into account a higher value is obtained, in good agreement with the ESR results. A tilted arrangement was recently proposed for porphyrin–fluorohectorite intercalates based on X-ray diffraction data but with a much smaller tilt angle (ϕ = 7°). Note, however, that the low-charge fluorohectorite used in the previous study possesses a charge intermediate to the natural hectorite and fluorohectorite used in the present study.

Thus, intercalation of layered solids can be used to manipulate the structure of supermolecular assemblies. Specific guest–host interactions significantly influence the molecular organization (orientation and alignment) of guest molecules in the galleries of the layered template. By controlling these subtle interactions, one can mediate the architecture of a material at the molecular level. Experiments are in progress to evaluate the nonlinear optical and hole-burning properties of these new supermolecular assemblies.

Registry No. CuTMPyP, 48242-70-2; hectorite, 12173-47-6; fluorohectorite, 68084-70-8.

Molecular Composites of Rigid-Rod Polymers in the Matrix of Flexible-Coil Polymers. Preparation of Thin-Film Nonlinear Optical Materials via Soluble Complexes
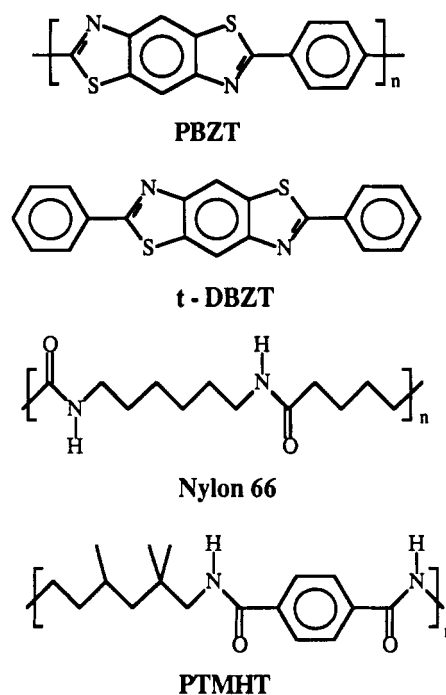
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Molecular composites[1-8] are composite materials in which a high-strength, high-modulus, rigid-rod polymer is molecularly dispersed in the matrix of a flexible-chain polymer. One important aim of such a material system concept is to improve the mechanical properties, such as tensile strength and modulus, by a complementary blend of the structural and physical properties of the component polymers. Rod/coil molecular composites whose preparation, processing, phase behavior, and mechanical prop-

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Scheme I

PBZT

t-DBZT

Nylon 66

PTMHT

erties have been investigated include poly(*p*-phenylene-benzobisthiazole) (PBZT)/poly(2,5(6)-benzimidazole) (ABPBI),[1,2] 1,1-PBZT/poly(2,5(6)-benzothiazole) (ABPBT),[1,2] PBZT/poly(hexamethyleneadipamide) (nylon 66)[5,6] poly(*p*-phenyleneterephthalamide) (PPTA)/nylon 66, and PPTA/poly(caprolactam) (nylon 6).[4] These rod/coil composite materials are generally prepared from ternary solutions in strong concentrated protonic acids such as methanesulfonic acid (MSA).[1-8] The electroactive, linear optical, and nonlinear optical properties of rod/coil molecular composites have so far not been investigated.

Molecular composites that contain an electroactive or nonlinear optical component or components such as the conjugated rodlike PBZT and semiflexible coils ABPBI and ABPBT expand the range of organic solid-state materials and can be expected to exhibit a complementary blend of electroactive and optical properties. In this regard, although it would seem that the upper limits on the electroactive properties of molecular composites are set by those of the components, such a class of materials is nevertheless of theoretical and practical interest. For example, such composite materials are important model systems for the investigation of the effects of morphology and composition on electroactive and nonlinear optical properties. Also, in the case of third-order nonlinear optical (NLO) properties, there is precedence for enhanced NLO properties of composite materials (e.g., metal- or semiconductor-doped glasses and polymers) compared to the starting component materials.[9,10]

We report the preparation of thin films of rod/coil molecular composites of PBZT/nylon 66 (see Scheme I) and PBZT/poly(trimethylhexamethyleneterephthalamide) (PTMHT) using a novel approach of ternary solutions of the Lewis acid complexes of the polymers in organic solvents. We also demonstrate that the PBZT/nylon 66 and PBZT/PTMHT molecular composites have interesting nonlinear optical properties as will be reported in detail elsewhere.[11] We have previously reported that Lewis acid

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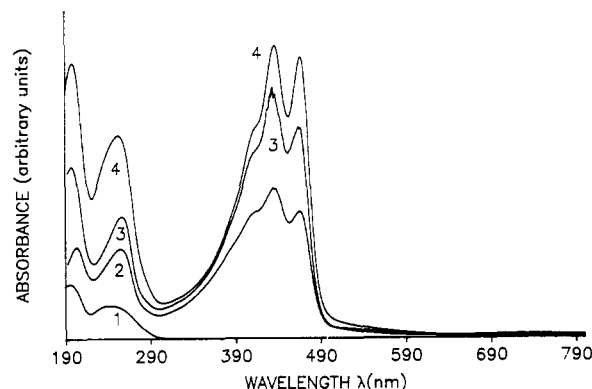| system	composite composition, wt %	solvent[a]	C_{cr}, wt %
1:1 PBZT/nylon 66	54/46	$AlCl_3$/NM	5.1
1:1 PBZT/nylon 66	54/46	$GaCl_3$/NM	9.0
1:1 PBZT/PTMHT	48/52	$AlCl_3$/NM	5.7
1:1 PBZT/PTMHT	48/52	$GaCl_3$/NM	9.5

[a] NM = nitromethane.

(e.g., $AlCl_3$ and $GaCl_3$) complexes of rodlike PBZT[12-14] and coillike polyamides[15] are soluble in organic solvents. In the case of PBZT–Lewis acid complexes, nematic liquid-crystalline solutions in organic solvents were obtained at about 7 wt % or higher.[13]

The PBZT sample used has an intrinsic viscosity of 18 dL/g and was provided by the Polymer Branch of the Air Force Materials Laboratories (Dayton, OH). The nylon 66 sample (Polysciences Inc., Warrington, PA) has a M_w ~ 12000–18000, a glass transition temperature (T_g) of 55 °C, and a crystalline melting temperature (T_m) of 260 °C. The PTMHT sample (Scientific Polymer Products, Inc., Ontario, NY) has a T_g of 153 °C and no observed T_m. Nitromethane (99+%, Aldrich), aluminum(III) chloride (99.9%, Aldrich), and gallium(III) chloride (99.99+%, Aldrich) were used as received.

The following solution preparations were done in a drybox filled with nitrogen. Ternary solutions of the polymer–Lewis acid complexes for preparing the PBZT/nylon 66 and PBZT/PTMHT composites were prepared by codissolving the polymers in $AlCl_3$/nitromethane or in $GaCl_3$/nitromethane. A minimum of 4 mol of Lewis acid/mol of PBZT repeating unit and 2 mol of Lewis acid/mol of polyamide repeating unit were found necessary to completely dissolve the polymers and form their complexes in solution.[14] In practice, 10–20 mol % Lewis acid in excess of these minima was used for preparing the present solutions. Polymer dissolution was aided by mechanical stirring in the case of dilute solutions and by gentle heating at 40–60 °C in the case of the more concentrated and viscous solutions. In this way homogeneous solutions of a range of total polymer concentrations were prepared with various mole ratios of PBZT/nylon 66 and PBZT/PTMHT. The total polymer concentration of solutions used to prepare the molecular composites was well below the critical concentration (C_{cr}) for anisotropic phase separation as ascertained by observation under a polarized microscope. The typical critical concentration and phase equilibria data for several PBZT/polyamide ternary solutions in Lewis acid/nitromethane are shown in Table I. The very high critical concentration in $GaCl_3$/nitromethane solutions is significant and very important for bulk molecular composites processing.

Free-standing or supported thin films of the rod/coil molecular composites were obtained from ternary solutions by either of two ways. In the first method, films of solution between glass substrates were immersed in deionized water or methanol for 12–16 h to coagulate or regenerate the solid composite and remove the Lewis acid. In the second

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Figure 1. Electronic spectra of thin films of PTMHT (1), PBZT (2), 1:1 PBZT/nylon 66 (3), and 1:1 PBZT/PTMHT (4).

method, solution cast liquid films were dried at 80–100 °C to obtain the solid composite–Lewis acid complex, which is subsequently immersed in deionized water or methanol to get the desired solid molecular composite. In each case the coagulated molecular composites were dried in a vacuum at 60–70 °C for 12–16 h. Only the results of films of molecular composites coagulated by the first method are presented here.

The solid composite complexes PBZT–$GaCl_3$/PTMHT–$GaCl_3$ were found to exhibit reproducible T_g's in the range 10–20 °C. The occurrence of such low T_g values for these rod/coil composite complexes is not unexpected since we have observed similar T_g behavior in the component polymer complexes.[14-16] This result is important for possible melt processing of molecular composites at relatively low temperatures where crystallization and phase separation phenomena might not occur. Also, this low T_g will allow stretch orientation of molecular composites, before coagulation, to deliberately induce anisotropic composite morphology.

The composition, morphology, and optical quality of thin films of the rod/coil composite materials were investigated by FTIR, UV-vis, thermal analysis, and optical microscopy. Although elemental analysis was not done on the coagulated composites, prior analytical data for the pure component polymers coagulated from similar Lewis acid solutions showed negligible $AlCl_3$ or $GaCl_3$ (<0.5%).[12,14] The FTIR spectra of the molecular composites were a superposition of the component spectra and did not reveal any evidence of cross-hydrogen-bonding between molecules of PBZT and those of the polyamides. The UV-vis spectra of thin films of some of the PBZT/nylon 66 and PBZT/PTMHT molecular composites are shown in Figure 1. The electronic spectra of the composite materials consisted of the superposed spectra of the components. All the absorption bands of the component polymers were well resolved down to 185 nm, including nylon 66 (λ_{max} ~ 200 nm), PTMHT (λ_{max} = 242, 195 nm), and PBZT (λ_{max} = 468, 437, 253, 200 nm). This suggests homogeneity of the molecular composites to at least the order 180 nm. In contrast, the thin films that were purposely heated to 200–300 °C to induce phase separation were largely opaque. The UV-vis spectra of Figure 1 also showed that nonresonant NLO measurements could be made above 500 nm. Thin films of the PBZT/polyamide composites were transparent yellow and of good optical quality suitable for the THG experiments that will be described later.

Differential scanning calorimetry (DSC) was also used to investigate the morphology and phase behavior of the rod/coil molecular composites. The as-prepared PBZT/

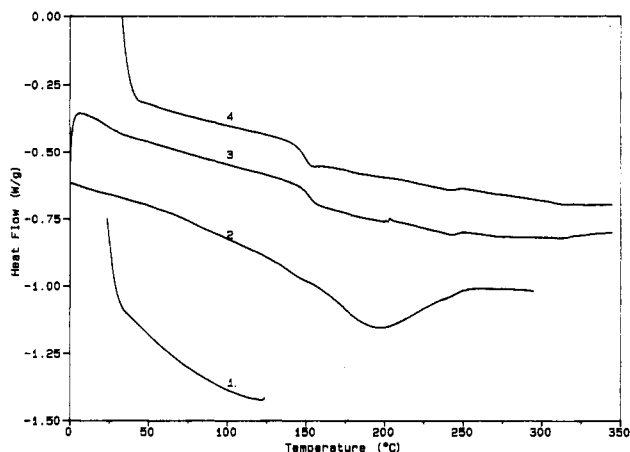(16) Roberts, M. F.; Jenekhe, S. A., manuscript in preparation.

Figure 2. DSC thermograms of the 1:1 PBZT/PTMHT composite heated at 20 °C/min. The first (1), second (2), third (3), and fourth (4) heating indicated.

PTMHT composites did not exhibit any T_g. However, as Figure 2 shows, after first and second heating to 300 °C, cooling, and reheating, the 1:1 PBZT/PTMHT composite showed a sharp T_g at 153 °C, which is identical with the T_g of the pure PTMHT. In the case of PBZT/nylon 66 composites, the DSC results revealed a broad endothermic transition with peak at 247 °C on first heating to 300 °C. Cooling and twice reheating the same sample to 300 °C resulted in a sharp endotherm with peak at 247 °C, which we interpret as the melting point of the nylon 66 phase in the phase-separated composite. These DSC results show that thermally induced phase separation had occurred due to heating of both rod/coil composites.

Direct visualization of the morphology and thermally induced phase separation of the PBZT/PTMHT and PBZT/nylon 66 composites was made by optical microscopy. A homogeneous featureless morphology was observed on the scale of 100 nm in the as-prepared molecular composites. However, when the same films were heated to 300 °C and cooled, a heterogeneous morphology containing a dispersed phase feature with a diameter of about 1–2 μm was observed. A similar observation of the morphology and thermally induced phase separation in the PBZT/nylon 66 composite system has previously been reported by others.[5]

The nonresonant third-order NLO coefficient, $\chi^{(3)}$ ($-3\omega;\omega,\omega,\omega$), of the molecular composites was investigated by picosecond third harmonic generation (THG) experiments whose details will be reported elsewhere.[11] The THG measurements on thin films with thicknesses in the range 120–640 nm were done at a fundamental wavelength of 1.9 μm and were accurate to ±20%. Each data point was obtained from the averages of several samples. Table II shows the $\chi^{(3)}$ values for the pure PBZT and four rod/coil molecular composites. The composition dependence of the $\chi^{(3)}$ of PBZT/nylon 66 composites shows the expected linear decrease with decreasing mole fraction of the NLO component, PBZT. However, the measured $\chi^{(3)}$ for the PBZT/PTMHT molecular composites shows significantly enhanced values compared to what is predicted from a linear mixing rule. The mechanism for this enhancement of the third-order NLO properties of PBZT/PTMHT molecular composites is yet to be elucidated.

In summary, thin films of molecular composites of the nonlinear optical rigid-rod polymer PBZT in the matrix of two flexible-coil polyamides, nylon 66 and PTMHT, have been prepared from ternary solutions of the Lewis acid complexes of the polymers in organic solvents. The measured nonlinear optical properties of the molecular

Table II. Composition Dependence of the Third-Order Nonlinear Optical Properties of Molecular Composites

sample	mol % PBZT	$\chi^{(3)}(-3\omega;\omega,\omega,\omega),$[a] 10^{-11} esu
PBZT	100	1.37
1:1 PBZT/nylon 66	50	0.70
1:2 PBZT/nylon 66	33	0.39
1:1 PBZT/PTMHT	50	1.07
1:2 PBZT/PTMHT	33	0.62

[a] All $\chi^{(3)}$ data accurate to ±20%.

composites showed a linear dependence with composition in the case of PBZT/nylon 66 composites and more enhanced optical nonlinearities than expected from a linear mixing rule in the case of PBZT/PTMHT composites. These results demonstrate that thin-film nonlinear optical composite materials with enhanced optical properties can be prepared from soluble complexes of the component polymers. The results also demonstrate that nonlinear optical techniques, such as third harmonic generation, constitute a promising sensitive probe of the solid-state structure of polymer molecular composites.

Bis(perfluorophenyl) Azides: Efficient Cross-Linking Agents for Deep-UV and Electron Beam Lithography

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The miniaturization of integrated circuits in the microelectronics industry[1] has spearheaded the development of alternatives to conventional photolithography.[2–4] Deep-UV,[5] electron beam (EB),[6] and X-ray lithography[7] techniques have thus emerged using resists with submicron resolution. However, these resists are not without limitation.

Deep-UV-initiated cross-linking of polymers such as poly(p-vinylphenol)[8] and novolac (polycresol–form-

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[‡] Department of Physics.
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