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In-situ photopolymerization of an oriented chiral liquid crystal acrylate in an electric field

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Summary

The effect of an external electric field on the photopolymerization rate of chiral liquid crystalline 4-acryloyloxy-undecanloxy-4'-[S(-)-2-methylbutyloxy]-biphenyl (monomer (I)) was studied using FT-IR. The orientation behavior of the thermally polymerized polyacrylate of monomer (I) under an electric field was observed by POM. The results showed that in-situ photopolymerization of the oriented monomer (I) under the application of an electric field proceeded at a higher rate than in the absence of an electric field and can fix mesogenic orientation.

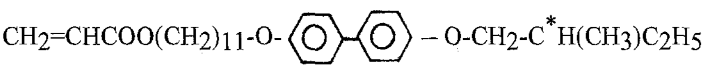
Introduction

Chiral liquid crystalline side-chain polymers (CLCSPs) have recently become the topic of intensified investigations[1]. The great interest in these CLCSPs stems mainly from their electrooptical properties and potential applications. CLCSPs possess ferroelectric properties in the chiral tilted smectic phase (S*c ...) and their alignment can be fixed into the glassy state[2]. These CLCSPs are expected to be utilized as new electrooptical, piezoelectric and nonlinear optical materials, etc.[3-4]. However, before these CLCSPs achieve practical applications the techniques to feasibly control the alignment of mesogenic moieties need to be developed . Up to now, to accomplish the macroscopic orientation many attempts such as surface treatments, application of shear stress, electric and / or magnetic fields have been made. Unfortunately, alignment of LC polymers is more difficult than equivalent low molar mass liquid crystals due to their higher viscosity and lower mobility[5]. Compared with the used techniques, in-situ photopolymerization of an oriented liquid crystal (SPOLC) [6] probably is the most prospective method of achieving a highly oriented liquid-crystalline side-chain polymer. In the previous paper[7], we reported our study on the effect of temperature on the birefringence of a surface-oriented chiral liquid-crystalline acrylate monomer and its polymer obtained by in-situ photopolymerization in the monomeric smectic A phase , the result showed that the highly homogeneous and oriented polymeric LC film could be prepared by in-situ photopolymerization of the surface-oriented chiral LC monomer.
Similarly, photopolymerization of oriented liquid crystalline monomer by an electric field has also been proved to be efficient for the fixation of orientation of monomers[5].

However, few studies have so far been reported on in-situ photopolymerization of electric field-oriented chiral LC monomers. Accordingly, in the present work, the effect of a dc electric field on in-situ photopolymerization of a chiral LC acrylate as well as the orientation behavior of the corresponding LC side-chain polyacrylate under the application of an electric field have been investigated.

Experimental

The chiral liquid crystal monomer used was 4-acryloyloxy- undecanloxy -4'-[S(-)-2-methylbutyloxy]-biphenyl (I), which was synthesized as described in ref.[8], its chemical structure is illustrated as follow:



Tab. 1 lists the phase transition temperatures of (I), the reaction sample (monomer (I) added with 2.5 wt.% photoinitiator α,α-dimethoxydeoxybenzoin (A)), and the polymerized sample of monomer (I) synthesized by solution polymerization ($\overline{M}n=1.11\times10^4$, $\overline{M}w/\overline{M}n=1.5$). Phase transition temperatures were determined on a Perkin-Elmer DSC 7. Phase textures and the alignment of mesogenic groups of the polyacrylate in the dc electric field were observed with POM(OLYMPUS transmission BH-2 polarizing microscopy connected with a Mettler FP-5 hot stage).

Tab.1 Phase transition temperature of the monomer (I) and its thermally polymerized polymer

Sample	Phase transition temperature
Monomer (I)	K62.0 °C S_A 69.0 °C I
(I) + 2.5 wt.% (A)	K55.0 °C S_A 67.1 °C I
Polymer of (I)	K65.1°CS*c95.7°CS_A115.5°CI

The reaction samples were prepared by adding 2.5 wt.% (A) into monomer (I), then dissolving both components in dichloromethane and subsequently evaporating the solvent.

In-situ photopolymerization proceeded in a glass cell with a gap of 20 μm (20±1μm) under a 30 V dc electric field. The glass cell was coated with indium tin oxide (ITO) and polyimide. The cell was filled with the reaction sample in its isotropic phase at 80 $^{\circ}$C using capillary suction on a hot stage. After the cell was filled with the sample, then cool the sample slowly (~2°C/min) to the temperature for photopolymerization. Photopolymerization was carried out with the irradiation of UV light (mainly λ >300 nm, ultrahigh pressure mercury lamp, GCQ200, 200W) in the monomeric smectic phase at 64 $^{\circ}$C after the desired temperature had been retained for 25 min under N_2 atmosphere in the case of non-electric field. If under the application of the electric field, the desired temperature had been kept for 2 hour prior to the photopolymerization. The smectic phase at 64°C was formed by cooling monomer (I) slowly from its isotropic phase.

The monomer conversion was measured by a BRUKER ISF113V FTIR spectrophotometer.

Results and discussion

Monomer conversion was measured by means of FT-IR as described in ref.[7].
The irradiation time dependence of monomer conversion for in-situ photopolymerization of monomer (I) in the presence /or absence of the electric field is illustrated in Fig.1, where monomer conversion is plotted as a function of irradiation time during photopolymerization in the smectic phase of monomer (I) at 64 °C. It can be seen that the photopolymerization under the application of the electric field proceeds at a higher rate than that without an external electric field.

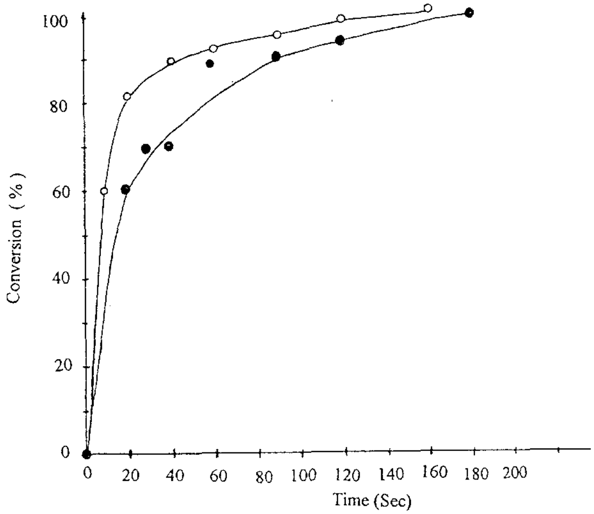
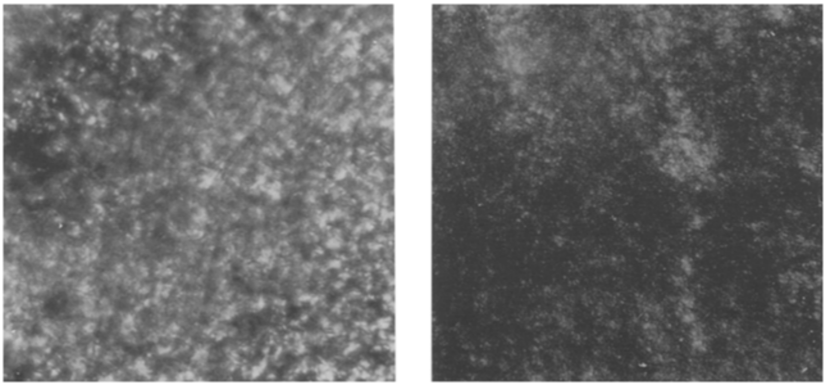


Fig.1 Monomer conversion as a function of irradiation time during photopolymerization in the monomeric S_A phase at 64 °C, (•) without using an electric field, (o) under a 30 V dc electric field

It is likely that the homeotropic alignment of the monomer induced by the electric field affects the photopolymerization rate remarkably. In the case of homeotropic alignment, the director of LC monomer (I) is perpendicular to the plate of the cell, reactive C=C double bonds of the monomer are arranged closely and regularly and consequently the possibility of efficient collision between monomer molecules, which leads to the polymerization, is incresed. On the other hand, under the application of electric field, the photoinitiator probably absorbs an appropriate photon and becomes excited more readily than without an electric field.

In order to check the possibility of fixing the monomer orientation in the cell under the application of the electric field by in-situ photopolymerization , the films obtained by complete photopolymerization in the monomeric smectic phase in the presence of 30V dc voltage and in the absence of the electric field, respectively (for a same irradiation time), were quenched from 64 °C to below room temperature by fast immersion of cell in ice water. Fig.2 shows the texture of the films observed by POM.

Fig.2 (a) illustrates the optical texture of smectic phase. This result indicates that photopolymerization of monomer (I) in its smectic phase can fix the monomer liquid crystalline structure. Furthermore, Fig.2 (b) exhibits that the intensity of transmitted light through the film which is obtained by in-situ photopolymerization of oriented monomer (I) under the application of 30 V dc voltage is much lower than that in the absence of electric field, but polarized light still to some extent transmits through the film. This observation means that the mesogenic orientation induced by an electric field can be fixed by in-situ photopolymerization in the aligned system in which some mesogenic groups are aligned at an angle with the plate of the glass cell. This is presumably because that the homeotropic texture of monomer (I) induced by the electric field is disturbed during in-situ photopolymerization in some degree.



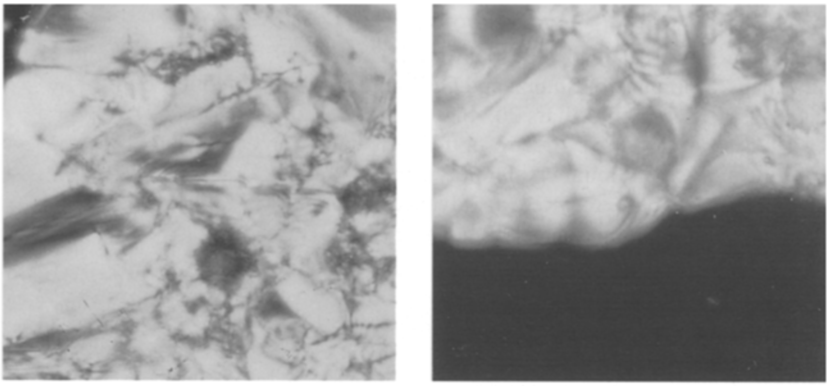
(a) (b)

Fig.2 Photomicrograph for optical texture of films obtained via photopolymerization of monomer (I) in its S_A phase at 64 ^oC, (a) without using an external electric field, (b) under the application of a 30 V dc electric field

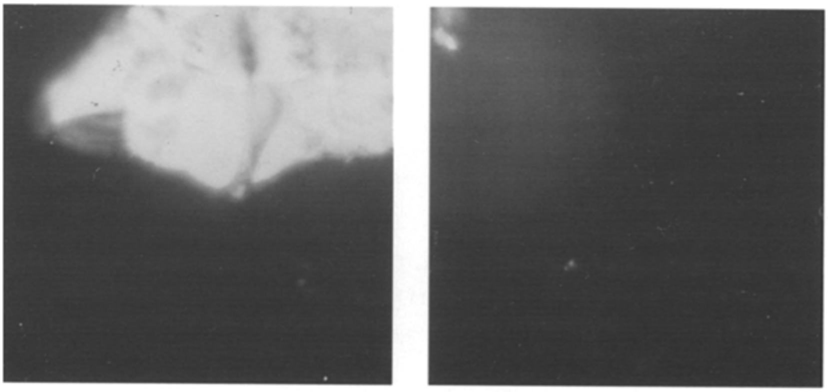
One prominent feature of the experimental results is that molecular orientation can be generated by external fields. Fig.3 shows the orientation behavior of the thermally polymerized polymer of monomer (I) in a 30 V dc electric field at 114.5 ^oC , just below 1 ^oC than its clearing point. With increasing the time for using the aligning electric field across the sample, the mesogenic side-chain of the polymer is oriented parallel to the electric field direction since the intensity of transmitted light through the film between crossed polars is reduced .

The dark area (as observed through crossed polars) implies an optically isotropic texture in the region of the electrodes[9]. At 114.5 ^oC, the sample is in S_A phase, therefore, this observation suggests a well-ordered homeotropic texture. Further increasing time leads to an increasing dark area, in the meantime, the bright color region, which shows the focal conic texture of S_A phase, gradually disappears. This course corresponds to a change from a scattering texture to a homeotropically aligned system. It took 30 V dc electric field about 3 hours to achieve the macroscopic homeotropic alignment. It is noted that at

93.5 ^{0}C, just 2 ^{0}C below the phase transition temperature $T_{SA \rightarrow S^{*}C}$, aligning of mesogenic side-chain of the polymer along the electric field direction is not obvious at all even at longer time in the electric field partly due to the higher viscosity of the polymer. In addition, Fig.2 and Fig.3 also demonstrate that in-situ photopolymerization of an oriented monomer in an electric field is advantageous with respect to achieving a highly oriented liquid-crystalline side-chain polymer, namely, in-situ photopolymerization of an oriented liquid crystal monomer is carried out quickly and the temperature at which the polymerization proceeds can be chosen relatively freely.



(a) t = 0 min (b) t = 20 min



(c) t = 50 min (d) t = 180 min

Fig.3 The effect of a 30V dc electric field on the alignment of mesogenic groups of the thermally polymerized polymer of monomer (I) in different time

In conclusion, in-situ photopolymerization in an electric field proceeds faster than without using aligning electric field and is relatively efficient to prepare an oriented liquid crystalline side-chain polymeric film.

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