$(CHCMe_3)(N(2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2){:}OCMe_3)_2$, 108969-04-6.

References and Notes

(1) *Polyacetylene. Chemistry, Physics and Material Science*; Chien, J. C. W.; Academic: New York, 1984.

(2) (a) Destri, S.; Catellani, M.; Bolognesi, A. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 353. (b) Tubino, R.; Dorinsville, R.; Lam, W.; Alfano, R. R.; Birman, J. L.; Bolognesi, A.; Destri, S.; Catellani, M.; Porzio, W. *Phys. Rev. B* **1984**, *30*, 6601. (c) Dorsinville, R.; Tubino, R.; Krimchansky, S.; Alfano, R. R.; Birman, J. L.; Bolognesi, A.; Destri, S.; Catellani, M.; Porzio, W. *Phys. Rev. B* **1985**, *32*, 3377. (d) Bolognesi, A.; Catellani, M.; Destri, S. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 29. (e) Piaggio, P.; Bolognesi, A.; Catellani, M.; Destri, S. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 311. (f) Porzio, W.; Bolognesi, A.; Catellani, M.; Destri, S. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 71. (g) Bolognesi, A.; Catellani, M.; Destri, S.; Porzio, W.; Meille, S.; Pedemonte, E. *Makromol. Chem.* **1986**, *7*, 1287. (h) Cuniberti, C.; Piaggio, P.; Dellepiane, G.; Catellani, M.; Piseri, L.; Porzio, W.; Tubino, R. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 471. (i) Bolognesi, A.; Catellani, M.; Destri, S.; Porzio, W. *Polymer* **1986**, *27*, 1128. (j) Bates, F. S.; Baker, G. L. *Macromolecules* **1983**, *16*, 707. (k) Baker, G. L.; Bates, F. S. Macromolecules **1984**, *17*, 2619. (l) VanNice, F. L.; Bates, F. S.; Baker, G. L.; Carroll, P. J.; Patterson, G. D. *Macromolecules* **1984**, *17*, 2626. (m) Baker, G. L.; Bates, F. S. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 15. (n) Kminek, I.; Trekoval, J. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 53.

(3) (a) Galvin, M. E.; Wnek, G. E. *Polymer* **1982**, *23*, 795. (b) Galvin, M. E.; Wnek, G. E. *Polym. Prep.* **1982**, *23*, 99. (c) Galvin, M. E.; Wnek, G. E. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2727. (d) Rubner, M. F.; Tripathy, S. K.; Georger, J.; Cholewa, P. *Macromolecules* **1983**, *16*, 870.

(4) (a) Aldissi, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1347. (b) Aldissi, M.; Bishop, A. R. *Polymer* **1985**, *26*, 622. (c) Aldissi, M. *Synth. Met.* **1986**, *14*, 13. (d) Aldissi, M. *Synth. Met.* **1986**, *13*, 87. (e) Ames, S. P.; Vincent, B.; White, J. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1525. (f) Galvin, M. E.; Wnek, G. E. *Polym. Bull. (Berlin)* **1985**, *13*, 109. (g) Galvin, M. E., Wnek, G. E. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 33.

(5) (a) Edwards, J. H.; Feast, W. J. *Polymer* **1980**, *21*, 595. (b) Edwards, J. H.; Feast, W. J.; Bott, D. C. *Polymer* **1984**, *25*, 395. (c) Feast, W. J.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1985**, *202*. (d) Bott, D. C.; Brown, C. S.; Edwards, J. H.; Feast, W. J.; Parker, D.; Winter, J. N. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 9.

(6) Polydispersities between 1.8 and 2.8 are the lowest that have been reported for polymer precursors to Feast polyacetylene; see: Harper, K.; James, P. G. *Mol. Cryst. Liq. Cryst.* **1985**, *117*, 55.

(7) (a) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.

(8) (a) Schrock, R. R.; Feldman, J.; Grubbs, R. H.; Cannizzo, L. *Macromolecules* **1987**, *20*, 1169. (b) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640.

(9) Knoll, K.; Krouse, S. A.; Schrock, R. R. J. *Am. Chem. Soc.*, in press.

(10) **1** (4.1 μL, 0.0205 mmol) was added to a solution of Mo$(CHCMe_3)(NAr)(OCMe_3)_2$ (1 mg, 0.00205 mmol) in toluene (1 mL) at −78 °C. After 10 min the solution was warmed and held at −20 °C for 60 min. Pivaldehyde (6 μL, 0.064 mmol) was added and solvents were removed in vacuo while keeping the solution temperature below −20 °C (in order to minimize the retro-Diels–Alder reaction[6]) to give light yellow colored powders quantitatively. Samples were analyzed immediately by GPC in dichloromethane at 25 °C: 5 equiv of **1**, $M_w = 1370$, $M_n = 1070$, $M_w/M_n = 1.28$; 10 equiv of **1**, $M_w = 1700$, $M_n = 1490$, $M_w/M_n = 1.15$; 20 equiv of **1**, $M_w = 2600$, $M_n = 2310$, $M_w/M_n = 1.13$; 20 equiv repeated, $M_w = 2400$, $M_n = 2200$, $M_w/M_n = 1.10$. With time the retro-Diels–Alder reaction yields polyene sequences that alter the hydrodynamic characteristics of poly-**1** and lead to higher apparent dispersities.

(11) A solution of norbornene (193 mg, 2.05 mmol) in toluene (10 mL) was added dropwise to a rapidly stirred solution of Mo$(CHCMe_3)(NAr)(OCMe_3)_2$ (20 mg, 0.041 mmol) in toluene (2 mL). After 5 min a solution of **1** (165 μL, 0.82 mmol) in toluene (4 mL) was added dropwise to the rapidly stirred solution. After 5 min another solution of norbornene (193 mg, 2.05 mmol) in toluene (10 mL) was added dropwise to the rapidly stirred solution. After 10 min, 20 μL of benzaldehyde (0.168 mmol) was added. The solvents were removed in vacuo. The residue was dissolved in a minimal amount of methylene chloride and precipitated by addition of excess methanol to obtain light yellow powders essentially quantitatively.

(12) The retro-Diels–Alder reaction was done in solution (methylene chloride or toluene) at 2.0 wt % (polymer weight to solvent weight) or as a thin film. All samples were heated at 90 °C for 60 min. Under these conditions we have shown that the retro-Diels–Alder reaction is complete.[9]

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Electronic Properties of an Electron Donor–Acceptor Polymer Blend

The phase-separation behaviors of organic polymer blends have attracted extensive studies for their effects on mechanical properties,[1] but few studies have been concerned with the relation between the phase-separation structure and the electrical properties. We have been interested in the phase-separation behavior of the photoconductive polymer blends containing electron donor–acceptor (EDA) complexes, because they can have interfaces similar to the p–n junctions of semiconductors and may have unusual electronic properties different from those of doped polymer systems.

Recently, Rodriguez-Parada and Percec reported that polymethacrylates containing a carbazole group as a donor chromophore are miscible with polymethacrylates containing a 3,5-dinitrobenzoyl group as an acceptor.[2] This miscibility was attributed to a relatively weak intermolecular electronic interaction, and the phase separation occurred at 186–230 °C with the concomitant dissociation of the EDA complex.

This finding motivated us to pursue further study on phase-separation behaviors of EDA polymer blends and their effect on photoelectrical properties. We have shown that the phase separation of partly miscible blends of the donor poly[(*N*-ethylcarbazol-3-yl)methyl acrylate] (I) and the acceptor poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate] (II) has a structure similar to the phase structure produced by spinodal decomposition. The effect of this structure on the photocurrent of the polymer blend is also presented.

Polymers I ($\bar{M}_w = 5.0 \times 10^4$) and II ($\bar{M}_w = 3.5 \times 10^4$) were prepared by the radical polymerization of the corresponding monomers[3] by using AIBN as an initiator in benzene. The THF solutions of these polymers were mixed at various ratios, and films were deposited on slide glasses or NESA glasses from the solutions at room temperature. The films are yellow by the EDA complex, which had a UV absorption around 400 nm.

The film of a 1:1 weight ratio of polymers I and II has a phase-separated, matrix–island structure (Figure 1a) in which isolated islands with irregular shapes and sizes (0.5–1 μm) dispersed in the continuous matrix. When this 1:1 film (containing ca. 10 mol % excess of carbazole group) was exposed to iodine vapor for several hours, the islands became green, indicating the formation of an EDA complex between carbazole and iodine. This result suggests that the islands were composed predominantly of the donor polymer and that the matrix was a solid solution of the donor and acceptor polymers with the interchain EDA complex.

When the films were heated, another phase separation started in the matrix, and islands were finally absorbed

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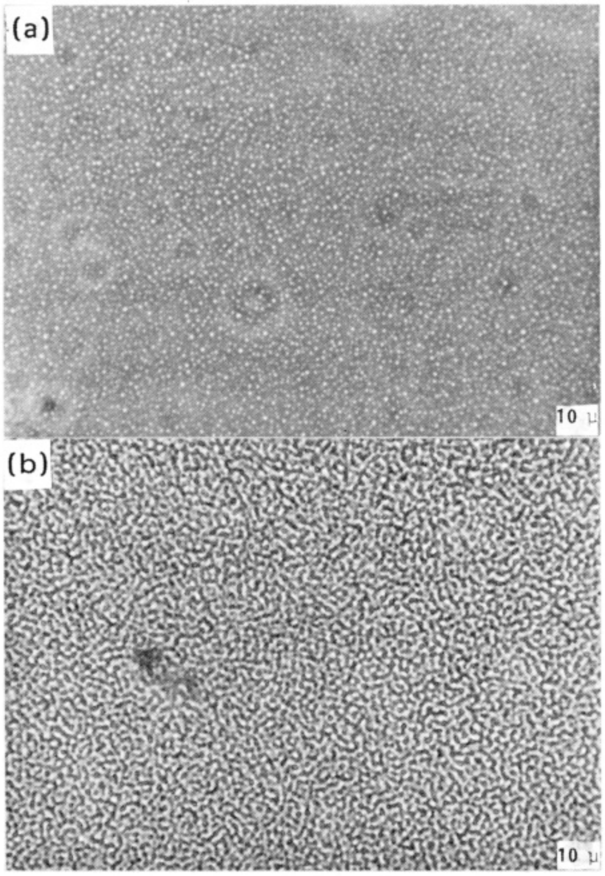

Figure 1. Phase-separation behavior of the polymer blend film of poly[(*N*-ethylcarbazol-3-yl)methyl acrylate] and poly[2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate] (1:1 weight ratio): (a) original; (b) heated at 190 °C for 2 min.

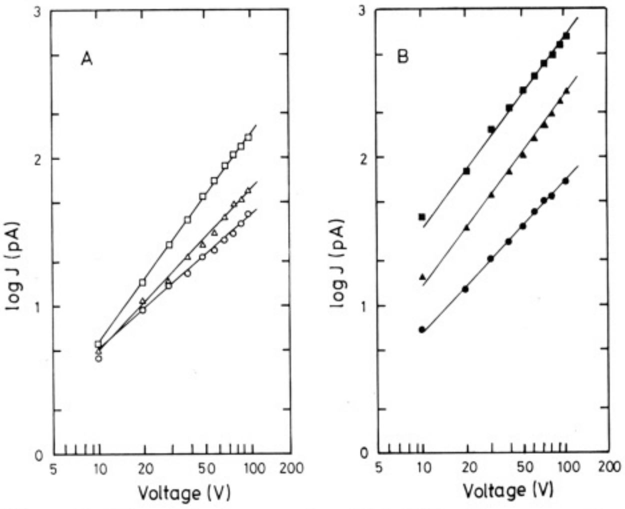

Figure 2. Transition temperature (T_s) of the phase-separation structure and T_g for various composition of poly[(*N*-ethylcarbazol-3-yl)methyl acrylate] (D) and poly[2-[(3,5-dinitrobenzoyl)oxy)]ethyl methacrylate] (A): (○) T_s; (△) T_g.

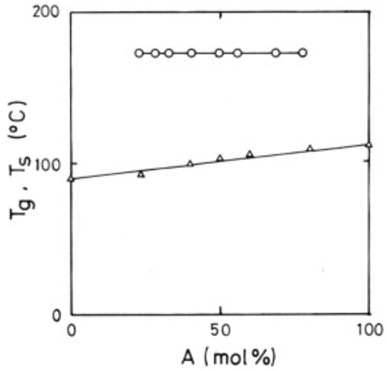

Figure 3. Current–voltage characteristics for the 1:1 polymer blend film: (A) original; (○) dark current, (△) photocurrent, (□) dark current after irradiation; (B) heated at 190 °C, (●) dark current, (▲) photocurrent, (■) dark current after irradiation.

into the newly separated phase. The phase-separation structure changed to a reticular tetrapod structure which was retained after cooled to room temperature at ca. 7 deg/min (Figure 1b). Examination of these films under a phase-contrast microscope with different varying focal point across the film thickness showed that each of two phases in this tetrapod structure was highly interconnective. This type of phase pattern is very similar to that produced by spinodal decomposition. The cooled samples retained the yellow color of the EDA complex.

The starting temperatures of phase-separation change for various II/I polymer molar ratios were determined by microscopic observation with a Mettler FP 800 hot stage at a heating rate of 5 deg/min. The change started at 173 °C and was completed at 183 °C, independent of acceptor compositions between 0.23 and 0.77 (Figure 2), implying that the new phase separation was closely related to dissociation of the EDA complex. The as-prepared films with acceptor contents less than 0.23 or higher than 0.77 were homogeneous and showed no phase separation by thermal treatment up to 200 °C.

The matrix–island structure of polymer blends with acceptor composition between 0.23 and 0.77 comprised islands with sizes of 0.5–1 μm composed of the donor-rich (p-type) phase, and the matrix comprised the EDA complexes. Because these polymer blends underwent a new phase-separation change on heating, whereas the homogeneous blends with compositions outside this range did not, it is assumed that the new separated phases are composed of an acceptor-rich phase (acceptor content ~0.77) and a donor-rich phase (acceptor content ~0.23) with an EDA complex layer between them. This result is in contrast to that reported by Percec et al[2] and reflects the difference in the polymer main chains.

It is known that dinitrobenzoyl-containing polymers show persistent conductivity[5] or the "memory effect".[6] Accordingly, we measured three kinds of current–voltage characteristics on the 1:1 blend film at 20 °C before and after thermal treatment:[7] (a) the dark current of blend film preheated at 80 °C for 1 min to erase any memory effect, (b) the photocurrent (light intensity 0.1 mW/cm^2, wavelength 400 nm), and (c) the dark current after irradiation by strong white light (light intensity 46 mW/cm^2) (Figure 3).

No appreciable difference in dark currents was observed for the original and the heat-treated films. The current (J) depended on applied voltage (V) as $J \propto V^n$. The values of n were 1.0 for both films and therefore both dark currents were ohmic. The photocurrent in heat-treated film was almost twice as high as the dark current in the original film (Figure 3B). Because the intensity of the light was low and the field dependence was not steep ($n = 1.2$), the measurement was made in an emission-limited region. Therefore, the difference in photocurrents in two films may be ascribed to an increase in carrier generation efficiency in the heat-treated sample. The photogeneration of electrons and holes may occur in the interfacial region between the donor-rich and acceptor-rich phases. These carriers might readily migrate to the latter two phases, thus preventing electron–hole recombination and increasing carrier generation efficiency.

After irradiation with a strong light, the heat-treated sample had a dark current five times higher than that before irradiation with the *n* value of 1.0. In contrast, the original sample showed only a slightly higher dark current after irradiation with the *n* value of 1.4. Since the dark current of the heat-treated film after irradiation was ohmic, the persistent conductivity in the heat-treated sample may be related to a phase-separation structure different from that reported by Abkowitz et al.[6] In the heat-treated sample, each carrier is in a different phase and has a longer lifetime than in a homogeneous system, because the recombination of carriers can occur only in the interfacial EDA complex layer. This situation could account for the persistent conductivity of the heat-treated sample.

Registry No. (I)(II) (copolymer), 114563-27-8; I (homopolymer), 71356-19-9; II (homopolymer), 82008-07-9.

References and Notes

(1) There are many books and reviews about the phase separation behavior. For example: Akiyama, S.; Nishi, T. *Polymer Blend*; Higaki, T., Ed.; CMC: Tokyo, 1981.
(2) Rodriguez-Parada, J. M.; Percec, V. *Macromolecules* **1984**, *19*, 55–64.
(3) 2-[(3,5-Dinitrobenzoyl)oxy]ethyl methacrylate was synthesized by the reaction of 2-hydroxyethyl methacrylate and 3,5-dinitrobenzoyl chloride in benzene (yield 67%; mp 71 °C, lit.[2] 70–71 °C). (*N*-Ethylcarbazol-3-yl)methyl acrylate was synthesized by the reaction of (*N*-ethylcarbazol-3-yl)methanol and acryloyl chloride in benzene (yield 75%; mp 71 °C, lit.[4] 72–73 °C).
(4) Simionescu, C. I.; Percec, V. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2287.
(5) Schaffert, R. M. In *Electrophotography*; Focal: London, 1965; pp 117–127.
(6) (a) Williams, D. J.; Abkowitz, M.; Pfister, G. *J. Am. Chem. Soc.* **1970**, *94*, 7970. (b) Pfister, G.; Abkowitz, M.; Williams, D. J. *J. Chem. Phys.* **1972**, *57*, 2979. (c) Williams, D. J.; Pfister, G.; Abkowitz, M. *Tappi* **1973**, *56*, 6, 129.
(7) The sample film containing equal weights of the two polymers with thickness of 12 μm was made on NESA glass, and a gold electrode (1 cm^2) was vapor-deposited on it. The thermal treatment was carried out at 190 °C for 2 min. The irradiation was carried out through NESA glass with an Ushio denki Xe lamp, and the positive voltage was applied on the gold side. The current of this sandwich device was measured with a Keithley 617 electrometer.

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Specular Reflectivity of Neutrons by Thin Polymer Films

Introduction. The reflectivity of neutrons provides a novel means of investigating a wide range of surface and interfacial phenomena with a spatial resolution that is on the nanometer size scale. Neutron reflectivity is emerging as a technique that can quantitatively address segment density depth profiles by simple isotopic substitution of light hydrogen by deuterium. Only recently has the utility of this technique in polymer science been realized. For example, Jannink and co-workers[1,2] have used the reflection of neutrons to evaluate the concentration profile of polymer segments in solution near the air–solution interface. There have also been preliminary reports on block copolymer solutions[3] and immiscible polymer bilayers.[4,5] In the present paper, we report the application of specular neutron reflection to investigate the interdiffusion of two layers, composed of polymer molecules where one of the polymers is deuteriated and the other is protonated.

Two different samples were studied. The first sample was a bilayer composed of deuteriated polystyrene on the top of protonated polystyrene; the latter layer was deposited on an optical flat of fused silica. The object here was not only to measure the segment profile for the specimen as prepared but to observe its evolution following an annealing treatment. The second sample consisted of a deuteriated/protonated bilayer of polyimide on fused silica.

Neutron Reflectivity. Neutron reflectivity principles have been extensively treated in the literature.[6] It is sufficient here to recall a few concepts to clarify which quantities can be obtained for the problem at hand. The neutron reflectivity profile is solely a function of the component of the neutron momentum perpendicular to the film:

$$q_{z0} = (2\pi/\lambda)\sin\theta \qquad (1)$$

where θ is the angle of incidence of the neutron beam with the surface and λ is the neutron wavelength. In a medium composed of nuclei with neutron scattering amplitudes[7] b in a volume[8] V, q_{z0} is modified such that

$$q_{zi} = (q_{z0}^2 - 4\pi b/V)^{1/2} \qquad (2)$$

The component of the neutron momentum parallel to the surface is identical with that in vacuum. For this reason the reflectivity process can be described in terms of the one-dimensional motion of a particle in a potential. The problem of finding the potential from the reflecitivity is nothing but the well-known "inverse problem" in quantum mechanics. The reflectivity cannot be described in an explicit form except for a few analytical forms of the potential; the simplest of which is a histogram of layers of different thicknesses and different refractive indices to which the effective profile can be approximated. The reflectance at the boundary between the *i*th and (*i* + 1)th layers is

$$r_{i,i+1} = \frac{q_{z,i} - q_{z,i+1}}{q_{z,i} + q_{z,i+1}} \qquad (3)$$

and the total reflectance of the system r_t is a suitable combination of the products of the reflectances at the single boundaries. In our case the system is vacuum/deuteriated polymer/hydrogenated polymer/silica; the reflectance takes the form[9]

$$r_t = [r_{01} + r_{12}\exp(2iq_{z1}d_1) + r_{23}\exp(2i(q_{z1}d_1 + q_{z2}d_2)) + r_{01}r_{12}r_{23}\exp(2iq_{z2}d_2)]/[1 + r_{01}r_{12}\exp(2iq_{z1}d_1) + r_{12}r_{23}\exp(2iq_{z2}d_2) + r_{01}r_{23}\exp(2i(q_{z1}d_1 + q_{z2}d_2))] \qquad (4)$$

where d_i is the thickness of layer *i*.

Using tabulated values for b and V, we obtain (for a bilayer of polystyrene) $(b/V)_{\mathrm{PSD}} = 6.1 \times 10^{10}$ cm^{-2}, $(b/V)_{\mathrm{PSH}} = 1.4 \times 10^{10}$ cm^{-2}, and $(b/V)_{\mathrm{silica}} = 3.48 \times 10^{10}$ cm^{-2}. The strongest reflectances occur at the front and back faces of the deuteriated layer. Hence, to a first approximation we can simply substitute the real system by a layer of deuteriated polystyrene over an infinitely thick layer of protonated polystyrene. For real values of q_{z1}, the reflectivity takes the simple form[10]

$$R = r_t^2 \simeq \frac{r_{01}^2 + r_{12}^2 + 2r_{01}r_{12}\cos(2q_{z1}d_1)}{1 + r_{01}^2r_{12}^2 + 2r_{01}r_{12}\cos(2q_{z1}d_1)} \qquad (5)$$

Equation 5 gives basically an interference function in

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