Thermoreversible Supramolecular Networks with Polymeric Properties

C. B. St. Pourcain and A. C. Griffin[*,†]

Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, U.K.

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ABSTRACT: Hydrogen bonding between carboxylic acids and pyridines can be used as a means of chain extension. However, the reversibility of hydrogen bond formation does not allow the chain-extended structure to be fixed, and a temperature-dependent chain length results. Complexation between a tetrapyridyl species and a diacid is shown to counteract the reversibility of the hydrogen bonding. These complexes form thermoreversible three-dimensional supramolecular networks which have properties typical of low molar mass materials at high temperatures but polymeric properties at low temperatures. The complexes exhibited a glass transition and could form fibers from the melt yet exhibited a low-viscosity isotropic liquid at elevated temperatures. Atypically, a complex incorporating a 2,2′,6,6′-tetrasubstituted biphenyl moiety was found to be liquid crystalline.

Introduction

Hydrogen bonding has recently been used in a number of supramolecular systems as a means of polymer formation or modification via a self-assembly process. There are two general approaches to preparing these systems.

In one, hydrogen bonding takes place in the side chain of a preformed polymer, thereby introducing new properties into the polymeric system. Fréchet[1-5] has described a variety of side-chain polymers, with various backbones, in which acid dimerization or the molecular recognition between a pyridyl species and a pendant aromatic carboxylic acid allows the self-assembly of liquid crystalline polymers. Bazuin and Brandys[6] have reported a related system in which the placements of pyridyl and carboxylic acid are reversed. Work on polymer blends has shown that the complexation between a pendant pyridyl and a pendant carboxylic acid is stronger than the dimerization of the acid; an association constant of approximately 500 was estimated for the pyridyl/carboxylic acid complex in this system.[7] In addition, Stadler[8-15] has investigated the properties of thermoplastic elastomers in which hydrogen bonding is used to cross-link polybutadiene-based chains; the hydrogen bonding is crucial to the thermal and mechanical properties of these materials.

In the other approach, hydrogen bonds between small molecules or oligomers are used as a method of self-assembly and of forming extended linear chains. Lehn has used triple hydrogen bond formation as a methodology for chain extension and for promotion of liquid crystallinity.[16,17] He has also reported the preparation of a number of supramolecular ribbons and strands formed by the cocrystallization of difunctional components.[18,19] Lillya[20] has recently described the chain extension of carboxy-terminated oligomers which associate through hydrogen bonding. Wuest has reported the self-assembly of dipyridones and tetrapyridones into supramolecular ribbons[21] and three-dimensional networks.[22] The complexation of a diacid and a dipyridyl, using only a single hydrogen bond per connection, to generate materials which through complexation both are liquid crystalline and have a chain-extended structure has recently been examined by this laboratory.[23-25] These heteromeric, complimentary hydrogen-bonded species were chosen to have a simplicity of structure which should facilitate establishment of predictive structure–property relations.

Although in this second approach there is considerable evidence for chain extension, these materials behave in some ways more like small molecules than polymers (with the exception of a system, reported by Lehn, which formed fibers[26]). Outside of the abovementioned reports, relatively little work has been done to design association structures, prepared by the molecular recognition driven self-assembly of small molecules, which possess polymeric properties. As an extension of our work with dipyridyl/diacid complexes, we have been investigating the use of tetrapyridyl species in place of dipyridyls as a means of counteracting the reversibility of the hydrogen bonding and thereby increasing the effective instantaneous chain extension in these systems. This approach also permits the preparation of supramolecular thermoreversible polymeric networks. We describe here the preparation and properties of two such systems which could have potential uses as reversible adhesives and as recyclable materials as well as serving as models for reversible gelling systems. It should be noted that in a recent paper Lehn[27] has suggested the possibility of preparing supramolecular polymer networks as well as the self-assembly of dendrimers.

Experimental Section

All starting materials were purchased from Aldrich Chemical Co. and were used as supplied. Melting points were determined on an Electrothermal IA9100 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 510 FTIR. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 250–MHz Fourier transform NMR spectrometer with TMS as internal reference. Elemental analyses were performed by the Department of Chemistry, University of Cambridge, Cambridge, U.K. Differential scanning calorimetry was recorded on a Perkin-Elmer DELTA DSC-7. Heating and cooling rates of 10 °C/min were used for DSC studies. Dynamic mechanical studies were performed on a Rheometric Dynamic Strain Rheometer II (Rheometrics, Inc). Samples were placed between paralled plates, and a strain of 2% and a frequency of 20 rad/s were employed. Samples for this study

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[†] Current address: Departments of Chemistry & Biochemistry and Polymer Science, University of Southern Mississippi, Hattiesburg, MS 39406.

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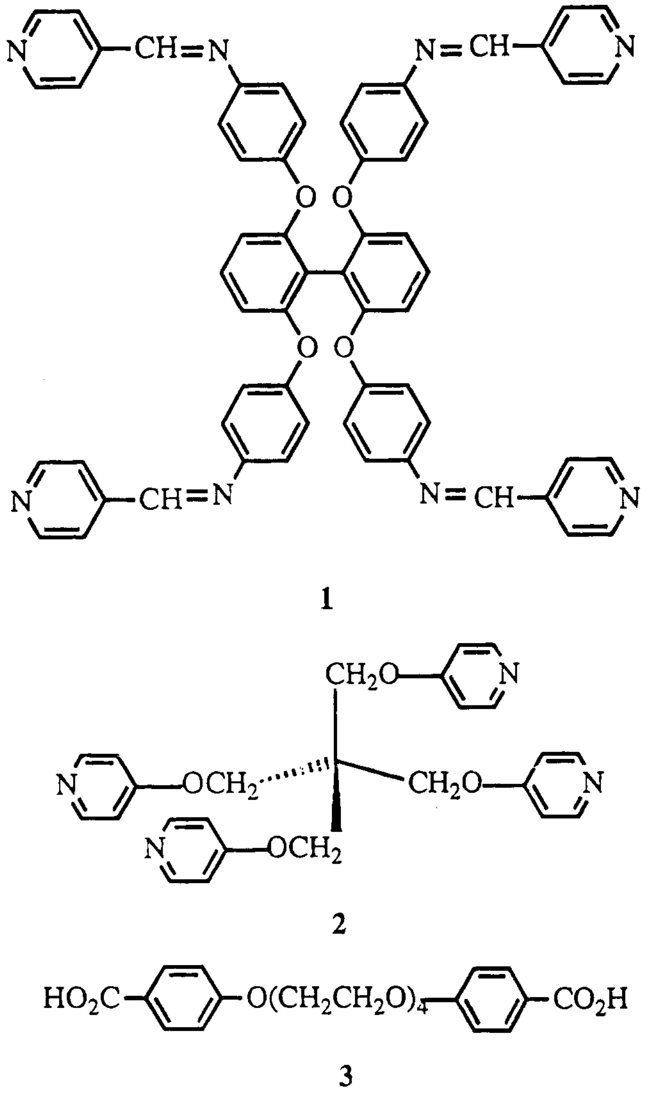

Figure 1. Reactants for self-assembly.

were prepared by compression molding. The complexes were heated in a mold to a temperature of 150 °C for 5 min while under a load of 2 tons/m^2. This load was maintained for 2 h as the sample cooled to room temperature. A Zeiss Axioskop polarizing microscope equipped with a Linkam TMS 91/THMS 600 heating stage was used for optical microscopic studies.

The compounds in Figure 1 were synthesized for this study.

2,2′,6,6′-Tetrakis[[(4-pyridylmethylene)imino]phenoxy]-biphenyl, 1. This compound was prepared from 2,2′,6,6′-tetrahydroxybiphenyl and 4-nitrofluorobenzene by standard methods.[28] Mp: 236–237 °C. IR (KBr, cm^{-1}): 3226, 3037, 1578, 1497, 1451, 1237, 1011, 839, 814, 546. ^{1}H NMR (DMSO-d_6, ppm): 4.30 (s, br, 4H, H_2O), 6.75 (d, 4H, J = 8.3 Hz, biphenyl), 6.98 (d, 8H, J = 8.7 Hz, Ar), 7.34 (d, 8H, J = 8.7 Hz, Ar), 7.35 (t, 2H, J = 8.0 Hz, biphenyl), 7.82 (d, 8H, J = 5.9 Hz, pyridyl), 8.68 (s, 4H, =CH), 8.72 (d, 8H, J = 5.8 Hz, pyridyl). Anal. Calcd for $C_{60}H_{42}N_8O_4{\cdot}2H_2O$: C, 73.91; H, 4.76; N, 11.48. Found: C, 73.87; H, 4.56; N, 11.36.

Tetrakis(4-pyridyl)pentaerythritol, 2. This compound was prepared from pentaerythritol tetratosylate and 4-hydroxypyridine by standard methods. Mp: 198 °C. IR (KBr, cm^{-1}): 3025, 2963, 2890, 1593, 1501, 1461, 1281, 1212, 1050, 1032, 872, 835. ^{1}H NMR ($CDCl_3$, ppm): δ 4.36 (s, 8H, CH_2), 6.72 (d, J = 6.3 Hz, pyridyl), 8.40 (d, J = 5.6 Hz, pyridyl). ^{13}C NMR ($CDCl_3$, ppm): δ 44.49, 65.88, 110.34, 151.45, 164.33. Anal. Calcd for $C_{25}H_{24}N_4O_4$: C, 67.56; H, 5.44; N, 12.60. Found: C, 67.39; H, 5.43; N, 12.65.

Tetraethylene Glycol Bis(4-benzoic acid), 3. The synthesis of this compound has been described elsewhere.[23]

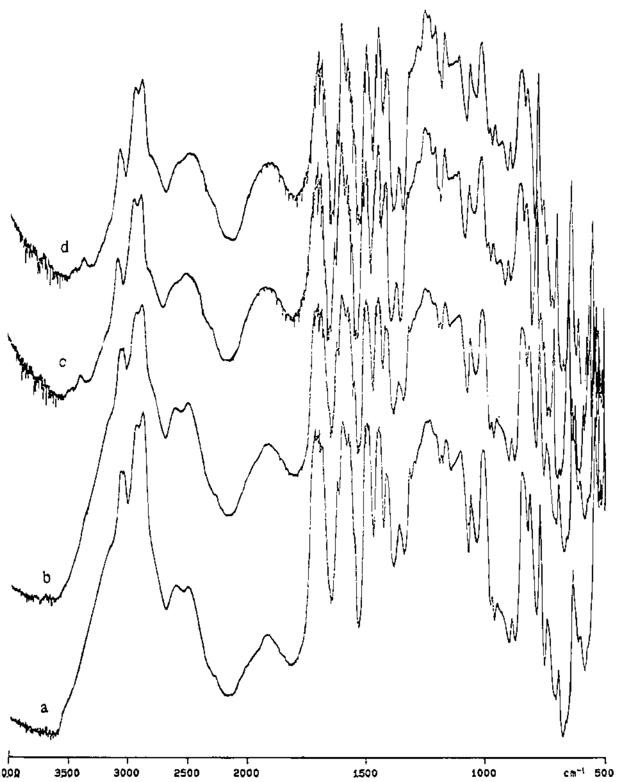

Figure 2. Temperature-dependent infrared spectra of **C1/3** at (a) 205, (b) 150, (c) 100, and (d) 50 °C.

Complex Formation. The complexes reported here were prepared in the melt from exact stoichiometric mixtures (1:1 ratio of acid/pyridyl groups) using the method described previously.[23]

Results and Discussion

Diacid **3** formed complexes readily with tetrapyridyls **1** and **2** to give complexes **C1/3** and **C2/3**, respectively. These systems can be described as arising from a reversible A_2B_4 polycondensation via hydrogen bonds.

Confirmation that complexation between carboxylic acid and pyridine has taken place is most easily obtained by infrared spectroscopy. Studies described in the literature show that new hydrogen-bonded OH absorption bands appear at about 1900 and 2500 cm^{-1} upon complexation.[29] A temperature-dependent infrared study of **C1/3** as it cools from an isotropic liquid is shown in Figure 2.

It can be seen that at 205 °C, when the complex is an isotropic liquid, there are absorptions at ~1900 and ~2500 cm^{-1} corresponding to the heteromeric hydrogen-bonded OH groups. In addition, there is significant underlying acid dimer OH absorption in the 3500–3000 cm^{-1} region. On cooling to 150 °C the intensity of the two absorptions from the complex increases with concomitant reduction in the acid dimer band intensity, and at 100 °C the OH absorptions from the complex become even more intense and thereafter remain constant. This study shows that the extent of complexation increases on cooling from the isotropic liquid to the solid state. Hydrogen bonding does occur in the isotropic liquid, but the dynamics of the hydrogen bond formation and dissociation are sufficiently rapid that a significant number of acid and pyridyl groups are uncomplexed at any instant.[25] As the temperature decreases, it is likely that the dynamics of this association/dissociation are slowed. The tetrafunctionality of the pyridyl species, **1**, leads to an A_2B_4 network with a reversibly branched

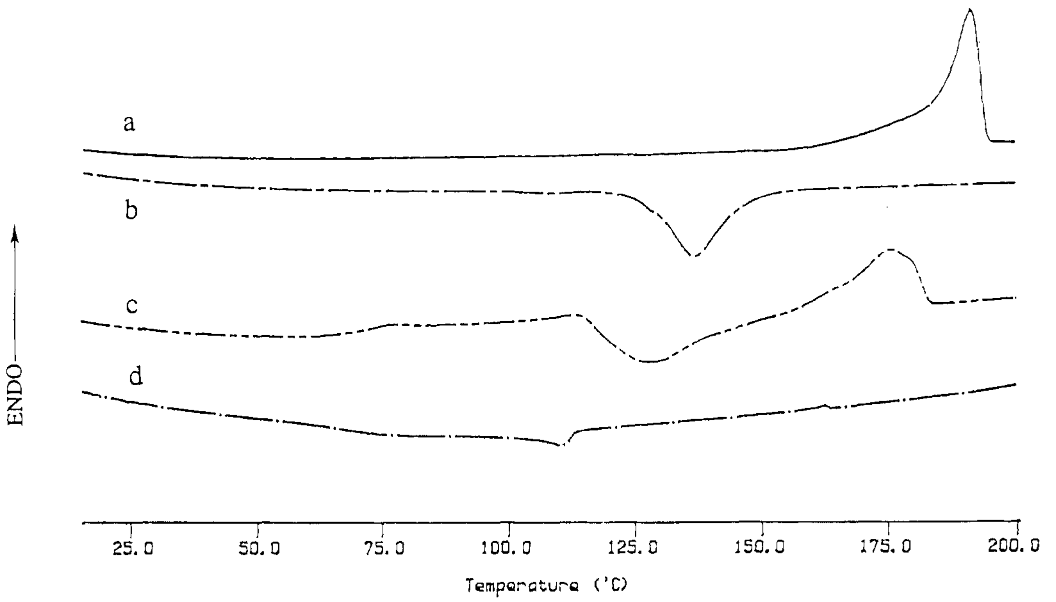

Figure 3. DSC of **C1/3**: (a) heating; (b) cooling; (c) heating after 30 min at 200 °C; (d) cooling after 30 min at 200 °C.

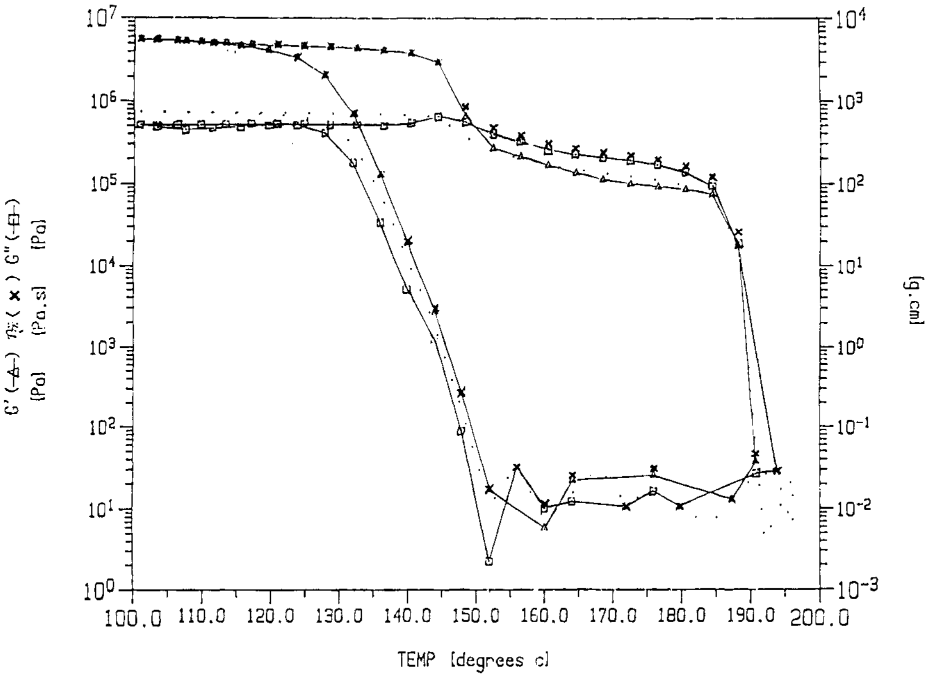

Figure 4. Temperature sweep rheological experiment for **C1/3**.

structure. A temperature-dependent IR study of the stability of low molar mass carboxylic acid/pyridine complexes has recently appeared[30] which is in general agreement with the behavior reported here.

Differential scanning calorimetry (DSC) and rheological studies of **C1/3** provide further insight into the behavior of this complex. DSC (Figure 3) shows that on heating the onset of the melting endotherm occurs at a temperature of ~160 °C, some 30 °C below the melting point. (A small pretransition effect is also seen in DSC studies of diacid/dipyridyl complexes but is much less pronounced.) This suggests that the sample is becoming more fluid over a significant temperature range. Moreover, a significant fraction of the heteromeric hydrogen bonds are disrupted at the melting point. This behavior is confirmed by the rheological study (Figure 4) which shows that the viscosity of the complex begins to decrease on heating at 150 °C. In the parallel-plate geometry the true low-temperature modulus would be considerably higher than that shown here. The flat plateau at $T < 140$ °C ($\approx 5 \times 10^6$ Pa) is reflective not of the material itself but of the instrument's compliance at the 2% strain level. This decrease is gradual until the melting point is reached, whereupon the viscosity of the complex drops sharply. The resulting liquid has a viscosity typical of low molar mass molecules rather than of polymers. Polarizing light microscopy confirmed this transition as melting to an isotropic liquid. This latter technique also revealed the slow growth of crystals on cooling from the isotropic liquid. This crystal growth is too slow to be clearly evident by DSC as the exotherm would be very broad and shallow. Rheology shows on cooling an increase in viscosity at 152 °C corresponding to the initiation of crystal growth. The small amount of crystal growth above this temperature does not appear to significantly affect the viscosity of the sample. Rapid cooling suppresses crystal formation. Both DSC and polarizing

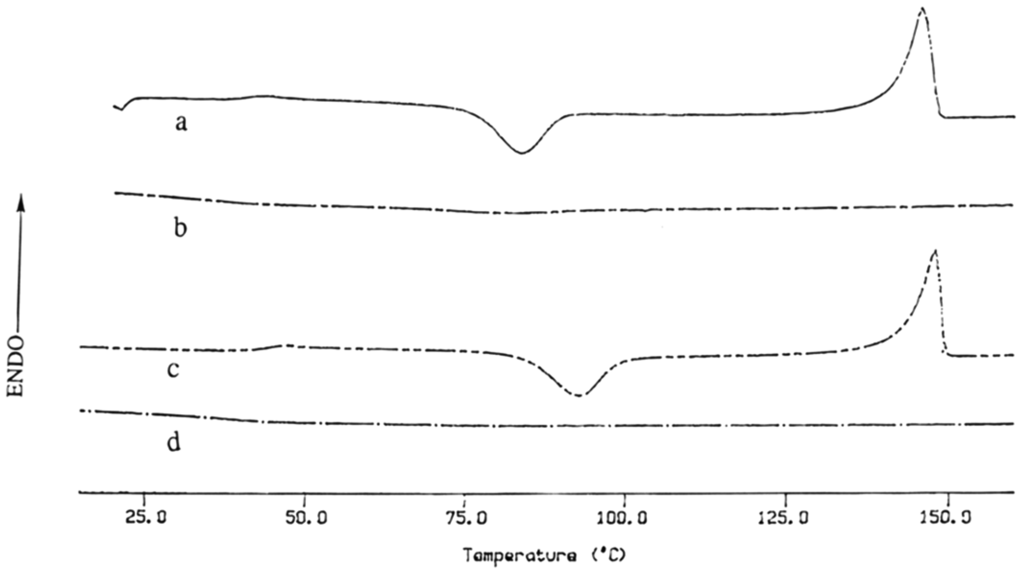

Figure 5. DSC of **C1/2**: (a) heating; (b) cooling; (c) heating after 30 min at 200 °C; (d) cooling after 30 min at 200 °C.

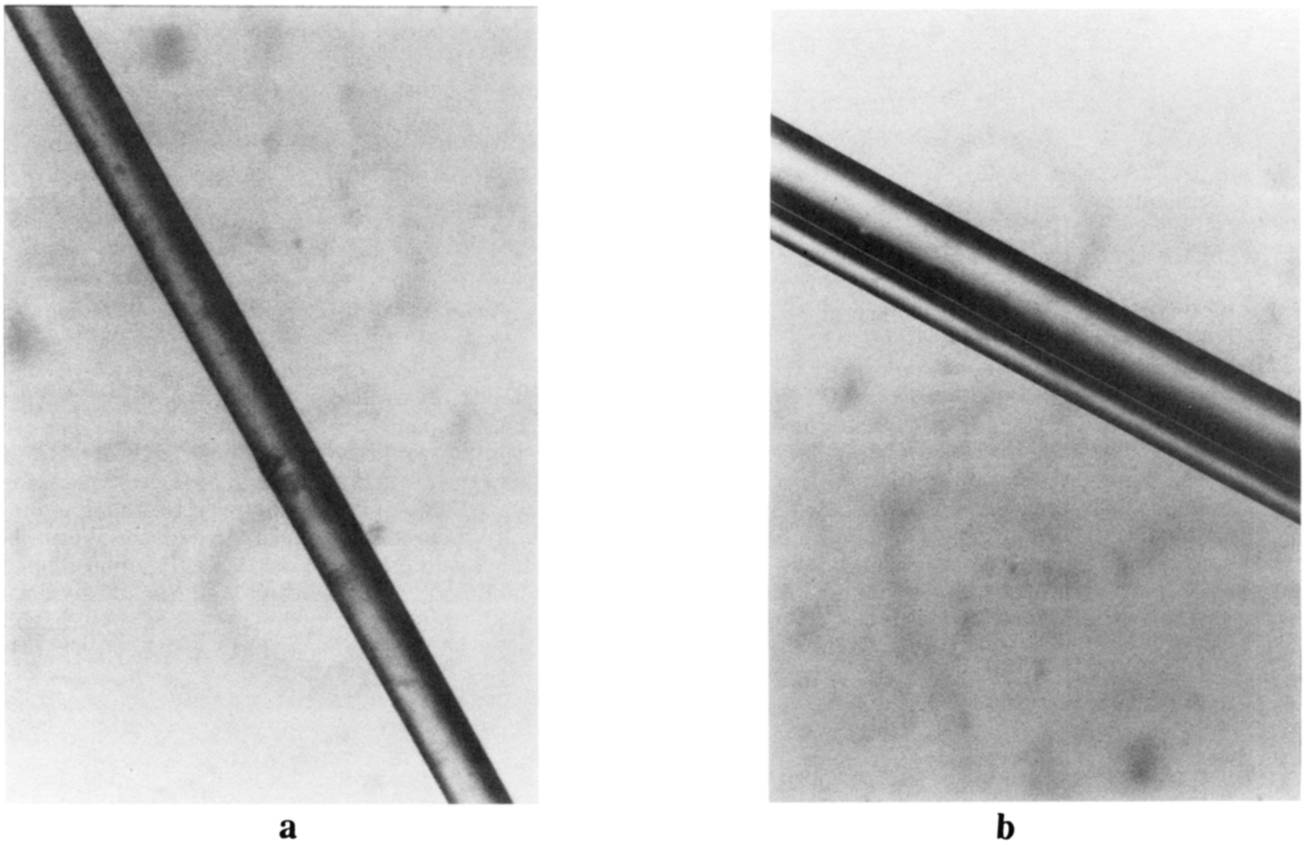

Figure 6. Fiber pulled from the melt of (a) **C1/3** (×100) and (b) **C2/3** (×320).

microscopy confirm the formation of a mesophase at 137 °C on rapid cooling from the isotropic liquid. The mesophase had a very fine, grainy optical texture. Rheology did not give evidence of a mesophase since the sample was almost completely crystalline at 137 °C due to use of a cooling rate of only 3 °C/min. Thermal cycling of **C1/3** causes the thermal behavior to change. After the **C1/3** complex is heated at 200 °C for 30 min and then cooled to room temperature, the melting endotherm broadens and the melting temperature decreases (Figure 3c,d). Crystallization on cooling is suppressed, but cold crystallization begins to occur on subsequent heating. The temperature at which the mesophase forms also decreases, and the mesophase becomes less apparent. A glass transition appears on heating at 71 °C. After heating **C1/3** at 200 °C for 2 h, the IR spectrum was essentially unchanged and no absorptions from possible decomposition products were observed. The DSC trace after this heat treatment was essentially featureless as the melting endotherm became very broad. Polarizing microscopy confirms these latter observations and showed that no crystallization occurred on cooling and that a transparent glass is formed.

Complex **C2/3** when prepared from the melt and cooled to room temperature was a transparent solid. The thermal behavior of this complex was studied by DSC and polarizing microscopy and was found to be similar to that of **C1/3**; see Figure 5. On heating **C2/3** under-

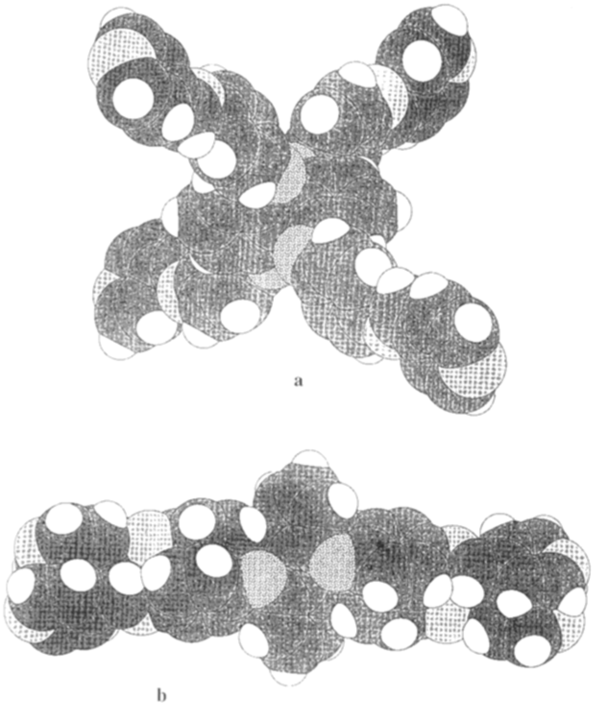

Figure 7. Conformations of tetrapyridyl **1**: (a) pseudotetrahedral; (b) rodlike.

went a glass transition at 41 °C. On further heating cold crystallization was observed followed by melting at 148 °C. The onset of this melting endotherm was ~15 °C below the melting point. DSC shows that on cooling little crystallization occurs, and this was confirmed by polarizing microscopy. Thermal cycling has little effect on the thermal properties of **C2/3**.

The diacid/dipyridyl complexes, reported earlier from this laboratory,[23,25] showed evidence of chain extension, but some of the properties of these complexes were typically those of low molar mass materials. In contrast, doubling the number of binding sites in the pyridyl component such as in complexes **C1/3** and **C2/3** resulted in glass transitions and in fibers which could be pulled from the melt; see Figure 6. These observations suggest that there can be significant chain extension in these materials, thereby giving rise to polymeric properties.[31]

Surprisingly, complex **C1/3** which contains the 2,2′,6,6′-tetrasubstituted biphenyl **1** crystallizes readily and forms a mesophase. The biphenyl unit in tetrapyridyl **1** is twisted about the aryl−aryl bond and might be expected to have a pseudotetrahedral geometry; see Figure 7a. Such a geometry would likely have difficulty packing into a crystalline form.

Indeed, when tetrapyridyl **1** is heated to the isotropic liquid and then cooled, no crystal formation is observed and the compound forms a glass instead. When complexed with a diacid, this pseudotetrahedral geometry would be expected to form a three-dimensional network. There is, however, an alternative rodlike conformation of **1** which, together with the pseudotetrahedral conformation, could account for the observed behavior of **C1/3**. CPK models show that in the rodlike conformation the arms of tetrapyridyl **1** are arranged in two pairs; one arm from each of the aromatic rings of the biphenyl is present in each pair; see Figure 7b. When complexed with a diacid, this rodlike structure might be expected to promote both crystallization and the formation of a mesophase. The driving force in the association of the arms would possibly be the $\pi-\pi$ interactions between the aromatic rings of each arm.[32] When initially prepared, compound **1** is crystalline, which may suggest that the rodlike conformation predominates. When this compound is melted, the $\pi-\pi$ interactions are overcome and the compound adopts the entropically more favored pseudotetrahedral conformation. When cooled, these pseudotetrahedra would have difficulty packing and a glass forms instead. However, when **C1/3** is prepared from the melt, complexation takes place some 30 °C below the melting point of **1** and it seems reasonable that the rodlike conformation might still predominate. Complexation with the acid would then produce a ladder-type linear structure which might be expected to crystallize and to form a mesophase; see Figure 8a. Repeated heating of the sample to an isotropic liquid would overcome most of the $\pi-\pi$ interactions, and the pseudotetrahedral geometry would then predominate, allowing the complex to adopt a more entropically favored network structure; see Figure 8b. The complex would become increasingly amorphous on heating, and both crystallization and mesophase formation would be less likely with each successive thermal

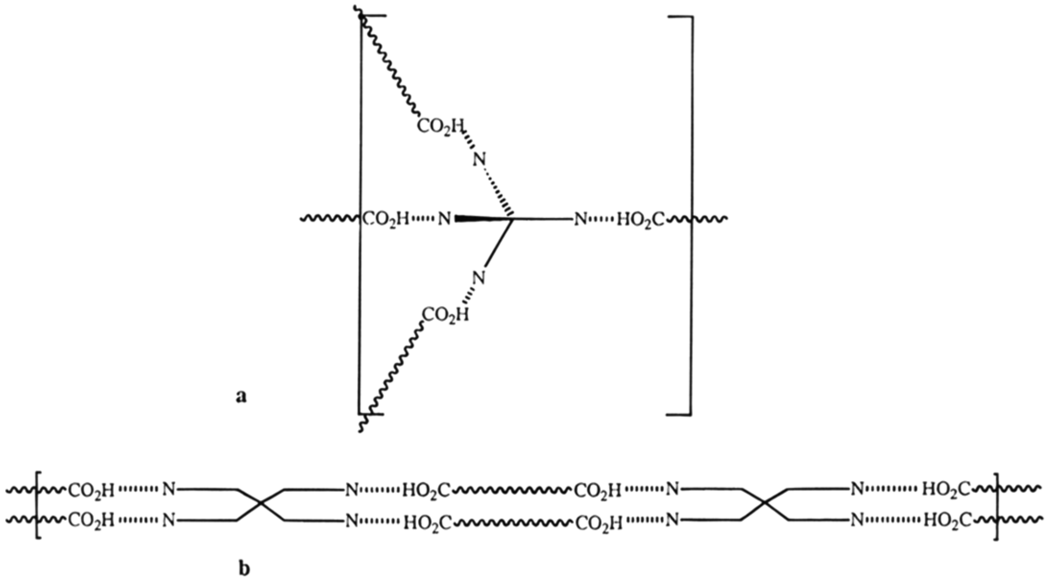

Figure 8. Schematic of (a) network structure and (b) ladder structure.

cycle. The best picture of this system may be one of ordered clusters connected by less ordered hydrogen-bonded regions. At temperatures above 150 °C the larger "crystallites" become mobile with a mechanical behavior dominated by viscous flow ($G'' > G'$), hydrogen bond dynamics. There is still some elasticity, however, due to the large number of hydrogen bonds.

In contrast, tetrapyridyl **2** has flexible arms and short aromatic segments and it would be expected that **C2/3** would adopt a three-dimensional network structure initially rather than a ladder type structure. The short aromatic segments do not allow formation of a liquid crystalline structure on complexation with diacid **3** and therefore there is no strong driving force for ordered "crystallite" clusters as in **C1/3**. This would account for the simple and repeatable thermal behavior of this complex. Further investigation of these thermoreversible networks to probe the dynamics of hydrogen bonding, such as recently reported by Stadler[33] for "sticky" polybutadiene chains, is warranted.

Conclusions

Hydrogen bonding is responsible for the complexation between carboxylic acids and pyridines. Although this simple, single hydrogen bond is capable of generating chain extension and also acting as a vehicle for introducing liquid crystallinity, the reversibility of the hydrogen bonding causes these materials to behave under some conditions more like low molar mass materials rather than polymers. We have prepared two complexes each from a diacid and a tetrapyridyl, which show polymeric properties. This suggests that the reversibility of the hydrogen bonding can be counteracted by increasing the number of hydrogen bonding sites per monomer unit. Remarkably, these three-dimensional supramolecular networks can combine the properties of small molecules at high temperatures yet can behave like polymers at low temperatures.

A mesophase was observed for the complex containing a tetrapyridyl based on a 2,2′,6,6′-tetrasubstituted biphenyl. A twisted structure such as this would not be expected to form a mesophase. It is proposed that the rigid arms in this tetrapyridyl can initially adopt a rodlike conformation which would be more conducive to mesophase formation and linear chain extension. Repeated thermal cycling of the complex containing this tetrapyridyl destroys the mesophase as the tetrapyridyl increasingly adopts a pseudotetrahedral geometry, thereby allowing the complex to form the entropically more favorable network structure.

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