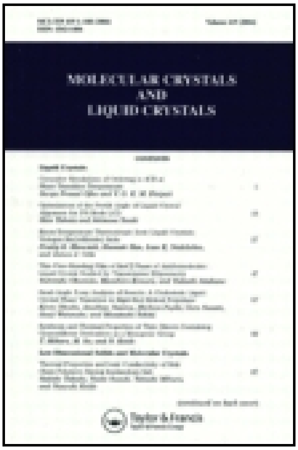

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Chirality in Some Liquid Crystalline Association Chain Polymers

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Chirality in Some Liquid Crystalline Association Chain Polymers

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Two series of sequence random association chain liquid crystalline polymers have been synthesized by melt mixing a bispyridyl with dicarboxylic acids, which in their individual states are not liquid crystals. The phase behavior of two classes of polymer complexes was examined using hot stage polarized light microscopy. It is shown that polymer complexes consisting of (+)-3-methyl adipic acid exhibit a chiral nematic fingerprint texture even at low molar concentration (1.5%) while polymer complexes with an (L)-tartaric acid derivative exhibit a weak fingerprint texture only at high concentration. The effects of the random association chain structure on the thermal behavior of the polymer complexes are also discussed.

Keywords: Random Association; Hydrogen Bond; Chiral; Liquid Crystalline Polymer

INTRODUCTION

The self-assembly of small molecular species to form a well-defined polymeric supramolecular structure through a molecular recognition is of much current interest. Association chain polymers in which the chain structure and liquid crystallinity arise through a hydrogen bonding coupling interaction represent one such example. Liquid crystallinity in this type of polymeric material can be induced by hydrogen bond association between otherwise non-liquid crystalline materials[1-4] or it can be modified by grafting via complexation of new components onto preformed polymers[5-9].

Covalently bonded chiral liquid crystalline polymers (LCPs) have been extensively studied because of their potential application in the field of electronic devices[10]. It is well known that introduction of a spacer containing a chiral carbon in the main chain of a LCP by copolymerizing different mesogenic units may lead to the formation of a chiral mesophase for the copolymer[11]. Recently, chiral mesophases have also been generated through self-assembly of suitable hydrogen-bond donors and acceptors. Yu[12] has reported a series of low molar mass liquid crystalline complexes which exhibit chiral nematic and/or chiral smectic phases made from suitable substituted 4-alkoxybenzoic acids and stilbazoles. Frechet[13] has described the grafting of an optically active stilbazole onto a pendant aromatic unit attached to a preformed polymer via hydrogen bond formation. These complexes exhibited chiral smectic phases. Lehn[1,14] used chiral tartaric acid derivatives and 2,6-diaminopyridine derivatives to generate helical, supramolecular liquid crystalline polymers. It is our interest to study the formation of a polymeric main chain LCP through hydrogen bonding interaction between dicarboxylic acids and bispyridyls. In previous papers, we have studied the packing structure of association chain LCPs[15-17], in particular how the sequence random association chains packed into a smectic phase[15]. It is the aim of this paper, however, to study the influence of concentration of a chiral third component and the resulting sequence random chain structure on the thermal behavior and liquid crystallinity of a typical association chain LCP.

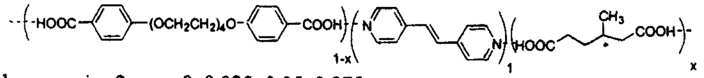
EXPERIMENTAL

Monomers: Tetraethyleneoxy bis-(4-benzoic acid) and the tartaric acid derivative were synthesized according to the literatures[3, 14]. The (+)-3-methyl adipic acid and trans-1, 2-bis-(4-pyridyl)ethylene were obtained from Aldrich.

Polymer Complexes: Polymer complexes, as shown in figure 1, 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 30-120 seconds.

A TA Instruments DSC was used for thermal measurements at heating and cooling rates of 10 °C /min. Polarized light microscopy analysis was done using a Leica series S polarizing light microscopy fitted with a Mettler heating stage.

Polymer series 1: x: 0, 0.025, 0.05, 0.075, 0.10, 0.125



Polymer series 2: x: 0, 0.025, 0.05, 0.075

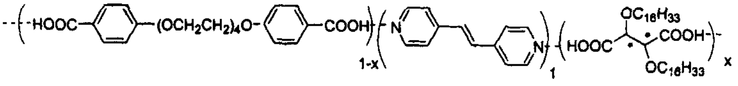


FIGURE 1. Chemical structures of polymer complexes

RESULTS AND DISCUSSION

Three-Component Complexes with (+)-3-Methyl Adipic Acid

Polymer series 1 consists of three components: a bispyridyl and two diacids having pKa values which are approximately equal. These three components in their individual states are not liquid crystalline. A two-component complex between bispyridyl and (+)-3-methyl adipic acid has a melting temperature of 161.5 °C but it is not liquid crystalline. However, the two-component complex between bispyridyl and tetraethyleneoxy bis-(4-benzoic acid) exhibits a nematic phase and a monotropic smectic phase. The thermal behavior of the individual monomers and their two-component complexes is shown in table 1.

TABLE 1 Thermal Behavior of Individual Monomers and their Complexes

Monomers & Complexes	Temperature (°C)
Tetraethyleneoxy bis-(4-benzoic acid)	M.p.: 186
(+)-3-Methyl adipic acid	M.p.: 81-84
Dialkoxytartaric acid	M.p.: 92
Trans-1, 2-bis-(4-pyridyl)ethylene	M.p.: 150-153
Tetraethyleneoxy bis-(4-benzoic acid)/ Trans-1, 2-bis-(4-pyridyl)ethylene	K176.5N178.5I (heating)* I174N168.5S_A159K (cooling)*
Trans-1, 2-bis-(4-pyridyl)ethylene/ (+)-3-Methyl adipic acid	M.p.: 161.5

* K: crystalline solid; N: nematic; S_A: smectic A; I: isotropic

If a small amount of tetraethyleneoxy bis-(4-benzoic acid) is substituted with an appropriate molar amount of (+)-3-methyl adipic acid, it is expected that the mesophase transition temperatures (I-N and N-S) of the resulting three-component complex would decrease for two reasons. Firstly, the effective concentration of the mesogen decreases. Secondly, the sequence randomness of chain structure due to the introduction of a third component frustrates the packing of the mesogenic groups and destabilizes the mesophase further. When the concentration of (+)-3-methyl adipic acid increases, the phase transition temperatures decrease further. Figure 2 is a plot of concentration of (+)-3-methyl adipic acid vs. phase transition temperature. A monotonic decrease of phase transition temperature with an increase of (+)-3-methyl adipic acid concentration was observed.

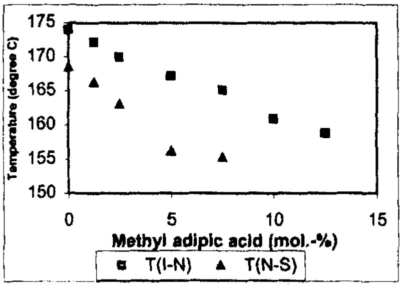


FIGURE 2: Relation between concentration of (+)-3-methyl adipic acid and phase transition temperature.

The phase transition temperatures and the concentration of (+)-3-methyl adipic acid show a linear relation. The slopes for the I-N and N-S curves are -1.2 and -1.9 °C/mol.-%, respectively. The slopes of these curves represent the extent of a third component affecting the mesophase stability, the larger the slope, the greater the effect of the (+)-3-methyl adipic acid in destabilizing the mesophase. Introduction of (+)-3-methyl adipic acid destabilizes the smectic phase more than the nematic phase. When the concentration of the (+)-3-methyl adipic acid exceeds 10 mol.-%, the complex loses its smectic phase. As is known, the formation of a smectic phase requires not only orientational order but also short range positional order of the mesogenic species (layer structure). High concentration of (+)-3-methyl adipic acid leads to an irregular chain sequence which, as we expected, could disrupt the positional order.

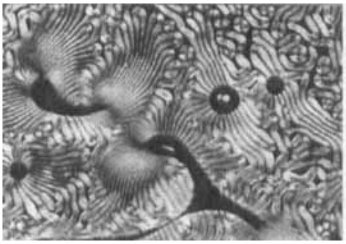


FIGURE 3

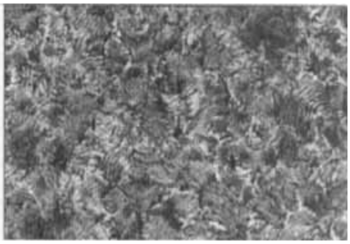


FIGURE 4

FIGURE 5

FIGURES 3,4 and 5: Fingerprint textures of polymer complexes with 1.5, 5.0, 7.5 mol.-% of (+)-3-methyl adipic acid at 168, 164 and 161 °C on cooling, respectively. Magnification X 320.

Polarized light microscopy showed a characteristic fingerprint texture when (+)-3-methyl adipic acid was introduced into the complex, even at the very low concentration of 1.5 mol.-%. This indicates that by doping the polymer with small amount of chiral diacid, the resulting polymer complex exhibits a chiral nematic phase. Figures 3, 4 and 5 are photomicrographs showing the fingerprint texture of polymer complexes with 1.5, 5.0 and 7.5 mol.-% of (+)-3-methyl adipic acid respectively at constant magnification of 320X. It can be seen 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-methyl adipic acid concentration. The increase in concentration of the chiral component twists the nematic director to a larger extent and results in a shorter pitch. In figure 5, the fingerprint structure of polymer complex with 7.5 mol.-% of (+)-3-methyl adipic acid, although present, is not as distinct as those of polymer complexes with 5 or 1.5 mol.-% of (+)-3-methyl adipic acid.

If the concentration of (+)-3-methyl adipic acid is increased up to 10 mol.-%, the fingerprint texture is lost and an unusual texture 'cat's eye' was observed. Further microscopy experiments were done to identify this phase by a contact preparation using this polymer complex and the parent two-component complex of tetraethyleneoxy bis-(4-benzoic acid) / trans-1,2-bis-(4-pyridyl)ethylene. The contact region exhibited a fingerprint texture. This was seen between the typical nematic Schlieren texture of the parent complex and the 'cat's eye' texture of the 10-mol.% chiral doped complex. The contact zone produces a range of concentration less than 10-mol.% dopant. It is apparent that the 'cat's eye' texture represents a highly twisted chiral nematic phase.

The pKa values for the alkyl carboxylic acid and the aromatic carboxylic acid are quite similar. Hence, the competition between these two acids for bispyridyls to form a hydrogen bonded association chain should not be much different. We expected the three-component complex to have a sequence random association chain structure. However, it is difficult to determine the monomer sequence of association chain polymers since they typically dissociate in common solvents. The microscopy study provided useful information regarding the association chain structure. We have seen that the line periodicity of the fingerprint, related to the half pitch of the helical nematic, increases with a decrease of (+)-3-methyl adipic acid concentration. Moreover, there is a linear relation between the line periodicity of fingerprint and the concentration of the (+)-3-methyl adipic acid. This indicates that the (+)-3-methyl adipic acid should be randomly distributed along the polymer chains. If the polymer chains had a blocky copolymer structure, the line periodicity of fingerprint would not be sensitive to (+)-3-methyl adipic acid concentration and the polymer may even exhibit a biphase texture.

Three-Component Complexes with (L)- Tartaric Acid Derivative

Similar to doping with (+)-3-methyl adipic acid, the introduction of the tartaric acid derivative into the polymer system destabilizes the mesophase and lowers the phase transition temperatures. Nevertheless, in the concentration range of this study (2.5 - 7.5 mol.-% of tartaric acid derivative), polymer series 2 exhibits both nematic and smectic phases. The relation between the concentration of tartaric acid derivative and the transition temperatures is shown in figure 6. With an increase in the concentration of the tartaric acid derivative, the phase transitions for both I-N and N-S decrease accordingly. The relations between phase transition temperatures and the concentration of tartaric acid are not linear. The transition temperatures have a larger decrease at a low concentration of tartaric acid. Upon further concentration increase, the phase transition temperatures remain essentially unchanged.

The tartaric acid derivative contains two long alkyl chains ($OC_{16}H_{33}$) at the 2 and 3 positions. These two long alkyl chains would be expected to destabilize a nematic phase. In contrast to the I-N temperatures, the N-S transition temperatures are higher for polymer series 2 than for polymer series 1, indicating a more stable smectic phase. This can be explained using our proposed 'length emulation layer" model for the packing of sequence random association chain polymers in smectic phase[15]. In a random association chain polymer, the formation of a smectic phase depends strongly on the length of the different structural units in the polymer chain. As long as the resulting 'structural units' (mesogenic and/or non-mesogenic) have a similar length, they can be accommodated into the same smectic layer. In polymer series 2, the length of the association structure formed from trans-1,2-bis-(4-pyridyl)ethylene and the tartaric acid is about half of that of the association structure formed from trans-1,2-bis-(4-pyridyl)ethylene / tetraethyleneoxy bis-(4-benzoic acid), which makes it possible for the polymer to form a 'length emulation layer' structure and hence a stable smectic phase by having two 'half-length' structures match laterally with the twice-as-long species. The smectic phase is observed even at about 20 mol.-% of the tartaric acid derivative. For polymer series 1, the length of the association structure between trans-1,2-bis-(4-pyridyl)ethylene and (+)-3-methyl adipic acid is longer than half of the length between trans-1,2-bis-(4-pyridyl)ethylene / tetraethyleneoxy bis-(4-benzoic acid), which does not favor formation of a smectic and the smectic phase was lost when the adipic acid concentration exceed 10 mol.-% phase due to high concentration of defect in the packing structure. It must be mentioned that the long C16 chain could additionally lead to lateral register by interdigitation.

It is interesting that we found only a weak fingerprint texture in a contact preparation experiment at high tartaric acid concentration.

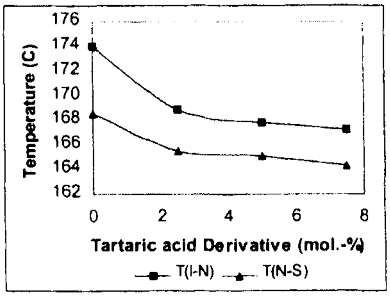


FIGURE 6: Relation between phase transition temperatures and concentration of tartaric acid derivative.

Acknowledgements

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