Macromolecules **2003,** *36,* 5195−5200

Crystallization and Phase Behaviors of Multicomponent Supramolecular Complexes through Hydrogen-Bonding Association

Xuehong Lu,[†] Chaobin He,*[,‡] and Anslem C. Griffin[§]

School of Materials Engineering, Nanyang Technological University, Singapore 639798; Institute of Materials Research and Engineering, 3 Research Link, Singapore 117602; and School of Textile and Fiber Engineering, Georgia Institute of Technology, 801 Ferst Drive Atlanta, Georgia 30332-0295

Received September 30, 2002; Revised Manuscript Received January 6, 2003

ABSTRACT: Two series of hydrogen-bonded association chain polymers have been prepared by melt mixing of diacids and bispyridyl. Liquid crystallinity and crystallization behavior of the polymers were studied using DSC, polarized microscopy, and X-ray scattering methods. It is shown that these two polymer series exhibit smectic liquid crystallinity and also crystallinity despite their random chain structures. The two polymer series show very different capabilities in forming the smectic and crystalline phases. This is due to their difference in monomer length, which may lead to different crystallization mechanisms. The study indicates that when the random association chain polymers are made of two types of blocks, one of which has nearly twice the length of the other, the corresponding crystallization behavior can be explained by the existence of “length emulation” crystals.

Introduction

Hydrogen-bonded association chain supermolecules, or “polymers”, have attracted much attention due to their scientific values and potential technological applications.[1−6] Over the past quarter century, supramolecular chemistry has grown into a major field and has fueled numerous developments at the interfaces with biology and physics.[7] Unlike conventional covalent bonded polymers, association chain polymers are formed by noncovalent interaction, such as hydrogen bonding. Through such noncovalent bonding, liquid crystallinity can be induced by combining two or more otherwise non-liquid-crystalline compounds or liquid crystallinity of one component can be modified by addition of a second component. The association process of hydrogen bonding mimics biological self-assembly. Understanding of this process could lead to new approaches in the synthesis of functional materials.

There are two types of hydrogen-bonded association chain liquid-crystalline polymers, namely main-chain and side-chain hydrogen-bonded LCPs. In the area of side-chain hydrogen-bonded LCPs, pyridyl species have been “grafted” onto pendant aromatic acid units on preformed polymer chains.[8−12] In the area of main-chain hydrogen-bonded LCPs, Lehn et al. have described association through triple hydrogen bonding of ditopic species,[13,14] while Griffin et al. have synthesized a class of association chain LCPs by hydrogen bonding of diacids and bispyridyls, neither of which are liquid crystalline by themselves.[15,16] Meijer et al.[17] have described a non-liquid-crystalline association chain polymer having a quadruple hydrogen-bonding motif which remains associated even in a solvent. The property of the polymer solution is similar to that of covalent bond polymers.

In contrast to the work done in the synthesis area, structures of hydrogen-bonded LCPs, particularly main-chain hydrogen-bonded LCPs, have not been intensively studied. In our previous papers, we have studied the nature of interaction between diacids and bispyridyls and have reported the structure of a main-chain hydrogen-bonded LCP formed by mixing two complementary components.[18−21] In this paper we will report crystallization behaviors of two series of random association chain LCPs consisting of three components.

Liquid crystalline polymers with random chain sequence, such as copolymers consisting of 4-hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA), have been intensively investigated. These polymers can crystallize even under quenched conditions despite their random chain sequence and different length of the comonomers. Their X-ray diffraction patterns show sharp but aperiodic peaks. Several hypotheses have been put forward to explain the observations. Windle’s group has proposed the “non-period lattice” (NPL) model,[22,23] which suggests that the crystallinity in rigid chain random copolymers may result from the segregation and lateral matching of similar yet random sequences of the neighboring chain segments. Later, the NPL crystal model has been extended to semirigid chain polymers.[23−25] Parallel with the NPL model, Gutierrez et al. have proposed the “plane start register model” to account for crystallinity in HBA−BNA random copolymers, which suggests that the three-dimensional order observed is due to the parallel arrangement of a number of random but nonidentical chain segments with just one monomer in register in the center of each segment.[26] Nevertheless, both models agree that the ordered zones have random sequence in the chain direction and some degree of register in the lateral direction, and both models can predict aperiodic X-ray peaks. Crystallinity has also been observed in flexible chain random copolymers, such as atactic poly(vinyl chloride) (PVC) and poly(acrylonitrile) (PAN). The phenomenon has been attributed to the existence of “shape emulation” crystals, in which one type of unit is included in the crystal lattice for the other type of units since two types of units have similar shape.[27,28] However, all of the crystal models mentioned above have been emerged from studies of

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[†] Nanyang Technological University.

[‡] Institute of Materials Research and Engineering.

[§] Georgia Institute of Technology.

* To whom correspondence should be addressed.

10.1021/ma021544j CCC: $25.00

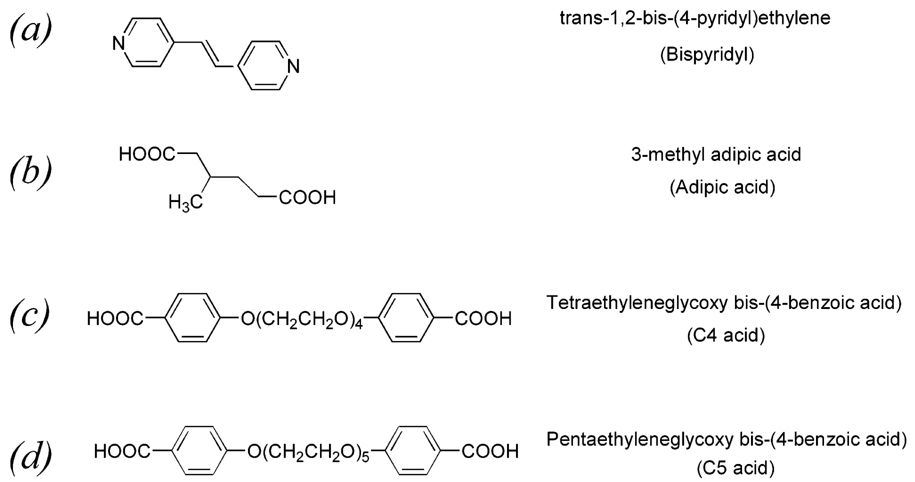

Figure 1. Chemical structures of the monomers: (a) *trans*-1,2-bis(4-pyridyl)ethylene (bispyridyl); (b) 3-methyladipic acid (adipic acid); (c) tetraethyleneglycoxybis(4-benzoic acid) (C4 acid); (d) pentaethyleneglycoxybis(4-benzoic acid) (C5 acid).

covalent bonded random copolymers. This opens the question as to whether these models can also be applied to random association chain polymers, especially considering the relatively low energy required to break hydrogen-bonded polymer chains to alter their sequence distribution. We have found that random associate chain polymers may also be highly crystalline, while the corresponding crystallization mechanisms have not yet been addressed. To study crystallization mechanisms of random association chain polymers, in this study we synthesized two series of random association chain polymers, each of which consists of three components with a random sequence. The polymer series I consists of bispyridyl, adipic acid, and a diacid, C4 acid, and the series II consists of bispyridyl, adipic acid, and another diacid, C5 acid. The C4 and C5 acid have almost identical chemical structure except that the C4 acid is shorter than the C5 acid by a (OCH$_2$CH$_2$) segment. The study on the two series polymers allows us to address the question raised above.

Experimental Section

Monomer Synthesis. Three diacids and a two-ring bispyridyl were used to prepare the two series of hydrogen-bonded association chain polymers. Their chemical structures are shown in Figure 1. *trans*-1,2-Bis(4-pyridyl)ethylene (bispyridyl) and 3-methyladipic acid (adipic acid) were obtained from Aldrich and used without further purification. Tetraethyleneglycoxybis(4-benzoic acid) (C4 acid) and pentaethyleneglycoxybis(4-benzoic acid) (C5 acid) were synthesized according to ref 16.

Polymer Preparation.. Each series of hydrogen-bonded association chain polymers were synthesized by mixing two diacids and bispyridyl in their melt state. Polymers containing adipic acid and C4 acid is denoted as HBP4 series. Polymers containing adipic acid and C5 acid is denoted as HBP5 series. The molar ratio of diacids to bispyridyl is kept at 1:1, i.e., at a stoichiometric ratio, for all the polymers, while the molar ratio of adipic acid to C4 or C5 acid changes from 0:1 to 1:0. The polymerization procedure has been reported in a previous paper.[15] The polymers were synthesized by mixing the three components with the requirement that the stoichiometric ratio of total −COOH and pyridyl nitrogen be 1:1. The mixtures were put in a small vial which is then placed in an oil bath at 190−200 °C under argon and stirred vigorously for about 120 s. Chemical structures of these two series of polymers are shown in Figure 2.

Thermal Study. Thermal behaviors of the two series of polymers and the corresponding monomers were studied using a TA-2920 DSC under a heating and cooling rate of 10 °C/min, respectively. The phase behaviors of the polymer complexes were also examined using a Leica polarized light microscope fitted with a heating stage.

X-ray Scattering. X-ray powder scatterings of the polymer complexes were obtained using a Siemens XPD-700P diffractometer fitted with a 2-D gas filled detector. Cu Kα radiation was used. The data were then corrected by subtracted a background scattering and divided by the detector response. 1-D data were obtained by integrating the 2-D data. During the integration, the data integration step is 0.05° (2θ), which is within the resolution of the detector. The polymer samples used X-ray scattering experiments were initially heated to their isotropic melt state and then cooled to room temperature in air.

Calculation of Monomer Lengths. The lengths of all the monomers were calculated on the basis of their optimized conformations, which were generated using the MOPAC AM1 routine, CERIUS Molecular Modeling Software for Materials Research from Molecular Simulation Inc. of Burlington, MA, and Cambridge, UK.[27]

Results and Discussion

Liquid Crystallinity. When diacids and bispyridyl are melt-mixed, polymerization occurs which generates a polymer structure in which a diacid (donor) is always associated with a bispyridyl (acceptor), as shown in Figure 2. This is because that, except ionic interaction, hydrogen bonding is the strongest one among the noncovalent interaction forces between two molecules. The association between “donor” and “acceptor” effectively induces hydrogen bonds that lead to a more stable structural organization. More importantly, it is the hydrogen bonds that link the rigid parts of the “donor” and “acceptor” together so that the effective length of mesogenic groups is increased which leads to liquid crystallinity of the resulting complexes. This is clearly demonstrated by the fact that all the monomers used in this study do not exhibit any liquid crystallinity by themselves, while by melt mixing them together liquid crystallinity was observed in all the cases.

DSC and microscopy studies show that all the polymers under study exhibit monotropic liquid crystallinity; i.e., the liquid crystallinity is only observed when the polymer is cooled from its isotropic melt. Figure 3 is a summary of phase transition temperatures of the HBP4 series measured using DSC. This series of polymers exhibits nematic and smectic liquid crystallinity in the

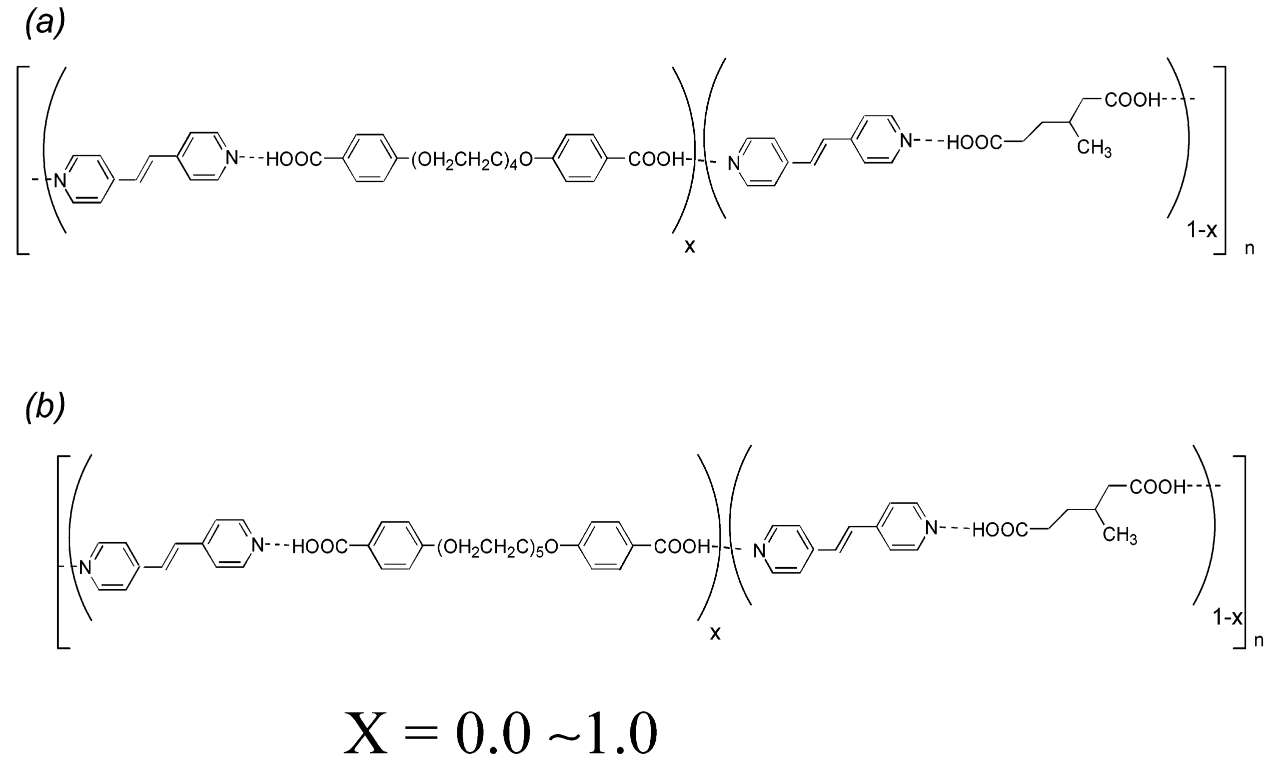

Figure 2. Chemical structures of the hydrogen-bonded association chain polymers. (a) The HBP4 polymer series which contains tetraethyleneglycoxybis(4-benzoic acid) (C4 acid); HBP400, HBP402, HBP404, HBP406, HBP408, and HBP410 represent polymers containing 0, 20, 40, 60, 80, and 100 mol % adipic acid out of the total acid contents, respectively. (b) The HBP5 polymer series which contains pentaethyleneglycoxybis(4-benzoic acid) (C5 acid); HBP500, HBP502, HBP504, HBP506, HBP508, and HBP510 represent polymers containing 0, 20, 40, 60, 80, and 100 mol % adipic acid out of the total acid contents, respectively.

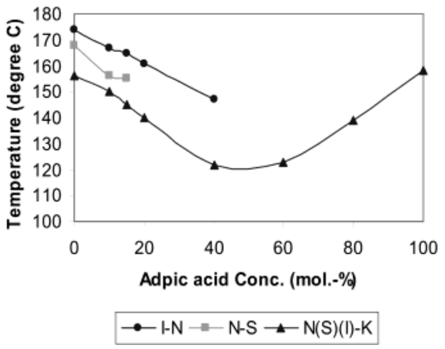

Figure 3. Phase transition temperatures of the HBP4 polymer series as a function of adipic acid molar concentration (out of the total diacid contents) measured using DSC. The data were obtained on cooling with a cooling rate of 10 °C/min. (●) represents isotropic−nematic transition; (■) represents nematic−smectic transition; (▲) represents nematic (or smectic, or isotropic)−crystalline transition.

composition range of 0−40 and 0−20 mol % of adipic acid, respectively. Note that the molar percentage of adipic acid here is based on the total diacid contents only rather than the total contents of diacids and bispyridyl, and this convention will be used throughout this paper. Representative optical textures for the observed nematic and smectic phase are shown in parts a and b of Figure 4, respectively. The HPB5 series does not exhibit any nematic liquid crystallinity whereas exhibits a smectic phase in a wider range of composition, i.e., from 0 to 60 mol % of adipic acid, as shown in Figure 5.

It is interesting to see that the capability of the two polymer series in forming the smectic phase is fairly different. While the HBP4 series can only exhibit the smectic phase when the adipic acid concentration is lower than 15 mol %, the HBP5 series exhibits the smectic phase up to 60 mol % of adipic acid.

Crystallization. For these two series of polymers, the two pair of diacid components, i.e., adipic acid/C4 acid and adipic acid/C5 acid, have similar pK_a values. This means that the reactivities of adipic acid and C4 or C5 acid are similar in competing to attract a bispyridyl to form an association structure. As a result, the complexation of the three components, i.e., adipic acid/C4 acid/bispyridyl or adipic acid/C5 acid/ bispyridyl, likely leads to a random distribution of the diacids along the resulting polymer chains. The sequence random characteristic has also been confirmed in a previous study using (+)-3-adipic acid/C4 acid/bispyridyl association chain system.[19] The association chain polymers exhibit a chiral nematic phase. Polarized light microscopy showed a characteristic fingerprint texture when (+)-3-methyladipic acid was introduced into the complex, even at the very low concentration of 1.5 mol %. Moreover, it was showed that the line periodicity of the fingerprint, which is related to the half pitch of the helical nematic phase, increases with the decrease of (+)-3-methyladipic acid concentration. The increase in concentration of the chiral component twists the nematic director to a larger extent and results in a shorter pitch. These results clearly indicate that, first, the adipic acid takes part in the formation of the liquid crystalline phase as the association between adipic acid and pyridyl alone does not lead to liquid crystallinity. Second, the change of the pitch of the line periodicity of the fingerprint with the increase of (+)-adipic acid also indicates that the adpic acid is randomly distributed along the polymer chain.

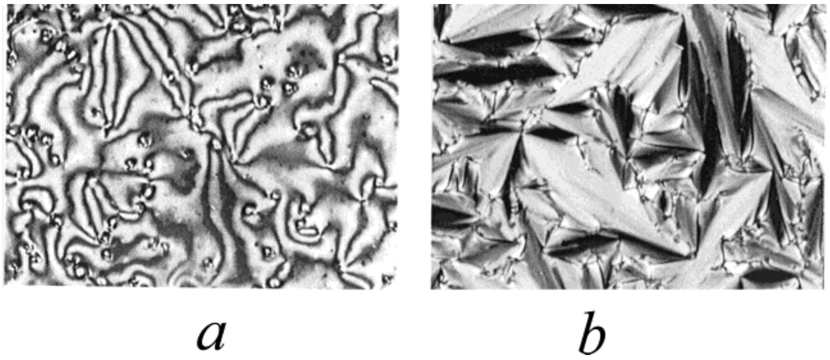

Figure 4. Optical textures observed from the HBP4 polymer series show (a) a nematic phase at 167 °C and (b) a smectic phase at 158 °C. Molar ratio of C4 acid to adipic acid is 90:10. Magnification is 200.

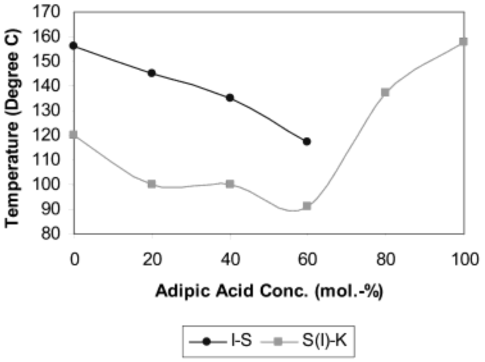

Figure 5. Phase transition temperatures of the HBP5 polymer series as a function of adipic acid molar concentration (out of the total diacid contents) measured using DSC. The data were obtained on cooling with a cooling rate of 10 °C/min. (●) represents isotropic−smectic transition; (■) represents smectic (or isotropic)−crystalline transition.

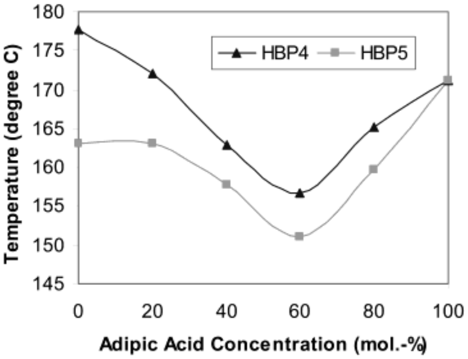

Figure 6. Melting temperatures of the two polymer series as a function of adipic acid concentration measured using DSC. The data were obtained on heating with a heating rate of 10 °C/min. (▲) represents the HBP4 polymer series; (■) represents the HBP5 polymer series.

Despite their random chain structures, our experiments show that melting peaks appear on DSC traces for all the polymers, which indicates the existence of crystallinity. The melting temperatures of the polymers measured using DSC from the first heating traces are recorded in Figure 6. It can been seen that the melting temperatures of the two polymer series decrease as the adipic acid concentration increases up to 60 mol % and then increase when the concentration of adipic acid increases further. Both polymer series display a lowest melting temperature at around 60 mol % of adipic acid concentration.

The extent of melting temperature depression for the two series of polymers is, however, different. The melting temperature depression for the HBP4 series is larger than that for the HBP5 series. This is more significant when the concentration of adipic acid is less than 20 mol %, as shown in Figure 6. In this composition range, the melting temperature for the HBP4 series decreases by about 7 °C while that for the HBP5 series is nearly kept at a constant level. The difference in melting temperature depression between the two systems is caused by their difference in monomer length, and this will be addressed in detail later.

It is interesting to see that there is a significant degree of undercooling observed in these association chain polymers. Undercooling crystallization is often observed in polymers (or molecular chain) but not in small molecules where the arrangement of small molecule into a crystal lattice is easy and rapid. The significant degree of undercooling, on the other hand, indicates a polymeric characteristic of the association chain polymers.

The crystalline structures of the polymer complexes and their individual monomer components were studied using the powder X-ray scattering method. In a previous report,[18] we have shown that when two complementary monomers are melt-mixed together forming an association chain polymer through hydrogen bonding, the resulting polymers not only show liquid crystallinity but also develop new crystalline structures that is different from those of the individual monomers. The polymer systems studied here consist of three components. Similar to the two-component system, they not only exhibit liquid crystallinity but also develop new crystal structures. This is clearly shown by the fact that some strong scatterings from the monomers are not shown in the polymer spectra, while some strong scatterings which do not appear in the monomer spectra show up in the polymer scattering patterns, as shown in Figures 7−9. The new crystalline structures observed obviously arise from the association chain structure.

Figure 8 shows the powder X-ray scatterings of the HBP4 polymer series. There are six polymers in this series, HBP400, HBP402, HBP404, HBP406, HBP408, and HBP410, for which the concentrations of adipic acid are 0, 20, 40, 60, 80, and 100 mol %, respectively. The curve at the bottom is the X-ray scattering from HBP400, a copolymer formed by melt-mixing C4 acid and bispyridyl. It can be, in fact, seen as a homopolymer of bispyridyl-C4 acid blocks since it has a regular chain structure. Similarly, HBP410 can be seen as a homopolymer of bispyridyl−adipic acid blocks.

When adipic acid is partially substituted by C4 acid, the resulting polymers are random copolymers of bispyridyl−C4 acid and bispyridyl−adipic acid blocks, and

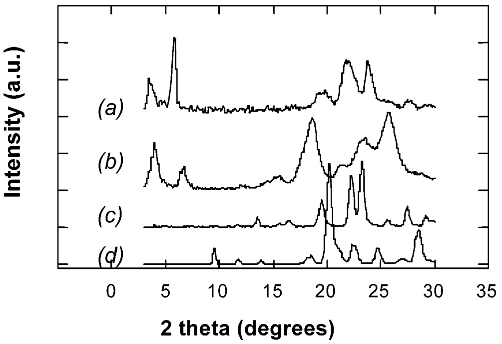

Figure 7. X-ray scatterings from the monomers: (a) pentaethyleneglycoxybis(4-benzoic acid) (C5 acid); (b) tetraethyleneglycoxybis(4-benzoic acid) (C4 acid); (c) *trans*-1,2-bis(4-pyridyl)ethylene (bispyridyl); (d) 3-methyladipic acid (adipic acid).

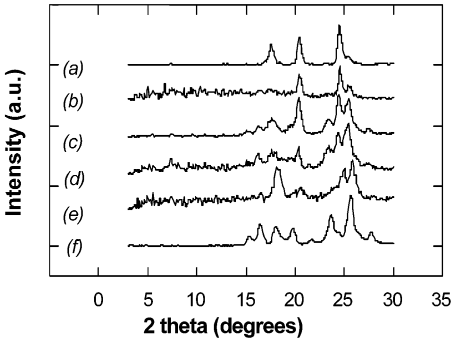

Figure 8. X-ray scatterings from the HBP4 polymer series; From bottom to top the curves are for polymer HBP400, HBP402, HBP404, HBP406, HBP408, and HBP410, which represent polymers containing 0, 20, 40, 60, 80, and 100 mol % adipic acid out of the total acid contents, respectively.

their X-ray scattering patterns are very different from those of the homopolymers, i.e., HBP400 and HBP410. The X-ray diffraction patters of the random copolymers also cannot be reproduced by adding together the two homopolymer X-ray diffraction patterns at any ratio. This clearly indicates that the ordered zones in these random copolymers are not composed of homopolymer sequences. Moreover, crystallinity of the polymers is also decreased significantly when C4 acid is introduced into the polymer chains. It can be seen that a large scattering halo is superimposed with the crystalline peaks for the polymers HBP410, HBP408, and HBP406. All the evidence suggests that although in association chain polymers the linkage between monomers is weaker than that in covalent bonded polymers, they do not tend to break up to rearrange their sequence distributions to form regular crystal structures. Instead, it is likely that the crystal zones are formed with segments of random sequences. In fact, the hydrogen-bonding association chain is strong enough to sustain shear force.[20]

Figure 9 shows the X-ray scattering patterns from the HBP5 polymer series. There are also six polymers in this series, HBP500, HBP502, HBP504, HBP506, HBP508, and HBP510, for which the concentrations of adipic acid are 0, 20, 40, 60, 80, and 100 mol %, respectively. The curve at the bottom is the scattering from HBP500, a copolymer from complexation of C5 acid and bispyridyl. The structure of this two-component copolymer has been studied and reported in a previous paper.[18] When adipic acid is partially substituted by C5 acid, the resulting polymers would be terpolymers, in which the two diacids are distributed randomly along the chains. It is interesting to see that the scattering signatures for polymer complexes HBP510, HBP508, and HBP506, for which adipic acid concentrations are 100, 80, and 60 mol % respectively, are quite similar, in contrast to the polymer HBP4 series.

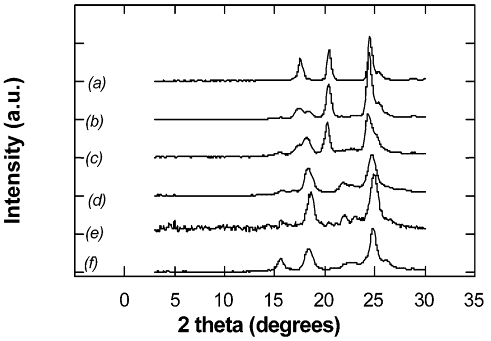

Figure 9. X-ray scatterings from the HBP5 polymer series. From bottom to top the curves are for polymer HBP500, HBP502, HBP504, HBP506, HBP508, and HBP510, which represent polymers containing 0, 20, 40, 60, 80, and 100 mol % adipic acid out of the total acid contents, respectively.

It is striking to see that the HBP5 series of polymer complexes exhibit very high crystallinity despite the random character of the polymer chains and the crystallinity of the polymer complexes is not significantly reduced even in the middle range of composition. The crystallinities for polymer HBP500, HBP502, and HBP504 are all about 86% based on estimation from X-ray data, which means that incorporation of 40 mol % of adipic acid into the polymer chains does not significantly interrupt the crystal packing.

The X-ray scattering signatures and crystallinity of the HBP5 polymer series is in contrast to those of the HBP4 polymer series. The crystalline structure and crystallinity of the HBP4 polymer series is very sensitive to the substitution of the adipic acid by C4 acid in the whole range of compositions. The fact that the crystalline structure and crystallinity of the HBP5 polymer series hardly change when the C5 acid is substituted with adipic acid up to 40 mol % of adipic acid rises a question as to what is the crystallization mechanism for the HBP5 polymer series.

Before answering this question, we need to consider how the three components in the polymers arrange along the polymer chains. Although both HPB4 and HBP5 series consist of three monomer components, these three components are not randomly distributed along the polymer chains. As mentioned earlier, along a polymer chain, a bispyridyl is always followed by a diacid through hydrogen bond association. As a result, the HBP4 polymer series can be considered as random copolymers of bispyridyl−tetraethyleneglycoxybis(4-benzoic acid) (C4 acid) blocks (BT blocks) and bispyridyl−adipic acid blocks (BA blocks), while the HBP5 series can be considered as random copolymers of bispyridyl−pentaethyleneglycoxybis(4-benzoic acid) (C5 acid) blocks (BP blocks) and BA blocks. The concentration of the BA blocks ranges from 0 to 100% for both series, i.e., from HBP400 to HBP410 for the HBP4 series and from HBP500 to HBP510 for the HBP5 series.

The difference between polymer series HBP5 and HBP4 is only the length difference of one of the diacids; i.e., the C5 acid is longer than the C4 acid. The lengths for bispyridyl, adipic acid, and pentaethyleneglycoxybis(4-benzoic acid) (C5 acid) were calculated as 9.5, 10.1, and 30.7 Å, respectively.[29] As mentioned before, the

HBP5 series consist of BT and BA blocks which are randomly distributed along the polymer chains. Given the length of the hydrogen bond is 1.74 Å and bond angle of 167°,[30] the lengths of the BP blocks and BA blocks are about 43.6 and 23.0 Å, respectively. The simulated data indicate that the lengths of polymer repeat units for HBP500 and HBP510 block are 40.8 and 20.5 Å, respectively. This gives that the length of the BP blocks is roughly twice of the length of the BA blocks. At low C5 concentration it is very likely that a BP block would emulate two BA blocks and packed into the crystal lattice for BA blocks. Therefore, by introduction of C5 (BP block), the main crystal scattering signatures and crystallinity are hardly changed up to 40 mol % of C5 acid incorporation. The fact that the melting temperature of the HPB5 series is hardly changed even up to 20 mol % of adipic acid incorporation also suggest the possible length emulation packing structure for the crystals. At higher concentration of C5 acid, it is likely that two BA blocks would emulate a BP block and packed into the crystal lattice for BP blocks. Therefore, in the whole range of compositions, crystallinity of the HBP5 series is fairly high compared to those of the HBP4 series, especially in the middle range composition.

The existence of smectic phase in the HPB5 polymer series even up to 60 mol % of adipic acid incorporation, on the other hand, also provides indication of the possible length emulation packing structure. A smectic liquid crystalline polymer has not only a long-range orientational order but also a short-range positional order, i.e., layer structure. The existence of a smectic phase in the HPB5 series at high adipic acid concentration, 60 mol %, suggests that the short BA blocks should be included into the layer packing but not only act as defects. Small-angle X-ray scatterings from the polymer HPB500 also shows a low-angle scattering with a length roughly equal to the length of the BP blocks.[17] The absence of smectic phase at the high concentrations of adipic acid is attributed to flexible nature of adipic acid.

The HBP4 series has a short version of acid. The length of tetraethyleneglycoxybis(4-benzoic acid) (C4 acid) is about 3.5 Å shorter than that of pentaethyleneglycoxybis(4-benzoic acid) (C5 acid) so that the length of BT blocks is only about 40.1 Å. The length of the BT blocks is much shorter than that of twice the length of the BA blocks, which make it difficult for two BA blocks packing into the crystal lattice for the BT blocks. X-ray scattering from the HPB4 series clearly indicates an increase of amorphous halo with an increase of adipic acid incorporation, which means an increase of amorphous region. The HBP4 series exhibits smectic phase only at very low adipic acid concentration (<15 mol %). This is also a clear evidence that BA blocks cannot emulate the length of BT block well due to their large difference in length and hence become defects in smectic liquid crystals, which leads to an unstable smectic phase.

Conclusions

The two series of hydrogen-bonded association chain polymers studied in this paper exhibit not only liquid crystallinity but also crystallinity despite their random chain sequence. Their capabilities in forming the crystalline and smectic phase are very different, which is due to their difference in the monomer length. When the random association chain polymers are made of two monomers, one of which has nearly twice of the length of the other, the crystallization behavior can be explained by the existence of "length emulation" crystals.

References and Notes

(1) Lehn, J. M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem. Soc., Chem Commun.* **1990**, 479.
(2) Lehn, J. M.; Mascal, M.; DeCian, A.; Fischer, J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 461.
(3) Hilger, C.; Stadler, R. *Makromol. Chem.* **1991**, *192*, 805.
(4) Hilger, C.; Stadler, R. *Polymer* **1991**, *32*, 3244.
(5) Freitas, L. del; Stadler, R. *Colloid Polym. Sci.* **1988**, *266*, 1095.
(6) Hilger, C.; Drager, M.; Stadler, R. *Macromolecules* **1992**, *25*, 2498.
(7) (a) Lehn, J. M. *Science* **2002**, *295*, 2400. (b) Kato, T. *Science* **2002**, *295*, 2414.
(8) Kato, T.; Frechet, M. J. *Macromolecules* **1989**, *22*, 3818.
(9) Kumar, U.; Kato, T.; Frechet, M. J. *J. Am. Chem. Soc.* **1992**, *114*, 6630.
(10) Kato, T.; Hihara, H.; Uryu, T.; Fujishima, A.; Frechet, M. J. *Macromolecules* **1992**, *25*, 6836.
(11) Kumar, U.; Frechet, M. *J. Adv. Mater.* **1992**, *4*, 665.
(12) Kumar, U.; Kato, T.; Frechet, M. J.; Ujiie, S.; Timura, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1531.
(13) Lehn, J. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304.
(14) Lehn, J. M. *Makromol. Chem. Macromol. Symp.* **1993**, *69*, 1.
(15) Alexander, C.; Jariwala, C. P.; Lee, C.-M.; Griffin, A. C. *Macromol. Symp.* **1994**, *77*, 283.
(16) Lee, C.-M. Jariwala, C. P.; Griffin, A. C. *Polymer* **1994**, *35*, 4550.
(17) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J. H. K. K.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601.
(18) He, C. B.; Donald, A. M.; Waigh, T.; Griffin, A. C.; Windle, A. H. *J. Polym. Sci., Phys. Ed.* **1998**, *36*, 1617.
(19) He, C. B.; Lee, C.-M.; Griffin, A. C. Bouteiller, L.; Lacoudre, N.; Boileau, S.; Fouquey, C.; Lehn, J.-M. *Mol. Cryst. Liq. Cryst.* **1999**, *A332*, 2761.
(20) Lu, X. H.; He, C. B.; Terrell, C. D.; Griffin, A. C. *Macromol. Chem. Phys.* **2002**, *203*, 85.
(21) Xu, J. W.; He, C. B.; Chua, T. K.; Lu, X. H. *Macromolecules* **2002**, *35*, 8846.
(22) Windle, A. H.; Viney, C.; Golombok, R.; Donald, A. M.; Mitchell, G. R. *Faraday Discuss. Chem. Soc.* **1985**, *79*, 55.
(23) Hanna, S.; Romouribe, A.; Windle, A. H. *Nature (London)* **1993**, *366*, 546.
(24) Lu, X.; Windle, A. H. *Polymer* **1995**, *36*, 451.
(25) Lu, X.; Windle, A. H. *Polymer* **1996**, *37*, 2027.
(26) Gutierrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* **1983**, *24*, 937.
(27) Hobson, R. J.; Windle, A. H. *Polymer* **1993**, *34*, 3582.
(28) Hobson, R. J.; Windle, A. H. *Macromolecules* **1993**, *26*, 6903.
(29) *CERIUS Molecular Modeling Software for Materials Research* from Molecular Simulation Inc. of Burlington, MA, and Cambridge, UK.
(30) Jeffery, G. H.; Maluszynska, *J. Mol. Struct.* **1986**, *147*, 127.

MA021544J