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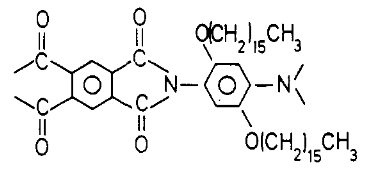
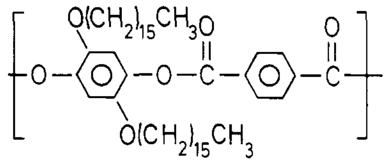
Rigid-Rod Polymers with Flexible Side Chains. 6. Ordered Phases from Solid Solutions of Two-Component Blends As Investigated by Wide-Angle X-ray Scattering

Many examples of classical isotropic polymers are known which give miscible blends. The techniques of characterizing these blends are also rather well understood.[1] Miscibility in the case of liquid-crystalline (LC) polymers has received much less attention. For mixtures of LC side-chain polymers and low molecular weight LCs studies have been performed.[2,3] Miscibility between two stiff-chain polymers presents a different situation. On the one hand, the classical techniques of investigating compatibility are difficult to apply to these systems. On the other hand, these materials are frequently intractable and insoluble leading to difficulties in blend preparation. As shown in a number of recent publications[4–7] the solubility of a number of stiff-chain polymers has been considerably improved by appending flexible side chains to the backbone. In addition, these flexible side chains lead to the formation of LC phases at temperatures where thermal degradation is not a problem. If the side chains are long enough, these systems generally form layered mesophases manifested by strong Bragg reflections characteristic of the side-chain length. The layering seen in these substances by wide-angle X-ray diffraction (WAXS) provides a unique opportunity to study their mixtures at a molecular level. In this paper we present preliminary results from a study of one series of blends of polyimides with polyesters by WAXS and discuss their compatibility.

The polymers considered were a poly(2,5-bis(hexadecyloxy)-1,4-phenylene terephthalate) (abbreviated PE16) and a polyimide prepared from pyromellitic anhydride and 2,5-bis(hexadecyloxy)-1,4-phenylene diisocyanate (abbreviated PI16).



PI 16



PE 16

Polymer PE16 was prepared as described previously;[4] η_{inh} was measured as 2.07 dL/g in $CHCl_3$ at 25 °C. Polymer PI16 was prepared as described by Wenzel.[6] He quotes η_{inh} values of 0.45 dL/g in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone, DMPU, at 25 °C. Blends were prepared by dissolving the polymers in hot (about 100 °C) DMPU to form a clear solution which was subsequently reprecipitated in methanol to give fine powders. The powders were dried at 100 °C under vacuum for 72 h. A series of five blend compositions was made, PI16 with 10, 30, 50, 70, and 90 wt % PE16. Before study, all materials were heated to 220 °C and slowly (about 1 K) cooled to ambient temperature to avoid sample preparation and thermal history related artifacts. The blends were studied by X-ray diffraction (Siemens D500 diffractometer in reflection mode with Ni filtered Cu Kα radiation), DSC (Perkin-Elmer DSC-7), and polarizing optical microscopy.

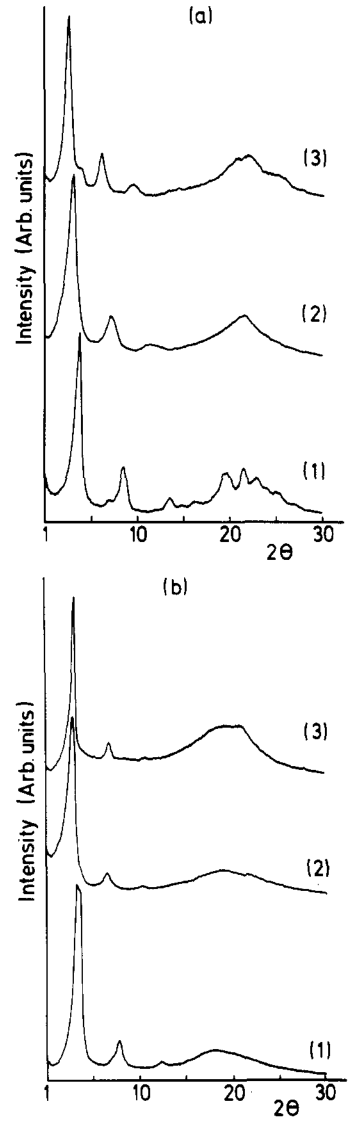


Figure 1. X-ray diffractograms of blends and pure components (a) at 30 °C and (b) at 200 °C; (1) PI16; (2) 50 wt % PI16/PE16 blend; (3) PE16.

After study, one blend was extracted with $CHCl_3$, which only dissolves the polyester. The resulting solid was analyzed and consisted of the pure PI16 material, indicating that no chemical reactions between the two components occurred during heating.

The X-ray diffractograms taken for pure PE16, PI16, and the 50 wt % blend at 30 and 200 °C are shown in Figure 1. The pure PE16 at 30 °C (Figure 1a, curve 3) shows three sharp reflections in the small-angle region at spacings of 25.8, 12.7, and 8.5 Å, respectively, indicating a lamellar-type structure termed A which has been described previously.[5] The wide-angle region presents several reflections superimposed on a broad halo. These are primarily due to ordering of the side chains. A shoulder is observed at a spacing of approximately 19.5 Å in "as reprecipitated" material due to small amounts of a second crystalline modification termed B and described elsewhere.[5] This 19.5 Å shoulder disappears following the first melting and was not seen in any of the blends. At 200 °C (Figure 1b, curve 3), the X-ray diffractogram again consists of three orders of reflections in the small-angle region. Only an amorphous halo is seen in the wide-angle region indicating disorder of the side chains. The PE16 polymer melts at about 215 °C to give a diffractogram consisting of a broad amorphous halo centered around a spacing of

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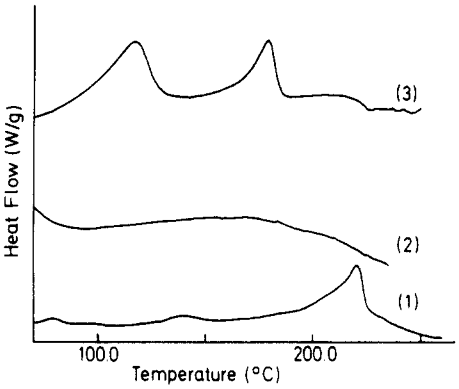

Figure 2. DSC heating curves taken at 20 K and normalized per gram of material; (1) PE16; (2) 50 wt % PI16/PE16 blend; (3) PI16.

23.5 Å and a second amorphous halo centered around 5 Å. The DSC heating scan of PE16 taken for temperatures higher than 100 °C (Figure 2, curve 1) consists of a small endotherm at about 140 °C associated with the formation of the mesophase and another endotherm at about 215 °C corresponding to the transition to the isotropic melt. Transition temperatures determined by optical microscopy were in agreement with the DSC analysis.

The X-ray diffractograms of pure PI16 are shown in curves 1 of Figure 1a,b. At 30 °C (Figure 1a) this polymer also shows three orders of small-angle reflections at spacings of 20, 9.8, and 6.5 Å, respectively, indicating a lamellar structure with a layer spacing of 20 Å. The wide-angle region consists of a broad halo under several sharp reflections due to ordering in the side chains. The shoulder at 11.7 Å has been assigned to the polyimide backbone repeat unit.[6] At temperatures between about 110 and 175 °C a layered phase of intermediate ordering is seen and has been described elsewhere.[6] At 200 °C (Figure 1b, curve 1) the X-ray diffractogram also consists of three orders of small-angle reflections, indicating lamellar layering. An amorphous halo centered around 5 Å is attributed to disorder of the packing of the side chains. The DSC heating scan of the PI16 polymer (Figure 2, curve 3) consisted of an endotherm at about 110 °C and a second endotherm at about 175 °C corresponding to the formation of the mesophase. The PI16 polymer did not show further changes on heating in the X-ray diffractograms, DSC curves, or under the polarizing optical microscope until it thermally decomposed at temperatures of about 350 °C.

It should be noted that the PE16 and PI16 polymers show vastly different layer spacings (about 26 and 20 Å, respectively) even though the length of the pendant side chains is the same. This has been discussed previously.[4,5]

Diffractograms from the 50 wt % blend of PE16 with PI16 are shown in curves 2 of Figure 1a,b. At 30 °C (Figure 1a, curve 2) the blend shows three orders of small-angle reflections at spacings of 22.8, 11.4, and 7.6 Å, corresponding to a layer repeat of 22.8 Å. No evidence was seen for reflections in either the 20 or 26-Å region. The wide-angle region consists of a single rather sharp halo at a spacing of about 4.3 Å. At 200 °C (Figure 1b, curve 2) the diffractogram also shows three orders of small-angle reflections corresponding to a layer spacing of 24.7 Å and an amorphous halo centered at 4.9 Å in the wide-angle region. On heating above this temperature, no further changes were seen by X-ray diffraction or polarizing optical microscopy. The DSC heating curve (Figure 2, curve 2) did not show any endotherms.

The WAXS diffractograms of the blends thus clearly indicate miscibility of the two polymers. If a two-phase system was formed during blending, one would expect to see a superposition of the WAXS scattering corresponding to each pure component. It is obvious from the small-angle region of Figure 1a,b that here one sees not the superposition of the two pure components but new peaks intermediate between those of the pure polyester and polyimide. Furthermore, though the presence of extremely small domains of phase-separated material might give rise to an intermediate maximum, the presence of three orders of small-angle reflections observed for the blend rules out this possibility. The absence of distinct reflections in the wide-angle region of the blend at 30 °C indicates that the side chains are less ordered than those of either the pure polyimide or polyester at 30 °C. The DSC curves in Figure 2 also indicate that the blend does not show thermal transitions associated with either pure component. Here, presumably the long side chains induce molecular miscibility of the polyester and polyimide backbones, but due to the different geometries of these backbones, the side chains are not able to order as well as in the pure components alone.

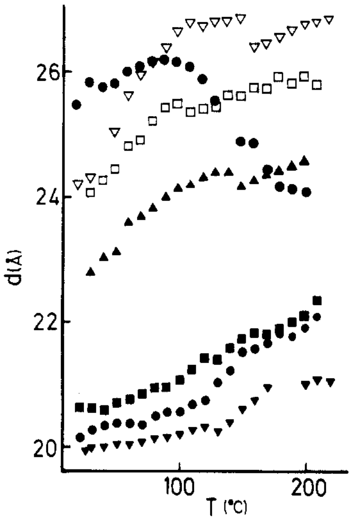

Figure 3. Temperature dependence of layer spacing, d, for different blend compositions; (1, ●) pure PE16; (2, ▽) PE16 with 10 wt % PI16; (3, □) PE16 with 30 wt % PI16; (4, ▲) PE16 with 50 wt % PI16; (5, ■) PE16 with 70 wt % PI16; (6, ○) PE16 with 90 wt % PI16; (7, ▼) PI16.

While miscibility of polymers to produce compatible amorphous phases is well-known,[1] here an ordered phase is seen to form a miscible polymer/polymer blend. It should be pointed out, however, that miscibility of low molecular weight liquid crystals to give liquid-crystalline mixtures[8] and miscibility of metals to give ordered solutions[9] are well-known. This seems to be an analogous case in the area of polymers. The possibility of continuously tailoring structure by blends of self-organizing polymers is worthwhile to be explored further from a theoretical as well as a practical viewpoint.

The temperature dependence of the observed layer spacing as a function of composition is shown in Figure 3. The pure PI16 (curve 7) shows a monotonic increase in layer spacing as a function of temperature. The pure PE16 (curve 1), on the other hand, behaves quite differently. The layer spacing increases with temperature to about 80 °C; then in the mesophase the layer spacing decreases with temperature as has been seen previously.[5] The PI16/PE16 blends (curves 2–6) show monotonically increasing layer spacing as a function of temperature.

One interesting difference between the blends and the pure components is the behavior of the blends with low polyimide content. With only 10 wt % polyimide, the

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negative layer spacing temperature coefficient of the polyester disappears and the positive coefficient of the polyimide seems to dominate. The thermal behavior of the 30 wt % blend is similar. In fact, the transition to an apparently isotropic melt seen with the pure polyester disappears and a layered mesophase is seen to about 350 °C, where thermal decomposition becomes a serious problem. One explanation for this might be a "stiffening" of the polyester backbone by the very rigid polyimide component. This behavior is currently being investigated in detail.

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Registry No. PI16 (copolymer), 115563-56-9; PI16 (SRU), 112231-33-1; PE16 (copolymer), 115563-54-7; PE16 (SRU), 115563-57-0.

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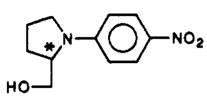
Persistent, Efficient Frequency Doubling by Poled Annealed Films of a Chromophore-Functionalized Poly(*p*-hydroxystyrene)

All synthetic strategies for polymeric second-harmonic generation (SHG) materials[1] must address the crucial issues of maximizing chromophore densities while achieving maximum, persistent noncentrosymmetry. An attractive alternative to poling glassy polymers simply doped with nonlinear optical (NLO) chromophores[2–4] are materials in which NLO chromophores are covalently linked to the polymer backbone,[5,6] thus offering potential impediment both to phase separation at high chromophore densities and to deleterious relaxation[4a] of poling-induced chromophore alignment. We report here an embodiment[7] of this strategy which employs structure–enforcing hydrogen-bond networks,[8] achieves high chromophore densities, and affords polymer films with persistent (on a timescale of months) second-harmonic coefficients d_{33} ($^1/_2\chi^{(2)}_{333}(-2\omega;-\omega,\omega)$) equal to or in excess of the corresponding value for $LiNbO_3$. General observations relevant to NLO film processing and the applicability of current theoretical models[3] are also reported.

Poly(*p*-hydroxystyrene)[9] ($\bar{M}_W \approx 6000$; $T_g \approx 155$ °C) was functionalized[10] to varying levels (15–60% of phenol rings) with the tosylate[11] of *N*-(4-nitrophenyl)-L-prolinol (NPPOH,[12] eq 1) and was purified by washing with acetone

$$\text{(PS)OH} + \text{NPPOTs} \xrightarrow{H_2O,\ OH^-} \text{(PS)O-NPP} + \text{HOTs} \qquad (1)$$

NPPOH =


and repeated precipitation from THF with methanol. Products were characterized by 400-MHz ^{1}H NMR, FT-IR, elemental analysis, DSC, and optical spectrophotometry.[13] In a class 100 laminar-flow clean hood, 1–5-μm films of (PS)O-NPP were cast onto ITO-coated conductive glass from multiply filtered THF solutions. The films were then annealed at 100 °C for 2 h prior to dc poling. The effect of annealing is to enhance the ultimate poling fields which can be achieved and the temporal stability of the SHG capacity (vide infra). The reason appears to be removal of traces of THF and other volatiles (verified by FT-IR) which plasticize the material and enhance macromolecule mobility (supported by DSC[14]), independent or concurrent changes in the hydrogen-bonding network[15] (verified by FT-IR[16]) which may also affect mobility and changes in film morphology (suggested by SEM) which may seal imperfections leading to dielectric breakdown during poling.[17] The annealed films were covered with an aluminum electrode, heated to 80 °C, and poled by incrementally increasing the field with online current monitoring (to detect the onset of dielectric breakdown processes). The film was held at the maximum field for 0.5 h and then cooled in the presence of the field. Careful film fabrication and annealing allowed poling at dc fields as high as 1.8 MV/cm, which appears to be near the limit of what is practicable for typical polymer thin films.[17] In contrast, experiments with *doped* NPPOH/PS or (PS)OH films indicated phase separation (and opacity) at chromophore concentrations as low as 5 mol %, frequent breakdown at low poling fields (presumably reflecting greater mobility), and weak, shorter lived SHG performance (presumably reflecting greater chromophore mobility).

Table I
Second-Harmonic Coefficients for Chromophore-Functionalized Polystyrenes[a]

material	functionalization level % phenyl rings	poling field, MV/cm	d_{33},[b] 10^{-9} esu
(PS)CH_2-DR	12.5	0.3	2.7[c]
(PS)CH_2-DASP	4.5	0.3	0.12[c]
(PS)O-NPP	15.0	0.7	5.1 (5.7)
(PS)O-NPP	25.0	0.3	3.0 (3.6)
(PS)O-NPP	48.0	0.6	11.6 (10.9)
(PS)O-NPP	48.0	1.6	18.0 (29)

[a] Measured within 0.5 h of poling; λ = 1.064 μm. [b] Experimental SHG coefficients. Quantities in parentheses are theoretical values of d_{33} estimated from eq 2 and 3. [c] From ref 5. DR = 2-[4-[(4-nitrophenyl)azo]-*N*-ethylanilino]ethoxy; DASP = 4-(4-(dimethylamino)styryl)pyridinium iodide.

Second-harmonic coefficients of the (PS)O-NPP samples were measured at 1.064 μm in the p-polarized geometry by using the instrumentation and calibration techniques described previously.[5] Second-harmonic coefficients were calculated from the angular dependence of the second-harmonic intensity and the formalism of Jerphagnon and Kurtz for uniaxial materials, assuming also that $d_{31} = d_{24} = d_{15} = {}^1/_3 d_{33}$.[3,10,18] Film thicknesses were measured after SHG experiments by using a Tencore Alpha-Step 200 profiler. Representative data are set out in Table I. It can be seen that the (PS)O-NPP second-harmonic coefficients are rather large, exceeding the corresponding d_{36}

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