Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Hongli, Yang , Xuqin, Wu and Shijin, Li(1996) 'Synthesis and characterization of block copolymers having liquid crystalline behaviour', Liquid Crystals, 20: 2, 261 — 264
To link to this Article: DOI: 10.1080/02678299608031134
URL: http://dx.doi.org/10.1080/02678299608031134

LIQUID CRYSTALS, 1996, VOL. 20, NO. 2, 261–264

Preliminary Communication

Synthesis and characterization of block copolymers having liquid crystalline behaviour

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(*Received 19 January 1995; in final form 6 September 1995; accepted 7 September 1995*)

A series of four block copolymers based on aromatic acetoxy-polysulphone (Ac-PSF), terephthalic acid (TPA), *m*-phthalic acid (MPA), acetoxy-benzoic acid (Ac-HBA), and a di(acetoxy)bisphenol monomer were synthesized. Their structures were determined by IR, thermal mechanical analyses and solubility tests. They all exhibit liquid crystalline behaviour.

In recent years there has been a great deal of interest in the liquid crystal behaviour of block copolymers having a rigid rod attached to a semi-flexible chain [1]. In 1981, Lenz *et al.* [2] introduced BPA and BPS into the main chains of copolymers based on chlorohydroquinone (CHQ) and terephthalate chloride (TC). Their results showed that under a suitable BPA or BPS concentration, the final copolymer acted as a liquid crystal. In 1988, Zhang Zhibin *et al.* [3] reported the block copolymers of low molecular weight polysulphone with rigid rods consisting of CHQ and TC and obtained the same results as above for certain compositions. Further systems have also been studied [1, 4, 5].

In this communication, the synthesis of novel block copolymers containing rod-like and semi-flexible moieties will be discussed. The rod-like part is formed during the reaction, and is made from four monomers: Ac-HBA, TPA, MPA and diacetoxybisphenol. The semi-flexible chain is acetoxypolysulphone. These block copolymers will be used to improve the compatibility of *in situ* composites [6].

The materials used (and their respective abbreviations) were terephthalic acid (TPA), *m*-phthalic acid (MPA), 4,4′-diacetoxybisphenol A (Ac-BPA), 4,4′-diacetoxybisphenyl (Ac-BP), *p*-acetoxybenzoic acid (Ac-HBA), 4,4′-diacetoxy bisphenylmethane (Ac-BPM), 4,4′-diacetoxybisphenylsulphone (Ac-BPS). Acetoxy polysulphone (Ac-PSF) (molecular weight is 1100) were prepared in the conventional manner [1].

IR analyses were performed on a Nicolet 5DX FT-IR spectrophotometer. Samples were analysed as powders ground with KBr powder and pressed into pellets. Leitz Orthoplan-Pol hot stage optical microscopy was used. Samples were viewed between crossed polarizers at a magnification of 320 ×. The thermal–mechanical analyses were performed on a DJY-1 thermal–mechanical analyser (Shanghai) under a load of 5 g at a heating rate of 20°C min^{-1}. DSC measurements were obtained from a Du-Pont-912 DSC at a heating rate of 10°C min^{-1}.

The scheme shows the synthetic route to the block copolymers. When replacing Ac-BP with $CH_3COOArCH_2ArOCOCH_3$ (AC-BPM), another block copolymer, BPM-PSF, is obtained. If Ac-BP is replaced by $CH_3COOArC(CH_3)_2ArOCOCH_3$ (Ac-BPA) or $CH_3COOArSO_2ArOCOCH_3$ (AC-BPS), we get the block copolymers BPA-PSF or BPS-PSF respectively.

The detailed process of the first two steps in the scheme is given in reference [1]; the last step is as follows: Ac-PSF (0·02 mol), TPA (0·014 mol) and MPA (0·006 mol) were placed into a three-necked round-bottomed flask. The reaction vessel was purged well with N_2. The flask was heated to 180°C for 1–1·5 h. The byproduct (acetic acid) distilled from the molten mass was removed via the steady N_2 flow. During the reaction the mixture was stirred to aid removal of the acetic acid and promote good mixing of the reactants. The system was allowed to cool and Ac-HBA (0·03 mol), Ac-BP (or another Ac-Bisphenol monomer) (0·01 mol), and a little catalyst $Pb(Ac)_2{\cdot}3H_2O/Sb_2O_3$ were added. The temperature was increased to 200°C for 1 h, and gradually up to 300°C, then stirred for an additional 4 h. The stirring was halted and a vacuum was applied to the system over a 15 min period. The pressure was reduced to 10–20 mmHg, and at this point the temperature was raised to 320°C and held there for 0·5 h. Afterwards, the reaction vessel was brought to atmospheric pressure by

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$HO{-}Ar{-}C(CH_3)_2{-}Ar{-}OH + Cl{-}Ar{-}SO_2{-}Ar{-}Cl$
(BPA) (DCDPS)

$\downarrow K_2CO_3$

$HO{-}Ar{-}C(CH_3)_2{-}Ar{-}(O{-}Ar{-}SO_2{-}Ar{-}O{-}Ar{-}C(CH_3)_2{-}Ar)_n{-}O{-}Ar{-}SO_2{-}Ar{-}Cl$
(HO−PSF−Cl)

$\triangle \downarrow CH_3{-}CO{-}O{-}CO{-}CH_3$ $((Ac)_2O)$

$CH_3{-}COO{-}Ar{-}C(CH_3)_2{-}Ar{-}(O{-}Ar{-}SO_2{-}Ar{-}O{-}Ar{-}C(CH_3)_2{-}Ar)_n{-}O{-}Ar{-}SO_2{-}Ar{-}Cl$
(Ac−PSF)

$HOOC{-}Ar{-}COOH$ (TPA) $\downarrow$ $CH_3{-}COO{-}Ar{-}COOH$ (Ac−HBA)
$HOOC{-}Ar\backslash COOH$ (MPA) $CH_3{-}COO{-}Ar{-}Ar{-}O{-}CO{-}CH_3$ (Ac−BP)

$Cl{-}Ar{-}SO_2{-}Ar{-}PSF{-}[{-}O{-}(CO{-}Ar{-}CO)_x{-}(O{-}Ar{-}Ar{-}O)_y{-}(CO{-}Ar\backslash CO)_z{-}(O{-}Ar{-}CO)_w{-}]_m$
(BP−PSF)

Scheme Synthesis of block copolymers.

bleeding in N_2. The polymer was extracted with acetone and dichloromethane for 12 h and 24 h respectively. The samples were dried at 60°C *in vacuo* for several days prior to analysis.

The mnemonics used, BP-PSF, BPM-PSF, BPS-PSF, BPA-PSF, refer to the series of block copolymers with different Ac-bisphenol monomers. BP-LCP, BPM-LCP, BPS-LCP and BPA-LCP refer to liquid crystalline polyesters based on TPA, MPA, Ac-HBA, Ac-BP (or Ac-BPM, Ac-BPS, Ac-BPA), which have been discussed in reference [7].

Figure 1 shows the FTIR spectra of (*a*) BP-LCP, (*b*) the copolymer of Ac-PSF and BP-LCP, and (*c*) Ac-PSF. In figure 1 (*a*), in addition to the very strong band due to the carbonyl group of the ester (at 1750 cm^{-1} $\nu_{C=O}$), a band at 1048 cm^{-1}, typical of the ester vibration ($\nu_{C\text{-}O\text{-}C}$) is also readily observed. In figure 1 (*c*) showing the spectrum of Ac-PSF, a weak signal can be observed corresponding to the carbonyl group at 1750 cm^{-1}, a typical sulphone group peak (ν_{SO_2}) at 1150 cm^{-1}, a band due to the isopropyl group at 1380 cm^{-1}, and a strong aromatic C–C vibration at 1500 cm^{-1}. The FTIR spectrum of a typical copolymer BP-PSF (see figure 1 (*b*)), exhibits bands characteristic of the BP-LCP (1750 cm^{-1} (s) and 1048 cm^{-1}) as well as those exclusive to Ac-PSF (1150 cm^{-1}, ν_{SO_2} sym, 1500 cm^{-1} aromatic C–C vibration). Additionally a band due to the isopropyl group at 1380 cm^{-1} can be seen.

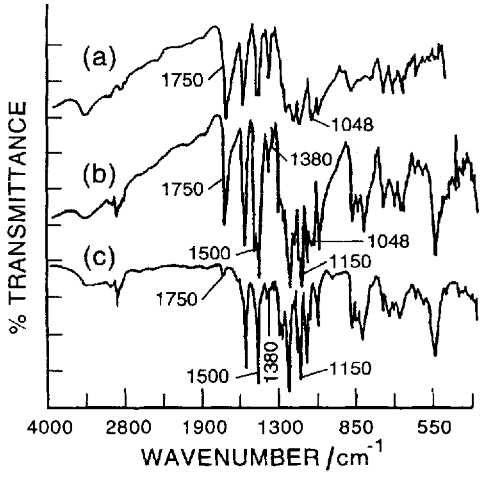


Figure 1. FTIR spectra of (*a*) BP-LCP, (*b*) the copolymer of Ac-PSF and BP-LCP and (*c*) Ac-PSF.

Temperature–strain curves are shown in figure 2 of (*a*) BP-PSF and (*b*) the BP-LCP/PSF blend. The two curves are very different: in figure 2 (*b*) two turning points can be seen at 200 and 250°C, whereas in figure 2 (*a*) only the one turning point at 185°C is observed, indicating that the BP-PSF is a single polymer and not a mixture of BP-LCP and PSF.

Polysulphone is soluble in many solvents, for example, chloroform, dicloromethane (DCM) and tetrahydrofuran. However it is difficult to find a solvent for the wholly aromatic copolymers. Two solvents have been used here, DCM and a mixture of chloroform and *p*-chlorophenol (CF/PCP) (1 : 1), and the results of this solubility test are shown in the table. It is clear that all the samples were insoluble in DCM except Ac-PSF, so no Ac-PSF remained in the block copolymer. Alternatively the block copolymers were soluble in CF/PCP, however, the LCPs were not. Thus, there were no rigid rod polymers in the block copolymers either.

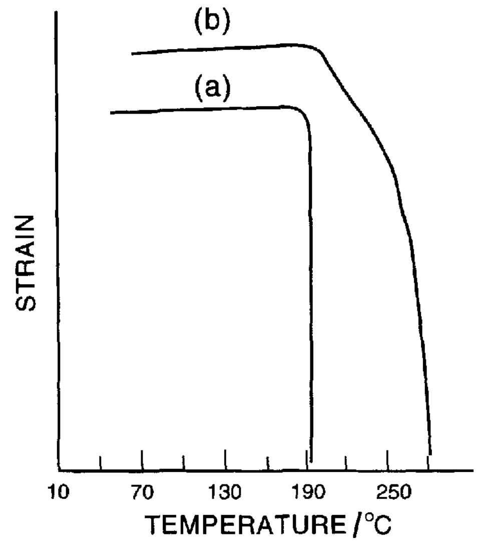


Figure 2. Temperature versus strain curves for (*a*) BP-PSF and (*b*) BP-LCP/PSF (25/75) blend.

Solubility test of the copolymers.

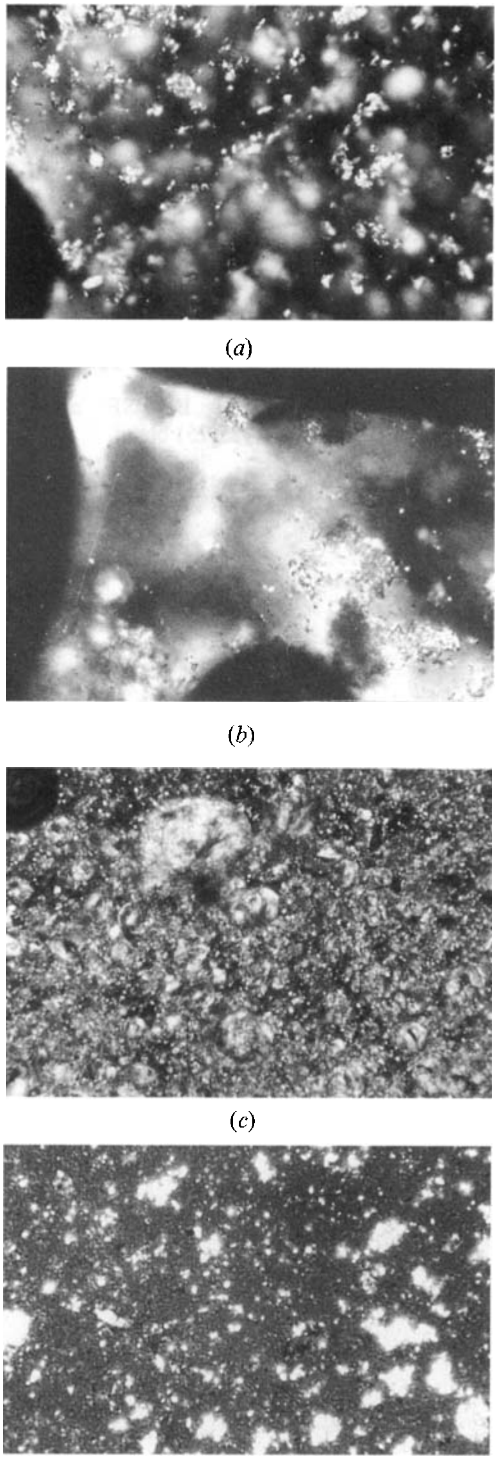
Samples	DCM	CF/PCP (1:1)
AC-PSF	Soluble	Soluble
BPA-PSF	Insoluble	Soluble
BPA-LCP	Insoluble	Insoluble
BPM-PSF	Insoluble	Soluble
BPM-LCP	Insoluble	Insoluble
BP-PSF	Insoluble	Soluble
BP-LCP	Insoluble	Insoluble
BPS-PSF	Insoluble	Soluble
BPS-LCP	Insoluble	Insoluble

These results, with the above analyses, suggest that block copolymers were formed.

Optical micrographs of segmented copolymers are given in figure 3. As expected, liquid crystal textures are observed. In all cases in which crystalline to liquid crystalline transitions were recorded by differential scanning calorimetry (DSC), birefringence was observed by microscopy (between crossed polarizers), and the melts could be readily sheared and aligned by the movement of the cover slide.

The thermal characterization of the copolymer BP-PSF by DSC is illustrated in figure 4(*a*). It has a glass transition temperature at 153°C, and melts at 280°C. This DSC spectrum is quite different to that of the BP-LCP/PSF blend (see figure 4(*b*), indicating that BP-PSF is not a mixture of BP-LCP and PSF, but is a single copolymer.

In conclusion, block copolymers of low molecular mass Ac-PSF and rigid rod chains were synthesized. Optical microscopy and thermal studies verified their liquid crystallinity.


(*a*)

(*b*)

(*c*)

(*d*)

Figure 3. Optical micrograph of the block copolymers (320 ×) (*a*) BPA-PSF, (*b*) BPM-PSF, (*c*) BP-PSF and (*d*) BPS-PSF.

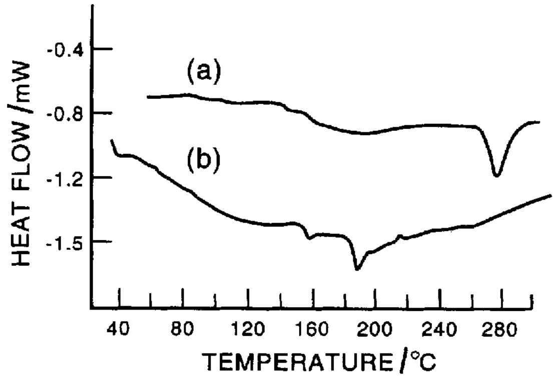


Figure 4. DSC spectra of (*a*) BP-PSF and (*b*) the BP-LCP/PSF (25/75) blend.

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