Notes

Poly[2,4,7-trinitro-9-fluorenyl methacrylate-*co*-1-(2-anthryl)ethyl methacrylate]: An Intramolecular Donor–Acceptor Copolymer

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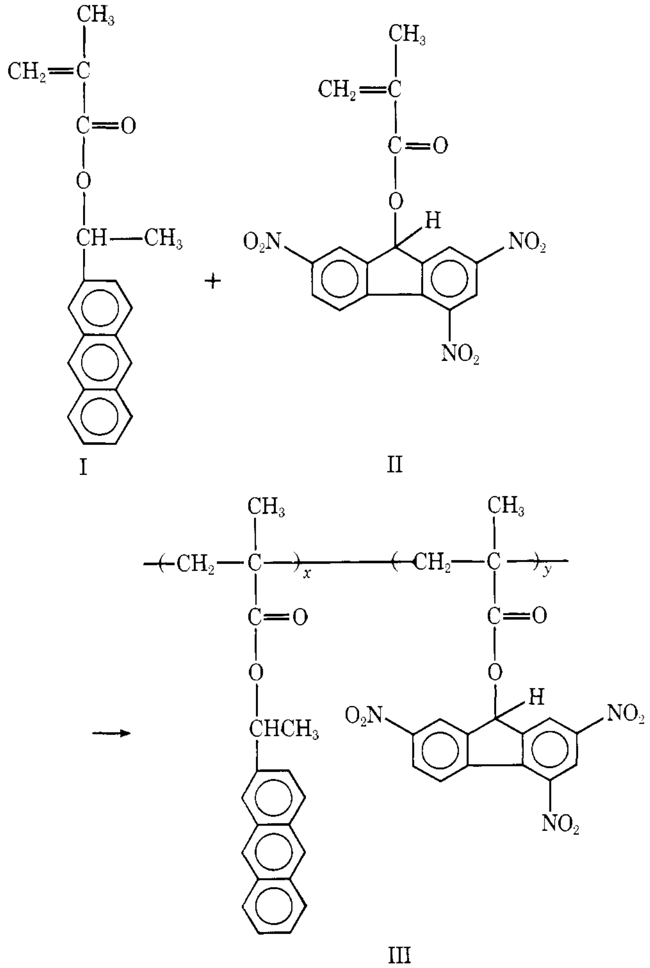
Intramolecular charge-transfer complexes, where the interacting chromophores are constrained in a nondissociative arrangement, are materials of considerable interest.[1] Although charge-transfer complexes in polymeric systems have received much attention in recent years,[2] there have been only a few cases reported of intramolecular complexes formed from copolymers containing both donor and acceptor groups. The results of an early study describing the alternating copolymers of trinitrostyrene as acceptor and vinyl pyridines or *p*-dimethylaminostyrene as donor[3] have now been shown to be questionable.[4] Mulvaney et al.[5] have recently reported copolymers containing pendant carbazole and either dinitrobenzoate- or chloranil-like groups. Some intramolecular complexation was suggested for the chloranil case. Schulz et al.[2] prepared copolyesters based on spirocyclopropanetetranitrofluorene/fluorene monomers and reported broad intramolecular charge-transfer effects. Tsuchida et al.[6] have prepared a Mannich-type polymer from dinitrotoluene, 1,3-di-4-piperidylpropane, and formaldehyde and observed intramolecular complexation.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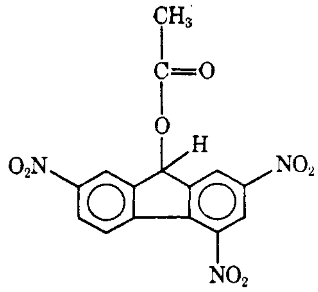
IV

Two recent reports from this laboratory have described the synthesis and polymerization of a new electron-donor monomer 1-(2-anthryl)ethyl methacrylate (I)[7] (AEMA) and a new electron-acceptor monomer 2,4,7-trinitro-9-fluorenyl methacrylate (II)[8] (TNFMA). This report describes the preparation and spectral properties of the 1:1 copolymer (III) of these two monomers. This copolymer is believed to be the first addition type intramolecular charge-transfer polymer prepared from polynuclear aromatic donor and acceptor monomers.

Experimental Section

Monomer Synthesis. The syntheses of TNFMA[8] and AEMA[7] have been described previously.

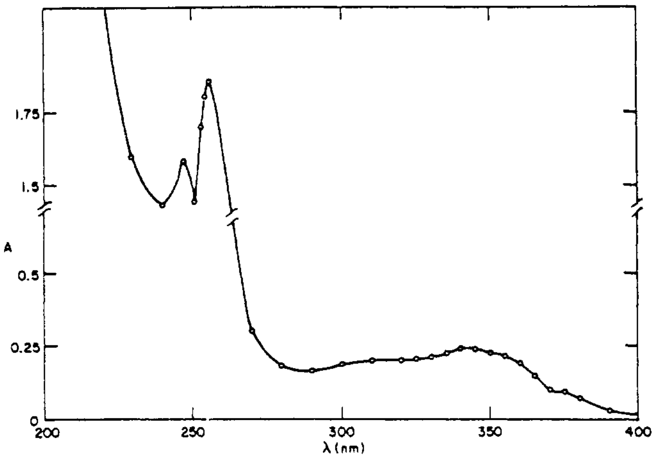

Figure 1. UV spectrum of poly(TNFMA-*co*-AEMA) in THF (7.72×10^{-4} g/dL) at 25 °C and 1-cm cell.

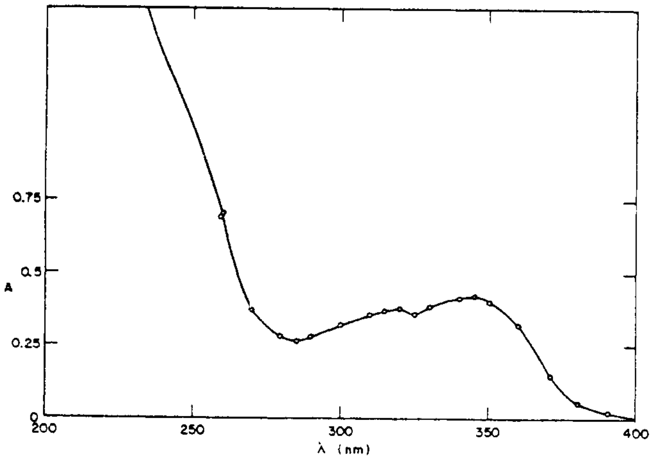

Figure 2. UV spectrum of poly(TNFMA) in THF (7.72×10^{-4} g/dL) at 25 °C and 1-cm cell.

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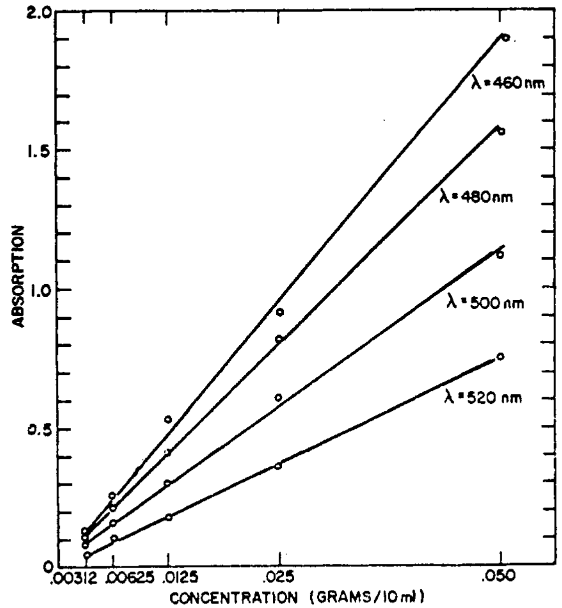

Figure 3. Linear dependence of absorption of concentration for poly(TNFMA-*co*-AEMA) charge-transfer band, THF, 25 °C, 1-cm cell.

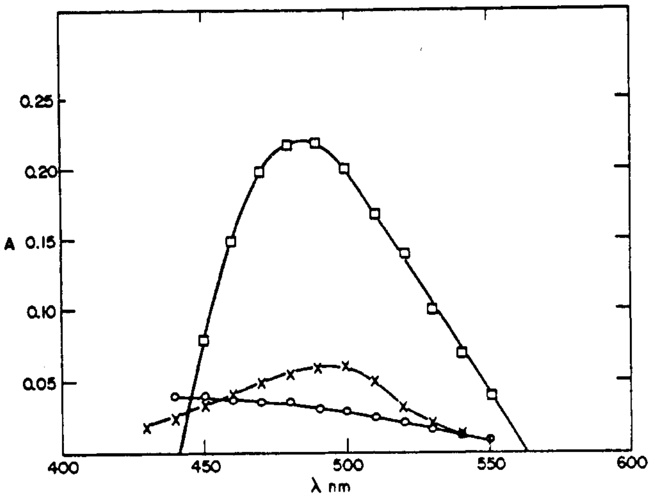

Figure 4. Charge-transfer spectra of (O) anthracene/2.47-trinitro-9-fluorenyl acetate; (×) anthracene/poly(TNFMA); (□) poly(TNF-*co*-AEMA)] 5 × 10^{-3} M in each chromophore, THF, 25 °C and 1-cm cell.

Polymerization. TNFMA (0.2 g, 5 × 10^{-3} M) and AEMA (1.5 g, 5 × 10^{-3} M) were dissolved in 20 mL of reagent grade acetone. AIBN (0.5 wt %) was added as the free-radical initiator. The polymerization tube was sealed under vacuum after two freeze–thaw cycles and the polymerization was carried out for 18 h at 60 °C. The product was isolated by precipitation into methanol followed by reprecipitation from THF into hexane. Approximately 2.0 g (57% conversion) of an orange powder, freely soluble in THF, DMF, and Me_2SO, was obtained. The IR spectrum of the copolymer showed "inter alia" a broad carbonyl band at 1730 cm^{-1}, nitro group bands at 1340 and 1540 cm^{-1}, and aromatic bands at 1600 and 730 cm^{-1}. GPC analysis in THF gave a single peak and $\bar{A}_n$ = 280, $\bar{A}_w$ = 560, with MWD = 2.0. An intrinsic viscosity of $[\eta]$ = 0.062 was measured in THF at 30 °C.

Anal. Calcd for $C_{37}H_{29}O_{10}N_3$ (1:1 copolymer): C, 65.80; H, 4.30; N, 6.20. Found: C, 65.79; H, 4.40; N, 6.29.

Results and Discussion

Spectral Studies. Measurements were made on a Cary 14 spectrophotometer using standard techniques. Charge-transfer bands were determined by subtracting out the contribution due to the acceptor from the absorption of the donor/acceptor mixture in all cases except the 2,4,7-trinitro-9-fluorenylacetate–anthracene model system where the acceptor solution was used in the reference beam and the difference read directly. As reported earlier,[8] THF was found to react slowly with the acceptor polymer, therefore, all spectra were determined from freshly prepared solutions.

Copolymer Composition. Elemental analysis showed that the copolymer had an equimolar composition. This composition was confirmed using UV analysis by comparing the absorption of the trinitrofluorenyl group of the copolymer to that of poly(2,4,7-trinitro-9-fluorenyl methacrylate) at 345 nm. The UV spectrum of the copolymer to 400 nm is shown in Figure 1. Figure 2 shows the UV spectrum of poly(TNFMA) (note the absence of the anthracene band at ca. 260 nm). The weight percent of II in the equimolar copolymer is 57. At equal weight concentrations, the absorption from the trinitrofluorenyl group of the copolymer was 57% of that of the homopolymer.

Charge-Transfer Interactions. The intramolecular character of the charge-transfer interaction of the pendant anthracene and trinitrofluorenyl groups was established by showing that the absorption of the charge-transfer band varied linearly with concentration (see Figure 3) at several different wavelengths. An intermolecular interaction would be expected to vary in a nonlinear fashion with concentration because of the equilibrium between the donor and acceptor components.

Comparison of the charge-transfer spectra of the copolymer with the model systems, anthracene/2,4,7-trinitro-9-fluorenyl acetate (IV), and anthracene/poly(2,4,7-trinitro-9-fluorenyl methacrylate),[8] shows an enhanced absorption for the copolymer (see Figure 4). The intensity of the charge-transfer band in the 490-nm range is about an order of magnitude greater than the charge-transfer band in the model systems. This enhancement is attributed to the influence of the polymer environment on the interacting chromophores. A constrained intramolecular chromophoric interaction thus results and therefore a higher effective concentration of complex, in comparison to the model systems, is obtained. Such an effect is consistent with the observation of donor–acceptor cyclophane systems where strong charge-transfer complexes are formed despite little if any interactions being observed in the model components.[1,9]

References and NOTES

(1) P. M. Keehn and R. Luhowy, *J. Am. Chem. Soc.*, **99**, 3797 (1977); J. G. O'Connor and P. M. Keehn, *Tetrahedron Lett.*, 3711 (1977).
(2) R. C. Schulz, D. Fleischer, A. Henglein, H. M. Bössler, J. Trisnadi, and H. Tanaka, *Pure Appl. Chem.*, **38**, 227 (1974).
(3) N. C. Yang and Y. Gaoni, *J. Am. Chem. Soc.*, **86**, 5022 (1964).
(4) G. B. Butler and K. Sivaramakrishran, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **17(2)**, 608 (1976).
(5) D. M. Chang, S. Gromelski, R. Rupp, and J. E. Mulvaney, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 571 (1977).
(6) T. Tomono, E. Hasegawa, and E. Tsuchida, *J. Polym. Sci., Polym. Lett. Ed.*, **12**, 139 (1974).
(7) M. Stolka, *Macromolecules*, **8**, 8 (1975).
(8) S. R. Turner and C. AuClair, *Macromolecules*, **9**, 868 (1976).
(9) H. A. Staab and H. Haffner, *Tetrahedron Lett.*, 4397 (1974).

Chain Deformations in Rubber

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Small-angle neutron scattering (SANS) has made possible direct determinations of the chain dimensions of polymers in

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