in phase separated systems. SEM analysis offers adequate support to justify the DSC behavior; indeed, whereas the 20% E7 mixture has a fracture surface similar to that of the unblended matrix, the 40% E7 composite shows a LC separated droplet morphology with a low connection grade. The morphology changes considerably upon increasing the E7 concentration in the blend or lowering the curing temperature; heterogeneous LC-droplet and polymer-ball morphologies appear, arising from differences in the rate of polymerization of ECA between two early separated phases: a LC-poor one, rich in ECA/PECA and a LC-rich phase, still containing substantial amount of monomer.

Keywords: liquid crystal dispersions; phase separation; droplet morphology; polymer-ball morphology

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INTRODUCTION

Acrylate and methacrylate chemistry has been extensively used as polymerization induced phase separation (PIPS) method to create PDLC films; both monomeric and oligomeric acrylates, as well as multifunctional acrylates have been reported as components of the starting solutions[1]. The common morphology of monofunctional acrylate-based polymer dispersed liquid crystal is the droplet morphology, in which the liquid crystal domains appear as relatively distinct droplets within the polymer matrix. Noh et al.[2] have investigated the morphology of a number of polymeric structure that can be formed using acrylate-based PIPS systems; they observed that dramatic changes in film morphology, in terms of droplet sizes, shapes and interconnectivity can be achieved through relatively minor changes of the polymerization rate and of the solubility between the liquid crystal and the polymer-forming components. A peculiar kind of PDLC film morphology, which is referred to as the reverse or polymer-ball morphology, first reported by Yamagishi et al.[3] has been also observed in acrylate PIPS systems[1]; it consists of small polymer-balls which merge to form a larger network structure with narrower and irregular voids filled with the liquid crystal. PDLC films with the polymer-ball morphology tend to exhibit memory states in which transparency is preserved after the voltage is removed[4].

n-Alkyl α-cyanoacrylates, which are endowed with remarkable chemical and physical properties, have been never considered, to our knowledge, to prepare PIPS systems. α-Cyanoacrylic esters are widely used as adhesives in industry and medicine, because of their ability to polymerize virtually instantaneously on almost any surface at room temperature without any added catalyst[5,6]. Moreover, due to their highly polar character, these polymers bring to the formation of very strong bonds between a wide variety of materials and this combination of properties sets the cyanoacrylates apart from conventional adhesives[7]. In-

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deed, the unusual electronic environment, created by the highly electronegative nitrile and ester groups, allows the initiation of an anionic polymerization by weak bases such as water and alcohol. However polyalkyl-α-cyanoacrylates can be successfully prepared also by free radical initiation if an effective inhibitor of the anionic mechanism is added to the monomer[8-10]. In this way, by carefully choosing the experimental conditions, a better control of the polymerization rate can be achieved.

In the present paper isothermal polymerization between 80 and 92°C of ethyl α-cyanoacrylate (ECA) in the presence of different amounts of nematic E7 was performed; azobisisobutyronitrile (AIBN) was used as initiator and methane sulphonic acid (MSA) was added to inhibit the anionic mechanism. Thermal and morphological characterizations were carried out on the resulting composite systems.

EXPERIMENTAL

The liquid crystal chosen for this work is the eutectic four-component mixture E7 (Merck) of substituted cyanobiphenyls and a cyanoterphenyl. The acrylic monomer ECA, kindly provided from Loctite (Ireland) Ltd., was protected against anionic polymerization with 5 % w/w of MSA; polymerization was carried out by using 2 % w/w of AIBN as thermal initiator between 80 and 92°C in presence of different amounts of E7, ranging from 0 to 80 % w/w.

Samples for a calorimetric study of the curing process were prepared by mixing appropriate amounts of ECA, MSA, AIBN and E7 and stirring the various components together for about 15 min to achieve suitable homogeneous mixtures (the polymer precursor cures very slowly in these conditions). Mixture samples of 10-12 mg were then pipetted into aluminum pans and transferred to a Mettler TA 3000 DSC System (equipped with a software package Graphware TA72) to be analyzed in both temperature-scanning and isothermal modes. To obtain isothermal

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data the samples were placed in the DSC cell at room temperature and the temperature programmed rapidly to the chosen value; the heat release was followed until the cure process was essentially complete. The conversion/time plots were derived by normalizing partial heat releases of the polymerization process to the overall heat release of the E7-free sample. After isothermal cure, temperature scans were run in order to measure possible residual exotherms.

Samples for phase behavior and morphological analyses were prepared in the form of films 50-100 μm thick by mixing and stirring the various components at room temperature until a homogeneous mixture was obtained and 8 min at 90°C; the prepolymerized mixture was then coated onto a polypropylene sheet along with Mylar spacers and a second polypropylene sheet was then laminated with pressure to form a uniform film; the choice of polypropylene was dictated by the poor adhesion of PECA to this material. The specimens were then cured in an oven at temperatures ranging between 50 and 100°C for 1-70 h and finally removed from the supports after being cooled to room temperature. The phase behaviors of the films were determined by DSC operating in its temperature scanning mode, measuring glass transitions temperatures of PECA and E7 together with the heat capacity change associated to the latter and the E7 nematic-isotropic transition temperature and enthalpy. A Leica Stereoscan 440 Scanning Electron Microscope (20 kV accelerating voltage) was used to carry out morphological studies on the composite films fractured in liquid nitrogen; E7 was extracted with n-hexane at room temperature and the fracture surface coated with gold.

RESULTS AND DISCUSSION

Radical polymerization of ECA/E7 mixtures

The DSC technique provides a convenient and useful method of monitoring the course of exothermic reactions involved in the free radical polymerization of 2-cyanoacrylates[10]. Since it is quite simple and quick, it

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was carried out in this work to get information on the effect of E7 on the polymerization process of ECA. Preliminary experiments in the scanning-temperature mode were performed to identify the proper temperature range for isothermal polymerization. The comparison between non-isothermal reaction curves from 25 to 150°C for pure ECA and a mixture ECA/E7 60/40 w/w is shown in Fig.1; since isothermal method is inaccurate at the higher temperatures[11], polymerization was carried out between 80 and 92°C. Data for pure ECA and ECA/E7 60/40 w/w are given in Table I where tp is the time of the exothermic peak, ΔHp the polymerization enthalpy and ΔHp^ the enthalpy of the residual exotherm evolved during a successive scan.

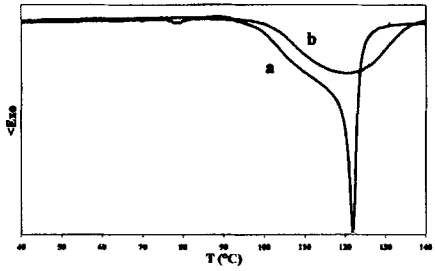

FIGURE 1 Non-isothermal polymerization of ECA (curve a) and ECA/E7 60/40 w/w (curve b).

TABLE I Isothermal polymerization of ECA and ECA/E7 60/40 w/w

E7 (% w/w)	Tiso (°C)	tp (min)	ΔHp (kJ/mol)	ΔHp^ (kJ/mol)
0	80	18	51	5
0	84	14	54	2
40	84	26	58	1
40	88	13	55	1
40	92	11	40	2

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Although the reactions appeared to go to completion, a little further heat was evolved on raising the temperature over that at which the isothermal experiments had been performed; a similar effect for bulk polymerization of methyl 2-cyanoacrylate was shown to be due to incomplete consumption of the monomer at the lower temperatures[10]. Reactions were completed in this second stage since there was no heat evolution during a further scan. The overall heat of polymerization measured at different temperatures and compositions appears to be almost constant and close to the literature value of 58 kJ/mol[7]; the lower enthalpy measured at the higher temperature (92°C) could arise from the occurrence of a significant degree of polymerization before the establishment of temperature equilibrium at the beginning of the experiment.

Conversion/time plots are given in Fig. 2: curves *a* compare the behavior of ECA and ECA/E7 60/40 at the same temperature (84°C), curves *b* illustrate the effect of temperature on the polymerization of the monomer/liquid crystal mixture; the results indicate that the monomer conversion is unaffected by the presence of E7 which acts only as a diluent for ECA, slowing the rate of reaction and reducing the pronounced auto-acceleration effect shown by the neat monomer.

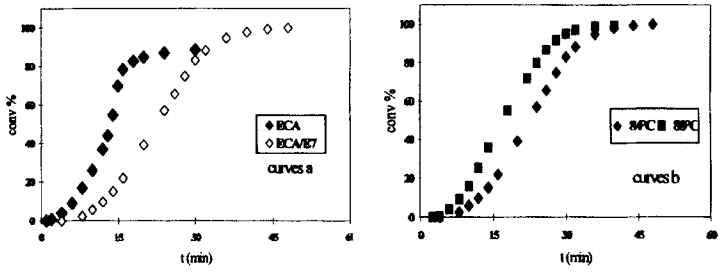

FIGURE 2 Fractional conversion vs. time for isothermal experiments. Being a few percent residual enthalpy of polymerization still noticeable in the successive scan, conversion of pure ECA does not approach 100%.

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Phase behavior

The phase behavior of the cured PECA sample is quite simple: only the glass transition appears at 134°C. PECA/E7 composites, on the other hand, exhibit the glass transition and isotropization of E7, as well as the glass transition of PECA. DSC data of scans performed at a rate of 20°C/min on film samples obtained after different polymerization times (t_{pol}) at the temperature T_{pol} are collected in Table II, normalized on the real amount of E7; the use of lower scan rates does not affect these results. Both ΔCp and ΔHi of E7 appear to be affected by variation of composition and curing temperature, whereas transition temperatures are slight influenced; a certain inclusion of the monomeric component in the segregated E7 domains can justify the reduction of the liquid crystal nematic-isotropic transition in the composites. Not too relevant is the role played by the curing time, at least when the E7 content is lower than 80%.

TABLE 2 Phase behavior of PECA/E7 composites

PECA/E7 (w/w)	T_{pol} (°C)	t_{pol} (h)	Tg E7 (°C)	ΔCp E7 (J/gK)	Ti E7 (°C)	ΔHi E7 (J/g)	Tg PECA (°C)
100/0	90	1	-	-	-	-	134
80/20	90	1	-	-	-	-	114
60/40	75	4	-62	0.20	56	2.3	118
60/40	75	27	-62	0.19	56	2.1	118
60/40	90	1	-61	0.21	55	2.7	118
40/60	90	1	-62	0.24	56	2.6	117
40/60	100	1	-60	0.30	55	3.2	117
20/80	90	1	-62	0.09	56	1.0	116
20/80	90	17	-60	0.03	56	0.3	117
20/80*	90	17	-62	0.34	57	4.0	117
0/100	-	-	-62	0.47	59	5.8	-

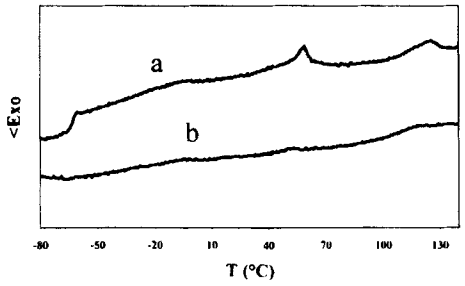

FIGURE 3 DSC curves of PECA/E7 20/80 (17 h at 90°C; curve *a* 20/80*, curve *b* 20/80)

DSC data can be applied to the evaluation of the solubility limit of the liquid crystal in the polymeric matrix. The PECA glass transition of the mixed samples, depressed by the plasticizing action of the liquid crystal indicates this limit to be close to 20%. A parameter useful to determine the amount of free liquid crystal within the film is the increase of ΔCp E7 at the glass transition; a second parameter is the enthalpy change ΔHi E7 at its clearing temperature[12-14]. Values of ΔCp E7 and ΔHi E7 = 0 for the 80/20 mixture indicate that in this sample the liquid crystal is below the solubility limit. The comparison of ΔCp and ΔHi of E7 for the 60/40 and 40/60 films cured at 90°C to those of the pure liquid crystal, leads to evaluation of solubility limit of about 20 and 30%, respectively. The former value substantially agrees with the behavior of the 20% mixture; the latter indicates that ΔCp E7 and ΔHi E7 of the 40/60 composite are lower than expected. ΔCp and ΔHi at fixed E7 content increase on increasing the curing temperature. Samples incorporating 80% E7 macroscopically separate in two regions: a free-E7 poor solid film (DSC analysis given in Table II as 20/80) and a free-E7 rich gel (20/80* in the same Table); the scanning profiles are shown in Fig. 3. Long curing times enhance this separation evidenced by migration of the gel phase to the edge of the film.

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Morphological analysis

SEM morphological analysis offers adequate support to justify the DSC behavior. Indeed, the 20% E7 sample exhibits a fracture surface just like that of the undiluted matrix, indicating lack of phase separation for this composition; the 40% E7 mixture, after 1 h curing at 90°C, generates a film with isolated droplets (Fig. 4). Some changes occur on increasing the E7 content since, next to the droplets, which decrease in average number per unitary surface area going from 40 to 80% E7, a polymer-ball like morphology appears. At intermediate E7 concentrations this morphology seems to be confined in large cavities within the polymer matrix, at high E7 contents the system separates into macroscopic droplet and polymer-ball like regions (Fig. 5). Polymer-ball like domains practically disappear in 60% E7 films if the curing temperature is raised to 100°C and appear in 40% E7 samples after polymerization of 4 or 27 h at 75°C (Fig.6). The morphology of the composites seems to be independent of the curing time. In order to obtain a homogeneous polymer-ball morphology from the 40% E7 mixture we tried to reduce the curing temperature down to 50°C; the result is given in Fig. 7.

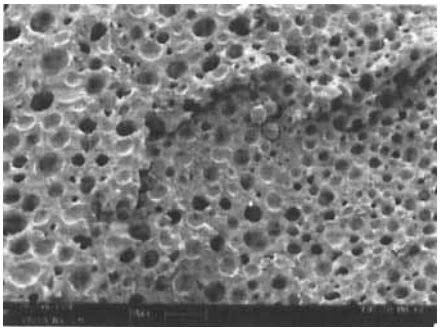

FIGURE 4 SEM of a 40% E7 sample cured for 1 h at 90°C

PECA/E7 film morphology as a function of composition and cure temperature can be therefore summarized as follows: i) at low E7 content an

amorphous polymer single phase appears; ii) at intermediate E7 contents and high curing temperature the system forms a droplet morphology; iii) at intermediate compositions and low curing temperature a polymer-ball morphology is observed; iv) droplet and polymer-ball morphologies co-exist at intermediate compositions and curing temperature; v) at high E7 content the system separates into macroscopic LC-rich and polymer-rich regions.

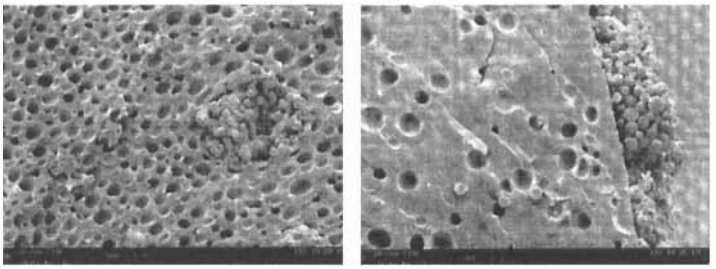

FIGURE 5 SEM of 60 and 80% E7 samples cured for 1 h at 90°C

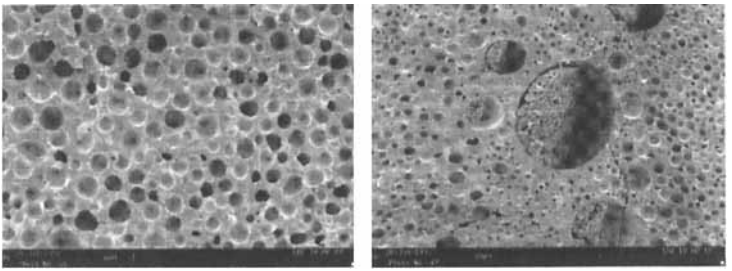

FIGURE 6 SEM of 60 (1 h at 100°C) and 40% E7 (27 h at 75°C)

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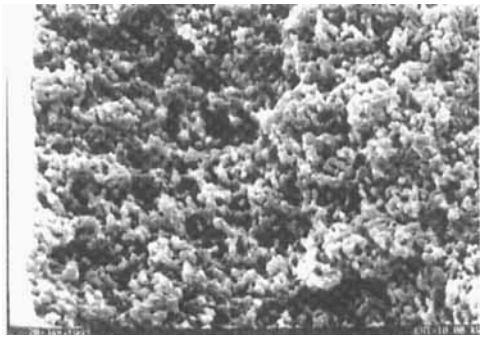

FIGURE 7 SEM of a 40% E7 sample cured for 70 h at 50°C

CONCLUSIONS

The cure of ECA/E7 system begins at the chosen temperature in the single-phase region of the temperature/composition phase diagram, since the starting mixtures show good solubility between the components; this diagram, as generally observed for PIPS systems[1,15], can be supposed to show upper critical solution temperature (UCST) behavior. As polymerization proceeds, the area of the two-phase region moves to higher temperature, broadens in composition and becomes asymmetric[1,16], due to the decreased entropy of mixing of larger molecules; when the displacement of the phase boundary line moves the system into the two-phase regime phase separation occurs, even if temperature and composition of the system do not change. The mixtures separate into an E7-rich phase and an E7-poor phase; because of the multi-component nature of the system (liquid crystal and monomer/polymer solutions) segregation can occur at different concentrations in the two phases.

The final size of the E7 domains is determined by their rate of formation, their growth through diffusion, coarsening and coalescence process and the freezing of the structure due to the formation of the solid

polymer matrix. Fast polymerization reactions result in smaller domain size both because of increased rate of formation of E7 droplets and sudden increase of the polymer-rich phase viscosity. On the contrary slow cure rate leads to larger E7-rich regions, since the phase separated domains have enough time to grow and coalesce. As the phase separated E7 domains are still rich in monomeric ECA, polymerization continues within such domains with a rate that continuously decreases with the lowering of ECA concentration; as a consequence the size of the separate liquid crystal domains dictates polymer-ball size and interconnectivity.

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