

WHOLLY-AROMATIC THERMOTROPIC LIQUID CRYSTALLINE POLYMER AND ITS BLOCK COPOLYMER

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ABSTRACT

A wholly-aromatic thermotropic liquid crystalline polymer (WATLCP) composed of p-hydroxybenzoic acid (HBA), 4,4'-dihydroxy bisphenyl (BP), terephthalic acid (TPA), m-phthalic acid (MPA) was synthesized. It was symbolized by BP-LCP. Using a similar method, a new copolymer BP-PSF was prepared. BP-PSF has a semi-flexible chain polysulfone and a rigid-rod chain like BP-LCP. By FT-IR, polarizing microscope and DSC technique, the structures and properties of BP-LCP and BP-PSF were studied.

INTRODUCTION

In recent years, many papers were published^[1-3] on wholly-aromatic liquid crystalline polymers (WATLCP) because of their unique properties. But their main shortcoming—high processing temperature, made them difficult to be used. For example, Xydar, an America product^[4], which is composed of terephthalic acid (TPA), p-hydroxybenzoic acid (HBA) and bisphenol A (BPA), should be processed over 400°C. In order to lower the processing temperature, a lot of works have been done^[5-7]. A series of low melting point WATLCPs were synthesized^[8] and were used to reinforce thermoplastic resins polysulfone (PSF), polycarbonate (PC) etc.

The blend of thermotropic liquid crystalline polymer and thermoplastic resin was called in-situ composites by Kiss,^[9]. It is a new kind of composites with high mechanical properties. Liquid crystalline polymer can form microfiber structure during processing and reinforce the matrix resin, but the poor compatibility of liquid crystalline polymer with the matrix limits the reinforcing effect. How to improve the compatibility remains a difficult problem in this field.

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In order to improve the compatibility of WATLCP/PSF in-situ composites^[10], a compatibilizer is necessary. This paper presents the method of synthesizing a block copolymer composed of polysulfone chain and WATLCP chain, and the results of comparing the properties of this block copolymer with the WATLCP. The block copolymer can act as a compatibilizer for WATLCP/PSF blend.

EXPERIMENTAL

Materials

Terephthalic acid (TPA), m-phthalic acid (MPA), bisphenol A (BPA) were bought from Shanghai Chemical Reagents Factory, chemically pure. acetoxy-benzoic acid (Ac-HBA), 4,4'-diacetoxy bisphenyl (Ac-BP), 4,4'-dichlorodiphenylsulfone (DCDPS) and a wholly-aromatic thermotropic liquid crystalline polymer BP-LCP were prepared by ourselves^[8].

Apparatus

IR analyses were performed on Nicolet 5DX FT-IR spectrophotometer. Samples were analyzed as powders ground with KBr powder and pressed into pellets. Samples were viewed between cross-polarizer with a Leitz Orthoplan-P01 hot stage optical microscopy at a magnification of 320. DSC results were obtained from a Dupont-912 DSC at a heating rate of 10°C/min.

Synthesis of low molecular weight polysulfone

According to the conventional manner^[11], BPA (22.8g) and DCDPS (28.3g) were added into a reactor together with 27.9g potassium carbonate and 400ml dimethyl sulfoxide. The system was heated till 190°C under N₂. After that pumped vacuum for 40—60 minutes, stopped heating. The reactants was poured into methanol, white precipitates were obtained, washed the solids with boiling water and methanol to get pure products, it has a molecular weight of 1100 by end group titration.

Synthesis of block copolymer

Put the PSF (0.01 mol), TPA (0.014mol), MPA (0.006mol) into a three-necked flask. The contents were purged well with N₂ for several times. Then heated it to 180°C, and allowed to remain there for 1—1.5h. The by-product acetic acid was removed by a steady N₂ flow via the N₂ exit port. Stirring was kept during this cycle to the by-product removal and to allow for good mixing of the compounds. Then cooled the system and added Ac-HBA (0.03mol), Ac-BP (0.01mol) and a little catalyst Pb (Ac)₂·3H₂O/Sb₂O₃. Increased the temperature to 200°C for 1h, and up to 300°C step by step. Stirred for an additional 4h. After that stirring was halted and vacuum was applied to the system over a 15min period. The pressure was reduced

to 10–20 mmHg, and at this point the temperature was raised to 320°C and held there for 0.5h. Afterwards, the reaction vessel was brought to atmospheric pressure by bleeding in N₂. The polymer was extracted with acetone and dichloromethane for 12h and 24h respectively. The samples were dried at 60°C in vacuo for several days prior to analysis.

RESULTS AND DISCUSSION

FT-IR analyses

Fig. 1 shows the FT-IR spectra of acetoxy-PSF, BP-LCP and the block copolymer BP-PSF. In Fig. 1a, in addition to the very strong band due to the carbonyl group of the ester linkages (1750cm^{-1} , $\nu_{\text{C=O}}$), a band at 1048cm^{-1} , typical of the ester vibration ($\nu_{\text{C—O—C}}$) is readily observed. Fig. 1c shows the spectrum of Ac-PSF in which there is a weak signal of the carbonyl group ($\nu_{\text{C=O}}$, 1750cm^{-1}), a typical peak of sulfone group (ν_{SO_2} , 1150cm^{-1}), a separate band of isopropyl group (1380cm^{-1}) and a strong aromatic C—C vibration band (1500cm^{-1}). The FT-IR spectrum of the copolymer BP-PSF is shown in Fig. 1b. This spectrum shows the characteristic bands of the BP-LCP (1750cm^{-1} (s), 1048cm^{-1}) (Fig. 1a), as well as bands exclusive to Ac-PSF (1150cm^{-1} , sym. ν_{SO_2} , 1500cm^{-1} , aromatic C—C vibration). Besides, an intense carbonyl band of the ester linkage is noted at 1750cm^{-1} , and a separate band of the isopropyl group appears at 1380cm^{-1} .

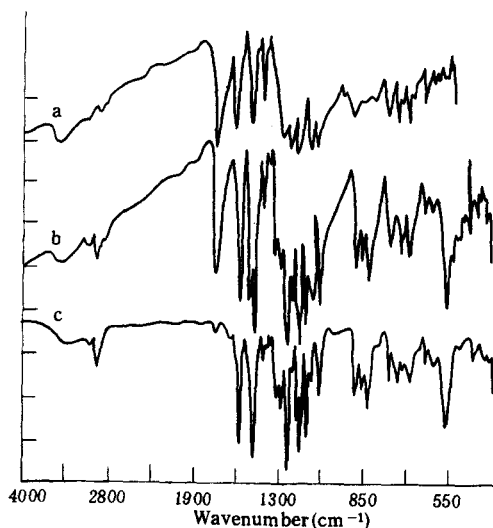
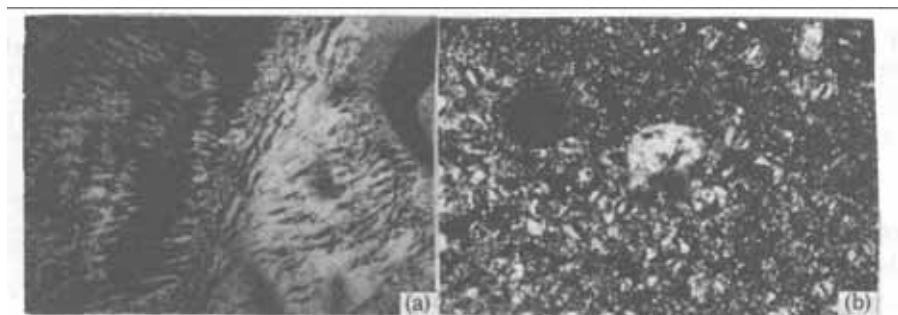


Fig. 1. FT-IR spectra of (a) BP-LCP, (b) BP-PSF, and (c) Ac-PSF

Liquid crystallinity of polymers

The optical micrographs of BP-LCP and BP-PSF are given in Fig. 2. Both BP-LCP and BP-PSF have nematic liquid crystallinity. In order to examine the nematic phase, BP-LCP and BP-PSF were sandwiched between two glass plates, and placed under the crossed polarizers. For BP-LCP, typical interferences can be observed because of the variations of the optical axis with respect to the incident light. Many inclination lines can be found, which is the typical texture of nematic phase. For BP-PSF, the texture is visualized as a lot of flashing balls under crossed polarizers (Fig. 2b).



(a) BP-LCP (340°C)

(b) BP-PSF (300°C)

Fig. 2 Optical micrographs of (a) BP-LCP and (b) BP-PSF

DSC analyses

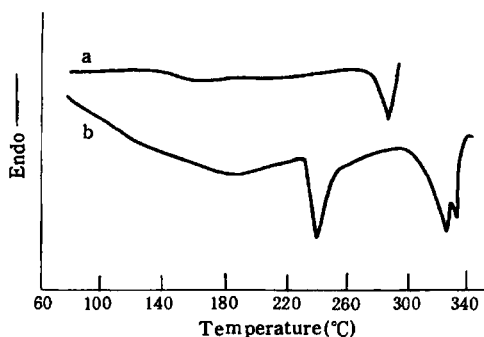


Fig. 3 DSC curves of (a) BP-PSF (b) BP-LCP

Fig. 3 shows the DSC curves of BP-LCP and BP-PSF. They have two transition temperatures, but BP-LCP has a T_{kk} (crystal-crystal) at 240°C, and a T_{kn} (crystal-nematic) at 330°C, while BP-PSF exhibits a T_g at 153°C and a T_{kn} at 280°C. The differences in their thermal properties may be explained that the crystallinity of the copolymer is decreased by the presence of PSF chain. Different results were reported by Auman, B.C. et al.^[12]. Their block copolymer and LCP had similar DSC curves

with two transition temperatures T_{kk} and T_{kn} in both curves.

CONCLUSIONS

A block copolymer BP-PSF, composed of short PSF chain and four monomers TPA, MPA, HBA, BP, was synthesized according to the method of preparing BP-LCP. Both polymers have nematic liquid crystallinity. But BP-LCP shows better liquid crystallinity than BP-PSF. Introducing PSF chain to BP-LCP chain can decrease the crystallinity of the copolymer.

Keywords:

Liquid crystalline polymer; Block copolymer; Polysulfone, Melt polymerization

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