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Polyimines from Terephthalaldehyde and Aliphatic Diamines. 7. Charge-Transfer Complexes of Some Copolyimines with *p*-Chloranil and 2,4,7-Trinitrofluorenone

H. Yang and A. Natansohn*

Department of Chemistry, Queen's University, Kingston, Ontario K7L 3N6, Canada

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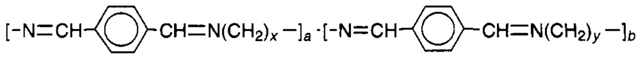
Copolyimines from terephthalaldehyde and combinations of odd–even and even–even numbers of methylene groups in the spacers have been doped with *p*-chloranil (C) and 2,4,7-trinitrofluorenone (TNF) and analyzed by DSC, polarized light microscopy, and X-ray diffraction. The smectic G phase is disrupted for charge-transfer complexes with both dopants, but TNF is much less effective. In fact, the smectic G phase is transformed into a smectic C phase in complexes with C, indicating mixing at a molecular scale. The difference is explained by the different geometry of the electron-accepting dopant. C has a shape similar to the structural unit of the copolyimine (electron donor). TNF is more suited for discotic columnar mesophase formation.

Introduction

There is a significant amount of research in the area of charge-transfer complexes of discotic liquid-crystalline polymers. Typically, electron-donor groups such as substituted triphenylenes are incorporated into the main chain or the side chain of a polymer, and a small molecular electron-acceptor (2,4,7-trinitro-9-fluorenone [TNF], for example) is added to either form or reinforce the columnar discotic phase.[1,2] The opposite example has also been published: a polymer based on the electron-acceptor compound doped with the electron-donor molecule.[3] The addition of the dopant and the charge-transfer complexation provide a stronger tendency to organize in columnar mesophases.

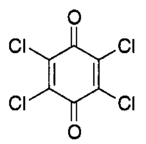
In contrast, very little research has been reported on polymeric calamitic mesophases when charge-transfer complexes are involved. Calamitic liquid crystals contain rodlike mesogenic groups. Polyimines containing dicarbazolylcyclobutane in the main chain form charge-transfer complexes with chloranil and TNF, but no mesophases are induced.[4] A "model" compound for polyimines obtained from terephthalaldehyde and aliphatic diamines has been shown to form charge-transfer complexes with a variety of electron acceptors.[5] This paper presents a followup study of the influence of charge-transfer complexation on the mesophases of two copolyimines: one with an even–even combination of the number of methylene groups in the flexible spacer (8 and 10)[6] and the other with an odd–even combination (3 and 10)[7]. Unlike the initial polyimines,[5] the copolyimines are all soluble in common organic solvents;[6,7] thus their charge-transfer complexes can be prepared by slow evaporation from a common solution. The general formula of a copolyimine and the nomenclature is



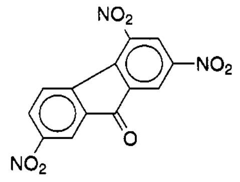
COPI-*x*-*y*(*a*/*b*)

For example, COPI-3-10(9/1) is a copolyimine containing 90 mol % of a 3-methylene spacer and 10% of a 10-methylene spacer. Although the above formula may suggest block copolymers, all copolyimines have a perfectly random distribution of the two structural units.

The electron acceptors used in this study are *p*-chloranil and 2,4,7-trinitro-9-fluorenone:



C



TNF

Experimental Section

The copolyimines were synthesized according to the previously described methods.[5,7] The molecular weights were also reported.[7] *p*-Chloranil (Aldrich) and 2,4,7-trinitrofluorenone (Polysciences) were used as received. Charge-transfer complexes were prepared by mixing chloroform solutions of the two components in the appropriate ratios and letting the solvent slowly evaporate. Drying was performed in vacuum for at least 24 h at room temperature. DSC analysis was performed on a Mettler TA-3000 at heating and cooling scans of 10 °C/min. Optical observations were made on a Nikon Labophot-2 microscope under cross-polarized light and using

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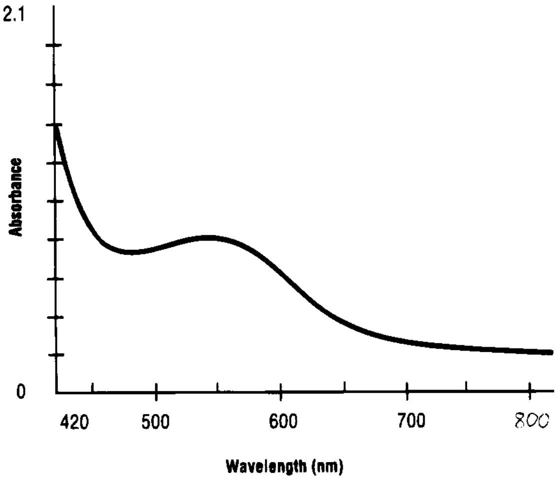

Figure 1. Electronic spectrum of a film containing COPI-3-10(1/9) and C in a 1:1 molar ratio (average structural unit: C).

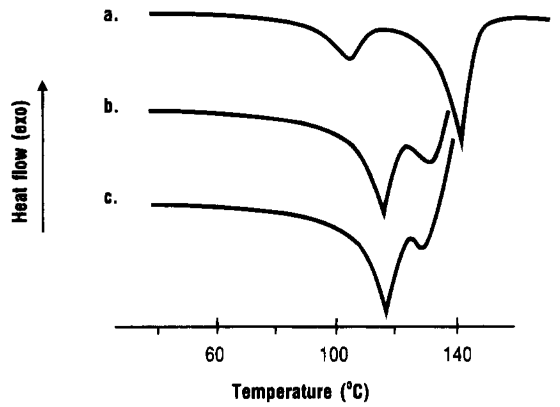

Figure 2. DSC scans on heating of (a) COPI-3-10(1/9), (b) COPI-3-10(1/9) doped with C (10 mol %), and (c) COPI-3-10-(1/9) doped with C (20 mol %).

a Wild-Leitz heating stage. X-ray powder diffraction patterns were obtained using a CSS/STOE 2P/L two-circle diffractometer with a high temperature attachment. Cu radiation was used (λ = 1.5418 Å). Electronic spectra were run on a Hewlett-Packard 8452A UV–vis spectrophotometer.

Results and Discussion

The existence of charge-transfer complexes is clearly proven by the appearance of a color upon mixing the two components, which are colorless by themselves (TNF is light yellow). Complexes with C are purple, while complexes with TNF are brown. However, their electronic absorbances are not very different. Complexes with TNF show a continuous absorbance with a shoulder in the visible region at about 540 nm. Complexes with C have a well-separated visible absorbance with a maximum at about 550 nm, as shown in Figure 1. The copolyimines have no absorbance tail in this region of the spectrum. All electronic spectra are very similar to the spectra of the respective complexes of the model structural unit.[5] A maximum of about 20 mol % C or TNF can be doped into a copolyimine without phase separation. All complexes are stable in air at room temperature.

Complexes with *p*-Chloranil. The DSC curves for complexes of COPI-3-10(1/9) with C are presented in Figure 2. The curves were obtained on heating only, because these complexes start decomposing as they go through their liquid crystalline-to-isotropic transition. COPI-3-10(1/9) is crystalline at room temperature, goes to a smectic G liquid crystalline phase at 99 °C, and clears into an isotropic phase at 136 °C.[7] The smectic G phase is a highly ordered liquid-crystalline phase, being sometimes considered quasi-crystalline.[8] In the undoped COPI-3-10(1/9) the enthalpy of transition from crystal to liquid-crystal phases is smaller than the enthalpy of the clearing transition, mainly because more order is being lost at clearing than by transforming a highly ordered crystalline phase into a relatively highly ordered liquid-crystalline phase. It clearly appears from Figure 2 that upon doping the liquid-crystalline interval narrows progressively with increasing C concentrations. It is also obvious that the ratio of intensities of the two transitions are different in the doped copolyimine as compared with the pure one. The first transition is the dominant one in the complexes, suggesting that the nature of the liquid-crystalline phase may be changed.

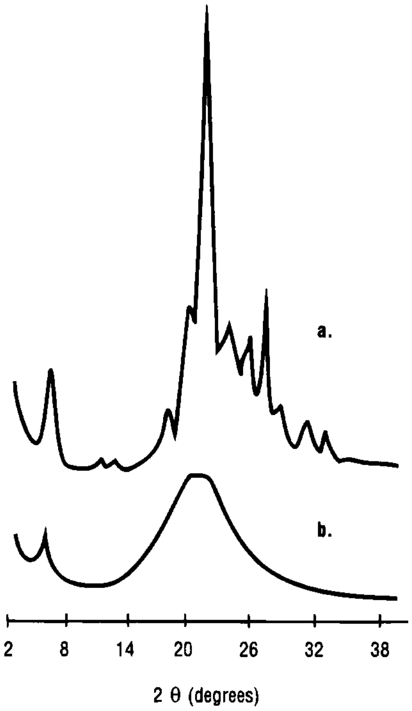

Figure 3. X-ray diffraction pattern of COPI-3-10(1/9) doped with 10 mol % C at (a) room temperature and (b) 127 °C.

Polarized light microscopy supports this hypothesis, the texture of the liquid-crystalline complex looks like a smectic C phase. The best technique to identify the phase is X-ray diffraction, and a diffraction pattern taken at two temperatures is presented in Figure 3. At room temperature, the complex is crystalline, and the presence of a peak at a 2θ value of 26° indicates that some of the *p*-chloranyl is phase separated and forms independent crystals. The diffraction pattern at 127 °C shows that all *p*-chloranil is complexed now (the melting point of pure *p*-chloranil is 289 °C) and that the liquid-crystalline phase is definitely not of a smectic G type, but much less ordered. The fact that the X-ray diffraction pattern is consistent with a smectic C phase, combined with the optical microscopy data and with the fact that the copolyimine smectic G phase was tilted (as

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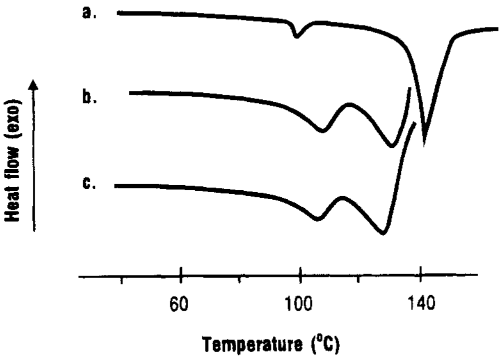

Figure 4. DSC scans on heating of (a) COPI-8-10(5/5), (b) COPI-8-10(5/5) doped with C (10 mol %), and (c) COPI-8-10-(5/5) doped with C (20 mol %).

smectic C is) strongly suggests that the liquid-crystalline phase of these complexes is smectic C. This also agrees with the DSC data. A crystalline-to-smectic C transition would be more intense than a smectic C-to-isotropic transition. The enthalpy changes associated with the smectic-to-isotropic transition are about 3 kJ/mol for a complex containing 10 mol % C and about 2 kJ/mol when the complex contains 20 mol % C.

The DSC curves for complexes of COPI-8-10(5/5) with C are shown in Figure 4. The effect of adding chloranil to COPI-8-10(5/5) is similar to its effect on COPI-3-10-(1/9). The liquid-crystalline interval is narrower in the complexes than in the copolyimine, but it does not change much when an increasing amount of C is present in the complex. In this instance as well, the complex is much more unstable upon heating than the copolyimine and decomposes as it becomes isotropic. There is an increase in the enthalpy of crystalline to smectic transition in the complex, but the enthalpy is still lower than the enthalpy of the smectic to isotropic transition. On the basis of the DSC curves, it is reasonable to assume that the smectic phase is still of the same type as in the copolyimine.

Complexes with 2,4,7-Trinitrofluorenone. The DSC scans of a COPI-3-10(1/9) sample doped with increasing amounts of TNF are presented in Figure 5. When TNF exceeds about 20 mol %, its melting peak starts being visible at 178 °C, indicating that this is probably the maximum amount of TNF which forms homogeneous mixtures with the copolyimine. Unlike chloranil, TNF has no major effect on the transition temperatures exhibited by the copolyimine. The ratio of the enthalpies of the two transitions (crystalline to smectic G and smectic G to isotropic) remains about constant, and the only change is a narrowing of the smectic G range from both directions. The crystalline phase is slightly stabilized while the smectic G phase is less stable upon doping with TNF. X-ray diffraction patterns indicate the presence of the same smectic G phase in the complexes as in COPI-3-10(1/9).

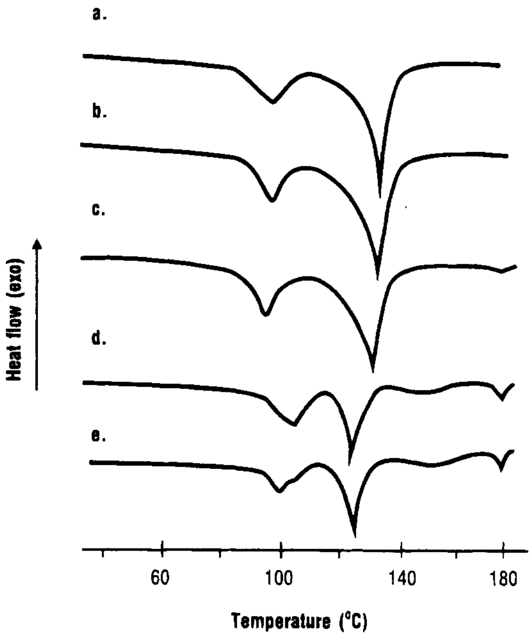

Figure 5. DSC scans on heating of (a) COPI-3-10(1/9), (b) COPI-3-10(1/9) doped with 10 mol % TNF, (c) COPI-3-10(1/9) doped with 20 mol % TNF, (d) COPI-3-10(1/9) doped with 30 mol % TNF, and (e) COPI-3-10(1/9) doped with 50 mol % TNF.

Analysis of these charge-transfer complexes confirms that the shapes of the mesogen (electron donor in this case) and of the complexing agent (electron acceptor) are very important for determining the properties of the resulting change-transfer complex. Chloranil is fairly similar in shape to the terephthalimine unit with which it forms the complex. This allows for a better packing, with the dopant penetrating between copolyimine chains and disrupting its self-organization behavior. Thus, a more ordered smectic G phase becomes a smectic C phase when complexation takes place. TNF has a more ringlike geometry, very useful in forming various discotic liquid-crystalline phases, but inefficient in the copolyimine case, where it only seems to produce a narrower liquid-crystalline interval without actual disruption of the polymer geometry and arrangement. It is likely that TNF forms complexes mainly with the amorphous part of the copolyimine; in the amorphous phase the supramolecular arrangement of the complexing groups has a lesser effect on the organized structures.

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