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Electron-Donor-Acceptor Copolyacrylates with High Photosensitivity

Since the success of the PVK–TNF complex in electrophotographic applications,[1] a number of studies have attempted to prepare copolymers containing intramolecular charge-transfer complexes.[2] Vinyl or acrylate/methacrylate compounds having a carbazole group were often employed as donor monomers, while acceptor monomers always contained strong electron-withdrawing units like nitro or cyano groups. In these investigations, due to either the high homopolymerizability of vinyl carbazole[3] or to inhibition of free radical copolymerization in particular by a nitrophenyl group,[4] it was extremely difficult to obtain copolymers with high enough molecular weights and good film quality. Hence, only a limited number of reports are available that describe the photoconductive properties of copolymers with intramolecular charge-transfer complexes.[5]

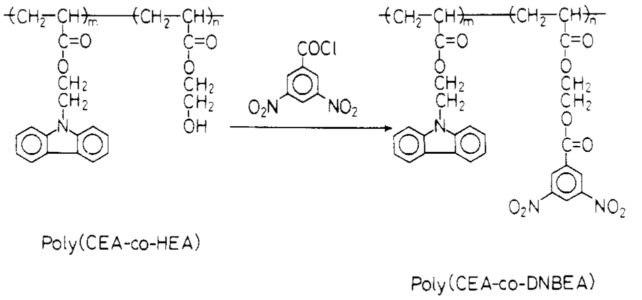
Previously we synthesized copolyacrylates having carbazole donor and trinitrofluorenone acceptor chromophores and first reported that the photogeneration efficiency of this electron-donor–acceptor (EDA) copolymer was higher than that of the donor polymer doped with the corresponding small acceptor molecule.[6] A similar effect was also confirmed for copolymers having a carbazole-containing acrylate and a dinitrobenzoate (DNB) containing methacrylate.[7] However, because of the low molecular weight resulting from inhibition of polymerization by acceptor monomers and high T_g's resulting from a specific interchain EDA interaction,[6–8] only samples with a low acceptor content (5 mol %) had the film quality required for the photogeneration measurement.

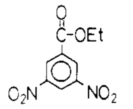
To circumvent this problem, we chose an alternative way to prepare poly[(2-*N*-carbazolylethyl acrylate)-*co*-2-[[(3,5-dinitrobenzoyl)oxy]ethyl acrylate]] [poly(CEA-*co*-DNBEA)], viz., the reaction between dinitrobenzoyl chloride and the precursor copolymer, poly[(2-*N*-carbazolylethyl acrylate)-*co*-(2-hydroxyethyl acrylate)] [poly(CEA-*co*-HEA)] with different molar ratios of carbazole/hydroxyl groups. By this method, we succeeded in obtaining EDA copolyacrylates with rather low T_g's and high molecular weights (Table I), which could not be obtained from the direct copolymerization of corresponding acrylate monomers.[6,7,9] This enabled us to perform photoconductivity measurements on EDA copolymers with high contents of the acceptor chromophore. These EDA copolymers show definitely higher photosensitivities than the donor homopolymer doped with small acceptor molecules.

Table I
Properties of Poly(CEA-*co*-DNBEA)

sample	Cz cont,[a] mol %	DNB cont,[a] mol %	$\bar{M}_w{}^b \times 10^4$	$\bar{M}_n{}^b \times 10^4$	T_g,[c] °C
1	98.5	1.5	3.5	1.6	100
2	90	10	4.2	2.7	102
3	87	13	3.6	1.8	106
4	75	25	5.2	3.0	107
5	66	34	5.1	2.2	109
6	55	44	5.5	3.1	108

[a] Determined by 270-MHz ^{1}H NMR spectra in solutions in chloroform (for no. 1–3) and elemental analysis (for no. 4–6). [b] Determined by GPC with polystyrene as standard. [c] Determined by DSC.





EDNB

A typical synthetic procedure is as follows: To a solution of poly(CEA-*co*-HEA)[10] (200 mg, carbazole/hydroxyl ratio, 3/1) and dry pyridine (259 mg, 3.27 mmol) in 20 mL of dry THF, a solution of 3,5-dinitrobenzoyl chloride (754 mg, 3.27 mmol, 15-fold equiv to the hydroxyl group in the precursor copolymer) in 10 mL of anhydrous THF was added dropwise in 10 min with stirring. The stirring was continued for 48 h at 50 °C. After pyridinium hydrochloride was removed by filtration, the resulting polymer solution was poured into methanol, and the precipitates formed were reprecipitated thrice from THF into methanol, giving a bright yellow powder of the EDA copolymer. The reaction between poly(CEA-*co*-HEA) and dinitrobenzoyl chloride was quantitative since the IR absorption of the hydroxyl group around 3500 cm^{-1} disappeared from the resulting poly(CEA-*co*-DNBEA).

Films were prepared by pouring a THF solution of the copolymer onto NESA glass plates and drying in vacuo for at least 1 day. The thickness and surface area of films were 7 μm and 4 cm^2, respectively. Photosensitivity of copolymer films was determined by the photoinduced discharge technique used in the previous paper.[6,7,11] After corona charging to a positive surface potential, a film was exposed to monochromatic light from a 500-W xenon lamp through a grating monochromator. A photoinduced surface-potential decay was observed with a Monroe Model 263 isoelectric voltmeter through a transparent probe,

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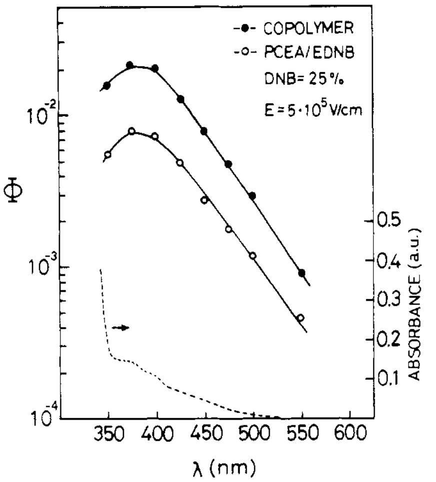

Figure 1. Wavelength dependence of photogeneration efficiency for poly(CEA-*co*-DNBEA) and EDNB-doped poly(CEA), both with 25 mol % of DNB content.

followed by manipulation with a digital storage oscilloscope and a microcomputer. The photogeneration efficiency (Φ) was obtained from the initial rate of photoinduced potential decay, $(\mathrm{d}V/\mathrm{d}t)_0$, observed under illumination of monochromatic light weak enough to avoid a space-charge effect, using the equation

$$\Phi = -(\epsilon_0\epsilon/eLP)(\mathrm{d}V/\mathrm{d}t)_0 \qquad (1)$$

where e is the electronic charge, L is the film thickness, P is the absorbed light intensity in photons/cm^2·s, ϵ_0 is the permittivity in vacuum, and ϵ is the dielectric constant of a specimen.

The wavelength dependence of Φ for the EDA copolymer and poly(2-*N*-carbazolylethyl acrylate) (poly(CEA)) doped with ethyl 3,5-dinitrobenzoate (both with 25 mol % of DNB) is depicted in Figure 1. The maximum Φ values are observed at 375–400 nm for both samples, which coincide well with a charge-transfer absorption band peak around 375–400 nm. The shape of the absorption spectrum shows no appreciable difference for these two systems. The optical band gap is about 2.48 eV (500 nm) for both samples. Photogeneration efficiency then decreases at longer wavelengths and becomes too low to be detected above 550 nm.

Figure 2 shows plots of the photogeneration efficiency versus the DNB content at 400 nm and 5×10^5 V/cm for EDA copolymers and poly(CEA) molecularly doped with EDNB. Both of the systems show a decreasing photogeneration efficiency with increasing DNB content. This result is in contrast with that of the TNF–PVK system in which photogeneration efficiency increases as the TNF to PVK monomer molar ratio increases. The reason for the increase in efficiency has been attributed to an increase in the initial separation of the electron–hole pairs.[12] It is noted that the definition of photogeneration efficiency used here is somewhat different from that in ref 12, where the uncorrected absorptivity may result in a lower value of efficiency for a sample with a lower acceptor content. The optical density of the present copolymer system was the same as that of the doped system at the same DNB content and was less than 1 even at maximum DNB content. In the EDA polymer system carriers emit in the bulk, hence either hole or electron transport contribute to the discharge current. For eq 1 to apply in a photogeneration measurement, both electrons and holes must have sufficient mobility to reach the surface of the film during the time of experiment.[12] However, according to theoretical studies, even when electron mobility is $^1/_{100}$ of the hole mobility, the discharge rate shows only slight change at the same electrical field.[13] The decrease in Φ values with increasing DNB content for the system under study, therefore, may correlate with decreased hole mobility due to a decreased number of uncomplexed carbazole chromophores.

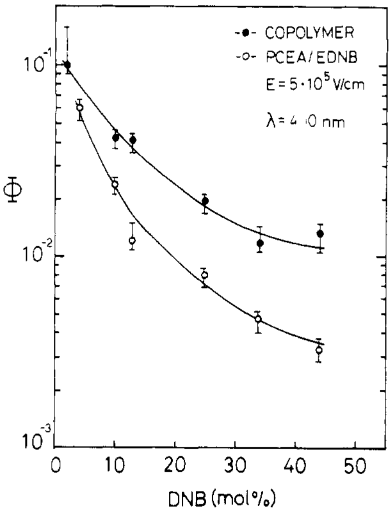

Figure 2. Photogeneration efficiency for poly(CEA-*co*-DNBEA) and EDNB-doped poly(CEA) versus DNB contents.

Photogeneration efficiency of the copolymer is definitely higher than that of the doped system as shown in Figure 2. It is remarkable that the efficiency for the doped system decreases to a larger extent than that of the copolymer with an increase in DNB content. By preliminary computation using Onsager's "geminate recombination" model,[14] we found that copolymers have higher primary quantum yield values (Φ_0) for formation of a bound electron–hole pair but almost the same thermalization radius, r_0 (15–21 Å), compared with those of the corresponding doped systems. In the copolymer the donor and acceptor chromophores are aligned in the polymer backbone, thus the chemical nature of the copolymer seems quite favorable for a photophysical process which may take place prior to the formation of the initial electron–hole pair. The detail of the computation results will be published elsewhere.

Registry No. (CEA)(HEA) (copolymer), 113793-26-3; (CEA)(DNBEA) (copolymer), 84943-52-2; 3,5-$(NO_2)_2C_6H_3COCl$, 99-33-2.

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ferent carbazole/hydroxyl group molar ratios were synthesized similarly.

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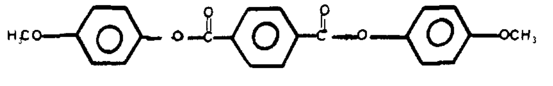
Two-Dimensional NMR and Proton Spin-Lattice Relaxation Studies of Thermotropic Homopolyesters Containing a Bicyclo[2.2.2]oct-2-ene Ring System

Due to their ordered nature, liquid crystals have been a subject of very intense scientific investigation.[1-5] It has been earlier reported[6-8] that several compounds that form a nematic mesophase contain a *p*-phenylene unit which serves a dual role: viz., (a) provides rigid linear grouping and (b) contributes to the polarizibility of the molecule. Dewar et al.[9] studied the factors influencing the stability of nematic liquid crystals by replacing the central benzene ring of bis(*p*-methoxyphenyl) terephthalate (I), with 1,4-bicyclo[2.2.2]octane. They observed that the introduction of a double bond into the bicyclooctane moiety led to an increase in mesophase stability.

In this paper, we describe the detailed proton nuclear magnetic resonance, homonuclear two-dimensional shift correlation (COSY) and proton spin–lattice relaxation studies to determine the structures of homopolyesters: poly[oxy(bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxyterephthaloyl] (II); poly[oxy(bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxycarbonyl(1,4-bicyclo[2.2.2]octylene)carbonyl] (III); poly[oxy(1,4-bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxycarbonyl(*trans*-1,4-cyclohexyl)carbonyl] (IV). We also show evidence for the influence of the electron density of the aromatic ring on bicyclo[2.2.2]oct-2-ene double bond in the homopolyester II by two-dimensional homonuclear dipolar correlated NMR (NOESY) studies.



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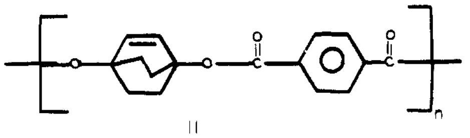

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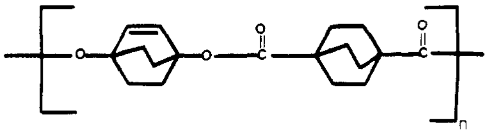

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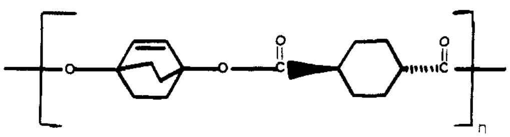

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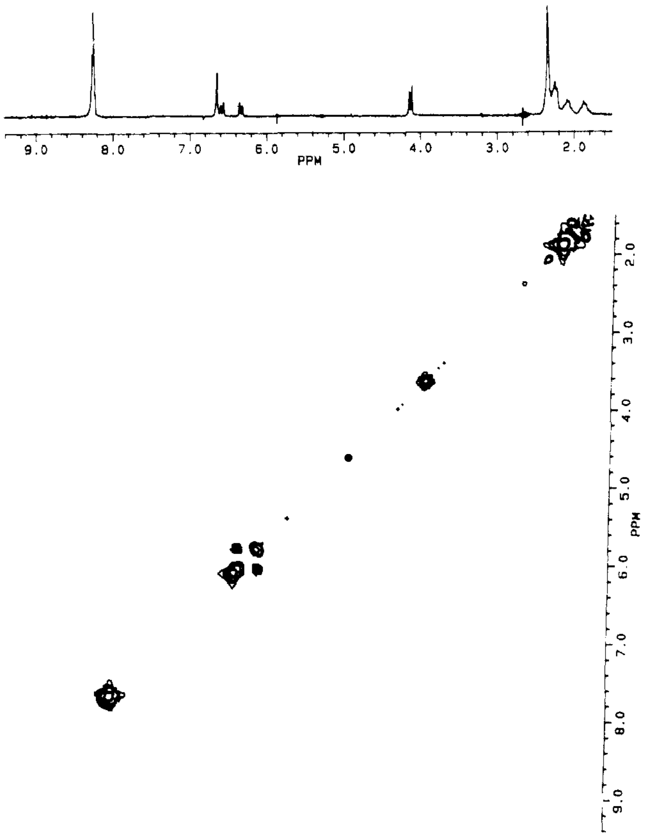

Figure 1. 250-MHz ^{1}H NMR 2D-COSY spectrum of poly[oxy(bicyclo[2.2.2]oct-2-ene-1,4-diyl)oxyterephthaloyl] (II), recorded at 25 °C in CF_3COOD.

Two-dimensional COSY[10-16] and two-dimensional NOESY[10,15,17-20] techniques have been applied extensively to the interpretation of proton spectra of biological macromolecules and synthetic macromolecules such as poly(vinylbutyral),[21] poly(methyl methylacrylate),[22] poly(vinyl alcohol),[23] and a vinylidene chloride–isobutylene copolymer.[24]

Experimental Section. The homopolyesters II, III, and IV were synthesized[25] by the polycondensation of bicyclo[2.2.2]oct-2-ene-1,4-diol with terephthaloyl chloride, bicyclo[2.2.2]octane-1,4-dicarbonyl chloride, and *trans*-1,4-cyclohexanedicarbonyl chloride, respectively.

All the NMR spectra were acquired on a Bruker WM250 spectrometer, equipped with an Aspect 3000 computer, operating at the frequency 250 MHz for proton. The routine ^{1}H NMR, two-dimensional NMR, and proton spin–lattice relaxation studies were done in deuteriotrifluoroacetic acid with tetramethylsilane (TMS) as internal standard at 25 °C. In the ^{1}H NMR spectrum, the peak at 4.1 ppm is due to an impurity in the solvent (CF_3COOD), and the peak at 4.12 is due to moisture (Figure 1). Homonuclear 2-D correlated spectroscopy (COSY) was performed by using the standard pulse sequence RD–90°–t_1–90°–t_2.[26] It was obtained by collecting an initial time domain spectrum ($S(t_1,t_2)$), consisting of 1024 × 256 complex data points for t_2 and t_1, respectively. The initial delay time, in which the spin system comes to equilibrium, was kept at 5 s. Each increment of t_1 was scanned 64 times. The spectral windows in f_1 and f_2 dimensions were ±1350 Hz each, so that the total sweep width was 2700 Hz. A sine-bell filtering function was used in both dimensions, prior to Fourier transformation, to improve resolution. Homonuclear 2-D spectra were all symmetrized to eliminate the bands of "t_1 noise" arising from spectrometer instabilities during the extended acquisition time associ-

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