Polymer 50 (2009) 4775–4780

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

New synthesis and characterization of ionic polyurethane-urea liquid crystals

Sellamuthu N. Jaisankar [a,b], Donna J. Nelson [a,*], Christopher N. Brammer [a]

[a] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA
[b] Polymer Division, Central Leather Research Institute, Adyar, Chennai 600 020, India

ARTICLE INFO

Article history:
Received 23 October 2008
Received in revised form
13 July 2009
Accepted 22 July 2009
Available online 5 August 2009

Keywords:
Polyurethane-urea
Schlieren texture
Liquid crystal

ABSTRACT

A new series of thermotropic ionic polyurethane-urea (PUU) liquid crystals (LCs) were synthesized, each by using the corresponding diisocyanate, 4,4′-bis(6-hydroxyhexoxy)biphenyl, and sodium 2,5-diaminobenzenesulfonate. Morphology, phase transition temperatures, and spectroscopic characteristics of the PUU LCs are reported. Each PUU exhibits a monotropic liquid crystal phase upon slow cooling. The PUU LC phase texture is visible by polarized optical microscopy (POM) and is dependent upon the PUU isocyanate precursor; 1,6-diisocyanatohexane (HDI) and 5-isocyanato-1-(isocyanatomethyl)-1,3,3,-trimethylcyclohexane (IPDI) polymers have schlieren textures, whereas 2,4-diisocyanato-1-methylbenzene (TDI) and methylenebis(4-phenylisocyanate) (MDI) polymers show grain textures.

1. Introduction

Liquid crystalline polymers (LCPs) [1,2] have been actively studied recently because of their technological potential [1a–c] and scientific challenges [1d,e]. Main chain LCPs without ionic groups generally has poor miscibility with and adhesion to other polymers, hindering their uses in blends of LC polymers and conventional polymers [1f]. Therefore, ionic LCPs have the simultaneous dual advantages of LCPs, such as microfiber reinforcement, and of ionomeric polymers, such as increased miscibility [1g]. Polyurethane-ureas (PUUs) are of interest due to their excellent thermoplastic characteristics [3], but their design as liquid crystals has not been so explored [3d–f]; there appear to be few reports of nonionic PUU LCs, whether smectic [3d,e] or nematic [3f], and even fewer of PUU LCs [3i–k] which could be ionic under some conditions. Therefore, in designing an ionic PUU LC synthesis, we drew from design strategies used in other similar systems.

Liquid crystal (LC) characteristics of polyurethane (PU) produced from 2,4-toluenediisocyanate (24TDI) and 4,4′-bis(6-hydroxyhexoxy)biphenyl (BHHBP) are reported to be due to structural features, including the asymmetric methyl in 24TDI, rigid biphenyl units, flexible methylene spacers of BHHBP, but less from intermolecular hydrogen bonding of urethane linkages [2a]. Hydrogen bonding in PUs was reported to be "only of secondary importance" in mesophase formation and morphology [2a], but important to dimensional stability [2b]. In contrast, hydrogen bonding in PUUs is expected to influence these characteristics differently, not only because NH bonds in urea linkages provide additional protons for donation, but also because the lone pair on N will form stronger hydrogen bonds than those on O; this is because the lower-electronegative N holds its electron pair more loosely, enabling it to participate more efficiently as an electron pair donor in hydrogen bonding. Indeed, reports have indicated that hydrogen bonding is important in PUUs [3a,b]. Therefore, polyurethane-ureas (PUUs) seem more likely candidates for liquid crystals, due to this potential for different hydrogen bonding, consisting of more and stronger bonds. There are two reports of PUU LCs, which could be ionic under some conditions [3i,j] and one report of a PUU LCs [3k], which is ionic; all used the same synthetic route using 3,5-diaminobenzoic acid.

The effects of PU and PUU precursor characteristics on product features help guide designing an ionic PUU likely to have LC properties. Many PUU syntheses used a diol, a diisocyanate, and a diamine chain extender [3]. In order to design an ionic PUU LC with compatibility in polymer blends, we incorporated into that design the characteristics which were reported to promote desired properties in other polymer systems: (1) an aromatic diamine as the chain extender [3d], (2) BHHBP as the mesomeric diol, which yielded an LC in the PU system [2a], (3) unbranched hard segments, which increase packing and hydrogen bonding in PUUs [3a], (4) an ionic hard segment, which gives better mechanical properties in multiple systems [2c,4], and (5) selecting sulfonate as the ionic group, because in PUs, sulfonate produced stronger intermolecular interactions than carbonate [2c]. Although the ionic nature of the product might be expected to reduce its LC properties [5], this is offset by the expectation that ionic groups have been shown to increase polymer compatibility in blends [1g,6a,b]. Blended

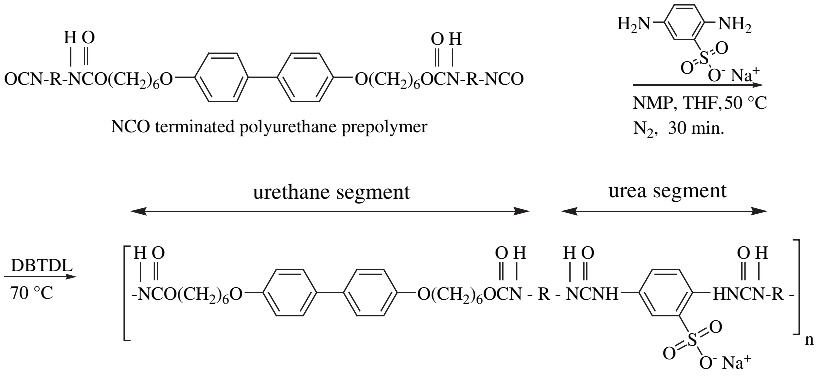
---

* Corresponding author. Tel.: +1 405 325 2288; fax: +1 405 325 6111.
E-mail address: djnelson@ou.edu (D.J. Nelson).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.07.049

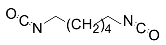
polymers often can be used simultaneously [1a] as novel compatibilizers [1c,g], processing aids [1b,c], and reinforcing agents [1g,6c], for polymer blends [1a], new types of advanced materials, and other commercially important systems [6d,e]. Therefore, it was of interest to develop a new route to ionic PUU LCs and to examine their characteristics. This PUUs based low molecular weight polymers are able to control the ionic content in the range of 6–12%, leads hydrophobic linear main-chain LC PUUs are insoluble in water.

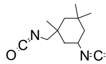
BHHBP was reacted with a representative diisocyanate eq. (1), followed by treatment with the ionic chain extender sodium 2,5-diaminobenzenesulfonate (DBS), by iterating 4× through a modified two-step procedure [3a] to give the corresponding PUU eq. (1), (R = diisocyanate). We report herein the synthesis and characteristics of four PUUs by this route.

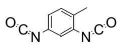


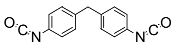
(1)

R = diisocyanate (see below)


1,6-diisocyanatohexane
HDI (→ PUU1)


5-isocyanato-1-(isocyanatomethyl)-
1,3,3,-trimethylcyclohexane IPDI (→ PUU2)


2,4-diisocyanato-1-methylbenzene
2,4-TDI (→ PUU3)


methylenebis(4-phenylisocyanate)
MDI (→ PUU4)

2. Results and discussion

Four series of PUUs were synthesized by reacting BHHBP and DBS with a linear aliphatic diisocyanate (HDI), a cyclic aliphatic diisocyanate (IPDI) and in order to find out the effect of an aromatic diisocyanate on the liquid crystalline property, the hexyl space mesogenic diol was reacted with TDI and MDI. FTIR was used for structural characterization of the PUUs as KBr pellets (sample: KBr = 1:80). FTIR spectra (Fig. 1) confirmed each PUU formation by disappearance of the very broad peak at 3535–3350 cm^{-1} (O–H stretch) and appearance of a new sharper peak at 3330 cm^{-1} (urethane N–H stretch). Absence of an isocyanate antisymmetric stretching band at 2280–2260 cm^{-1} in the product also evidences complete reaction between hydroxyl and diisocyanate. Similarly, IRs of PUUs1–4 each show a band at 1610 cm^{-1} (urethane C=O stretch) with a shoulder at 1545–1540 cm^{-1} (urethane N–H bend), and a second band at 1258–1225 cm^{-1} (N–C stretch of N–COO); these indicate formation of functionalities characteristic of a PUU. The spectra for PUUs1–4 have typical overlapping free and hydrogen bonded N–H stretch bands at about 3500–3300 cm^{-1}. These agree with IR changes observed upon blending polyurethanes with polyamides [7]. The counter-ion to SO_3^- in these PUUs (Na^+) complexes with the nitrogen lone pair electrons and reduces the N–H bond length. This produces the observed shift of N–H peaks from 3500 to 3330 cm^{-1}, as it does in polyester PUUs [8].

The ionic PUUs reported herein were also characterized by using cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR. The ^{13}C NMR of PUU1 (Fig. 2) shows peaks (in ppm) at 29.5 (CH_2), 45.2 (CH_2), 65.3 (CH_2–OPh), 69.6 (CH_2-OC(=O)NH), 119.0 (C=C), 131.8 (C=C), 160.1 (urea C=O), and 162.1 (sm shoulder, urethane C=O). PUUs1–4 show number average molecular weights ($\overline{M}_n$) in the range 25,000–35,000, as determined by VPO (Vapor-Phase Osmometry) in tetrahydrofuran (THF). All the PUU LC ionomers are insoluble in water because the ionic content of each is below 15 mol% in the main-chain PUU [9].

PUU thermal properties (Table 1) were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The two decomposition temperatures for each PUU studied herein were in the range of 315–359 °C for the first decomposition temperature (T_{d1}) and 399–496 °C for the second decomposition temperature (T_{d2}); all were dependent upon the diisocyanate used. This shows that all the PUUs were thermally stable [5] (i.e., no weight loss) up to 315 °C and that decomposition occurs after the clearing temperature of the ionic LC, as observed by optical microscope. The PUU2 DSC trace (Fig. 3) shows two endothermic transition temperatures on heating [2a], glass transition (T_g) and melting (T_m) at 123.9 °C and 179.1 °C, respectively (Table 1). In the cooling scan (Fig. 3b), PUU2 exhibits a sharp exothermic peak at 168.5 °C, which agrees with formation of an LC phase of the polymer [10]. The differences in T_m between DSC and POM may be due to the difference in a heating rate and the instrumentals differences (2–6 °C). Mormann and coworkers [10b] reported similar observations of crystallization upon cooling as same as the evidence of the crystallization melting point upon heating for the unsegmented polyurethane liquid crystals [10c].

Textures of PUUs1–4 were observed (Fig. 4) by cross polarized optical microscopy (POM) with a hot stage; these are characteristic of liquid crystals [10,11b,12,13]. PUU1–4 POM melting temperatures (Table 1) generally agree with the PUU1–4 DSC melting points. However, comparing these results for PUU1–4 with those for other LC polymers is difficult due to differences in $\overline{M}_n$, functional groups, polymeric architectures, etc. PUU2 LC began melting at 184.9 °C and reached its isotropic state at 290 °C; upon cooling, the thermotropic LC started to appear at 168.9 °C. At 126.8 °C the PUU2 LC was fully formed and is shown in an optical photograph (Fig. 4b). PUUs1–4 exhibit monotropic liquid crystallinity upon cooling; they exhibit mesophases with well-defined textures and are stable

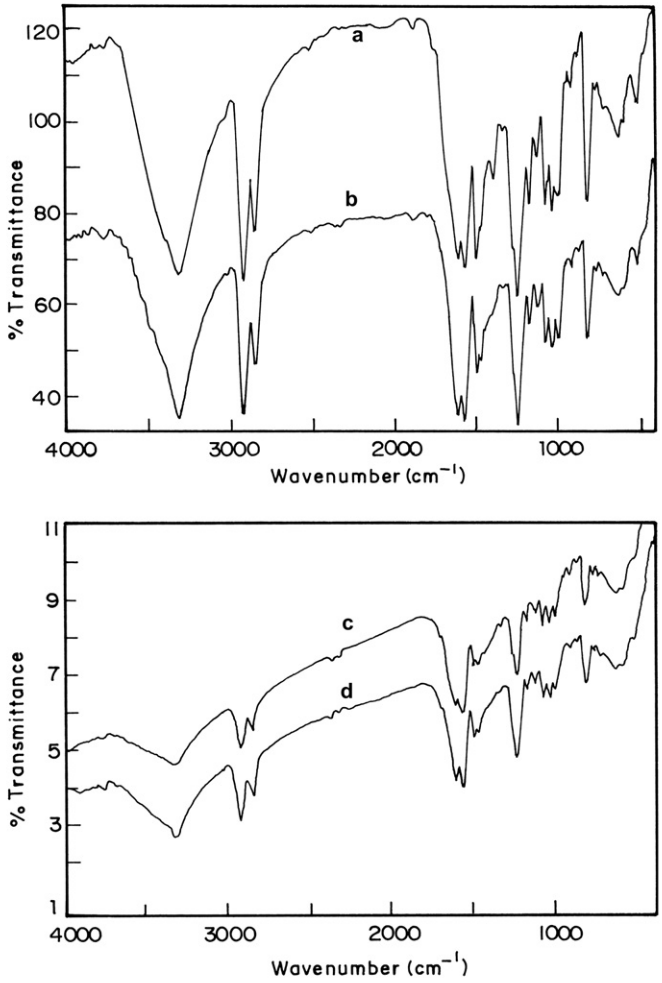


Fig. 1. FTIR spectra of (a) PUU1 (b) PUU2 (c) PUU3 and (d) PUU4.

Table 1
PUU heating temperatures (°C) of glass transition (T_g), melting (T_m), and first (T_{d1}) and second decompositions (T_{d2}).

Codes	T_g	T_m		T_{d1}	T_{d2}
	DSC	DSC	POM	TGA	TGA
PUU1	–	185.2	189.2	343	399
PUU2	123.9	179.1	184.9	359	445
PUU3	–	255.4	248	315	467
PUU4	–	269.8	262.5	340	496

macromolecules. These PUU LCs do not form lyotropic mesophases, probably because each has a hydrophobic linear main-chain, that is insoluble in water [11a].

The micrograph of each PUU (Fig. 4a–d), taken after cooling from its isotropic state, shows an LC phase. PUU1 and PUU2 each shows a schlieren LC double axial texture, characterized by two-brush and four-brush point singularities [10,11b,12,13e–g]. Each PUU3 and PUU4 shows a grain LC texture [10,13a–c]. In order to assist viewing this important two-brush point singularity, Fig. 4e and f provides a magnified portion of the photomicrographs of PUU1 (from Fig. 4a) and PUU2 (from Fig. 4b) respectively, in which an arrow designates the two-brush point singularity. Because of their electrostatic interactions, the ionic groups in the domains; this forces the soft main chains of the (PUUI and PUU2) hexyl units to fold and form a nematic threaded like LC [13h]. Such observations of texture variations with mesogens were made by Szczepaniak [13i]. In PUU3 and PUU4 ($\overline{M}_n = 29,000$ and $30,000$) respectively, due to difference in the molecular weight and temperature anneal cycles to coarsen the mottled the sand-like texture. Mesophase variation is observed when the diisocyanate is changed from aliphatic to aromatic. In the PUUs containing the aromatic diisocyanates MDI and TDI, grain texture is observed and in the PUUs containing the aliphatic diisocyanates HDI and IPDI exhibits threaded texture.

In each PUU sample, a mechanical force, such as slight shearing of the melt, caused microscopic orientation of the double axial domain. The low viscosity, which was temporarily induced by the slight shearing, also gives evidence for the presence of mesophases in PUUs1–4 [1a,14]. Patterns in the effects of lateral substituents upon the type of mesophase observed are hard to formulate, due to the large number of variables which must be considered, such as the structure of the mesogen and the type, size, and position of the substitutent [12,15–17].

X-ray scattering was used to verify the existence of a liquid crystalline phase and to confirm the nature of the phase observed by the DSC and POM. The least-ordered liquid crystal phase is the nematic phase [17e]. The diffractogram of the PUU1 copolymers

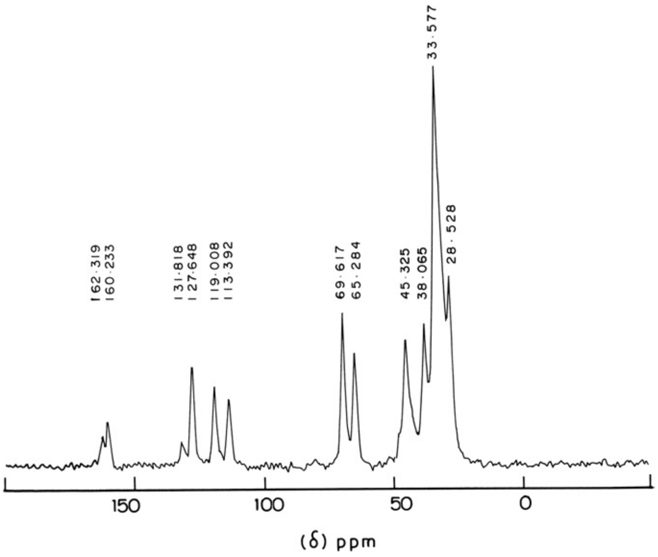


Fig. 2. CP/MAS ^{13}C NMR spectrum (ppm) of PUU1.

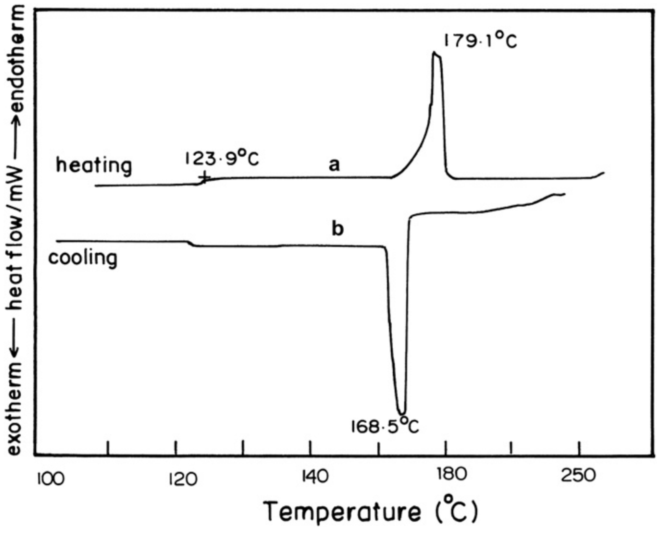


Fig. 3. DSC cooling traces of PUU2 (IPDI).

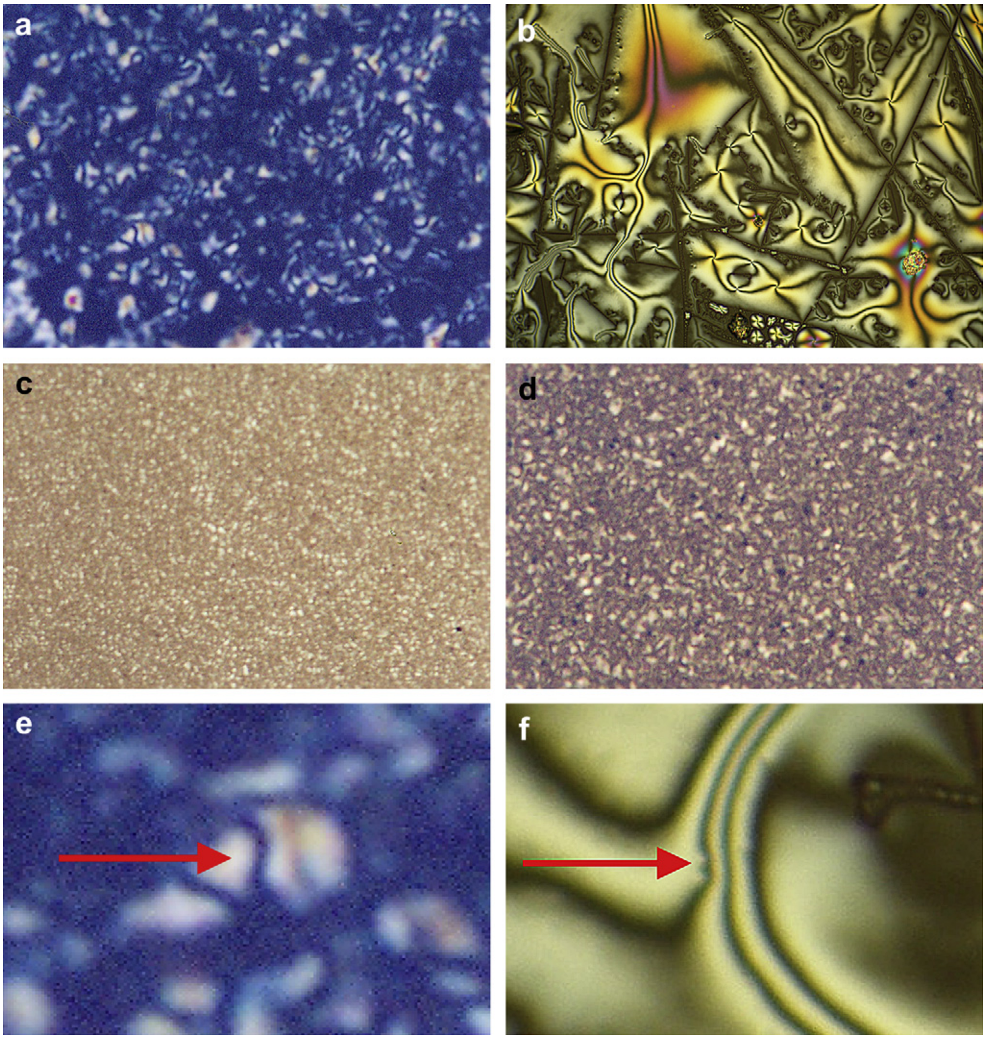


Fig. 4. Photomicrographs (cooling, liquid crystal texture 100×): (a) PUU1 at $T = 130$ °C, (b) PUU2 at $T = 126.8$ °C, (c) PUU3 at $T = 110.3$ °C, (d) PUU4 at $T = 116.1$ °C, (e) detail of Fig. 4a, and (f) detail of Fig. 4b.

(Fig. 5a) was similar to that of PUU2 shown in Fig. 5b as a representative example. The diffraction pattern obtained from powder samples at room temperature exhibited some sharp peak reflections in the wide angle region ($2\theta = 19$–$25°$) consistent with their amorphous nature [17e–f]. No peak was observed in the low angle region (see Fig. 5a–b). The location and relative intensities confirmed the presence of a nematic mesophase [23d]. WAXD studies indicated that the synthesized PUU copolymers possessed LC properties and exhibit a nematic phase [23f,g].

There are insufficient data to conclude definitely whether the LCs are nematic or smectic, but determinants found in other systems enable predictions through analogy. (1) According to Gray

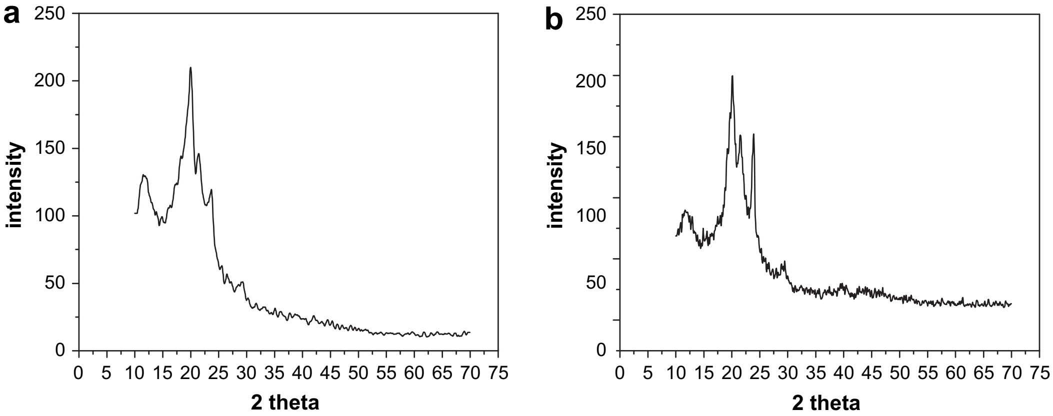


Fig. 5. Wide-angle X-ray diffractogram of (a) PUU1 and (b) PUU2.

[11a] and Han [18], lateral substitution results in additional molecular twisting (a steric effect), hinders molecular packing [19a], and depresses smectic properties greatly. This decreased crystallization is reasonable, because the steric requirements caused by chain periodicity inhibit crystallization markedly, and the resulting reduced crystalline order is a characteristic of the nematic phase [11a]. (2) Ionomeric pendants, which are attached to the polymer backbone via hard segments (ionic incorporation), lead to decreased crystallinity for the PUUs [5,19,20]. The presence of sulfonate ionic groups in the PUU1–4 main chain urea segments might be expected to depresses smectic properties in these PUUs similarly. (3) The grain textures observed for TDI and MDI based PUUs are similar to those previously observed for other reported nematic mesophases [13a–c]. (4) The combination of both twofold and fourfold brush arrangements such as those observed in Fig. 4b and f is reported [1b,13d] to be a characteristic of schlieren texture and typical of a nematic phase [13e–g]. The above conclusions from previous reports in other polymeric systems indicate that this new PUU could be a nematic LC, and additional studies exploring this possibility are planned.

3. Conclusion

Upon cooling, each PUU described herein exhibits a liquid crystal mesophase. Both structure and properties of each PUU depend upon the isocyanate used in its synthesis; although PUUs1–4 have different isocyanate precursors, all are monotropic LCs. Due to the combination of (1) their thermotropic liquid crystal properties, (2) their low ($\overline{M}_n$) molecular weights (~25,000–30,000), (3) the presence of ionomers on their main chain polymers, and (4) their possible lower order in liquid crystals [11a,21], these new ionic PUU LCs could have unusual physical properties which merit study.

4. Experimental section

4.1. Materials

4,4′-Dihydroxybiphenyl, hexane-1,6-diol, 2,5-diaminobenzenesulfonic acid, 1,6-diisocyanatohexane (HDI), 5-isocyanato-1-(isocyanatomethyl)-1,3,3,-trimethylcyclohexane (IPDI), 2,4-diisocyanato-1-methyl-benzene (2,4-TDI), and methylenebis(4-phenylisocyanate) (MDI) were purchased from Aldrich. All other chemicals and solvents were of analytical grade or better and used as obtained.

4.2. Synthesis of PUUs

To obtain each polyurethane-urea (PUU), the diisocyanate was reacted with 4,4′-bis(6-hydroxyhexoxy)biphenyl (BHHBP) in order to give the isocyanate terminated polyurethane prepolymer. The BHHBP was obtained eq. (1) in 86% yield, by using a previously reported method [1a]. In each of the following steps, the system was gently purged with nitrogen. The BHHBP was dissolved in THF and then heated to 70 °C for 30 min. A diisocyanate in THF was added slowly in order to yield the isocyanate (NCO) terminated polyurethane prepolymer. When the NCO content reached 5.5%, as determined by using an *n*-dibutylamine titration method [22], a solution of the ionic chain extender sodium 2,5-diaminobenzenesulfonate (DBS) and *N*-methyl-2-pyrrolidone (NMP) in THF [22], was added slowly to the prepolymer at 50 °C. After 30 min, 0.001% of dibutyltin dilaurate (DBTDL) in THF (the catalyst) was added. The reaction temperature was raised to 70 °C and maintained for at least two hours until all NCO groups were reacted, as confirmed by the disappearance of the IR absorption band at 2272 cm^{-1} (C=N stretch) [22]. The mixture was poured into cold methanol, and the product was filtered and re-precipitated. PUUs were obtained by iterating 4 times through the above solution polymerization procedure.

4.3. Characterization of PUUs

FTIR (Nicolet Impact 400 Spectrophotometer) was used for structural characterization of the thermotropic liquid crystalline PUUs as KBr pellets (sample:KBr = 1:80). The PUUs were also characterized by using cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR. The ^{13}C NMR spectrum was obtained at room temperature by using a 300 MHz FT-NMR spectrometer (Brucker MSL 300P). The resulting spectrum from the MAS experiment was recorded by spinning the sample at the magic angle of 54.74° with respect to the external magnetic field and with a spinning frequency of 4.0 kHz, in order to avoid overlapping the spinning side bands of other resonance lines [1d,23]. Contact time for the CP process was 2.0 ms, and the recycle time after acquisition of the free induction decay was 5 s [23b]. The molecular weight of each PUU was determined by vapor-phase osmometer (VPO) (KANUER vapor-phase osmometer), in THF solvent at 45 °C, with benzyl (Ph–CO–CO–Ph) as standard. The textures of the LC PUUs were observed by using a cross polarized optical microscope (POM) equipped with a hot stage (OLYMPUS BX50 polarizing microscope, which had a LINKAM THMS 600 heating stage and digital camera). Thermal properties of the PUUs were determined by differential scanning calorimetric (DSC) and by thermogravimetric analysis (TGA). Each DSC (A Seiko SSC 5200H thermal analysis unit attached to a DSC module) thermogram was obtained in nitrogen atmosphere at a heating rate of 5 $^\circ\text{C min}^{-1}$. Thermal stability was also determined by using a TG/DTA 220 module under nitrogen atmosphere, with a heating rate of 15 $^\circ\text{C min}^{-1}$. Wide-angle X-ray diffraction (WAXD) experiments were performed at room temperature [23d] on powder samples using a Seifert JSO debyeflex diffractometer; operating at 30 mA; 40 kV with Cu Kα radiation at a scanning rate of $0.02^\circ\ \text{s}^{-1}$.

Acknowledgments

We acknowledge the National Science Foundation and the Ford Foundation for support. SNJ appreciates financial support from the Science and Engineering Research Council, Department of Science and Technology (SERC-DST) India.

References

[1] (a) ACS symposium series 435. In: Weiss RA, Ober CK, editors. Liquid-crystalline polymers. Washington, DC: American Chemical Society; 1990;
(b) Donald AM, Windle AH. Liquid crystalline polymers. 1st ed. Cambridge, UK: Cambridge University Press; 1992. p. 232;
(c) ACS symposium series 632. In: Isayev AI, Kyu T, Cheng SZD, editors. Liquid-crystalline polymer systems. Washington, DC: American Chemical Society; 1996;
(d) Narasimhaswamy T, Lee DK, Yamamoto K, Somanathan N, Ramamoorthy A. J Am Chem Soc 2005;127:6958–9;
(e) Gao X, Liu R, Zhang J. Ind Eng Chem Res 2008;47:2590–6;
(f) Xue Y, Hara M, Yoon H. Macromolecules 2001;34:844–51;
(g) Zhang A, Zhang B, Feng Z. J Appl Polym Sci 2002;85:1110–7.

[2] (a) Papadimitrakopoulos F, Hsu SL, MacKnight WJ. Macromolecules 1992;25:4671–81 and references therein;
(b) Sheth JP, Aneja A, Wilkes GL. Polymer 2004;45:5979–84;
(c) Santerre J, Brash J. Ind Eng Chem Res 1997;36:1352–9.

[3] (a) Sheth J, Wilkes G, Fornof A, Long T, Yilgor I. Macromolecules 2005;38:5681–5;
(b) Curgul S, Yilgor I, Yilgor E, Erman B, Cakmak M. Macromolecules 2004;37:8676–85;
(c) Sung CSP, Hu C. Macromolecules 1981;14:212–5;
(d) Wolinska-Grabczyk A, Muszynski J, Penczek P. Polymer 1997;42:55–8;
(e) Stebani U, Lattermann G, Wittenberg M, Wendorff JW. J Mater Chem 1997;7:607–14;
(f) Simoes M, de Campos A. Phys Rev E 2004;69:061704/1–9;

(g) Wolinska-Grabczyk A, Muszynski J, Penczek P. Proc SPIE Int Soc Opt Eng 1998;3319:297–300;
(h) Figueiredo Neto AM, Godinho MH, Toth-Katona T, Palffy-Muhoray P. Braz J Phys 2005;35:184–9;
(i) Leea SM, Chena C, Wang C. Electrochim Acta 2003;48:3699–708;
(j) Leea SM, Chena C, Wang C. Electrochim Acta 2004;49:4907–13;
(k) Shevchenko VV, Vasil'evskaya GA, Loshkareva SN. Plasticheskie Massy 1987;9:32–4.

[4] (a) Xue Y, Hara M. Macromolecules 1997;30:3803–12;
(b) Xue Y, Hara M. Polymer 2005;46:7293–300.

[5] Xue Y, Hara M, Yoon H. Macromolecules 1998;31:7806–13.

[6] (a) He J, Liu J. J Appl Polym Sci 1998;67:2141–51;
(b) Binnemans K. Chem Rev 2005;105:4148–204;
(c) Kim SY, Kim JY, Kim SH. Polym Int 2008;57:378–84;
(d) Ghadage RS, Ponrathnam S, Nadkarni VM. J Appl Polym Sci 1989;37: 1579–88;
(e) Kihara H, Kishi R, Miura T, Kato T, Ichijo H. Polymer 2001;42:1177–82.

[7] Mattia J, Painter P. Macromolecules 2007;40:1546–54.

[8] Wang HL, Kao HM, Digar M, Wen T. Macromolecules 2001;34:529–37.

[9] (a) Nomula S, Cooper SL. Macromolecules 2001;34:2653–9;
(b) Eisenberg A, Kim JS. Introduction to ionomers. New York: Wiley & Sons; 1998. p. 2;
(c) Oswald P, Pieranski P, Constantin D. Nematic and cholestric liquid crystals: concepts and physical properties illustrated by experiments. In: Gray GW, Goodby JW, Fukuda A, editors. The liquid crystals book series, vol. 1. Boca Raton, FL: CRC Press; 2005.

[10] Wang XJ, Zhou QF. Liquid crystalline polymers. New Jersey: World Scientific Pub; 2004. p. 209–23;
(b) Mormann W, Brahm M. Makromol Chem Phys 1995;196:529–42;
(c) Tanaka M, Nakaya T. J Macromol Sci Chem 1987;A24:777–85.

[11] (a) Gray GW. Molecular structure and the properties of liquid crystals. New York: Academic Press; 1962. p. 13–4;
(b) Itoh M, Lenz RW. J Polym Sci Part A 1991;29:1407–19.

[12] Kumar S. In: Kumar S, editor. Liquid crystals: experimental study of physical properties and phase transitions. Cambridge, UK: Cambridge University Press; 2001. p. 29–64, 444–5.

[13] (a) Padmavathy T, Srinivasan KSV. J Polym Sci Part A 2002;40:1527–38;
(b) Sakthivel P, Kannan P. Polym Int 2005;54:1490–7;
(c) Kumar RM, Balamurugan R, Kannan P. Polym Int 2007;56:1230–9;
(d) Slaney AJ, Takatoh K, Goddby JW. Defect textures in liquid crystals. In: Elston S, Sambles R, editors. The optics of thermotropic liquid crystals. 1st ed. Colchester, UK: Taylor & Francis; 1998. p. 334–40;
(e) Tang H, Zhu Z, Wan X, Chen X, Zhou Q. Macromolecules 2006;39:6887–97;
(f) Kricheldorf HR, Richter M, Schwarz G. Macromolecules 2002;35:5449–53;
(g) Watanabe J, Harkness BR, Sone M, Ichimura H. Macromolecules 1994;27:507–12;
(h) Martin-Rapun R, Marcos M, Omenat A, Barbera J, Romero P, Serrano JL. J Am Chem Soc 2005;127:7397–403;
(i) Szczepaniak B, Frisch KC, Penczek P, Mejsner J, Leszczynska I, Rudnik E. J Polym Sci Polym Chem Ed 1993;31:3223–30;
(j) Srinivasan KSV, Padmavathy T. Macromol Symp 2003;199:277–93.

[14] Smyth G, Valles EM, Pollack SK, Grebowicz J, Stenhouse PJ, Hsu SL, et al. Macromol Symp 1990;23:3389–98.

[15] (a) Andersch J, Tschierske C. Liq Cryst 1996;21:51–63;
(b) Pugh C, Pukun Z. Polym Prepr (Am Chem Soc Div Polym Chem) 1999;40: 534–5.

[16] Arehart SV, Pugh C. J Am Chem Soc 1997;119:3027–37.

[17] (a) Zhou QF, Li HM, Feng XD. Macromolecules 1987;20:233–4;
(b) Hessel F, Finkelmann H. Polym Bull 1985;14:375–8;
(c) Kim GH, Pugh C, Cheng SZD. Macromolecules 2000;33:8983–91;
(d) Pugh C, Schrock RR. Macromolecules 1992;25:6593–604;
(e) Vries Adriaan de. Mol Cryst Liq Cryst 1985;131:125–45;
(f) Minli X, Chaocan Z. Liq Cryst 2007;34:12751283.

[18] Chang S, Han CD. Macromolecules 1996;29:2103–12.

[19] (a) Zhang D, Zhou QF, Ma YG, Wang XJ, Wan XH, Feng XD. Liq Cryst 1997;23: 357–63;
(b) Quiram DJ, Register RA, Ryan AJ. Macromolecules 1998;31:1432–5.

[20] (a) Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23:4098–107;
(b) Baumeister U, Kosturkiewicz Z, Hartung H, Demus D, Weissflog W. Liq Cryst 1990;7:241–9.

[21] (a) Barmatov EB, Obrascov AA, Pebalk DA, Barmatova MV. Colloid Polym Sci 2004;282:530–4;
(b) Chang S, Han CD. Macromolecules 1997;30:1670–84;
(c) Bashir Z, Khan N. J Polym Sci Part B Polym Phys 1996;34:2077–84;
(d) Khan N, Patel VL, Bashir Z, Price DM. J Polym Sci Part B Polym Phys 1995;33:1957–67;
(e) Gaehde J, Pohl MM, Mix R, Dany R, Hinrichsen G. Adv Urethane Sci Technol 1996;13:140–66;
(f) Mix R, Gaehde J, Goering H, Schulz G. J Polym Sci Part A Polym Chem 1999;34:33–44;
(g) Mix R, Goering H, Schulz G, Gruendemann E, Gaehde J. J Polym Sci Part A Polym Chem 1995;33:1523–36;
(h) Pohl MM, Dany R, Mix R, Gaehde J, Hinrichsen G. Polymer 1996;37:2173–7.

[22] Jaisankar SN, Lakshiminarayana Y, Radhakrishnan G. Adv Polym Technol 2004;23:24–31.

[23] (a) Schaefer J, Stejskal E, Buchdahl R. Macromolecules 1977;10:384–405;
(b) Ishida H, Kaji H, Horii F. Macromolecules 1997;30:5799–803;
(c) Shekar SC, Lee DK, Ramamoorthy A. J Magn Reson 2002;157:223–34;
(d) Changhai H, Chaocan Z, Minli X, Shuangqing Z. Liq Cryst 2008;35: 1321–8;
(e) Sang OK, Chong MK, In JC, Hee-Tae J. Macromolecules 2001;34:8961–7;
(f) Sang OK, In JC. Macromolecules 2000;33:7549–56.