Scientific Paper

Hydrogen-Bonded Liquid-Crystalline Polyurethane Complexes with 4-Dodecyloxybenzoic Acid†

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Received 02-06-2005

† Dedicated to the memory of Prof. Dr. Tatjana Malavašič

Abstract

We prepared novel hydrogen-bonded liquid-crystalline polyurethane complexes from 4-dodecyloxybenzoic acid and polyurethane containing pyridyl units in the main chain, based on 2,6-bis(hydroxymethyl)pyridine. The complexes were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffractometry. The liquid-crystalline polyurethane complexes were formed at acid/pyridine molar ratios up to 0.4 exhibiting crystal-smectic and smectic-nematic transitions similar to those of the polyurethane complexes with pendant pyridyl units reported on recently. The analogous low-molar mass urethane complex exhibited lower isotropization temperature and a less ordered smectic phase than the polymeric complexes.

Key words: supramolecular polyurethanes, hydrogen bonding, 4-dodecyloxybenzoic acid, liquid-crystalline polymers (LCP)

Introduction

An important class of supramolecular polymers that self-assemble via hydrogen bonding into well-defined structures are liquid crystalline polymers. In contrast to supramolecular main-chain liquid crystalline polymers, where self-assembled bifunctional monomeric units with two complementary groups (H-bond donor and H-bond acceptor) are incorporated into the polymer backbone, the mesogens in supramolecular side-chain liquid crystalline polymers (SCLCP) are attached onto the polymer backbone directly or via a flexible spacer.[1–3] In these systems, liquid crystallinity is induced through hydrogen bonding interactions between complementary binding sites on the polymer main-chain and low molar mass rigid mesogens.[4–8] A number of supramolecular SCLCPs have been prepared, among which H-bonds between pyridyl and carboxylic acid functional groups are the most frequently used.[8–17]

Various synthetic strategies are used for the preparation of supramolecular hydrogen- bonded SCLP polymers. A mesogenic low molar mass compound can be attached to a pendant binding site on the polymer main chain[10] or the side chain with the mesogenic unit can be bound to the polymer backbone through an H-bond connector.[11] In both cases, a flexible spacer decouples the motion of the polymer main chain from the motion of the anisotropically oriented mesogenic side chain. Additionally, a small rigid molecule with an aliphatic tail can self-assemble with a complementary unit in the polymer backbone without a flexible spacer.[13,14] We have recently described a novel synthetic route for supramolecular SCLC polyurethanes formed by self-assembly via intermolecular hydrogen bonding between small rigid molecules with aliphatic tails (4-alkoxybenzoic acids) and complementary pyridyl units on pendant binding sites on the polyurethane chain (PUPyA, based on *N*,*N*-bis(2-hydroxyethyl)isonicotinamide).[15–17] The length of the aliphatic tail has an important influence on the stability of the supramolecular SCLCP.[17]

In this contribution, we report on novel hydrogen-bonded liquid-crystalline polyurethane complexes prepared by the self-assembly of 4-dodecyloxybenzoic acid (DOBA) as the H-bond donor and polyurethane containing complementary pyridyl units in the main chain, based on 2,6-bis(hydroxymethyl)pyridine (PUPyB or PUPyBNPG), as the H-bond acceptor. We also studied the miscibility of DOBA with the analogous low molar mass urethane PyB. The complexes were investigated by using differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffractometry (XRD).

Results and discussion

The thermal properties of polyurethanes and their mixtures with DOBA were determined using differential scanning calorimetry (DSC). We have already shown

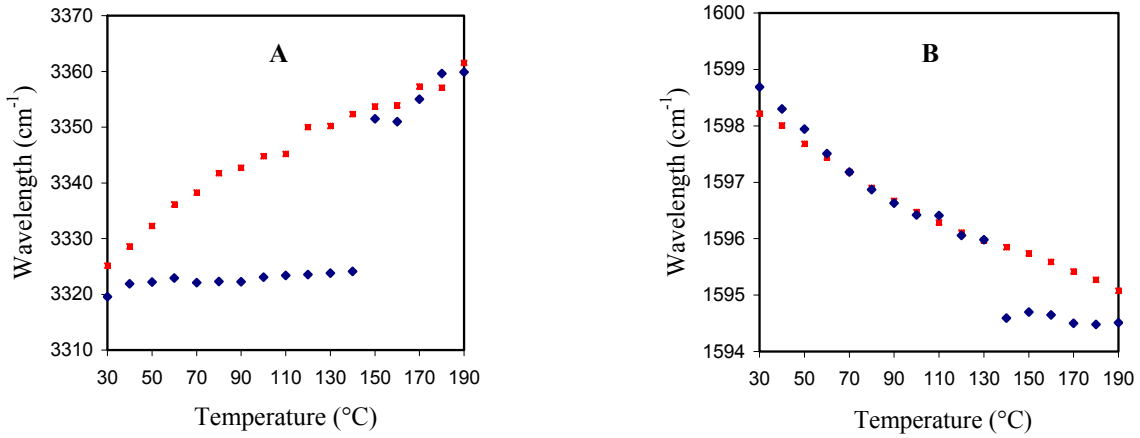


Figure 1. The temperature dependence of (A) N-H and (B) pyridine C=N stretching vibration wavelengths for PUPyB (**2**) taken during the first (♦) and second (■) heating.

that polyurethanes without pyridyl units in their backbones are practically immiscible with DOBA (below molar ratio 0.1).[17] In this case, dimerization of the acid molecules is a thermodynamically more favorable process than their binding to the urethane >C=O and/or –NH– groups.

During the slow drying and annealing of the polyurethane PUPyB (**2**) above the glass transition temperature (T_g), i.e. at 50 °C, the polyurethane segments tend to order as a consequence of their enhanced mobility. The first DSC heating curve of **2** therefore shows a broad melting transition peak (142 °C), which represents the non-linear hydrogen bonding dissociation between pyridine =N– or urethane >C=O and –NH– groups as shown by IR spectroscopy (Figure 1). During the second and third heating (10 °C/min), after the thermal treatment, the hydrogen bonds cleave gradually (Figure 1) and the polymer is amorphous with a T_g at 40 °C. However, it is known that urethane bonds dissociate and reassociate simultaneously above the critical temperature which is for polyurethane elastomers above 150 °C. It increases with the increasing hard segments content[18] or, in other words, crystallization stabilizes the urethane bond.[19] The temperature dependent dissociation of urethane bonds results in molar mass decrease thus influencing the polyurethane properties considerably.[20] Though polyurethane **2** consists of hard segments only it is likely that its molar mass decreases to some extent at temperatures above 160 °C[17] which may influence the stability of intra- and/or *homo*-intermolecular H-bonds of PUPyB molecules.

The DOBA/PUPyB mixtures were prepared in different molar ratios. The second heating DSC curve of DOBA/PUPyB = 0.1 consists of a T_g at 42 °C and three endothermic transitions: the peaks at 77 and 89 °C are due to transitions between highly ordered mesophases, and the endothermic transition at 141 °C is due to the PU main-chain melting. The cold crystallization transition is at 111 °C (Figure 2A).

The neat polyurethane PUPyB only exhibits a T_g at 40 °C and has no melting transitions during the second and third heating cycles (heating rate 10 °C/min). In the complex DOBA/PUPyB=0.1, the associated acid molecules slightly decrease the mobility of the polyurethane component and simultaneously facilitate the ordering of polymer segments, which interact mutually through hydrogen bonding. Above the molar ratio DOBA/PUPyB=0.1, a phase separation occurs, i.e. the DSC heating and cooling thermograms consist of additional transitions of DOBA molecules alone (Figure 2B). At the same time, the melting enthalpy values of PUPyB decrease with increasing amounts of DOBA. We have deduced that the non-bonded dimeric acid molecules most probably insert between the polymer chains of PUPyB and thus prevent the formation of polyurethane crystalline domains.

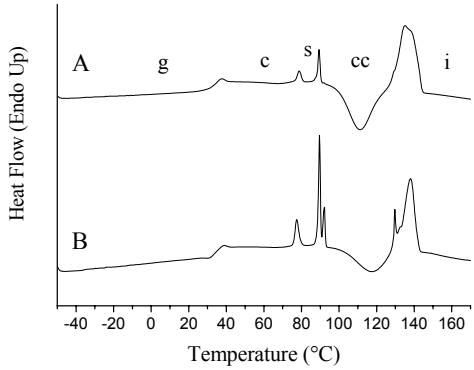


Figure 2. The second heating DSC curves (10 °C/min) of DOBA/PUPyB polyurethane complexes in various molar ratios: (A) 0.1 and (B) 0.3; g – glassy amorphous phase, c – crystal phase, s – smectic phase, cc – cold crystallization, i – isotropic phase.

It is known that the degree of crystallinity of polymers depends on the primary chemical structure,

which in turn determines the flexibility or stiffness of the main-chain and the types of non-covalent interactions between functional groups, all of which influence the polymer's conformation. The PUPyB with a heteroaromatic ring in the main-chain is more rigid than the PUPyA with a pyridyl unit as the pendant group. The linear chains of PUPyB without side groups and consequently no steric effects can easily interact through hydrogen bonding. As a result, PUPyB shows a tendency to crystallize and has, at comparable molar masses and polydispersities, a higher T_g than PUPyA (24 °C[16]). Additionally, the accessibility of the pyridyl group in PUPyB is lowered by intramolecular or *homo*-intermolecular hydrogen bonding with the urethane –NH– group. On the other hand, the pendant pyridyl unit in PUPyA as a side group introduces a structural irregularity to the polymer and is more accessible for the formation of H-bonds with DOBA.

In order to avoid crystallization of PUPyB, we synthesized amorphous PUPyBNPG from HDI, HMP, and NPG. The introduction of branched NPG and additional hexamethylene unit in the PUPyBNPG repeat unit enhances flexibility of the backbone (T_g=20 °C) as compared to rigid PUPyB (T_g=40 °C) and improves accessibility of pyridyl units for hydrogen bonding. The structural change in PUPyBNPG prevents the ordering of polymer main-chain segments via hydrogen bonding between pyridyl and urethane groups. In comparison to DOBA/PUPyB systems, the miscibility of the components in DOBA/PUPyBNPG complexes is improved. Similar observation was reported on hydrogen bonding in polymer blends where incorporation of an inert diluent moiety into the main chain reduces the self-associated hydrogen bonds and thereby enhances the formation of inter-associated hydrogen bonds.[21]

The components are miscible up to a mole ratio of 0.4; the obtained complexes are enantiotropic (Figure 3). The DSC cooling curves consist of overlapping nematic-smectic and smectic-crystal transitions. The T_g increases from 20 °C for PUPyBNPG to 29 °C for DOBA/PUPyBNPG=0.4 meaning that the introduction of DOBA leads to more stiff polymeric complexes in comparison to pure PUPyBNPG. The temperatures of the crystal-smectic and smectic-nematic transitions are at around 80 and 90 °C, respectively, and slightly decrease, whereas the isotropization temperature increases with an increasing molar ratio between DOBA and PUPyBNPG repeat unit from 106 °C for DOBA/PUPyBNPG=0.2 to 121 °C for DOBA/PUPyBNPG=0.3, and 125 °C for DOBA/PUPyBNPG=0.4. On the other hand, these temperatures are similar to those of DOBA/PUPyA complexes prepared with polyurethane with a pendant pyridyl unit, based on *N,N*-bis(2-hydroxyethyl)isonicotinamide.[15,16] We do not have an explanation for such behavior, since we expected changes in thermal properties due to the structural change in the backbone. However, similar behavior has been reported for complexes of polyacrylates with different spacer lengths of the complementary side-group bonding units and *trans*-(4-methoxy-4'-stilbazoles) or *trans*-(4-hexyloxy-4'-stilbazoles). The transition temperatures of the liquid-crystalline phases of the complexes did not change with structural modification of the polymeric component.[12]

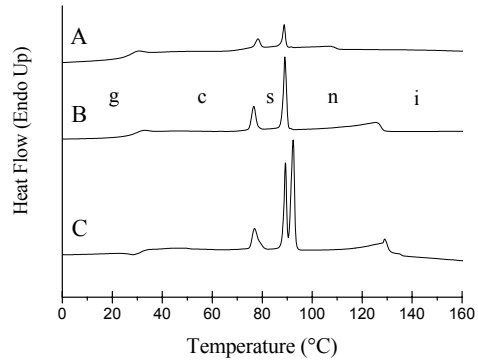


Figure 3. The second heating DSC curves (10 °C/min) of polyurethane complexes DOBA/PUPyBNPG with various molar ratios: (A) 0.1, (B) 0.4, and (C) 0.8; g – glassy amorphous phase, c – crystal phase, s – smectic phase, n – nematic phase, i – isotropic phase.

The high-angle regions in the X-ray diffractograms of DOBA/PUPyBNPG complexes, taken at room temperature, consist of an intensive diffraction signal distinctive of the distance between the side-chains. For the DOBA/PUPyBNPG=0.4 complex this signal is at 2θ=24.0° (3.7 Å), whereas in the diffractogram of DOBA/PUPyA=0.4 it is at 24.1° (3.1 Å). Evidently, the large distance between two pyridyl units in the PUPyBNPG repeat units does not have a significant effect on the ordering of side-chains. We presume that flexible oligomethylene units between pyridyl units of PUPyBNPG take on a random coil conformation that enables tighter contacts between the mesogenic side groups. Similarly, it was shown that the crystal-to-smectic transitions of the complexes of polyamides containing 2,6-diaminopyridine units and 3-substituted 4-alkoxybenzoic acid derivatives hardly changed with increasing numbers of methylene units between the main-chain pyridyl groups.[14] Eblinger and coworkers came to similar conclusion when they studied the influence of the length of oligomethylene chains between functional groups on the free energy of association for the series of complexes consisting of α,ω-dicarboxylates as H-bond acceptors and α,ω-diamides as H-bond donors, respectively. The $\Delta G_{association}$ values did not change drastically dependent on the number of $-CH_2-$ groups (up to the limit value). The flexible

aliphatic chains occupy the conformation defined by noncovalent interactions of complementary binding sites.[22]

The XRD signals representing a layered structure (smectic mesophase) in the complex DOBA/PUPyBNPG=0.4 at 85 °C are at higher angles and smaller distances between the layers than in DOBA/PUPyA complexes (Figure 4). The fourth order Bragg signal for DOBA/PUPyBNPG=0.4 is at 7.7° (45.0 Å), whereas for DOBA/PUPyA=0.4 it is at 7.3° (48.5 Å). The length of the fully extended *trans* planar conformation of the side chains of DOBA/PUPyBNPG complexes, based on a computational model, is 25.3 Å. This value is 1.8 times smaller than the smectic bilayer thickness (45.0 Å), which indicates that the interdigitation of oligomethylene chains is less intensive than in DOBA/PUPyA=0.4 where this length is 1.6.

In order to investigate the liquid-crystalline behavior of the low molar mass complex with the same mesogenic moiety as PUPyB, we synthesized urethane PyB (**4**). The 1:1 complex of **4** and DOBA shows a smectic phase, which is stable within a narrow temperature range (82–95 °C). The first heating DSC thermogram (10 °C/min) consists of two endothermic peaks at 85 and 95 °C (Figure 5A), whereas the second heating DSC curve has additional two-phase transitions present as well. The exothermic transition at 35 °C represents the formation of a new crystal phase, which melts at 77 °C (Figure 5B).

Figure 6 shows the X-ray diffractogram of the DOBA/PyB complex in the smectic phase obtained at 85 °C. The low angle diffraction peaks of the second, third, and fifth order represent the distance between smectic layers (34.1 Å). In the wide-angle region there is a diffuse signal called the Bragg reflection at approximately 2θ~20° (4.4 Å) due to the intermolecular spacing of the mesogenic units.

Figure 7 shows the crystal phase texture of the DOBA/PyB complex obtained on cooling the isotropic phase to room temperature. We were not able to obtain clear optical textures of the smectic phase, which was probably due to the strong tendency toward crystallization during the thermal treatment.

In comparison with the low-molar mass DOBA/PyB complex, the polymeric DOBA/PUPyBNPG complexes show higher isotropization temperatures and a more ordered smectic phase, which we explain by the denser lateral packing of DOBA along the polymer backbone.

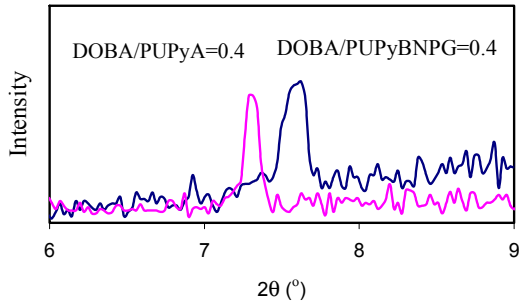


Figure 4. The small angle region in X-ray diffractograms of DOBA/PUPyA and DOBA/PUPyBNPG = 0.4 at 85 °C.

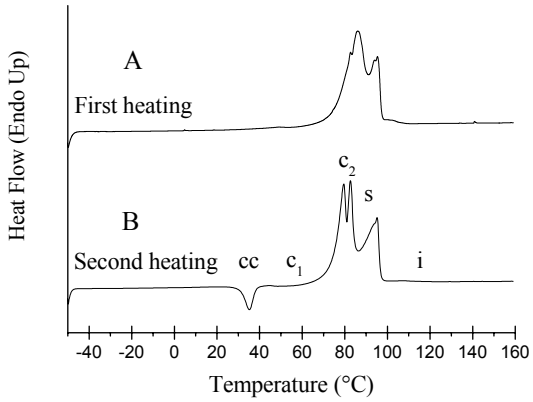


Figure 5. DSC first (A) and second (B) heating thermograms of DOBA/PyB complex; cc – cold crystallization, c – crystal phase, s – smectic phase, i – isotropic phase.

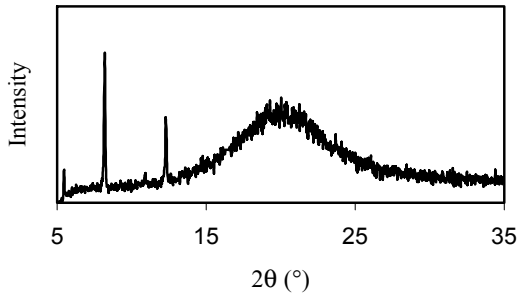


Figure 6. X-ray diffractogram of DOBA/PyB complex at 85 °C.

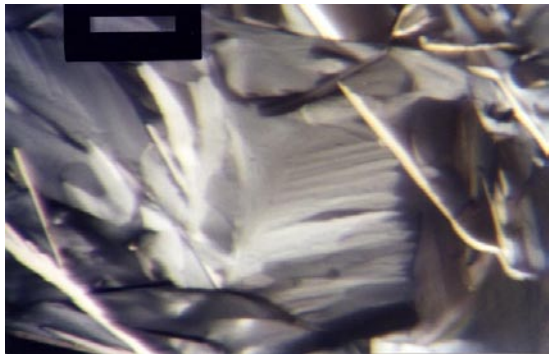
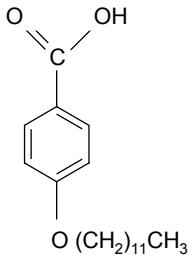


Figure 7. Crystal phase texture of DOBA/PyB complex (magnification 125x).

Experimental

Materials: 2,6-bis(hydroxymethyl)pyridine (HMP), hexamethylene diisocyanate (HDI),

2,2-dimethyl-1,3-propane diol (neopentyl glycol, NPG), and 4-dodecyloxybenzoic acid (DOBA, **1**) were obtained from Aldrich Chemicals and used as received. Compound **1** exhibits a smectic C phase between 94 and 131°C and a nematic phase between 131 °C and 138 °C on heating.

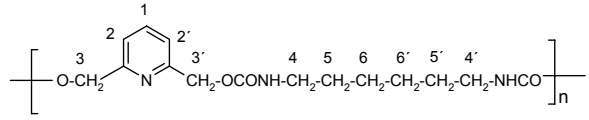


Characterization

The molar mass averages of the synthesized polyurethanes were determined by SEC-MALS on a Wyatt Technology Dawn-DSP instrument equipped with a He-Ne laser (λ_o=633 nm) and an Optilab-DSP differential refractometer. The eluent was 0.01M LiBr in DMF at a flow rate of 0.8 mL/min. Optical textures were obtained using a Carl Zeiss Stemi SV6 polarizing optical microscope equipped with a microscope camera MC 80 and a Mettler Toledo FP82 hot stage. Thermal properties were examined using a Perkin-Elmer DSC-7 differential scanning calorimeter with a heating and cooling rate of 10 °C/min. X-ray diffraction measurements were done by a Siemens D-5000 diffractometer using Cu K_α radiation (λ=1.54 Å). The sample was heated on a Pt-plate to 160 °C and then, prior to the measurements, cooled to room temperature. Infrared spectra were recorded on a Perkin-Elmer FTIR 1725X spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Varian Unity Plus-300 spectrometer at 300 and 75 MHz using TMS as an internal standard and DMSO-d_6 and $CDCl_3$ as solvents. Elemental analyses for C, H, and N were obtained on a Perkin-Elmer CHN Analyzer 2400.

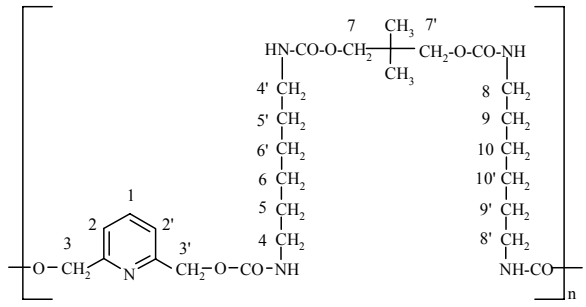
Synthesis of polyurethanes PuPyB (2) and PuPyBNPG (3)

Polyurethane **2** was synthesized from equivalent amounts of 2,6-bis(hydroxymethyl) pyridine (2.9 g, 21 mmol) and hexamethylene diisocyanate (3.4 mL, 21 mmol). The synthesis was carried out in a 20% solution of anhydrous *N*,*N*-dimethylformamide at room temperature under an argon atmosphere for 7 hours. The polymer was precipitated in methanol and dried at 50 °C under vacuum for one week. After thermal treatment, i.e. during the second and third DSC heating (10 °C/min), the polymer showed a glass transition temperature (T_g) at 40 °C, M_n=1.3 x 10^4, and M_w/M_n=1.5.

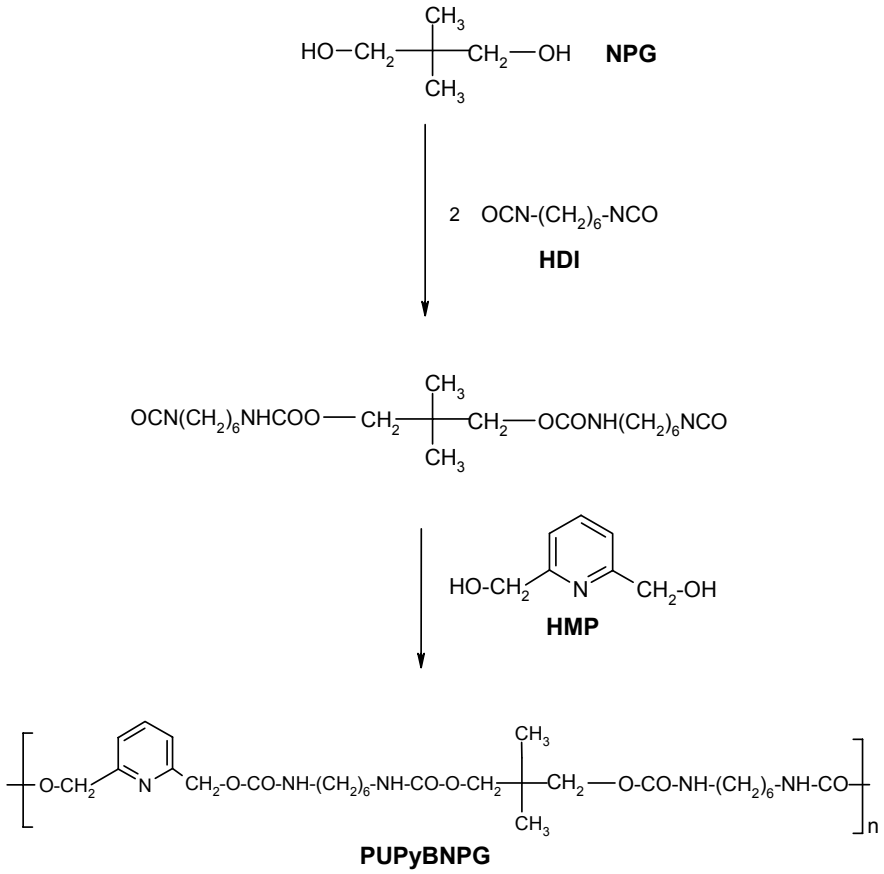


^{1}H NMR (300 MHz, DMSO-d_6) δ 7.83 (t, *J* 7.7 Hz, 1H, H_1), 7.37 (t, 2H, NHCOO), 7.26 (d, *J* 7.7 Hz, 2H, H_2, $H_{2'}$), 5.04 (s, 4H, $2H_3$, $2H_{3'}$), 2.98 (m, 4H, $2H_4$, $2H_{4'}$), 1.40 (m, 4H, $2H_5$, $2H_{5'}$), 1.25 (m, 4H, H_6, $H_{6'}$). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.5 (NHCOO), 155.8 (quaternary C), 137.7 (C_1), 119.9 (C_2, $C_{2'}$), 65.7 (C_3, $C_{3'}$), 40.2 (C_4, $C_{4'}$), 29.3 (C_5, $C_{5'}$), 25.9 (C_6, $C_{6'}$). IR (25 °C, KBr, cm^{-1}) ν 3325 (NH), 1699 (C=O), 1598, 1000 (C=N). Anal. Calcd for $(C_{15}H_{21}N_3O_4)_x$: C 58.61, H 6.90, N 13.67. Found: C 58.63, H 7.13, N 13.91.

Polyurethane **3** was synthesized in two reaction steps (Scheme 1). The first step involved the reaction of 2,2-dimethyl-1,3-propane diol (1.5 g, 14.3 mmol) and hexamethylene diisocyanate (4.8 g, 28.6 mmol) in a 20% solution of anhydrous *N*,*N*-dimethylformamide. The synthesis was carried out at 50 °C under an argon atmosphere for 15 hours. After cooling to room temperature, 2.0 g (14.3 mmol) of 2,6-bis(hydroxymethyl) pyridine was added to the synthesized intermediate diisocyanate. The reaction mixture was stirred for 12 hours at room temperature. The polymer was precipitated in methanol and dried at 50 °C under vacuum for a week. The polymer is amorphous with T_g at 20 °C, M_n=1.5 x 10^4, and M_w/M_n =1.7.



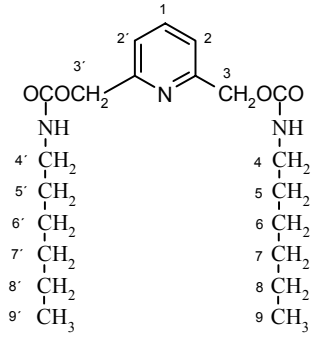
^{1}H NMR (300 MHz, DMSO-d_6) δ 7.83 (t, *J* 7.7 Hz, 1H, H_1), 7.37, 7.06 (t, 4H, NHCOO), 7.24 (d, *J* 7.7 Hz, 2H, H_2, $H_{2'}$), 5.04 (s, 4H, $2H_3$, $2H_{3'}$), 3.72 (s, 4H, $2H_7$, $2H_{7'}$), 2.94 (m, 8H, $2H_4$, $2H_{4'}$, $2H_8$, $2H_{8'}$), 1.40 (m, 8H, $2H_5$, $2H_{5'}$, $2H_9$, $2H_{9'}$), 1.24 (m, 8H, $2H_6$, $2H_{6'}$, $2H_{10}$, $2H_{10'}$), 0.84 (s, 6H, 2 CH_3). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.3, 156.5 (NHCOO); 155.8 (quaternary C), 137.7 (C_1), 119.9 (C_2, $C_{2'}$), 68.6 (C_7, $C_{7'}$), 65.7 (C_3, $C_{3'}$), 40.3 (C_4, $C_{4'}$), 40.2 (C_8, $C_{8'}$), 29.3(C_5, $C_{5'}$), 29.9 (C_9, $C_{9'}$), 26.1(C_6, $C_{6'}$), 25.9 (C_{10}, $C_{10'}$), 21.4 (2 CH_3). IR (25 °C, KBr, cm^{-1}): ν 3340 (NH), 1710 (C=O), 1596 (C=N). Anal. Calcd for $(C_{28}H_{45}N_5O_8)_x$: C 58.00, H 7.84, N 12.08. Found: C 57.75, H 8.21, N 12.27.



Scheme 1

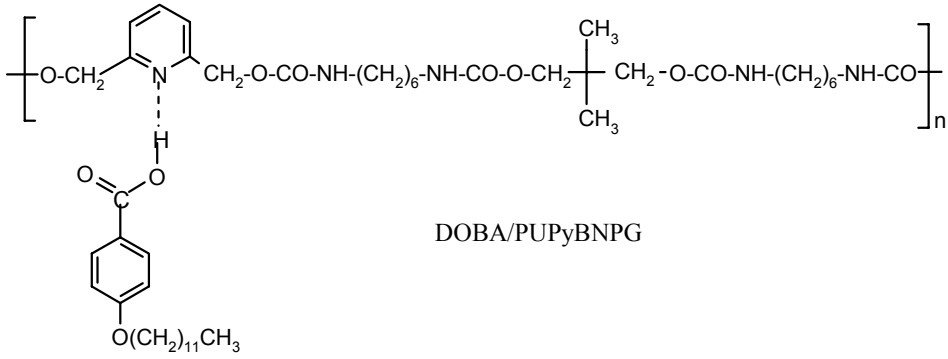
Synthesis of hexylcarbamic acid (6-hexylcarbamoyloxymethyl)-(pyridine-2-yl)-methyl ester PyB (4).

A mixture of 2,6-bis-(hydroxymethyl)-pyridine (6.0 g, 28.5 mmol) and hexyl isocyanate (9.1 g, 71.4 mmol) in DMF (40 mL) was heated at 80 °C for 24 h under an argon atmosphere. The reaction mixture was allowed to cool and precipitated in water. The precipitate was filtered and extracted several times with chloroform; the organic layer was washed with water and dried with sodium sulfate. After evaporation of the solvent, the crude product was purified on a silica-gel column using ethyl acetate. The product was crystallized from ethyl acetate/n-hexane.



Yield 76%. mp 89 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.83 (t, *J* 7.8 Hz, 1H, H_1), 7.36 (t, *J* 5.7 Hz, 2H, NHCOO,), 7.26 (d, *J* 7.8 Hz, 2H, H_2, $H_{2'}$), 5.04 (s, 4H, $2H_3$, $2H_{3'}$), 2.50 (m, 4H, $2H_4$, $2H_{4'}$), 1.40 (m, 4H, $2H_5$, $2H_{5'}$), 1.25 (m, 12H, $2H_6$, $2H_{6'}$, $2H_7$, $2H_{7'}$, $2H_8$, $2H_{8'}$), 0.86 (t, *J* 4.2 Hz, 6H, $3H_9$, $3H_{9'}$). ^{13}C NMR (75 MHz, DMSO-d_6) δ 156.5 (NHCOO), 155.8 (quaternary C), 137.6 (C_1), 119.9 (C_2, $C_{2'}$), 65.7 (C_3, $C_{3'}$), 40.3 (C_4, $C_{4'}$), 29.3 (C_5, $C_{5'}$), 30.9 (C_6, $C_{6'}$), 25.9 (C_7, $C_{7'}$), 22.0 (C_8, $C_{8'}$), 13.9 (C_9, $C_{9'}$). IR (25 °C, KBr, cm^{-1}) ν 3317 (NH), 1686 (C=O), 1596 (C=N). Anal. Calcd for $C_{21}H_{35}N_3O_4$: C 64.08, H 8.98, N 10.68. Found: C 64.15, H 9.25, N 10.68.

Preparation of the hydrogen-bonded complexes: All hydrogen-bonded complexes (Chart 1) were prepared by mixing the components in the molten state for 10 min at 160 °C under an argon atmosphere. The molar ratios between 1 and polymer repeat units in 2 and 3 were 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, and 1.0, whereas the molar ratio between 1 and 4 was 1:1. The products were cooled to room temperature and used for the measurements.



DOBA/PUPyBNPG

Chart 1

Conclusions

We prepared novel hydrogen-bonded liquid-crystalline polyurethane complexes from 4-dodecyloxybenzoic acid (DOBA) and polyurethane containing pyridyl units in the main chain, based on 2,6-bis(hydroxymethyl)pyridine (PUPyB and PUPyBNPG). The miscibility of the components depends on the strength of the intra- or *homo*-intermolecular H-bonds between pyridine =N– groups and urethane >C=O and –NH– groups, the flexibility of the polymer chain, and the accessibility of PU pyridyl units for binding.

PUPyB with linear polymer chains exhibits a strong tendency toward crystallization and is practically immiscible with DOBA, whereas the miscibility of DOBA and amorphous polyurethane PUPyBNPG with an additional hexamethylene unit and branched neopentyl glycol unit was enhanced. The liquid-crystalline polyurethane complexes were formed at DOBA/PUPyBNPG molar ratios up to 0.4 exhibiting crystal-smectic and smectic-nematic transitions at around 80 and 90 °C, respectively, and isotropization temperatures over 105 °C, which is similar to the polyurethane complexes with pendant pyridyl units based on *N*,*N*-bis(2-hydroxyethyl)isonicotinamide.[16] The analogous low-molar mass urethane complex exhibited a lower isotropization temperature and a less ordered smectic phase than the polymeric complexes.

Acknowledgement

The authors gratefully acknowledge the financial support of the Slovenian Research Agency (Project Z2-5403-104, program P2-0145-104) and the participation in the EU NoE Nanofun-Poly. The authors are also grateful to Prof. Dr. Branko Stanovnik and Mrs. Tatjana Stipanovič for elemental analysis.

References

1. J.-M. Lehn, Supramolecular Chemistry - Scope and Perspectives, in: A. Ciferri (Ed.): Supramolecular Polymers, Marcel Decker, Inc., New York, 2000, 615–642.
2. P. S. Corbin, S. C. Zimmerman, Hydrogen-Bonded Supramolecular Polymers, in: A. Ciferri (Ed.): Supramolecular Polymers, Marcel Decker, Inc., New York, 2000, 147–176.
3. C. T. Imrie, *Trends Polym. Sci.* **1995**, *3*, 22–29.
4. T. Kato, J. M. J. Fréchet, *Macromol. Symp*. **1995**, *98*, 311–326.
5. T. Kato, *Struct. Bond*. **2000**, *96*, 95–146.
6. T. Kato, *Science* **2002**, *295*, 2414–2418.
7. C. M. Paleos, D. Tsiourvas, *Liq. Cryst.* **2001**, *28*, 1127–1161.
8. T. Kato, N. Mizoshita, K. Kanie, *Macromol. Rapid Comm*. **2001**, *22*, 797–814.
9. T. Kato, J. M. J. Fréchet, *Macromolecules*, **1989**, *22*, 3818–3819.
10. U. Kumar, J. M. J. Fréchet, T. Kato, S. Ujiie, K. Timura, *Angew. Chem., Int. Ed. Engl*. **1992**, *31*, 1531–1533.
11. T. Kato, N. Hirota, A. Fujishima, J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem*. **1996**, *34*, 57–62.
12. T. Kato, H. Kihara, S. Ujiie, T. Uryu, J. M. J. Fréchet, *Macromolecules* **1996**, *29*, 8734–8739.
13. T. Kato, Y. Kubota, T. Uryu, S. Ujiie, *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1617–1618.
14. O. Ihata, H. Yokota, K. Kanie, S. Ujiie, T. Kato, *Liq. Cryst.* **2000**, *27*, 69–74.
15. G. Ambrožič, M. Žigon, *Macromol. Rapid Commun*. **2000**, *21*, 53–56.
16. G. Ambrožič, J. Mavri, M. Žigon, *Macromol. Chem. Phys*. **2002**, *203*, 439–447.
17. G. Ambrožič, M. Žigon, *Polym. Int*. **2005**, *54*, 606–613.
18. D. J. Martin, G. F. Meijs, P. A. Gunatillake, S. J. McCarthy, G. M. Renwick, *J. Appl. Polym. Sci.* **1997**, *64*, 803–817.

19. J. T. Koberstein, I. Gancarz, T. C. Clark, *J. Polym. Sci., Polym. Phys.* **1986**, *24*, 2487–2498.
20. T. Hentschel, H. Münstedt, *Polymer*, **2001**, *42*, 3195–3203.
21. Y. He, B. Zhu, Y. Inoue, *Prog. Polym. Sci.* **2004**, *29*, 1021–1051.
22. F. Eblinger, H.-J. Schneider, *Angew. Chem. Int. Ed.* **1998**, *37*, 826–829.

Povzetek

Pripravili smo nove tekočekristalinične poliuretanske komplekse, ki nastanejo z vodikovo vezjo med 4-dodeciloksibenzojsko kislino (DOBA) in poliuretanom na osnovi 2,6-bis(hidroksimetil)piridina s piridinskimi enotami v glavni verigi (PUPyB, PUPyBNPG). Lastnosti poliuretanskih kompleksov smo raziskali z diferenčno dinamično kalorimetrijo, polarizacijsko optično mikroskopijo in rentgensko difraktometrijo. Tekočekristalinični poliuretanski kompleksi so nastali pri molskih razmerjih med DOBA in ponavljajočo se enoto PUPyBNPG do 0,4. Zanje sta značilni smektična in nematična faza, podobno kot pri tekočekristaliničnih poliuretanskih kompleksih, kjer so piridinske enote del stranskih skupin. Analogni nizkomolekularni kompleks med uretanom in DOBA ima nižjo temperaturo izotropizacije in manj urejeno smektično fazo kot polimerni kompleksi.