Preparations and Polymerizations of [(Tricyanophenyl)thio]ethyl and [(Tricyanophenyl)sulfonyl]ethyl Methacrylates and Intramolecular Charge-Transfer Interaction and Photoconductivity of Their Copolymers with Bis(*N*,*N*-dimethylamino)phenyl Methacrylates

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ABSTRACT: 2-[(2,4,6-Tricyanophenyl)thio]ethyl methacrylate (1) and 2-[(2,4,6-tricyanophenyl)sulfonyl]-ethyl methacrylate (2) were synthesized as new types of methacrylates resistant to hydrolysis. Moreover, 3,5-bis(*N*,*N*-dimethylamino)phenyl methacrylate (3) and 2-[3,5-bis(*N*,*N*-dimethylamino)phenoxy]ethyl methacrylate (4) were prepared as new methacrylates carrying strong electron-donating groups. Copolymerizations of 1 and 2 with styrene (St) in dimethyl sulfoxide (DMSO) and copolymerizations of 3 and 4 with St in tetrahydrofuran (THF) were carried out at 60 °C. The monomer reactivity ratios against St obtained were alike among 1–3, probably due to the fact that polymerizing methacrylates for those monomers are linked to the same ethylene group. Copolymerizations in bulk of 1 with 3 and 4 and of 2 with 4 afforded the high molecular weight polymers, capable of being cast into a tough film as utilized for photoconductivity measurement. It was found in comparison of UV–vis spectra in THF or DMSO between monomer mixtures and the copolymers of the 1–3 system, 1–4 system, and 2–4 system under given concentrations of donor and acceptor units that the intramolecular charge-transfer interactions are much larger than the corresponding intermolecular ones and the charge-transfer interaction among the systems increases in both intensity and magnitude as follows: 1–3 system < 1–4 system < 2–4 system. Photocurrents for films of poly(1-*co*-3), poly(1-*co*-4), and poly(2-*co*-4) were found to run in irradiation with UV–vis light of wavelength 200–700 nm. The film of poly(2-*co*-4) exhibited photoconductivity in a semiconductor range of 1.0×10^{-9} Å at a wavelength of 375 nm under an electric field of −50 kV/cm. A hole drift mobility was measured to run only within a very short length. Photoconductivity and charge-transfer complex transition exhibited the same wavelength dependence. It can be said that the generation of electron carriers plentifully takes place due to excitation of the strong intramolecular charge-transfer complexes under irradiation, but the mobility of the carrier is very low, then resulting in a semiconductor range of the photoconductivity for the film.

Introduction

It is known that poly(vinylcarbazole) and trinitrofluorenone exhibit photoconductivity in a visible wavelength region owing to an intermolecular charge-transfer complex between them and are applicable in electrophotography.[1] Subsequently, incorporating both acceptor and donor units into the same polymer chains was carried out, for instance, in the preparation of poly[2-*N*-carbazoylethyl acrylate-*co*-2-[(3,5-dinitrobenzoyl)oxy]ethyl acrylate],[2] poly[2-*N*-carbazoylethyl acrylate-*co*-2-[(3,5-dinitrobenzoyl)oxy]-ethyl methacrylate],[3] poly[2-*N*-carbazoylethyl methacrylate-*co*-2-[(3,5-dinitrobenzoyl)oxy]ethyl methacrylate],[4,5] poly[2-*N*-carbazoylethyl acrylate-*co*-(2-acryloylethyl)-4,5,7-trinitrofluorenone-2-carboxylate],[6] and poly-[2-*N*-carbazoylethyl acrylate-*co*-2-[(3,5-dinitrobenzoyl)oxy]propyl acrylate].[7,8] These polymers afforded high photogeneration efficiency[2,3,6] and photoconductivity even in a near-infrared wavelength region[7,8] due to much strong interaction of their intramolecular charge-transfer complexes, and they were able to retain the properties for a long time because of no exuding small molecules of an acceptor.

An electron-accepting unit in the polymers consists of polynitrophenyl groups which are generally susceptible to a radical species. It is conceivable therefore that a vinyl monomer containing polynitrophenyl groups is not so polymerizable with a radical initiator that high molecular weight polymers can not be obtained.

A cyano group is almost as electron-accepting as a nitro group, but it is much less sensitive toward a radical species compared to the nitro group. Instead of the polynitrophenyl group, attention was paid to the polycyanophenyl group as an electron-accepting group, and we previously reported preparations and polymerizations of 2,4,6-tricyanophenyl methacrylate (TCPM) and 2,4,6-tricyanophenyl acrylate (TCPA) carrying tricyanophenyl groups as ester groups.[9] Unfortunately, TCPM and TCPA were susceptible enough to hydrolysis to give yellow solutions of 2,4,6-tricyanophenolate anion when dissolved in highly polar solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF). Accidentally, their hydrolysis was slow enough in tetrahydrofuran (THF) that the solutions were able to remain colorless for a few days. TCPM or TCPA was copolymerized with *m*-(*N*,*N*-dimethylamino)phenyl methacrylate (mDMAM) in THF to obtain copolymers with a strong intramolecular charge-transfer interaction between an electron-donating (dimethylamino)phenyl group and an electron-accepting tricyanophenyl group. However, the copolymerizations of TCPM with mDMAM under various conditions were carried out, but the copolymers obtained were not so high in molecular weight that they did not manage to form tough films for the measurement of photoconductivity. The terpolymerization of TCPM, mDMAM, and methyl methacrylate (MMA) was carried out in order to obtain a polymer of high molecular weight. The larger feed ratios of MMA in the terpolymerization allowed the higher molecular weight polymers to be formed but at the same time caused the concentration of tricyanophenyl and (dimethylamino)phenyl groups in the polymers to be lowered, eventually resulting in a decrease in the concentration of the intramolecular charge-transfer complex.

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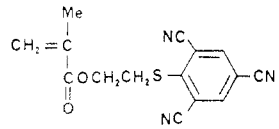
In this work, new methacrylates containing tricyanophenyl groups were prepared such as 2-[(2,4,6-(tricyanophenyl)thio]ethyl methacrylate (1) and 2-[(2,4,6-tricyanophenyl)sulfonyl]ethyl methacrylate (2), in which ethylene was inserted as a spacer between methacryloyloxy and tricyanophenyl groups for the purpose of reducing the hydrolytic lability and also improving their low polymerizability due to *o,o'*-disubstituted phenyl methacrylates. In addition, 3,5-bis(*N,N*-dimethylamino)phenyl methacrylate (3) and 2-[3,5-bis(*N,N*-dimethylamino)phenoxy]ethyl methacrylate (4) were prepared in order to obtain the monomer with greater electron-donating ability compared to that for mDMAM. Radical polymerizations of 1–4 and copolymerizations of 1 with 3 and 4 and of 2 with 4 were studied. The copolymers were used to investigate the intramolecular charge-transfer interaction between the tricyanophenyl and bis(*N,N*-dimethylamino)-phenyl groups and the photoconductivity of their tough films due to the strong charge-transfer interaction.



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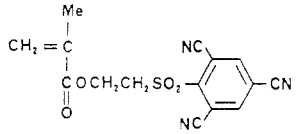

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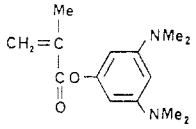

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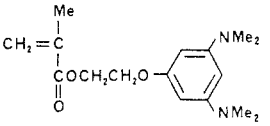

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Experimental Section

2-[(2,4,6-Tricyanophenyl)thio]ethanol (6): 1-Bromo-2,4,6-tricyanobenzene[10] (5; 1 g, 4.3 mmol) and 0.39 g (5 mmol) of 2-mercaptoethanol were dissolved in 20 mL of *p*-dioxane, and then 0.51 g (5.0 mmol) of triethylamine was added dropwise with stirring at room temperature, resulting in deposition of a triethylammonium bromide salt which was filtered off. The filtrate was placed under reduced pressure to remove volatile materials to obtain 0.85 g of a pale yellow solid, which was recrystallized from chloroform to give 0.72 g (73% yield) of 2-[(2,4,6-tricyanophenyl)thio]ethanol (6) as white needles: mp 115–116 °C; IR (KBr) ν_{OH} 3500, 3200, ν_{CN} 2225 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 2 H), 3.95 (t, J = 6 Hz, 2 H), 3.45 (t, J = 6 Hz, 2 H), 2.05 (s, 2 H). Anal. Calcd for $C_{11}H_7N_3OS$: C, 57.64; H, 3.08; N, 18.33; O, 6.99; S, 13.96. Found: C, 57.46; H, 3.10; N, 18.35; S, 13.88.

2-[(2,4,6-Tricyanophenyl)thio]ethyl methacrylate (1): Compound 6 (0.8 g, 3.8 mmol) and 0.8 g (5.2 mmol) of methacrylic anhydride[11] were mixed in the presence of 5 mg of 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as an inhibitor for radical polymerization. After 2 or 3 drops of concentrated sulfuric acid was added, the mixture was heated for about 5 min to result in a homogeneous solution, which was poured into 30 mL of ice water. The resulting mixture was extracted twice with 10 mL of dichloromethane. The combined extract was washed twice with 10 mL of water and twice with 10 mL of 5% aqueous potassium bicarbonate solution and then dried over anhydrous magnesium sulfate. The solution was concentrated to a 5-mL volume and then passed through a silica gel column using dichloromethane as eluent. The first elution band collected was placed under reduced pressure to remove volatile materials to afford 0.8 g of a white solid, which was recrystallized from a mixture of benzene and hexane (1/2 by volume) to give 0.66 g (59% yield) of 2-[(2,4,6-tricyanophenyl)thio]ethyl methacrylate (1) as white flakes: mp 99–100 °C; IR (KBr) ν_{CN} 2240, $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1640, ν_{CO} 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.10 (s, 2 H), 5.96 (m, 1 H), 5.50 (m, 1 H), 4.40 (t, J = 6 Hz, 2 H), 3.63 (t, J = 6 Hz, 2 H), 1.90 (s, 3 H). Anal. Calcd for $C_{15}H_{11}N_3O_2S$: C, 60.60; H, 3.74; N, 14.10; O, 10.78; S, 10.78. Found: C, 60.76; H, 3.69; N, 14.08; S, 10.54.

2-[(2,4,6-Tricyanophenyl)sulfonyl]ethyl methacrylate (2): Compound 1 (0.4 g, 1.35 mmol) was dissolved in 15 mL of acetic acid, and then 5 mL of a 30% aqueous hydrogen peroxide solution was added with stirring at room temperature. After stirring for an additional 24 h, the solution was poured into 30 mL of ice water. The resulting mixture was extracted twice with 10 mL of dichloromethane. The combined extract was washed with water and then dried over anhydrous magnesium sulfate. The solution was concentrated to a 5-mL volume and then passed through a silica gel column (1.5 cm diameter × 15 cm high) using dichloromethane as eluent. The first elution band collected was placed under reduced pressure to remove volatile materials to afford 0.3 g of a white solid, which was recrystallized from a mixture of dichloromethane and hexane (1/3 by volume) to give 0.23 g (52% yield) of 2-[(2,4,6-tricyanophenyl)sulfonyl]ethyl methacrylate (2) as white needles: mp 110–111 °C; IR (KBr) ν_{CN} 2250, $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640, ν_{SO} 1320, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.24 (s, 2 H), 6.00 (s, 1 H), 5.61 (s, 1 H), 4.73 (t, J = 6 Hz, 2 H), 3.58 (t, J = 6 Hz, 2 H), 1.90 (s, 3 H). Anal. Calcd for $C_{15}H_{11}N_3O_4S$: C, 54.70; H, 3.37; N, 12.80; O, 19.40; S, 9.73. Found: C, 55.08; H, 3.22; N, 12.83; S, 9.64.

3,5-Bis(*N,N*-dimethylamino)phenyl methacrylate (3): 3,5-Bis(*N,N*-dimethylamino)phenol[12] (7; 13.9 g, 56 mmol) was dissolved in 150 mL of a 10% aqueous sodium hydroxide solution, and then 8.0 g (77 mmol) of methacryloyl chloride[13] was added dropwise with stirring at room temperature. After stirring for an additional 1 h, the solution was extracted three times with 30 mL of benzene. The combined extract was washed with a 5% aqueous sodium hydroxide solution and water and then dried over anhydrous magnesium sulfate. The solution was concentrated to a 10-mL volume and then passed through a silica gel column (2 cm diameter × 20 cm high) using benzene as eluent. The first elution band collected was placed under reduced pressure to remove benzene to afford 5 g of a white solid, which was recrystallized from hexane to give 4.15 g (30% yield) of 3,5-bis(*N,N*-dimethylamino)phenyl methacrylate (3) as white needles: mp 67–68 °C; IR (KBr) $\nu_{C=O}$ 1750, $\nu_{C=C}$ 1640, ν_{CO} 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.30 (s, 1 H), 5.90 (s, 3 H), 5.70 (s, 1 H), 2.90 (s, 12 H), 2.00 (s, 3 H). Anal. Calcd for $C_{10}H_{20}N_2O_2$: C, 67.70; H, 8.12; N, 11.28; O, 12.90. Found: C, 67.79; H, 8.46; N, 10.54.

2-[3,5-Bis(*N,N*-dimethylamino)phenoxy]ethanol (8): 3,5-Bis(*N,N*-dimethylamino)phenol[12] (7; 4.0 g, 22 mmol) was dissolved in 80 mL of ethanol containing 1.5 g (65 mmol) of sodium metal, and then 2.7 g (22 mmol) of ethylene chlorohydrin was dropwise added with stirring at room temperature. The resulting solution was refluxed for 24 h under nitrogen and then placed under reduced pressure to remove volatile materials to give a dark red residue, to which 10 mL of benzene was added; the mixture was vigorously stirred and then filtered out to separate the precipitant of sodium chloride. The filtrate was placed under reduced pressure to remove benzene to give a dark red viscous residue, which was distilled at 170–175 °C under a pressure of 1 mmHg to give a red viscous oil. The oil was dissolved in 5 mL of benzene, and then the resulting solution was passed through a silica gel column (2 cm diameter × 20 cm high) by using benzene as eluent. The first elution band collected was placed under reduced pressure to remove benzene to given 2.66 g (54.5% yield) of 2-[3,5-bis(*N,N*-dimethylamino)phenoxy]ethanol (8) as a pale yellow viscous oil: IR (NaCl) ν_{OH} 3600, ν_{CH} 3025–2800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.35 (s, 1 H), 5.76 (s, 3 H), 4.01 (m, 4 H), 2.91 (s, 12 H). Anal. Calcd for $C_{12}H_{20}N_2O_2$: C, 64.25; H, 9.00; N, 12.48; O, 14.27. Found: C, 64.50; H, 8.95; N, 12.61.

2-[3,5-Bis(*N,N*-dimethylamino)phenoxy]ethyl methacrylate (4): Compound 8 (2.0 g, 9.0 mmol) and 1.66 g (10.8 mmol) of methacrylic anhydride were dissolved in 30 mL of tetrahydrofuran at room temperature in the presence of 3 mg of TEMPO, and then the solution was refluxed under nitrogen for 8 h. The reaction mixture was placed under reduced pressure to remove volatile materials to give a brown viscous oil, which was dissolved

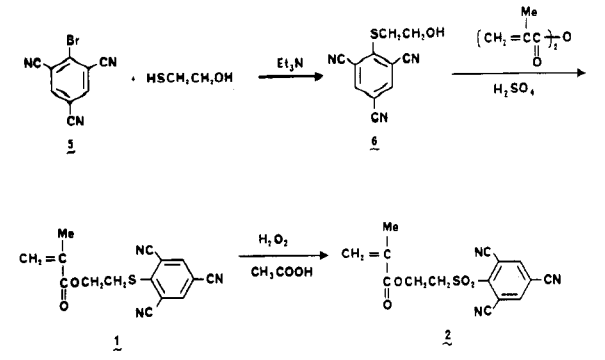
in 20 mL of benzene. The benzene solution was washed with a 5% aqueous sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, and then concentrated to give a brown viscous oil, which was distilled at 150–160 °C under a pressure of 0.01 mmHg by using a glass tube oven to give 1.7 g of an orange viscous oil. The oil was dissolved in 5 mL of benzene, and the resulting solution was passed through a basic alumina column (2 cm diameter × 20 cm high) by using benzene as eluent. The first elution band collected was concentrated to yield 1.3 g of a yellow viscous oil which was recrystallized three times from hexane to give 0.8 g (30% yield) of 2-[3,5-bis(*N,N*-dimethylamino)phenoxy]ethyl methacrylate (**4**) as white granules: mp 40–41 °C; IR (KBr) $\nu_{C=O}$ 1720, $\nu_{C=C}$ 1640, ν_{CO} 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.12 (s, 1 H), 5.63 (s, 2 H), 5.57 (s, 1 H), 4.42 (t, J = 5 Hz, 2 H), 4.12 (t, J = 5 Hz, 2 H), 2.19 (s, 12 H), 1.96 (s, 3 H). Anal. Calcd for $C_{16}H_{24}N_2O_3$: C, 65.30; H, 8.24; N, 9.52; O, 16.94. Found: C, 65.60; H, 8.33; N, 9.34.

Other Materials. Commercial styrene [St; bp 52 °C (30 mmHg)] was washed with a 2% aqueous sodium hydroxide solution and water, dried over anhydrous magnesium sulfate, stirred over calcium hydride at room temperature for 24 h, and distilled. Commercial benzene (bp 80 °C) was washed with concentrated sulfuric acid, water, a 5% aqueous sodium hydroxide solution, and water, dried over anhydrous magnesium sulfate, refluxed over metal sodium for 24 h, and distilled. Tetrahydrofuran (THF; bp 65 °C) was refluxed over lithium aluminum hydride for 12 h and distilled. Dimethyl sulfoxide [DMSO; bp 68 °C (10 mmHg)] was dried over 3-Å molecular sieves for 24 h and then distilled under reduced pressure. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from ethanol. Commercial di-*tert*-butyl peroxide (*t*-BPO) was used without further purification. Tetracyanoethylene (TCNE) was purified by sublimation (twice). *N,N*-Dimethyl-*p*-toluidine [DMT; bp 67 °C (4 mmHg)] was distilled over potassium hydroxide.

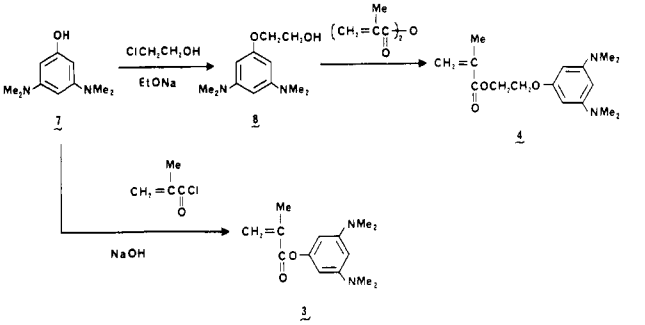
Polymerization Procedure. Given amounts of a monomer, an initiator, and a solvent, if necessary, were placed in an ampule, which was degassed by the freeze–thaw method (repeated three times) and sealed under reduced pressure. The ampule was set in a bath thermostated at a fixed temperature. After the time of polymerization, a small amount (1–2 mL) of THF or DMSO was added to the ampule to dissolve the contents. The resulting solution was poured into an excess of methanol to precipitate the polymer. In the case of solution polymerization, the reaction mixture was poured directly into an excess of methanol to precipitate the polymer, which was then dissolved in a small amount of THF or DMSO. The resulting solution was poured into an excess of methanol to reprecipitate the polymer. This dissolution–precipitation process was carried out at least three times for purification. The purified polymer was dried under reduced pressure until a constant weight was reached.

Charge-Transfer Complex Spectra. The electron-accepting property of **1** and **2** as well as the electron-donating property of **3** and **4** was determined by means of a charge-transfer transition band method.[14] Difference spectra were taken in THF at room temperature by placing the mixture solution in a sample cell and the solution of the compound under consideration in a reference cell. For monomers **1** and **2** with *N,N*-dimethyl-*p*-toluidine and for monomers **3** and **4** with tetracyanoethylene, absorptions due to DMT and TCNE, respectively, were substrated to obtain the difference spectra. The concentrations of solutions employed were as follows: for the former systems, [**1**] = [**2**] = 3.0 × 10^{-3} mol/L and [DMT] = 5.2 × 10^{-2} mol/L, for the system of **3** with TCNE, [**3**] = 1.1 × 10^{-2} mol/L and [TCNE] = 9.8 × 10^{-3} mol/L, and for the system of **4** with TCNE, [**4**] = 1.1 × 10^{-2} mol/L and [TCNE] = 1.2 × 10^{-2} mol/L. UV–vis spectra of poly(**1**-*co*-**3**) and poly(**1**-*co*-**4**) in THF and poly(**2**-*co*-**4**) in DMSO were measured at room temperature. Also, UV–vis spectra for **1** with **3** and **4** and for **2** with **4** were measured by adjusting the monomer concentration so that they were equivalent to the corresponding monomer units in the copolymers: 0.12 g/L of poly(**1**-*co*-**3**) (run no. 4 in Table V) in THF corresponds to concentrations of **1** and **3** in THF of 2.18 × 10^{-4} and 2.26 × 10^{-4} mol/L, respectively, 0.124 g/L of poly(**1**-*co*-**4**) (run no. 2 in Table VI) in THF corresponds to concentrations of **1** and **4** of 2.23 × 10^{-4} and 2.11 × 10^{-4} mol/L, respectively, 0.104 g/L of poly(**1**-*co*-**4**) (run no. 2 in Table VI) in DMSO corresponds to concentrations of **1** and **4** of 1.86 × 10^{-4} and 1.77 × 10^{-4} mol/L, respectively, and 0.096 g/L of poly(**2**-*co*-**4**) (run no. 3 in Table VI) in DMSO corresponds to concentrations of **2** and **4** of 1.58 × 10^{-4} and 1.62 × 10^{-4} mol/L, respectively.

Scheme I



Scheme II



The relationship of the intensity of the absorbance due to a charge-transfer complex versus the copolymer composition was considered as a sort of modified continuous variation method[15] to allow composition of an intramolecular charge-transfer complex to be determined. The absorbance of seven samples of poly(**1**-*co*-**3**) with various compositions was measured in THF at room temperature at wavelengths of 390, 400, 410, 420, 430, and 440 nm by adjusting the copolymer concentration to allow the sum of the concentrations of **1** and **3** units to be 0.01 mol/L.

Photoconductivity Measurement. The photoconductivity of films was measured in a dark chamber under reduced pressure below 10^{-2} mmHg in the wavelength range of 200–700 nm according to the method of Ieda et al.[16,17] A xenon lamp (500-W UXL-500 DO type, Ushio Inc.) was used as a light source, and the beam was monochromatized by means of a Shimadzu–Bausch and Lomb high-intensity grating monochromator. The gold–film–gold sandwich type specimen was prepared as follows: the copolymer was dissolved in THF or DMSO, and the resulting solution was passed through a Teflon-coated filter with a pore size of 5.0 μm (Fluoropore FP-500, Sumitomo Electric Co.) to remove small suspended dust particles. The solution was poured onto a gold-coated coverglass and was placed under reduced pressure to remove the solvent at a slow rate to obtain a film on which, then, a transparent gold electrode was deposited by a vacuum evaporating technique. The photocurrent direction is defined as positive when an electron flows from the irradiated surface of the specimen into the inside. The thickness of the film employed was measured by using a micrometer. Measurement of the hole drift mobility was carried out according to the method of Mikawa et al.[18] The gold–film–Nesa glass sandwich type specimen was prepared by a method almost similar to the above-mentioned preparation of the film for the photoconductivity measurement.

Characterization. The copolymer composition was established by elemental analysis. The number-average molecular weight, $\bar{M}_n$, of the copolymer was determined without correction by gel permeation chromatography (GPC) using standard polystyrenes as reference and THF as eluent. Solution viscosities of the polymers were determined at 30 °C by using an Ostwald viscometer and DMSO as solvent.

Instrumentation. Determination of the melting points was carried out on a Büch capillary melting point apparatus. ^{1}H NMR spectra were taken on a Hitachi R-60 spectrometer. Infrared and UV–vis measurements were made on Jasco A-100 and Jasco UVIDEC-430B spectrometers, respectively. Elemental

Table I
Homopolymerizations of 1–4

run no.	feed: monomer/mg	feed: initiator (mg)	feed: solvent (mL)	temp/°C	time/h	conv/%	$\bar{M}_n$[c]/10^4	η_{sp}/C[d]/(dL/g)
			Monomer 1					
1	100.2	AIBN (0.14)	THF (5)	60	24	83.0	2.2	
2	100.9	AIBN (0.12)	DMSO (5)	60	9.5	96.8	9.0	
3	99.3	*t*-BPO (1.0)		107	15 (min)	25.5	24.0	
			Monomer 2					
4[a]	50.8	AIBN (0.5)	THF (1)	60	2.2	39.8	*b*	0.19
5	50.2	AIBN (0.5)	DMSO (1)	60	4.0	59.1	*b*	0.94
6	50.2	*t*-BPO (1.6)		115	1.2	52.5	*b*	0.32
			Monomer 3					
7	100.1	AIBN (0.16)	THF (3)	60	20	62.1	1.3	
8	94.1	AIBN (0.15)	DMSO (3)	60	19.2	28.2	2.3	
9	104.4	AIBN (1.45)		70	10 (min)	14.9	11.0	
			Monomer 4					
10	82.5	AIBN (1.0)	DMSO (1)	60	12.5	42.3	1.0	
11	79.4	AIBN (1.0)		47	11.0	89.4	3.0	

[a] Polymer deposited. [b] Polymers are insoluble in THF. [c] Determined by GPC using THF as eluent and standard polystyrenes as reference. [d] Solvent: DMSO. Temp: 30 °C. C = 0.2–0.1 g/dL.

Table II
Copolymerizations[a] of 1 and 2 with St at 60 °C

run no.	monomer: St/mg	monomer: 1 or 2/mg	monomer: 1 or 2/(mol %)	time/h	conv/%	copolymer: S %	copolymer: 1 or 2/(mol %)	copolymer: $\bar{M}_n$[b]/10^4
				Monomer 1				
1	166.0	119.3	20.1	5.2	8.8	4.15	18.0	2.1
2	137.4	195.5	33.3	5	3.3	5.15	24.3	0.9
3	108.1	200.0	39.3	4	2.4	5.63	27.8	1.9
4	74.5	222.2	51.1	4	3.0	6.42	37.1	0.6
5	60.3	239.1	58.1	3	2.4	7.64	46.2	1.3
6	33.1	227.8	74.6	1.7	1.9	8.05	51.0	0.7
7	12.0	289.0	89.3	2	3.7	8.74	60.2	1.8
				Monomer 2				
8	99.2	34.9	10.0	11	8.9	3.62	15.8	1.0
9	98.3	50.9	14.1	14	11.9	4.67	22.6	1.0
10	79.5	104.4	29.4	7	3.9	6.27	36.4	0.9
11	47.5	146.7	49.4	7	5.1	6.69	41.1	0.9
12	26.9	229.0	72.9	9	18.4	7.91	57.9	1.6[c]

[a] Initiator: AIBN, 1 mg. Solvent: 5 mL of THF for the 1–St system and 5 mL of DMSO for the 2–St system. [b] Determined by GPC using THF as eluent and standard polystyrenes as reference. [c] $\bar{M}_n$ of the soluble part in THF.

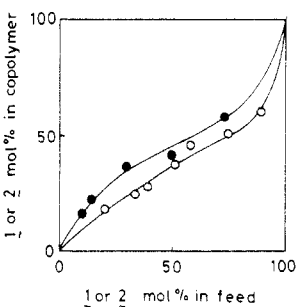


Figure 1. Copolymerization composition diagrams for the 1–St system (○) in THF and for the 2–St system (●) in DMSO at 60 °C.

analysis was performed by a Yanaco CHN corder MT-3. Number-average molecular weights ($\bar{M}_n$) of the polymers were measured on a Tosoh HLC-803D with a series of four columns, Tosoh G4000H, G3000H, G2500H, and G2000H.

Results and Discussion

Syntheses of 2-[(2,4,6-Tricyanophenyl)thio]ethyl Methacrylate (1) and 2-[(2,4,6-Tricyanophenyl)sulfonyl]ethyl Methacrylate (2). Compounds 1 and 2 were prepared via the reaction route shown in Scheme I. Thioethylene and oxyethylene were introduced as spacers between methacryloyloxy and 2,4,6-tricyanophenyl groups. The condensation reaction of 1-bromo-2,4,6-tricyanobenzene with ethylene glycol under basic conditions gave 2-(2,4,6-tricyanophenoxy)ethanol in poor yield (20%). On the other hand, the reaction of 1-bromo-2,4,6-tricyanobenzene with mercaptoethanol gave 2-[(2,4,6-tricyanophenyl)thio]ethanol (6) in satisfactory yield (73%). The sulfide bond is capable of being oxidized with hydrogen peroxide to sulfone which acts as a strong electron-accepting group instead of an electron-donating sulfide and enhances an electron-accepting property of 2,4,6-tricyanophenyl group. Therefore, on the basis of both the synthetic advantage and the easy conversion to sulfone to enhance an electron-accepting property of the 2,4,6-tricyanophenyl group, the thioethylene chain was preferred as a spacer to oxyethylene.

The esterification reaction of 6 with an excess of methacrylic anhydride in the presence of an acidic catalyst gave 1 in 60% yield. On the other hand, the Schotten–Baumann reaction of 6 with methacryloyl chloride under various experimental conditions failed to give the ester 1. The sulfide bond in 1 was subjected to oxidation with hydrogen peroxide in acetic acid to give 2 in 51% yield. Both 1 and 2 are soluble in DMF, DMSO, THF, chloroform, acetonitrile, acetone, ethanol, dichloromethane, and benzene and insoluble in hexane at room temperature. Compounds 1 and 2 in DMF and DMSO remained unchanged at room temperature for long periods of time in contrast to TCPM[9] and TCPA[9] which were readily

Table III
Copolymerizations[a] in THF of 3 and 4 with St at 60 °C

run no.	monomer St/mg	monomer 3 or 4/mg	monomer 3 or 4/(mol %)	time/h	conv/%	copolymer N %	copolymer 3 or 4/(mol %)	copolymer $\bar{M}_n$[b]/10⁴
				Monomer 3				
1	265.5	70.9	10.1	2	4.4	5.06	25.4	2.0
2	289.6	161.9	20.1	2	4.1	5.99	32.6	1.8
3	125.5	199.5	40.1	3	5.6	7.50	45.4	2.0
4	64.1	197.6	56.4	5	9.6	8.30	53.9	1.9
5	69.3	244.7	59.7	2	4.6	8.53	56.5	2.2
6	41.2	288.3	74.6	2	5.0	9.02	62.6	2.0
7	15.6	299.8	88.9	2	10.9	10.14	78.8	2.0
				Monomer 4				
8	95.4	30.7	10.2	4	10.9	4.11	21.1	1.5
9	49.2	65.1	31.9	4	6.2	6.30	40.6	2.1
10	25.5	101.5	58.5	4	8.0	6.89	48.3	1.8
11	25.8	154.0	67.9	4	7.5	7.64	58.4	2.2

[a] Initiator: AIBN, 1 mg. Solvent: 5 mL. [b] Determined by GPC using THF as eluent and standard polystyrenes as reference.

Table IV
Q and *e* Values of 1–4, 2,4,6-Tricyanophenyl Methacrylate, Phenyl Methacrylate, and Ethyl Methacrylate

monomer	*Q*	*e*
1	0.31	+0.67
2	0.63	+0.77
3	1.03	+0.75
4	0.85	+0.83
2,4,6-tricyanophenyl methacrylate	1.56	+0.82
phenyl methacrylate[23]	1.49	+0.73
ethyl methacrylate[23]	0.73	+0.52

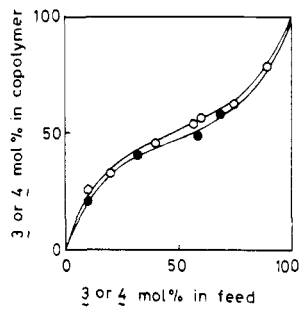


Figure 2. Copolymerization composition diagrams for the 3–St system (○) and the 4–St (●) system in THF at 60 °C.

hydrolyzed when dissolved in DMSO or DMF to produce yellow solutions of the tricyanophenolate anion.

Syntheses of 3,5-Bis(*N*,*N*-dimethylamino)phenyl Methacrylate (3) and 2-[3,5-Bis(*N*,*N*-dimethylamino)-phenoxy]ethyl Methacrylate (4). Compounds 3 and 4 were prepared via the reaction route shown in Scheme II. The esterification of 3,5-bis(*N*,*N*-dimethylamino)phenol (7) with methacryloyl chloride gave 3 in 30% yield. The condensation of 7 with ethylene chlorohydrin in the presence of sodium ethoxide gave 2-[3,5-bis(*N*,*N*-dimethylamino)phenoxy]ethanol (8) in 54% yield. Esterification of 8 with methacrylic anhydride in the presence of an acidic catalyst afforded 4 in 30% yield, while reaction of 8 with methacryloyl chloride did not give 4. Both 3 and 4 were capable of crystallizing only when purified carefully and were soluble in benzene, chloroform, isopropyl ether, methanol, ethanol, acetone, acetonitrile, and THF and slightly soluble in hexane.

Polymerization Behavior. Homopolymerizations of 1–4 took place readily with a radical initiator to give respective homopolymers as white powders as summarized in Table I. For the polymerization of TCPM, a steric interaction[19] was reported between the 2,6-disubstituted phenyl and the methacryloyl part to prevent homopolymerizability. For 1 and 2, this interaction is not present because the 2,6-disubstituted phenyl is not connected to the methacryloyl part directly. Homopolymers of 1–3 are soluble in THF, DMSO, and DMF except that poly(3) is insoluble in THF. Poly(1) and poly(4) are soluble in acetone, but poly(2) and poly(3) are insoluble in acetone. Poly(1), poly(2), poly(3), and poly(4) are insoluble in benzene, methanol, and chloroform. Hydrolysis of poly(1) and poly(2) in DMSO was studied. Poly(1) (run no. 1 in Table I) and poly(2) (run no. 5 in Table I) in DMSO-d_6 remained colorless and transparent for 8 days, and ^{1}H NMR spectra of these solutions were unchanged for that time, indicating that poly(1) and poly(2) are stable in DMSO.

Copolymerizations of 1 and 2 with St in DMSO were carried out. The results and composition diagrams are shown in Table II and Figure 1, respectively. The results of copolymerizations of 3 and 4 with St in THF and their composition diagrams are shown in Table III and Figure 2, respectively. The copolymerization results were analyzed according to the intersection[20] and Kelen–Tüdös[21] methods to give monomer reactivity ratios as follows: $r_1(1) = 0.11 \pm 0.05$ and $r_2 = 1.0 \pm 0.1$ at 60 °C for the 1–St system, $r_1(2) = 0.19 \pm 0.02$ and $r_2 = 0.45 \pm 0.02$ at 60 °C for the 2–St system, $r_1(3) = 0.32 \pm 0.07$ and $r_2 = 0.28 \pm 0.07$ at 60 °C for the 3–St system, and $r_1(4) = 0.22 \pm 0.05$ and $r_2 = 0.32 \pm 0.05$ at 60 °C for the 4–St system, respectively. Alfrey–Price's *Q* and *e* values for 1–4 were calculated on the basis of the above monomer reactivity ratios and are listed in Table IV, together with values for TCPM,[9] phenyl methacrylate, and ethyl methacrylate. It was obvious that the *Q* and *e* values of 1, 2, 4, and ethyl methacrylate fall into given ranges due to the fact that any polymerizing methacryloyloxy groups of these monomers are linked to the same ethylene group which allows an interaction between various functional groups and the methacryloyloxy group to be as small as negligible. On the other hand, methacryloyloxy in 3 is connected directly to the phenyl group, and the *Q* and *e* values of 3 are reasonably different from the ones for 1, 2, and 4.

The copolymerization of 1 with 3 was carried out in THF at 60 °C (Table V). Copolymers were obtained as powders, the color of which varied from orange to red, depending upon the copolymer composition, and their weights were (1–2) × 10⁴. These copolymers could be cast from THF solutions into transparent films, which, however, were not useful for the photoconductivity measurement because of their high brittleness probably due to their low molecular weight. For the purpose of preparing higher molecular weight copolymers, copolymerization of 1 with 3 was carried out in bulk. The molecular weight of the copolymer obtained was as high as 7.8 × 10⁴ (run no. 1 in Table VI), and it was capable of being cast from

Table V
Copolymerizations[a] in THF of 1 with 3 at 60 °C

run no.	monomer 1/mg	monomer 3/mg	monomer 1/(mol %)	time/min	yield/mg	conv/%	copolymer S %	copolymer 1/(mol %)	copolymer $\bar{M}_n$[b]/10⁴
1	69.3	230.9	20.0	23	37.6	12.5	1.39	10.0	1.3
2	140.1	196.1	39.9	90	24.5	7.8	3.59	29.4	0.95
3	168.3	137.8	50.5	50	36.3	11.9	4.52	37.9	1.9
4	200.3	111.5	60.0	60	69.4	22.3	5.86	49.1	1.5
5	248.1	52.3	79.9	90	64.6	21.5	7.57	66.4	1.8

[a] Initiator: AIBN, 1 mg. Solvent: 5 mL. [b] Determined by GPC using THF as eluent and standard polystyrenes as reference.

Table VI
Copolymerizations in Bulk of 1 with 3 and of 1 with 4 and Those in DMSO of 2 with 4

run no.	monomer 1/mg	monomer 2/mg	monomer 3/mg	monomer 4/mg	1 or 2/(mol %)	initiator (mg)	solv/mL	time/min	temp/°C	yield/mg	conv/%	copolymer S %	copolymer 1 or 2/(mol %)	copolymer $\bar{M}_n$[a]/10⁴	copolymer η_{sp}/C[b]/(dL/g)
						Monomer 1									
1	159.3		66.1		66.8	*t*-BPO (4.0)		6	106	160.0	71.0	7.03	61.0	7.8	
2	60.3			61.1	49.4	*t*-BPO (1.8)		90	106	31.0	25.5	5.55	51.3	4.0	
						Monomer 2									
3		38.7		37.6	48.0	AIBN (1.0)	1	950	60	24.8	32.5	5.08	49.4	*c*	1.52
4		39.7		47.7	47.7	AIBN (1.0)	1	420	60	27.3	34.0	4.98	48.0	*c*	1.48

[a] Determined by GPC using THF as eluent and standard polystyrenes as reference. [b] Solvent: DMSO. Temp: 30 °C. C = 0.027 g/dL. [c] Copolymers are insoluble in THF.

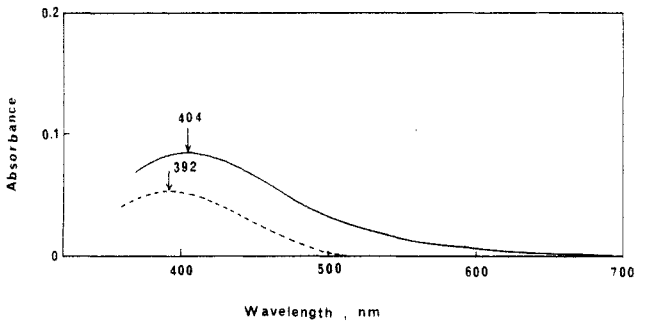


Figure 3. Intermolecular charge-transfer complex spectra between DMT and 1 (- - -) and between DMT and 2 (—) in THF solutions at room temperature. Concentration of the components: [1] = [2] = 3.0 × 10^{-3} mol/L and [DMT] = 5.2 × 10^{-2} mol/L.

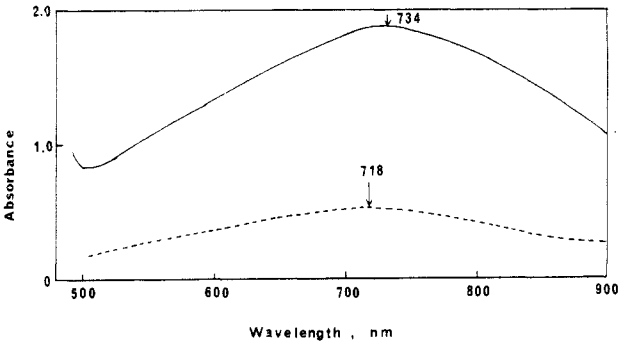


Figure 4. Intermolecular charge-transfer complex spectra between TCNE and 3 (- - -) and between TCNE and 4 (—) in THF solutions at room temperature. Concentrations of the components: [3] = 1.1 × 10^{-2} mol/L and [TCNE] = 9.8 × 10^{-3} mol/L for the 3–TCNE system and [4] = 1.1 × 10^{-2} mol/L and [TCNE] = 1.2 × 10^{-3} mol/L for the 4–TCNE system.

its THF solution into a tough film for use in the photoconductivity measurement. Copolymerizations of **4** with **1** in bulk and those of **4** with **2** in DMSO were also carried out. The results of those copolymerizations are summarized in Table VI. Poly(**1**-*co*-**4**) (run no. 2 in Table VI) was a red powder with a molecular weight of 4.0 × 10^4. Poly(**2**-*co*-**4**)s (run nos. 3 and 4 in Table VI) were dark red powders and exhibited the solution viscosities, η_{sp}/C, of 1.48 and 1.52 dL/g, respectively. Poly(**1**-*co*-**4**) (run no. 2 in Table VI) and poly(**2**-*co*-**4**)s (run nos. 3 and 4 in Table VI) were capable of being cast by using THF and DMSO as solvent, respectively, into tough films as utilized for photoconductivity measurement.

Intramolecular and Intermolecular Charge-Transfer Interaction. Difference spectra for the 1–DMT and 2–DMT systems are shown in Figure 3. Their absorption maxima are situated at 392 and 404 nm, respectively. It is obvious, in comparison with their positions of absorption maxima,[14] that **2** is stronger in electron-accepting property than **1**, probably because sulfonyl and sulfide groups are regarded as electron-accepting and electron-donating, respectively.

The difference spectra for the 3–TCNE and 4–TCNE systems exhibited absorption maxima at 718 and 734 nm, respectively, as shown in Figure 4, indicating that **4** is stronger in electron-donating property than **3**, corresponding well with the fact that the electron-donating property of ether is stronger than that of ester.

UV–vis spectra in THF for poly(**1**-*co*-**3**) (run no. 4 in Table V) and poly(**1**-*co*-**4**) (run no. 2 in Table VI) and those in DMSO for poly(**1**-*co*-**4**) and poly(**2**-*co*-**4**) (run no. 4 in Table VI) are shown in Figures 5 and 6, respectively, together with spectra of the corresponding monomer mixtures which were taken by adjusting each monomer concentration to be equivalent to the concentration of the corresponding monomer unit in the copolymer solutions. All of these copolymers were regarded as a one to one composition of the donor monomer unit to the acceptor monomer unit, and the concentrations of the copolymers were adjusted to be equivalent with regard to the corresponding individual monomer units. First, it is obvious in each system that the absorption for the copolymers is much larger than that for the monomers, probably indicating that the electron-accepting 2,4,6-tricyanophenyl and the electron-donating 3,5-bis(*N*,*N*-dimethylamino)-phenyl linked on the same copolymer chain allow these donor–acceptor pairs to form a charge-transfer complex much more easily and strongly because they could be considered to be locally more concentrated on the chain. In comparison with the position and broadness of the charge-transfer transition bands, it is found in Figure 5 that the charge-transfer interaction for the **1**–**3** system is weaker than that for the **1**–**4** system and also in Figure 6 that the interaction for the **2**–**4** system is much stronger

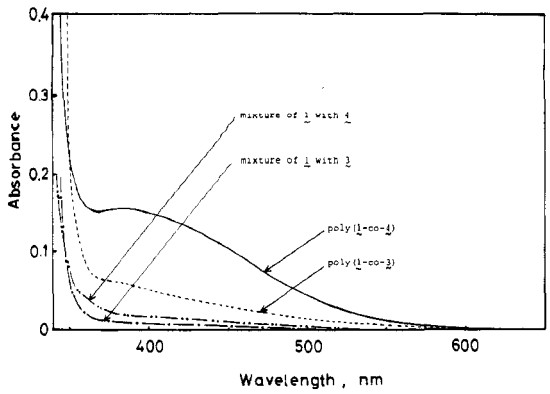


Figure 5. UV–vis spectra of poly(1-*co*-3) (run no. 4 in Table V) (- - -) and of poly(1-*co*-4) (run no. 2 in Table VI) (—) and of the mixture solution of 1 with 3 (– · –) and of 1 with 4 (– · · –) in THF at room temperature. [Poly(1-*co*-3)] = 0.120 g/L: concentrations of the 1 and 3 units in poly(1-*co*-3) correspond to 2.2×10^{-4} and 2.3×10^{-4} mol/L, respectively. [Poly(1-*co*-4)] = 0.124 g/L: concentrations of the 1 and 4 units in poly(1-*co*-4) correspond to 2.2×10^{-4} and 2.1×10^{-4} mol/L, respectively. [1] = 2.2×10^{-4} mol/L and [3] = 2.3×10^{-4} mol/L for the 1–3 system and [1] = 2.2×10^{-4} mol/L and [4] = 2.1×10^{-4} mol/L for the 1–4 system.

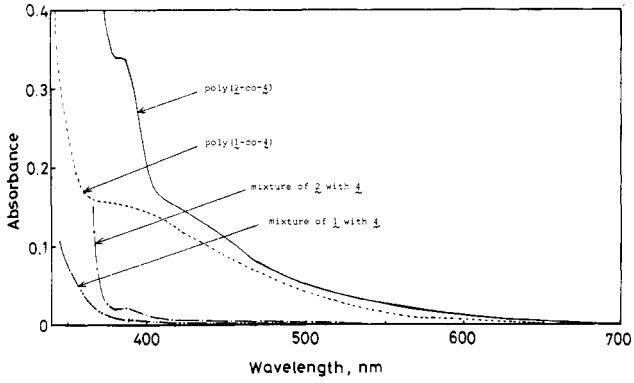


Figure 6. UV–vis spectra of poly(2-*co*-4) (run no. 2 in Table VI) (—) and of poly(1-*co*-4) (run no. 3 in Table VI) (- - -) and of the mixture solutions of 2 with 4 (– · –) and of 1 with 4 (– · · –) in DMSO at room temperature. [Poly(2-*co*-4)] = 0.096 g/L: concentrations of the 2 and 4 units in poly(2-*co*-4) correspond to 1.6×10^{-4} and 1.6×10^{-4} mol/L, respectively. [Poly(1-*co*-4)] = 0.104 g/L: concentrations of the 1 and 4 units in poly(1-*co*-4) correspond to 1.9×10^{-4} and 1.8×10^{-4} mol/L, respectively. [2] = 1.6×10^{-4} mol/ and [4] = mol/L for the 2–4 system and [1] = 1.8×10^{-4} mol/L and [4] = 1.7×10^{-4} mol/L for the 1–4 system.

than that for the 1–4 system. It is concluded therefore that both the intensity and the amount of charge-transfer interaction increase in the following order: 1–3 system < 1–4 system < 2–4 system in monomer mixtures as well as in the copolymers.

The composition of the charge-transfer complex formed in the poly(1-*co*-3)s was determined according to a modified continuous variation method[15] using copolymers with various copolymer compositions, i.e., absorptions at wavelengths of 390, 400, 410, 420, 430, and 440 nm were plotted against the copolymer compositions as shown in Figure 7 where absorption maxima at each wavelength were located at the copolymer composition of one to one, suggesting that intramolecular charge-transfer complex is made up of a one to one composition of the donor monomer unit to the acceptor one.

Photoconductivity of the Copolymer Films with the Intramolecular Charge-Transfer Interaction. Films of poly(1-*co*-3) (run no. 1 in Table VI), poly(1-*co*-4) (run no. 2 in Table VI), and poly(2-*co*-4) (run no. 4 in Table VI) showed orange, deep orange, and red, respectively, corresponding to the intensity and the amount of their intramolecular charge-transfer complexes. In the measure-

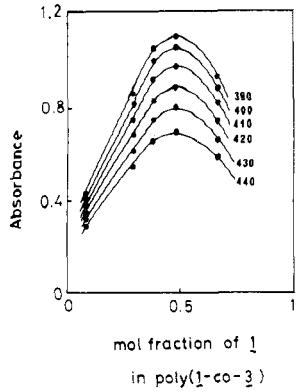


Figure 7. Intramolecular charge-transfer absorbance vs copolymer composition for the poly(1-*co*-3)s in THF at room temperature. [1 unit] + [3 unit] = 0.01 mol/L.

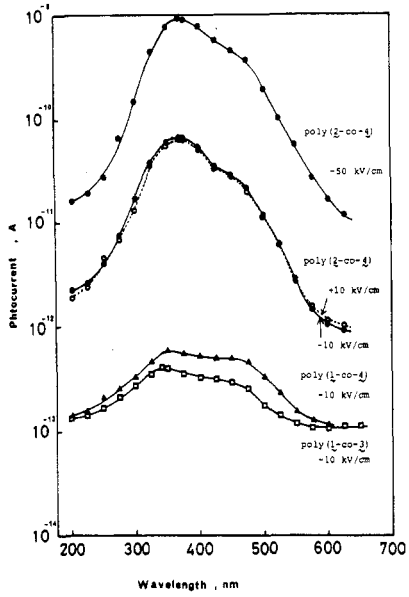


Figure 8. Spectral dependence of photocurrent in poly(1-*co*-3), poly(1-*co*-4), and poly(2-*co*-4). Film thickness: 9.1 μm for poly(1-*co*-3), 5.0 μm for poly(1-*co*-4), and 19.9 μm for poly(2-*co*-4).

ment of the photoconductivity of the films, some electric current immediately flowed when the electric field was applied to specimens, but it decreased gradually with time. This may be referred to as an absorption current. Therefore, after a specimen was placed in a given electric field for 30 min, an amount of electric current generated with UV-irradiation was measured as a photocurrent. Photocurrent measurements for the films of poly(1-*co*-3), poly(1-co-4), and poly(2-co-4) under an electric field of −10 kV/cm and additionally the measurement for the last film under that of −50 kV/cm were carried out under irradiation with UV–vis light of a wavelength range of 200–700 nm. The spectra of photocurrent vs wavelength of UV–vis light are shown in Figure 8, where all spectra exhibit a broad peak in wavelength from 300 to 600 nm with maximum peaks at 350–360 nm and a shoulder at 470–480 nm. The amounts of photocurrent for the films of poly(1-*co*-3), poly(1-co-4), and poly(2-*co*-4) at the wavelength of 450 nm under an electric field of −10 kV/cm were measured to be 3.0×10^{-13}, 5.0×10^{-13}, and 3.0×10^{-11} A, respectively. The order in the amounts of photocurrent appears to be in a good agreement with the order in the intensity and the amount of the intramolecular charge-transfer interaction in the copolymers: poly(1-*co*-3) < poly(1-*co*-4) < poly(2-*co*-4). The film of poly(2-*co*-4) was found to exhibit the highest photocurrent among them.

When the applied electric field was increased to −50 kV/cm, the photocurrent for the film of poly(2-*co*-4)

amounted to 1.0×10^{-9} and 4.5×10^{-10} A in UV-irradiation at wavelengths of 375 and 450 nm, respectively (Figure 7), corresponding to a semiconductor range of photoconductivity. Moreover, when an opposite electric field of +10 kV/cm was applied to the film of poly(**2**-*co*-**4**), a similar profile of the photocurrent vs wavelength of irradiating light was observed as shown in Figure 8.

For the film of poly(**2**-*co*-**4**), ratios of the photocurrent at a wavelength of 450 nm, I_{ph}^{450}, to the dark current, I_d, were estimated to be $I_{ph}^{450}/I_d = 86$ under an electric field of −10 kV/cm and $I_{ph}^{450}/I_d = 122$ under an electric field of −50 kV/cm. The amounts of photocurrent at 450 nm were found to be linearly proportional to the strength of an electric field in the range of −5 to −50 kV/cm, indicating that the photocurrent is ohmic.

It is obvious from the dependence of the photocurrent on the wavelength of irradiation light in Figure 8 that the photocurrent decreases drastically in the wavelength range below 350 nm, whereas it decreases gradually in the wavelength range above 350 nm and then sleeply in the wavelength range above 480 nm. On the other hand, UV–vis spectra of the copolymers were already mentioned to exhibit a strong intramolecular charge-transfer transition absorption band in the wavelength range from 350 to 500 nm as shown in Figure 5. Individual monomer unit components showed UV absorptions only in the wavelength range shorter than 350 nm. In the comparison of the wavelength dependence between photocurrent and the UV–vis absorption spectra, it is conceivable that the electron carrier generation takes place mainly with direct excitation of the intramolecular charge-transfer complex rather than with excitation of either donor or acceptor components followed by exciplex formation with respective opposite components. This concept is supported by the fact that the film with the strongest intramolecular charge-transfer interaction exhibits the largest amount of photocurrent generation, when irradiated by the UV light with a wavelength range above 350 nm.

The hole drift mobility, μ, in the film of poly(**2**-*co*-**4**) under an electric field of −100 kV/cm was measured by the time of flight method[18] to be below the lower limit of detection of 10^{-11} cm/V·s for the equipment employed. On the other hand, for the poly(vinylcarbazole) (PVCZ), the μ value was measured under the same experimental conditions to be 10^{-9} cm/V·s. Okamoto[22] and co-workers reported the photocurrent of 1×10^{-11} A for PVCZ in an irradiation at the wavelength of 360 nm in measurement using a gold–PVCZ–Nesa sandwich-type cell with PVCZ film with a thickness of 15 μm under an electric field of +35 kV/cm in vacuum.

It can be pointed out that the photocurrent for the poly(**2**-*co*-**4**) film is almost 50–100 times greater than that for the PVCZ film, whereas the hole drift mobility for the former is about one hundredth times as small as that for the latter. It could be concluded therefore that when irradiated, the poly(**2**-*co*-**4**) film can generate 10^3–10^4 times more electron carriers than that for PVCZ, but its drift length is so much shorter than that for PVCZ by a factor of about 10^{-3}–10^{-4}, suggesting that the greater number of electron carriers are generated from very strong intramolecular charge-transfer complexes in the film and the resulting carriers can run only within a very short length.

In summary, new methacrylates **1** and **2** with tricyanophenyl groups were successfully synthesized. These monomers exhibited high stability in polar solvents and high polymerizability and copolymerizability. Poly(**1**-*co*-**3**), poly(**1**-*co*-**4**), and poly(**2**-*co*-**4**) obtained in bulk polymerization were capable of being cast by using THF or DMSO into tough films for use in photoconductivity measurements. Both the intensity and the amount of the charge-transfer interaction increased in the following order: **1**–**3** system < **1**–**4** system < **2**–**4** system in monomer mixtures as well as in the copolymers. The amount of photocurrent in the copolymers was in good agreement with the intensity and the amount of the intramolecular charge-transfer interaction among them. By comparison of the wavelength dependence between the photocurrent and the UV–vis absorption spectrum, it was likely that the electron carrier generation takes place mainly through direct excitation of the intramolecular charge-transfer complex. It was also concluded from the values of the hole drift mobility of poly(**2**-*co*-**4**) and PVCZ that a large amount of electron carrier is generated in the poly(**2**-*co*-**4**) film under irradiation, but the carriers can run only within a very short length.

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References and Notes

(1) Schaffert, R. M. *IBM J. Res. Dev.* **1971**, *15*, 75.
(2) Hu, C. J.; Oshima, R.; Seno, M. *Macromolecules* **1988**, *21*, 1536.
(3) Hu, C. J.; Oshima, R.; Arai, U.; Seno, M. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2423.
(4) Simionescu, C. I.; Barboiu, V.; Grigoras, M. *Polym. Bull.* **1983**, *9*, 537.
(5) Simionescu, C. I.; Barboiu, V.; Grigoras, M. *Polym. Bull.* **1984**, *11*, 545.
(6) Hu, C. J.; Oshima, R.; Seno, M. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 1239.
(7) Natansohn, A.; Flaisher, H. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 579.
(8) Natansohn, A. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3161.
(9) Iwatsuki, S.; Itoh, T.; Shimizu, Y.; Iwata, Y.; Matsuhiro, S. *Macromolecules* **1985**, *18*, 1.
(10) Wallenfels, K.; Witzler, F.; Friedrich, K. *Tetrahedron* **1967**, *23*, 1353.
(11) Naworth, W. N.; Gregory, H.; Wiggins, L. F. *J. Chem. Soc.* **1946**, 488.
(12) Effenberger, F.; Nies, R. *Chem. Ber.* **1968**, *101*, 3787.
(13) Stempel, G. H., Jr.; Crosss, R. P.; Mariella, R. P. *J. Am. Chem. Soc.* **1950**, *72*, 2299.
(14) McConnell, H.; Ham, J. S.; Platt, J. R. *J. Chem. Phys.* **1953**, *21*, 66.
(15) Vosburgh, W. C.; Cooper, G. R. *J. Am. Chem. Soc.* **1941**, *63*, 437. Job, P. *Ann. Chem. Phys.* **1928**, *9*, 113.
(16) Morita, S.; Sawa, G.; Ieda, M. *Charge Storage, Charge Transport and Electrostatics with Their Applications*; Wada, Y., Perlman, M. M., Kolado, M., Eds.; Kodansha and Elsevier: Tokyo, 1979; p 397.
(17) Takai, Y.; Mori, K.; Mizutani, T.; Ieda, M. *Jpn. J. Appl. Phys.* **1976**, *15*, 2341.
(18) Fujino, M.; Mikawa, H.; Yokoyama, M. *Photogr. Sci. Eng.* **1982**, *26*, 84.
(19) Otsu, T.; Yamada, B.; Sugiyama, S.; Mori, S. *J. Polym. Sci., Polym. Chem.* **1980**, *18*, 2197.
(20) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1694.
(21) Kelen, T.; Tudos, F. *J. Macromol. Sci., Chem.* **1975**, *A9*, 1.
(22) Okamoto, K.; Kusabayashi, S.; Mikawa, H. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2324.
(23) Young, L. J. Tabulation of *Q*–*e* Values. In *Polymer Handbook*, 2nd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1975; pp II-387–II-404.

Registry No. **1**, 142189-20-6; **1** (homopolymer), 142189-26-2; **2**, 142189-21-7; **2** (homopolymer), 142189-27-3; **3**, 142189-22-8; **3** (homopolymer), 142189-28-4; **4**, 142189-23-9; **4** (homopolymer), 142189-29-5; **5**, 13520-05-3; **6**, 142189-24-0; **7**, 16857-98-0; **8**, 142189-25-1; (**1**)(**3**) (copolymer), 142189-34-2; (**1**)(**4**) (copolymer), 142189-35-3; (**1**)(St) (copolymer), 142189-30-8; (**2**)(**4**) (copolymer), 142189-36-4; (**2**)(St) (copolymer), 142189-31-9; (**3**)(St) (copolymer), 142189-32-0; (**4**)(St) (copolymer), 142189-33-1; 2-mercaptoethanol, 60-24-2; methacrylic anhydride, 760-93-0; methacryloyl chloride, 920-46-7; ethylene, 107-07-3.