

Rapid Communication

**SYNTHESIS OF DIACETYLENE-CONTAINING COPOLYESTERS AND
THEIR EFFECT ON ELECTRO-OPTICAL PROPERTIES OF
LIQUID CRYSTALS***

Xiao-fang Chen, Yao-wen Bai, Yu-guo Ma, Chen-hui Wang,
Dong Zhang, Xin-hua Wan and Qi-feng Zhou**

*Department of Polymer Science and Engineering, College of Chemistry,
Peking University, Beijing 100871, China*

Abstract Some diacetylene-containing copolyesters with different ratios of dipropargyl 1,10-decanate and dipropargyl terephthalate were synthesized. Properties of these copolymers were characterized by differential scanning calorimetry and polarizing optical microscopy. The copolymer could be cross-linked easily by UV irradiation in a liquid crystal matrix without adding any photoinitiator. The preliminary studies showed that the diacetylene-containing polymer network can assist liquid crystal molecules to align with the external electric field, thus reducing the response time of display devices.

Keywords Diacetylene-containing copolyesters, Polymer-stabilized liquid crystals, Electro-optical of liquid crystals

INTRODUCTION

Two types of composite materials consisting of liquid crystals and polymers have been reported for display applications so far: the polymer dispersed liquid crystals (PDLCs)^[1,2] and the polymer-stabilized liquid crystals (PSLCs). The systems containing a polymer of 20% or more are referred to as PDLCs^[3] and have been extensively studied because of their potential for applications in optical devices, such as optical switches, flat panel display screens. However, the refractive indices matching problem often exists in PDLCs systems. Therefore, PSLCs systems, in which a small amount (0.5~10%wt) of polymerizable monomer is dissolved in the liquid crystal matrix, have been designed to solve this problem^[4, 5]. Both types are commonly produced by spontaneous phase separation, which occurs during a UV radiation polymerization process. In the case of PSLCs, most of studies concentrated on diacrylates^[6-8], which formed polymer networks in the presence of photoinitiator. Here we synthesized a series of diacetylene-containing copolyesters (PDAs) and found that they could be cross-linked in a liquid crystal matrix by UV irradiation without adding any photoinitiator. The preliminary studies showed that the PDAs network can assist the alignment of liquid crystal molecules and reduce the response time of display devices.

EXPERIMENTAL

¹H-NMR spectra were obtained on a Varian 200 NMR spectrometer by using CDCl₃ as a solvent and TMS as an internal standard. Molecular weights were determined by GPC with polystyrene

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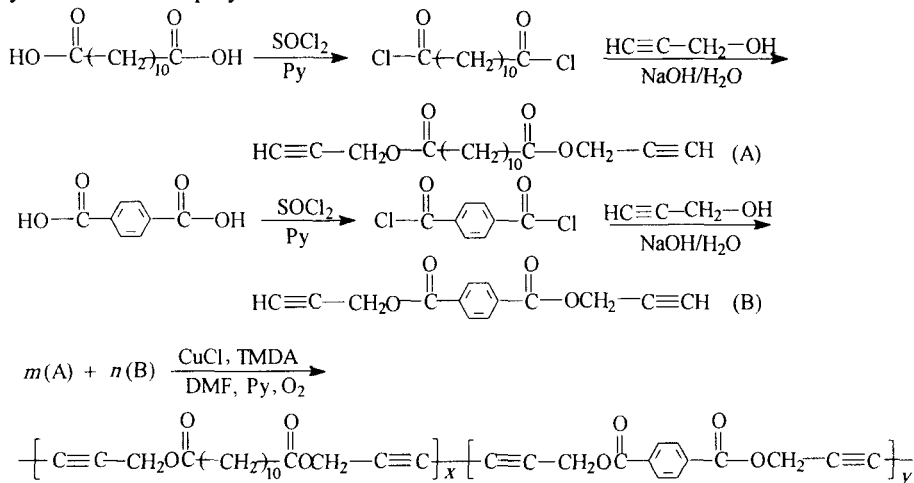
** Corresponding author: Qi-feng Zhou (周其凤), E-mail: qfzhou@pku.edu.cn

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standards in THF on a Waters 201 instrument. Differential scanning calorimeter (DSC) curves were recorded on a TA DSC-2010 instrument. The electro-optical properties of liquid crystals were tested on a LCT-5014 LCD Parameters Tester.

Synthesis of the Diacetylene-Containing Copolyesters

The syntheses of the copolymers and their monomers are summarized in Scheme 1.



Scheme 1 The synthesis of the copolyesters

Monomers synthesis

Dipropargyl 1, 10-decanate (A) was prepared from propargyl alcohol and 1, 10-decanedicarboxylic acid according to the literature^[9]. Dipropargyl terephthalate (B) was synthesized as follows: 1.232 g of propargyl alcohol was dissolved in 60 mL NaOH (0.33N) while a solution of 2.03 g terephthaloyl chloride in 30 mL toluene was added. The mixture was kept at 0–5 °C and was stirred vigorously. After 2–4 h, the mixture was filtered and the white solid was purified by recrystallization from ethanol. Yield: 40%, T_m = 107 °C.

Polymerization

A mixture of m moles of the monomer (A) and n moles of the monomer (B) with $m+n$ equal to 0.05 mol was dissolved in 8 mL of DMF and was then added slowly into a mixture of 0.021 g CuCl, 26.6 mL DMF, 8.4 mL pyridine and 0.035 mL N, N, N', N'-tetramethylenediamine (TMDA), while oxygen was bubbled through the reaction mixture. After 24 h at room temperature, the mixture was poured into acidified water. The yellow precipitate was filtered and dried in vacuum at room temperature.

Sample Preparation

The LC cells (TN type) were made by two indium-tin-oxide (ITO)-coated glass slides, which were coated with parallel rubbed polyimide layers, and separated by a 9- μm -thick spacer. 5CB and the desired amount of PDA80-20 ($m:n$ = 80:20) were mixed, heated into isotropic and then introduced into sample cells by capillary action. Finally the samples were irradiated under UV light for 15 min while a DC voltage of 24 volts was applied to the LC cells.

RESULTS AND DISCUSSION

The compositions of the copolymers x/y were determined from NMR spectra. As shown in Table I, the molar ratios x/y of monomers A and B in the copolymers were near to the feed ratios m/n in the reaction mixture. The molecular weight of the copolymers was moderate and listed in Table I.

Table 1 Some properties of DA-containing copolyesters

Copolymers	A:B molar ratio in feed		A:B molar ratio in the copolymers		T_m (°C)		M_w ($\times 10^{-3}$)
	m	n	x	y			
PDA80-20	4	1	3.8	1	69.1	75.9	11
PDA60-40	3	2	2.82	2	63.6		19
PDA50-50	1	1	-	-	64.4		10.4
PDA40-60	2	3	3	5	63.4	74.4	8.2

The melting points (T_m) of the copolyesters were recorded in Table 1 according to the DSC heating curves (heating rate was 20°C/min). The data collected in Table 1 were somewhat different from those reported in the literature^[9]. For example, PDA80-20 was reported only having a melting point at 77°C by Ogawa et al., while we found there were two endothermic peaks centered at 69°C and 76°C respectively in the heating process and only one exothermic peak in the cooling process (see Fig. 1). It was observed under polarizing optical microscope that the sample softened at about 68°C and became isotropic at 79°C. Birefringence can be observed in this temperature range, but neither typical liquid crystal texture, nor apparent phase transition was observed. We also found that the two endothermic peaks in DSC curves approached each other with an increase in heating rate and finally became one peak when the heating rate was 30°C/min (see Fig. 2, curves a, b and c). Also, if the sample was kept at 70°C for 15 min and cooled to room temperature, then heated at a rate of 20°C/min, there was only one endothermic peak at 76°C in the DSC heating curve (see Fig. 2, curve d). Thus, we conclude that this polymer is not liquid crystalline even though two endothermic peaks may be observed in DSC measurements. The occurrence of multi-melting of many polyesters was also observed for this polymer. The same phenomenon was observed for the polymer PDA40-60, which melted at 64 and 74°C on DSC (see Table 1). This is different from that of Ogawa, who reported that PDA40-60 could form a liquid crystal phase between 48°C and 67°C^[10].

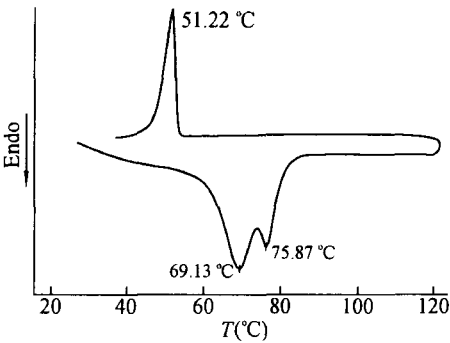


Fig. 1 The DSC curve of PDA80-20

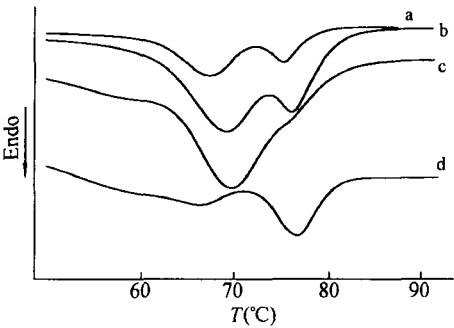


Fig. 2 The DSC heating curves of PDA80-20 at different heating rate
a) 10°C/min, b) 20°C/min, c) 30°C/min and
d) 20°C/min, pretreated sample

Some electro-optical properties of pure 5CB and 3%PDA40-60/5CB were compared in Table 2. We can see that when 3% PDA40-60 was added in 5CB, the response time was reduced and the threshold voltage (V_{th}) went down, but the contrast became poorer. These phenomena can be understood as follows. Before photopolymerization, PDA40-60 molecules can be aligned together with 5CB liquid crystal molecules by the applied electric field. After cross-linking, the polymer network may retain its orientation and can be used to assist the low molar mass liquid crystal to align and accelerate its response to the external field. So, the response time became

Table 2 Some electro-optical properties of 5CB and 3% PDA40-60/5CB

Samples	V_{th} (V)	V_{sat} (V)	Contrast	Response Time (T_{on}/T_{off}) (ms)
5CB	1.242	1.656	13.84	54/103
5CB/PDA40-60	0.858	1.992	9.97	28/49

shorter, and the threshold voltage lowered. However, the same retention of this molecular orientation of the rigid polymer network may also reduce the contrast. A more flexible polymer network may be needed to improve the contrast. Further studies are necessary in order to reach a good balance of the electro-optical properties.

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