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Syntheses of Novel Electron-Accepting Monomers Carrying the Polycyanophenyl Group and the Intramolecular Charge-Transfer Interaction of Their Copolymers

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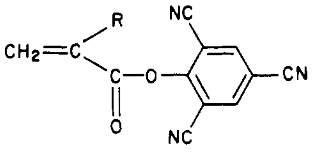
ABSTRACT: As novel electron-accepting monomers, 2,4,6-tricyanophenyl methacrylate (TCPM), 2,4,6-tricyanophenyl acrylate (TCPA), and 2,4-dicyanophenyl methacrylate (DCPM) were prepared. TCPM and TCPA are not homopolymerizable with α,α'-azobis(isobutyronitrile) (AIBN) at 60 °C for 70 h, while DCPM is homopolymerizable to yield its homopolymer with molecular weight $\bar{M}_n = 7.2 \times 10^3$. Their copolymerizations with styrene or methyl methacrylate (MMA) as comonomer were studied with AIBN at 60 °C to obtain their copolymerization parameters. In addition, copolymers between each of the monomers and *m*-(*N*,*N*-dimethylamino)phenyl methacrylate (mDMAPM) were examined in intramolecular charge-transfer complex formation in comparison with the corresponding intermolecular one between component monomers. A terpolymer of TCPM, mDMAPM, and MMA was prepared to obtain a tough film which was examined in photoconductivity.

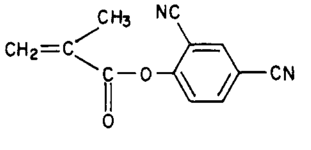
Several vinyl monomers with polynitrophenyl groups have been prepared such as 2,4,6-trinitrostyrene,[1-4] picryl methacrylate,[5-7] 2,4-dinitrophenyl methacrylate,[5,8] 4-nitrophenyl methacrylate,[5] 2′-ethylmethacryl 4,5,7-trinitro-9-oxofluorene-2-carboxylate,[9] and 2,4,7-trinitro-9-fluorenyl methacrylate[10,11] as electron-accepting monomers and as starting materials for speciality polymers with powerfully electron-accepting groups or with photoconductivity. However, since the nitro group is very susceptible to free radical reaction, free radical polymerizations of these monomers could not give polymeric productrs with high molecular weight to form tough films or fibers.

As compared with a nitro group, a cyano group is much less sensitive toward a free radical and is almost similarly strongly electron withdrawing, even though it ($\sigma_p = 0.66$)[12] is slightly less electron withdrawing than a nitro group ($\sigma_p = 0.78$)[12] in their Hammett substituent constants. Vinyl monomers with polycyanophenyl group instead of polynitrophenyl were thought to be interesting for preparing the high molecular weight specialty polymers. So far, a few vinyl compounds with monocyanophenyl groups have been known such as 2-cyanostyrene,[13] 3-cyanostyrene,[14] and 4-cyanostyrene,[15] but no vinyl compound with polycyanophenyl group has been prepared yet.

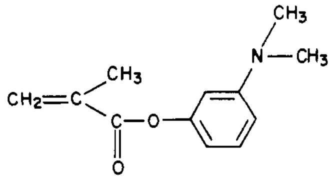
In this work, new vinyl monomers with 2,4,6-tricyanophenyl and 2,4-dicyanophenyl groups instead of picryl and 2,4-dinitrophenyl group were prepared, such as 2,4,6-tricyanophenyl methacrylate (TCPM), 2,4,6-tricyanophenyl acrylate (TCPA), and 2,4-dicyanophenyl methacrylate (DCPM) and their polymerization behavior was studied. In addition, copolymers between each of these monomers and *m*-(*N*,*N*-dimethylamino)phenyl methacrylate (mDMAPM) were examined in intramolecular charge-transfer complex formation in comparison with the corresponding intermolecular one between component monomers. A terpolymer of TCPM, mDMAPM, and methyl methacrylate was prepared to obtain a tough film which was examined briefly for photoconductivity.



R=H, TCPA
R=CH$_3$, TCPM



DCPM



mDMAPM

Experimental Section

Preparation of 2,4,6-Tricyanophenyl Methacrylate (TCPM) and 2,4,6-Tricyanophenyl Acrylate (TCPA). 1-

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Bromo-2,4,6-tricyanobenzene (2.0 g, 8.62 mmol), which had been prepared from bromomesitylene according to the method of Wallenfels et al.,[16] was dissolved in 70 mL of dry ethanol, and to this refluxing solution was added dropwise 1.13 g (17.1 mmol) of potassium hydroxide in 15 mL of dry ethanol with vigorous stirring over a period of about 5 min. When the potassium hydroxide solution was added, this solution immediately changed in color to yellow and gradually a powdery product was deposited. After the addition was completed, the reaction mixture was stirred under reflux for 0.5 h and then at room temperature for an additional 0.5 h. It was filtered out to obtain 2.3 g of pale yellow product, which was then mixed with 40 mL of dioxane, and 1.7 g (16.5 mmol) of methacryloyl chloride[17] was added dropwise. It was kept at room temperature with stirring for a half day. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure until dryness. The solid residue was dissolved in a small amount of chloroform, and then the chloroform solution was passed through the column packed with silica gel using chloroform as eluent. The eluate was evaporated under reduced pressure to obtain 1.20 g of a white solid product, which was recrystallized from dry ethanol to give white flake crystal of TCPM in 46% yield (0.94 g): mp 123–124 °C; UV (THF) 230 nm (ϵ 2.11 × 10^4); IR (KBr) 2230, 1750, 1630, and 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.08 (s, 2 H), 6.43 (m, 1 H), 5.95 (m, 1 H), 2.10 (m, 3 H). Anal. Calcd for $C_{13}H_7N_3O_2$: H, 2.97; C, 66.35; N, 17.01. Found: H, 2.99; C, 66.43; N, 17.08.

TCPA was prepared in a similar procedure using acryloyl chloride[17] instead of methacryloyl chloride: yield, 39%; mp 99–101 °C; UV (THF) 232 nm (ϵ 1.60 × 10^4); IR (KBr) 2230, 1750, 1630, and 1065 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 8.25 (s, 2 H), 7.00 (dd, 1 H), 6.60 (dd, 1 H), 6.32 (dd, 1 H). Anal. Calcd for $C_{12}H_5N_3O_2$: H, 2.26; C, 64.58; N, 18.82. Found: H, 2.28; C, 64.62; N, 18.98.

Preparation of 2,4-Dicyanophenyl Methacrylate (DCPM). 2,4-Dicyanophenol (1.10 g, 7.64 mmol), which had been prepared from salicylaldehyde according to the method of Hatano and Matsui,[18] was added to 0.54 g (7.71 mmol) of potassium methoxide in 20 mL of dry methanol with stirring. The resulting solution was evaporated under reduced pressure to give 1.07 g of potassium 2,4-dicyanophenoxide. To 1.07 g of potassium 2,4-dicyanophenoxide in 20 mL of dry THF was added dropwise 0.9 g (8.7 mmol) of methacryloyl chloride with stirring at room temperature and then it was kept for an additional 1.5 h. The resulting mixture was filtered. The filtrate was evaporated under reduced pressure to dryness to yield 1.0 g of a red viscous material, which was dissolved with hot excess *n*-hexane (ca. 100 mL). The colorless *n*-hexane solution was concentrated by evaporation to one-third volume and then cooled at 0 °C to deposit white needles of DCPM in 22% yield (0.2 g): mp 98–99 °C; UV (THF) 222 nm (ϵ 1.71 × 10^4); IR (KBr): 2240, 1740, 1630, and 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.23–8.00 (m, 3 H), 6.53 (m, 1 H), 5.95 (m, 1 H), 2.15 (m, 3 H). Anal. Calcd for $C_{12}H_8N_2O_2$; H, 3.81; C, 67.92; N, 13.19. Found: H, 3.92; C, 67.80; N, 13.28.

Other Materials. *m*-(*N*,*N*-Dimethylamino)phenyl methacrylate (mDMAPM) [bp 100 °C (0.25 mmHg)] was prepared from *m*-(*N*,*N*-dimethylamino)phenol and methacryloyl chloride according to the method of Shinkai et al.[19] Styrene (St), methyl methacrylate (MMA), α,α'-azobis(isobutyronitrile) (AIBN), THF, *p*-dioxane, and ethanol were purified from commercial products by conventional methods.

Polymerization Procedure. Given amounts of monomers, AIBN, and THF were placed in an ampule, which was degassed completely by the freeze–thaw method (repeatedly three times) and sealed. The ampule was set in a bath thermostated at 60 °C for the time of polymerization and opened. The reaction mixture was poured into excess methanol to precipitate the polymer. For purification, the following process was repeated more than three times: the polymer obtained was dissolved again in small amount of THF and the resulting solution was poured into excess methanol to precipitate the polymer, which was dried under reduced pressure.

Measurement of Charge-Transfer Transition Spectra. Absorption spectra of charge-transfer transition for the TCPM–mDMAPM, TCPA–mDMAPM, and DCPM–mDMAPM systems were measured in THF at room temperature. Concentrations of the solutions employed were as follows: [TCPM] = [TCPA] = [DCPM] = 0.01 mol/L and [mDMADM] = 0.10 mol/L.

Composition of the complex formed between TCPM and mDMAPM was determined according to the continuous variation method.[20] The measurement was carried out at wavelengths of 440, 425, 420, and 410 nm using THF as solvent at 25 °C. Concentrations of the solutions employed were as follows: [TCPM] = [mDMAPM] = 0.1 mol/L.

Determination of the equilibrium constant, K_{CT}, and the molar absorption coefficient, ϵ_{CT}, for the charge-transfer complex of the TCPM–mDMAPM system was carried out in THF at 15 and 25 °C according to the Benesi–Hildebrand equation. The wavelength at which the absorbance was measured was 420 nm by taking into account that an absorbance may be attributed much more to the charge-transfer complex than to the individual component compounds.

Absorption spectra of the intramolecular charge-transfer transition for the copolymers of the TCPM–mDMAPM, TCPA–mDMAPM, and DCPM–mDMAPM systems were measured in THF at 25 °C.

Characterization. Polymer composition was established by elemental analysis. Solution viscosity was determined in THF at 30 °C using the Ostwald viscometer. Concentrations of the solutions employed were in the range 0.15–0.25 g/dL. The number-average molecular weight ($\bar{M}_n$) of the polymers was determined by gel permeation chromatography (GPC) using standard polystyrene as reference and THF as eluent.

Instruments for Measurement. Instruments for UV–vis, IR, and ^{1}H NMR spectral determination were Shimadzu UV-200 and Hitachi Perkin-Elmer Model 139, Jasco A-100, and Varian A-60 D, respectively. Yanagimoto CHN Corder Model MT-2 was used for elemental analysis. GPC was performed on a Toyo Soda Model HLC-803D instrument with a series of four columns, Toyo Soda G 4000H, G 3000H, G 2500H, and G 2000H.

Results and Discussion

Preparation of Monomers. Dimroth and Kraft[21] reported that 2,4,6-tricyanophenol (pK_a of 1.0 at 20 °C) is a strong acid just as picric acid and melts at 185 °C with decomposition. However, they did not describe its detailed preparation procedure from methoxymesitylene. Wallenfels et al.[16] reported that mesitylene as a more readily available starting material was converted to 1-bromo-2,4,6-tricyanobenzene, which was reacted with 2 N sodium hydroxide solution immediately with strong yellow–green coloration, suggesting that 2,4,6-tricyanophenoxide anion was formed even though 2,4,6-tricyanophenol was not isolated as a pure compound. We attempted to obtain 2,4,6-tricyanophenol as a pure compound according to the method of Wallenfels et al. Because 1-bromo-2,4,6-tricyanobenzene is insoluble in 2 N alkali hydroxide solution at room temperature, their mixture was found to stay unreacted at room temperature over a few days. When the mixture was heated until refluxing, 1-bromo-2,4,6-tricyanobenzene instantly dissolved to yield a yellow solution with ammonia-like odor, implying an alkali hydrolysis of cyano groups. Ethanol was used as solvent instead of water in order to avoid the hydrolysis. 1-Bromo-2,4,6-tricyanobenzene and the two molar excess of potassium hydroxide were dissolved in dry ethanol. When the yellow solution was heated, a pale yellow solid product was precipitated, filtered, and dried under reduced pressure. The IR spectrum of the product showed no peak in the range 3700–2500 cm^{-1} due to stretching deformation of an oxygen–hydrogen bond but a peak in the range 1250–1000 cm^{-1} due to stretching deformation of a carbon–oxygen bond. The product was subject to combustion under oxygen in an electric furnace thermostated at 900 °C to leave a large amount of ash (inorganic salt). It was supposed, therefore, that the product is composed of potassium 2,4,6-tricyanophenoxide and potassium bromide. The product was dissolved in water, and hydrochloric acid was added dropwise until the solution became acidic. The resulting solution was extracted with dichloromethane or

Table I
Copolymerizations of TCPM with St and with MMA in THF at 60 °C[a]

run no.	monomer feed, mg TCPM	monomer feed, mg comonomer	amt of TCPM, mol %	time, h	polym yield, mg	conv, %	anal. % H	anal. % C	anal. % N	copolym comp, mol % TCPM	η_{sp}/C,[b] dL/g
				Copolymerization of TCPM with St							
A-1	71.8	179.9	14.9	3.0	18.6	7.39	5.56	77.42	9.24	32.9	
A-2	90.0	222.2	15.7	3.5	19.9	6.37	4.90	77.45	9.67	34.6	
A-3	147.8	192.2	25.2	3.0	37.6	11.1	5.00	77.95	9.60	34.6	0.191[c]
A-4	205.9	169.6	34.8	2.5	26.9	7.16	4.81	76.09	10.85	41.0	0.188
A-5	236.1	105.0	49.7	2.5	30.7	9.00	4.54	74.61	11.81	46.8	
A-6	309.2	76.9	63.9	2.2	30.0	7.77	4.48	73.92	12.26	49.7	
				Copolymerization of TCPM with MMA							
B-1	89.9	219.9	14.7	4.5	41.9	13.5	5.81	59.39	6.24	18.7	0.168[d]
B-2	119.2	200.0	20.1	4.0	30.5	9.56	5.32	60.54	7.68	24.4	0.149
B-3	148.1	187.2	25.0	4.0	32.6	9.72	5.25	60.02	8.53	28.2	0.163
B-4	207.2	163.4	34.9	3.0	26.3	7.10	4.99	60.01	9.63	33.5	
B-5	237.6	98.5	51.4	3.5	22.8	6.78	4.51	61.17	11.13	42.7	

[a] Initiator AIBN; 0.5 mol % with respect to total monomer concentration. Solvent, 5 mL. [b] Solvent, THF. Temperature, 30 °C. [c] $\bar{M}_n = 7.4 \times 10^4$. [d] $\bar{M}_n = 5.0 \times 10^4$.

Table II
Copolymerizations of TCPA with St and with MMA in THF at 60 °C[a]

run no.	monomer feed, mg TCPA	monomer feed, mg comonomer	amt of TCPA, mol %	time, h	polym yield, mg	conv, %	anal. % H	anal. % C	anal. % N	copolym comp, mol % TCPA	η_{sp}/C,[b] dL/g
				Copolymerization of TCPA with St							
C-1	83.2	219.8	15.0	3.5	42.9	14.2	4.70	77.62	10.04	34.8	
C-2	141.1	191.0	25.6	3.0	59.8	18.0	4.86	76.76	10.44	36.7	0.265
C-3	196.2	166.2	35.5	2.0	47.8	13.2	4.28	75.46	11.50	42.3	0.206
C-4	224.0	106.9	49.4	1.5	51.8	15.7	4.06	74.88	11.96	44.8	0.108
C-5	290.7	72.7	65.1	1.7	36.6	9.5	4.12	74.71	12.02	45.2	
				Copolymerization of TCPA with MMA							
D-1	83.4	207.6	15.3	3.0	19.9	6.84	6.01	57.32	4.15	11.3	
D-2	114.1	200.6	20.3	4.0	31.3	9.95	5.96	59.48	6.10	17.7	0.098
D-3	138.5	187.1	24.9	3.5	31.0	9.92	5.25	58.07	6.77	20.1	0.112
D-4	196.3	166.5	34.6	3.0	32.2	8.88	4.86	57.92	8.33	26.3	0.063
D-5	222.8	98.0	50.5	3.0	22.8	6.95	4.78	60.05	10.08	34.1	
D-6	293.3	68.1	65.9	3.5	33.9	9.38	4.36	61.49	11.22	39.8	

[a] Initiator AIBN; 0.5 mol % with respect to total monomer concentration. Solvent, 5 mL. [b] Solvent, THF. Temperature, 30 °C.

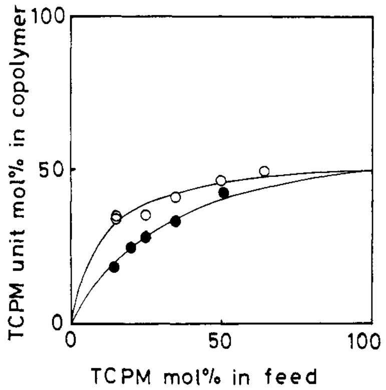

Figure 1. Copolymer composition curves of TCPM with (○) St and (●) MMA in THF at 60 °C.

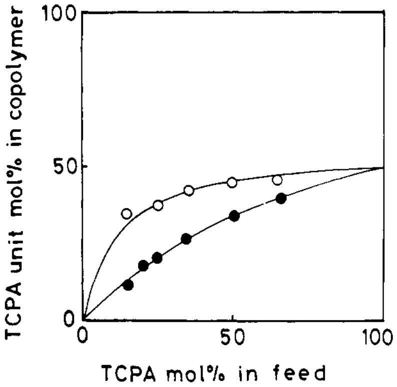

Figure 2. Copolymer composition curves of TCPA with (○) St and with (●) MMA in THF at 60 °C.

ethyl acetate. The extracts were evaporated under reduced pressure and no material was left as residue. Although 2,4,6-tricyanophenol could not be isolated as pure compound, the yellow solid product was reacted with methacryloyl chloride or acryloyl chloride in dioxane to obtain TCPM or TCPA successfully. TCPM and TCPA are soluble in THF, benzene, chloroform, acetonitrile, ethyl acetate, and acetone, and sparingly soluble in methanol and ethanol. When the transparent solution of TCPM or TCPA in chloroform or THF was allowed to stand in contact with the atmosphere at room temperature for a day, it changed in color to yellow, indicating that the ester linkage of their compounds is subject to hydrolysis with moisture in air to give yellow 2,4,6-tricyanophenoxide anion.

Polymerization Behavior of TCPM, TCPA, and DCPM. Homopolymerizations of TCPM and TCPA in THF were attempted with AIBN at 60 °C for 70 h. Their homopolymers were not obtained and unreacted monomers were recovered quantitatively, indicating that TCPM and TCPA are not homopolymerizable under this experimental condition. On the other hand, DCPM polymerizes at 60

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

run no.	monomer feed, mg DCPM	monomer feed, mg comonomer	amt of DCPM, mol %	time, h	polym yield, mg	conv, %	anal. % H	anal. % C	anal. % N	copolym comp, mol % DCPM	η_{sp}/C,[b] dL/g
				Copolymerization of DCPM with St							
E-1	81.2	242.8	14.0	3.5	25.2	7.8	5.62	79.31	6.72	33.7	0.14
E-2	133.5	193.9	25.3	3.0	24.3	7.4	5.16	78.52	7.38	38.4	
E-3	157.4	185.5	29.4	3.0	21.0	6.1	5.42	77.98	7.75	41.1	
E-4	186.6	172.3	34.8	3.0	22.4	6.2	5.43	78.70	7.37	38.3	
E-5	267.8	135.4	49.2	3.0	24.8	6.1	4.97	76.72	8.41	46.3	0.22[c]
E-6	258.0	66.7	65.6	3.0	32.5	10.0	4.78	75.50	8.82	49.7	0.19
E-7	358.3	35.5	83.3	3.0	32.5	8.3	4.83	75.40	9.16	52.7	
				Copolymerization of DCPM with MMA							
F-1	79.3	211.5	15.0	4.0	26.5	9.1	6.11	60.02	4.50	19.6	
F-2	106.2	154.6	25.0	4.0	28.6	11.0	5.71	60.71	6.27	29.9	0.22[d]
F-3	146.9	131.4	34.5	3.5	42.1	15.1	4.61	64.53	7.70	39.8	
F-4	183.4	119.8	41.7	3.5	51.9	17.1	4.83	66.89	8.85	46.4	0.17

[a] Initiator AIBN; 0.5 mol % with respect to total monomer concentration. Solvent, 5 mL. [b] Solvent, THF. Temperature, 30 °C. [c] $\bar{M}_n = 5.0 \times 10^4$. [d] $\bar{M}_n = 5.0 \times 10^4$.

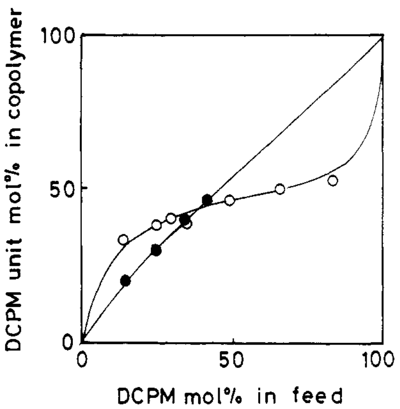

Figure 3. Copolymer composition curves of DCPM with (○) St and with (●) MMA in THF at 60 °C.

Table IV
Q and e Values of TCPM, TCPA, and DCPM

monomer (comonomer)	Q	e
TCPM (St and MMA)	1.56	+0.82
TCPA (St and MMA)	1.03	+1.18
DCPM (St)	0.91	+1.21
DCPM (MMA)	1.41	+1.05
phenyl methacrylate (St)[a]	1.56	+0.73
phenyl acrylate[b] (St)	0.90	+0.61

[a] Reference 13. [b] Reference 27.

°C with AIBN to yield a white powder of its homopolymer with molecular weight 7.2 × 10^3.

Tables I–III summarize the results of copolymerizations of TCPM with St and MMA, those of TCPA with St and MMA, and those of DCPM with St and MMA, respectively, and Figures 1–3 show the composition diagrams of these copolymerizations, respectively.

Monomer reactivity ratios were calculated according to intersection and Kelen–Tüdös methods as follows: $r_1 = 0$ and $r_2 = 0.18 \pm 0.05$ for the TCPM–St system, $r_1 = 0$ and $r_2 = 0.52 \pm 0.07$ for the TCPM–MMA system, $r_1 = 0$ and $r_2 = 0.20 \pm 0.05$ for the TCPA–St system, $r_1 = 0$ and $r_2 = 0.98 \pm 0.03$ for the TCPA–MMA system, $r_1 = 0.08 \pm 0.03$ and $r_2 = 0.22 \pm 0.05$ for the DCPM–St system, and $r_1 = 0.98 \pm 0.01$ and $r_2 = 0.68 \pm 0.02$ for the DCPM–MMA system. Table IV compiles the Alfrey–Price Q and e values for TCPM, TCPA, and DCPM, and also ones for phenyl methacrylate and phenyl acrylate for comparison. It was found out that three kinds of methacrylates, TCPM, DCPM, and phenyl methacrylate, and two kinds of acrylates, TCPA and phenyl acrylate, are almost similar in Q and e values, respectively, indicating that the cyano substituent on the phenyl group rarely influences the general reactivity and the polarity of the phenyl methacrylates and acrylates. On the other hand, a great difference was found in homopolymerizability between TCPM and DCPM, the latter being homopolymerizable but the former not. Otsu[22] et al. described a pronounced steric hindrance effect of two substituents at the 2- and 6-positions of the phenyl group up on free radical polymerization of phenyl methacrylates, when 2,6-di-*tert*-butylphenyl methacrylate was found to be not homopolymerizable with AIBN at 60 °C. Supposedly, the nonhomopolymerizability of TCPM also arises from a similar steric hindrance effect of 2,6-dicyano substituents of the phenyl group. All of the copolymers obtained are soluble in THF, acetone, chloroform, acetonitrile, dimethyl sulfoxide (Me_2SO), and *N*,*N*-dimethylformamide (DMF) and insoluble in methanol, *n*-hexane, and isopropyl ether. When the copolymers of TCPM or TCPA were dissolved in Me_2SO or DMF and their solutions were allowed to stand in contact with the atmosphere for a little while, their solutions became yellow readily. The ^1H NMR spectrum of the colorless solution in dimethyl-d_6 sulfoxide exhibited four kinds of peaks at 9.0, 7.0, 1.5, and 0.5 ppm whereas that of the yellow solution showed two additional peaks at 11.1 and 8.3 ppm. It was discovered on the basis of the peak areas at 0.5 ppm that the peak area at 9.0 ppm in the former spectrum is almost equal to the sum of the peak areas at 9.0 and 8.3 ppm in the latter. Since the yellow color is thought to be due to 2,4,6-tricyanophenoxide anion as reported by Wallenfels et al.,[16] the peak at 9.0 ppm is assigned to the phenyl protons of 2,4,6-tricyanophenyl group in the TCPM unit of the copolymer, and the peak at 8.3 ppm is assigned to the phenyl protons of the 2,4,6-tricyanophenoxide anion generated by ester hydrolysis of the TCPM unit in the copolymer. Peaks at 11.1, 7.0, 1.5, and 0.5 ppm are assigned to the acidic proton of methacrylic acid unit derived from hydrolysis of the TCPM unit, the phenyl proton of the St unit, the methylene proton of the TCPM unit and the methylene and methine protons of the St unit, and the α-methyl proton of the TCPM unit, respectively. On the other hand, the solutions of copolymers of DCPM in Me_2SO and DMF were found not to change in color even when they were allowed to stand for a long time. It is obvious that the 2,4,6-tricyanophenyl group in the copolymers is easily subject to hydrolysis with a trace amount of water in solvents, while the 2,4-dicyanophenyl ester

Table V
Copolymerizations of mDMAPM with TCPM, with TCPA, and with DCPM in THF at 60 °C[a]

run no.	monomer feed, mg: comonomer	monomer feed, mg: mDMAPM	amt of comonomer, mol %	time, h	polym yield, mg	conv, %	anal.: % H	anal.: % C	anal.: % N	copolym comp, mol % comonomer	η_{sp}/C,[b] dL/g
				Copolymerization of mDMAPM with TCPM							
G-1	77.0	452.7	12.8	3.0	77.9	14.7	7.13	69.37	8.26	11.7	0.219
G-2	152.7	393.8	25.1	1.5	51.0	9.33	6.56	66.88	8.98	17.6	0.205
G-3	222.0	321.9	37.4	1.0	33.4	6.14	5.87	66.69	9.86	25.1	
G-4	296.4	256.9	50.0	1.3	55.6	10.0	5.62	65.76	10.49	30.4	
G-5	371.6	192.3	62.6	1.3	24.9	4.42	4.87	64.33	10.92	34.3	
G-6	447.3	132.8	74.5	2.0	53.8	9.27	4.70	64.17	11.80	42.2	
G-7	148.8	387.2	25.0	24.0	391.9	73.1	6.66	68.61	9.56	22.5	0.209[c]
				Copolymerization of mDMAPM with TCPA							
H-1	132.0	380.1	24.0	24.0	318.7	62.3	6.52	67.43	8.37	12.0	0.090[d]
				Copolymerization of mDMAPM with DCPM							
I-1	133.0	387.5	24.9	18.0	393.7	75.6	5.78	68.42	8.12	40.3	0.16[e]

[a] Initiator, AIBN; 0.5 mol % with respect to total monomer concentration. Solvent, 5 mL. [b] Solvent, THF. Temperature, 30 °C. [c] $\bar{M}_n = 8.0 \times 10^4$. [d] $\bar{M}_n = 7.4 \times 10^4$. [e] $\bar{M}_n = 7.4 \times 10^4$.

Table VI
Copolymerizations[a] of TCPM with mDMAPM in Various Solvents at 60 °C

run no.	monomer feed, mg: TCPM	monomer feed, mg: mDMAPM	solvent[b]	time, h	polym yield, mg	conv, %	$\bar{M}_n \times 10^{-4}$
J-1	99.2	325.8	acetone	2.3	301.9	71.0	8.5
J-2	97.9	311.5	ethyl acetate	0.8	107.6	26.3	4.6
J-3	96.5	314.4	THF	18.3	320.0	77.9	7.0
J-4	92.2	301.0	acetonitrile	20.0	24.8	6.2	4.2
J-5	99.9	307.3	benzene	10.6	401.3	98.6	9.2
J-6	100.6	300.6	chloroform	10.6	114.0	28.4	7.4
J-7	101.4	307.0		0.3	107.2	26.3	38.0
J-8	102.7	302.2		2.4	gelation		

[a] Initiator AIBN, 1 mg. [b] 1 mL.

group is hardly subject to the hydrolysis, probably due to the weaker acidity of dicyanophenol compared to that of tricyanophenol.

Table V summarizes the results of the copolymerizations of TCPM, TCPA, or DCPM with mDMAPM. These copolymers were obtained as yellow or pale yellow powders. Colors of the copolymers of the TCPM–mDMAPM system deepened from yellow to yellow–brown with an increase in their TCPM unit content. The monomer reactivity ratios for the TCPM–mDMAPM system were obtained to be r_1(TCPM) = 0 and r_2(mDMAPM) = 1.25 ± 0.05 at 60 °C. The molecular weight of the copolymer prepared in THF at the monomer feed of 25 mol % TCPM (run no. G-7) was estimated by GPC measurement to be 8.0×10^4 in regard to the standard polystyrenes. Kadoma et al.[5] reported in the copolymerization of the picryl methacrylates and *p*-(*N*,*N*-dimethylamino)phenyl methacrylate (pDMAPM) with the monomer picryl methacrylate/pDMAPM feed ratio (mol) of 30/70 with AIBN in benzene at 60 °C for 72 h that the molecular weight of the copolymer with its composition picryl methacrylate/pDMAPM ratio (mol) of 22.9/77.1 was measured by vapor pressure osmometry in acetone to be 3.7×10^3. The copolymerizations of the picryl methacrylate–St and picryl methacrylate–MMA systems were attempted under experimental conditions similar to that of run no. A-3 and B-1 of Table I, respectively (the monomer picryl methacrylate/St feed (mg) ratio of 185.1/194.3 (25.0/75.0 in mol %) and the monomer picryl methacrylate/MMA feed (mg) ratio of 113.3/220.2 (14.8/85.2 in mol %) with 2 mg of AIBN in 5 mL of THF at 60 °C for 24 h). However, no polymeric product was obtained, and the unreacted monomers were recovered almost quantitatively. Moreover, the copolymerization of the 2,4-dinitrophenyl methacrylate–St system was attempted under experimental conditions similar to that of run no. E-5 of Table III (the monomer 2,4-dinitrophenyl methacrylate/St feed (mg) ratios of 319.2/140.0 (48.5/51.5 in mol %) with 2 mg of AIBN in 5 mL of THF at 60 °C for 7.5 h). No polymer was also obtained and the unreacted monomers were recovered. When the copolymerization of the 2,4-dinitrophenyl methacrylate–MMA system with the monomer 2,4-dinitrophenyl methacrylate/MMA feed ratio (mg) of 129.0/158.8 (24.5/75.5 in mol %) was carried out with 2 mg of AIBN in 5 mL of THF at 60 °C for 4.6 h, only 1.2 mg of the copolymer was obtained (0.4% conversion). Its molecular weight was found by GPC to be 6.6×10^3, being remarkably lower than that of the copolymer of DCPM with MMA (5.0×10^4 in run no. F-2 of Table III similar experimental conditions). Comparison of those copolymerizations among TCPM, DCPM, picryl methacrylate, and 2,4-dinitrophenyl methacrylate allowed us to point out that the former two monomers yielded the copolymer with a much higher molecular weight than the latter two monomers, suggesting that the cyano group is much less susceptible toward the free radical than the nitro group. The copolymer of TCPM and mDMAPM with molecular weight 8.0×10^4 in run no. G-7 of Table V could be processed by a film casting method into a transparent yellow but brittle film, implying that the molecular weight of the copolymer is still not so high to give sufficient toughness. Various conditions of the copolymerization were studied in order to prepare the copolymer with the higher molecular weight as summarized in Table VI, where run numbers J-1–J-6 using various solvents gave the copolymers with a similar molecular weight range (4–9) × 10^4. When the copolymerization in bulk was carried out until high conversion, the copolymer obtained was found to be insoluble in refluxing THF, hot Me_2SO, and DMF (at ca. 100 °C) (run no. J-8 in Table VI), indicating a

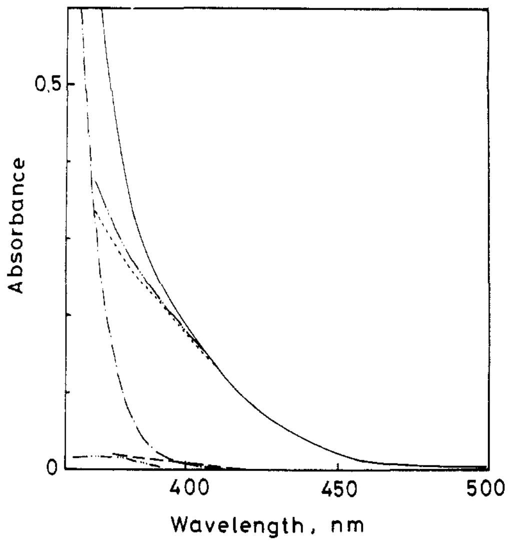

Figure 4. UV–vis spectra of mixture of TCPM and mDMAPM and their components and difference spectra between the mixture and their components for TCPM–mDMAPM, TCPA–mDMAPM, and DCPM–mDMAPM systems in THF at room temperature: (—) mixture of TCPM and mDMAPM; (–·–) mDMAPM; (–····–) TCPM; (···) difference spectrum. (–···–) Difference spectrum for the TCPA–mDMAPM system. (– – –) Difference spectrum for the DCPM–mDMAPM system. [TCPM] = [TCPA] = [DCPM] = 0.01 mol/L. [mDMAPM] = 0.1 mol/L.

formation of cross-linking probably due to polymer chain transfer reaction. When the bulk copolymerization was stopped at a conversion of 26.3%, the molecular weight of the copolymer obtained was found to be as high as 3.8×10^5 (run no. J-7 in Table VI). However, the film of this copolymer was found to be not tough but still brittle.

Inter- and Intramolecular Charge-Transfer Interaction of TCPM–mDMAPM, TCPA–mDMAPM, and DCPM–mDMAPM Systems. A yellow color developed immediately when TCPM, TCPA, or DCPM was mixed with mDMAPM in THF. For example, UV–vis spectra of the mixture of TCPM and mDMAPM and of individual monomers are shown in Figure 4, in which difference spectra between the mixture and the monomers for the three systems TCPM–mDMAPM, TCPA–mDMAPM, and DCPM–mDMAPM appear as broad band absorptions in the ranges 380–490, 380–490, and 380–430 nm, respectively, corresponding to the intermolecular charge-transfer transition of respective systems. In these systems, absorption maxima could not be observed. Both TCPM–mDMAPM and TCPA–mDMAPM systems were found to exhibit almost the same difference spectra, indicating that a difference in acceptor monomer structure between methacrylate and acrylate units exerts no influence on their intermolecular charge-transfer transition. TCPM–mDMAPM and TCPA–mDMAPM systems were regarded to have intermolecular charge-transfer transition at longer wavelength ranges than the DCPM–mDMAPM system, implying that TCPM and TCPA are stronger in electron-accepting character than DCPM.

Applications of the continuous variation method for the TCPM–mDMAPM system are shown in Figure 5 where absorption maxima are found at the equivalent volume fraction of donor and acceptor solutions with the same concentration in a wavelength range 400–440 nm, indicating that the complex is composed of equimolar amounts of TCPM and mDMAPM. The K_{CT} and ϵ_{CT} values for the complex formation of the TCPM–mDMAPM system in THF was estimated according to the Benesi–Hildebrand method using absorptions at 420 nm to be K_{CT} = 0.04 L/mol at 15 °C and 0.028 L/mol at 25 °C and ϵ_{CT} = 2500 L/(mol·cm). Kadoma et al.[5] reported that the picryl methacrylate–pDMAPM system in chloroform at room temperature has K_{CT} = 0.56 L/mol and ϵ_{CT} = 1100 L/(mol·cm). The $K_{CT}\epsilon_{CT}$ value for the TCPM–mDMAPM system ($K_{CT}\epsilon_{CT}$ = 100 at 15 °C) is about six times as small as that for the picryl methacrylate–pDMAPM system ($K_{CT}\epsilon_{CT}$ = 616 at room temperature) even though the comparison is in different solvents.

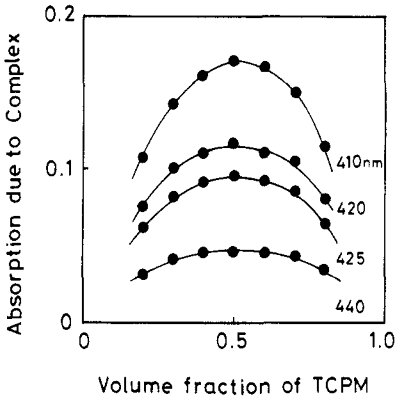

Figure 5. Continuous variation method of TCPM–mDMAPM system in THF at 25 °C. [TCPM] = [mDMAPM] = 0.10 mol/L.

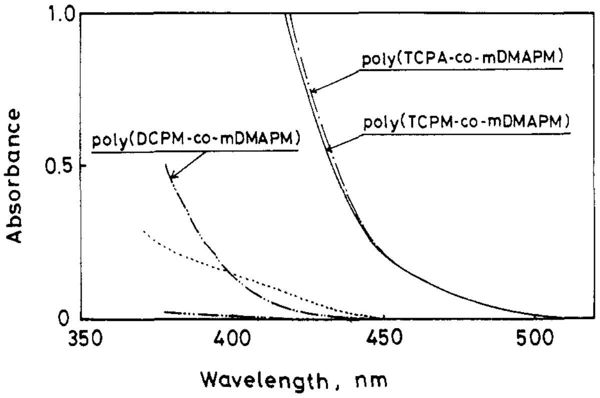

Figure 6. UV–vis spectra of the copolymers of the TCPM–mDMAPM (G-1), the TCPA–mDMAPM (H-1), and the DCPM–mDMAPM (I-1) systems in THF at 25 °C. (···) Difference spectra corresponding to intermolecular charge-transfer complexes of the TCPM–mDMAPM and TCPA–mDMAPM systems. Concentration = 0.0635 mol/L. (–····–) Difference spectrum corresponding to intermolecular charge-transfer complex of DCPM–mDMAPM system. Concentration = 0.048 mol/L.

Figure 6 shows UV–vis difference spectra of the copolymers of the TCPM–mDMAPM (run no. G-1 of Table V), the TCPA–mDMAPM (run no. H-1), and the DCPM–mDMAPM (run no. I-1) systems in THF. Difference spectra were obtained between copolymers and the sum of the two component monomers under the same concentrations of the monomers and the corresponding monomer units in the copolymers, being taken tentatively as intramolecular charge-transfer transitions in the copolymers. When copolymers of the TCPM–mDMAPM and the TCPA–mDMAPM systems with about similar contents of the acceptor monomer units, TCPM and TCPA units, were compared, their difference spectra were found to be almost identical, suggesting that a difference in acceptor monomer structure between methacrylate and acrylate exerts no influence in their intramolecular charge-transfer transition as well as intermolecular one. For comparison, additional difference spectra of the TCPM–mDMAPM and the TCPA–mDMAPM systems were taken between the mixture and the component monomers using the monomer concentrations corresponding to the monomer unit content in the above-mentioned copolymer. The DCPM–

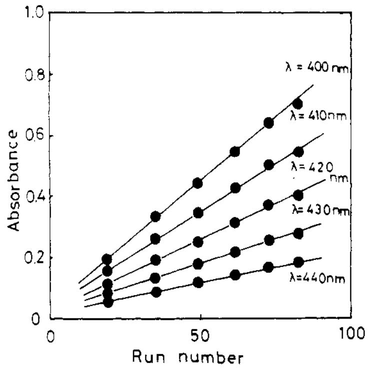

Figure 7. Charge-transfer complex absorption band linear dependence on run number in THF at 25 °C. Concentration = 0.02 mol/L.

mDMAPM system also was taken as both intramolecular and intermolecular difference spectra. It is obvious that intramolecular charge-transfer interactions are much stronger than the corresponding intermolecular ones. For the TCPM–mDMAPM and TCPA–mDMAPM systems, intramolecular charge-transfer interactions were found to be 16 times stronger than intermolecular ones at the wavelength of 420 nm and for the DCPM–mDMAPM system about 9 times stronger at the wavelength of 400 nm. These enhanced intramolecular charge-transfer interactions may be attributed to the unusual environment of interacting chromophores. Because donor and acceptor functional groups link together on the same polymer chain, they should be highly concentrated in the local region on the polymer chain in comparison with their overall concentrations and are forced to approach each other more closely and to interact with much ease.

As for the copolymers of the TCPM–mDMAPM system, plots of the intramolecular charge-transfer absorbance vs. the run number[23] of the copolymers are illustrated in Figure 7, where absorbances at wavelengths of 400, 410, 420, 430, and 440 nm increase linearly with an increase in the run number of the copolymers. Since a somewhat linear relationship is incidentally set up between run number and TCPM or mDMAPM monomer unit contents in the copolymer in the copolymerization of this system, it must be impossible to discuss the comparative merit between run number and acceptor monomer unit content with regard to intramolecular charge-transfer transition. However, the run number could be regarded to be more suitable than the copolymer composition because the donor and the neighboring acceptor monomer units on the same polymer chain should play an important role in the intramolecular charge-transfer transition. Simionescu et al.[8] pointed out in their papers about intramolecular charge-transfer transition in the copolymers of 9-carbazoyl-2-ethyl methacrylate with 2,4-dinitrophenyl methacrylate that the intensity of their absorbance is dependent upon copolymer composition and the maximal absorption is observed at the copolymer composition of equimolar amounts of donor and acceptor monomer units, indicating preference of a run number to a copolymer composition.

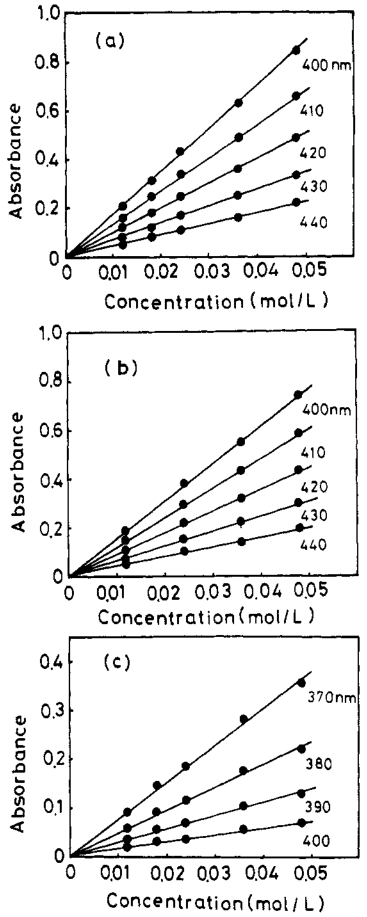

Figure 8. (a) Linear dependence of absorption of concentration for poly(TCPM-*co*-mDMAPM) (G-7) charge-transfer band in THF at 25 °C. (b) Linear dependence of absorption of concentration for poly(TCPA-*co*-mDMAPM) (H-1) charge-transfer band in THF at 25 °C. (c) Linear dependence of absorption of concentration for poly(DCPM-*co*-mDMAPM) (I-1) charge-transfer band in THF at 25 °C.

In the copolymers of the TCPM–mDMAPM (run no. G-7), TCPA–mDMAPM (run no. H-1), and DCPM–mDMAPM (run no. I-1) systems, absorbance of intramolecular charge-transfer transitions at given wavelengths were plotted against the concentration of the copolymers as depicted in parts a–c of Figure 8, respectively, where the absorbances were found to be related linearly with the copolymer concentrations. When diluted with solvent, an intermolecular charge-transfer complex theoretically decreases in its amount with the square of the concentration of the components, whereas the intramolecular charge-transfer complex decreases in its amount linearly with the concentration of the copolymer. Previously, Turner and Stolka[11] describe that the absorbance of the charge-transfer transition in the copolymers of 2,4,7-trinitro-9-fluorenyl methacrylate with 1-(2-anthryl)ethyl methacrylate varies in a linear fashion with the concentration of the copolymer at wavelengths of 460, 480, 500, and 520 nm, giving proof of an intramolecular charge-transfer interaction in the copolymer. It was therefore concluded that the copolymers of the TCPM–mDMAPM, TCPA–mDMAPM, and DCPM–mDMAPM systems exhibit an intramolecular charge-transfer interaction.

Photoconductivity of the Polymer Film with Intramolecular Charge-Transfer Interaction. The terpolymerization of the TCPM–mDMAPM–MMA system with the monomer feed TCPM/mDMAPM/MMA ratio of 0.5/0.46/3.22 in grams (5.8/6.2/85.9 in mol) in bulk with 5 mg of AIBN at 60 °C for 40 min gave 390 mg of the terpolymer with composition TCPM/mDMAPM/MMA ratio of 8.6/10.6/80.8 in mol with molecular weight of 8.0 × 10^5 by GPC, which could be fabricated into tough film by the casting method. Photoconductivity of this terpolymer was measured by a conventional technique.[24] The gold-film-gold sandwich-type specimen was prepared as follows: a chloroform solution of the terpolymer was poured onto a gold-coated coverglass and the solvent was evaporated slowly to obtain a film with a desired thickness as μ order, on which a transparent gold electrode was

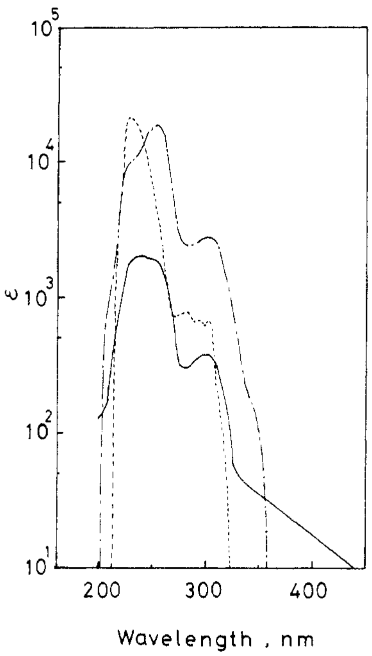

Figure 9. UV–vis spectra of the TCPM and mDMAPM monomers and the terpolymer of TCPM, mDMAPM, and MMA in THF at room temperature: (- - -) TCPM; (-·-) mDMAPM; (—) terpolymer. [TCPM] = 4.89 × 10^{-5} mol/L. [mDMAPM] = 3.97 × 10^{-5} mol/L. [terpolymer] = 0.158 g/L.

deposited by a vaccum evaporating technique. The photocurrent is defined as a positive one when an electron moves from its irradiated surface into its inside.

UV–vis spectra of the TCPM and mDMAPM monomers and the terpolymer of TCPM, mDMAPM, and MMA are shown in Figure 9. The absorption band in the wavelength range 350–450 nm for the terpolymer was assigned to an intramolecular charge-transfer transition between tricyanophenyl and (dimethylamino)phenyl groups because it was found to be linearly related with the concentration of the terpolymer similarly as shown in Figure 8.

The electric field applied to the terpolymer film was found to cause an electric current which decreases with time, the so-called absorption current. Thus, when the electric field had been applied for 60 min, the observed current was regarded as the dark current. The electric conductivity of the terpolymer film in the dark was measured to be 10^{-17}–10^{-16} Ω^{-1} cm^{-1} at room temperature. Relationships of the photocurrent under short circuit and under an electric field of ±500 kV/cm vs. wavelength are shown in Figure 10, including dark currents under the same condition. Under the electric field, two photocurrent peaks were observed in the ranges 300 and 350–400 nm. Under short circuit in the wavelength range near 240 nm was observed only one photocurrent peak which could not appear under application of electric fields, presumably due to potential masking of the strong photocurrent in the wavelength range near 300 nm. The relationship of photocurrent vs. wavelength was found to correspond well to the UV–vis spectrum of the terpolymer as illustrated in Figure 9. For this terpolymer film, ratios of photocurrent at a wavelength of 300 nm, I_{ph}^{300}, and photocurrent at a wavelength of 350 nm, I_{ph}^{350}, to the dark current, I_{d}^{60}, were estimated to be $I_{\mathrm{ph}}^{300}/I_{\mathrm{d}}^{60} = 10$ and $I_{\mathrm{ph}}^{350}/I_{\mathrm{d}}^{60} = 5$, respectively. The photocurrent was also found to increase with the intensity of the electric field applied. For poly(*N*-vinylcarbazole) (PVK), a well-known photoconductive polymer, values of $I_{\mathrm{ph}}^{300}/I_{\mathrm{d}}^{20}$ and $I_{\mathrm{ph}}^{350}/I_{\mathrm{d}}^{20}$ were estimated to be about 7 and 5, respectively, from the data in the paper of Okamoto et al.,[25,26] who used a gold–PVK–Nesa sandwich-type cell with PVK film with a thickness of 15 μm and detected a dark current, I_{d}^{20}, when an electric field as high as +150 kV/cm had been applied for 20 min.

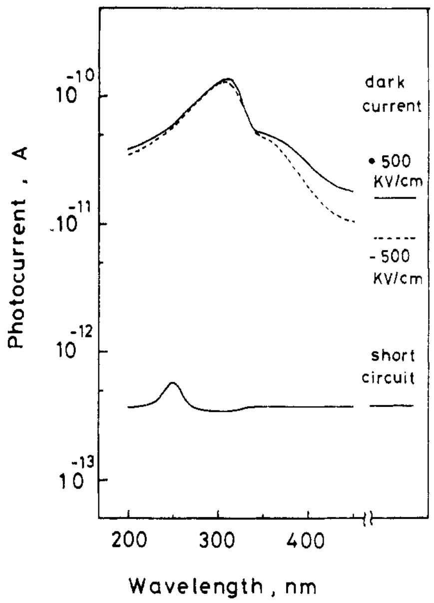

Figure 10. Relationships of photocurrent under a short circuit and under an electric field of ±500 kV/cm vs. wavelength.

A detailed study of the photoconductivity of the terpolymer film with an intramolecular charge-transfer interaction is now in progress.

Acknowledgment. We express our thanks to Professors G. Sawa and S. Nakamura of Mie University for photoconductivity measurements and valuable discussions.

Registry No. TCPM, 93806-47-4; TCPA, 93806-48-5; DCPM, 93806-49-6; St, 100-42-5; MMA, 80-62-6; (DCPM)·(*m*DMAPM) (copolymer), 93841-96-4; (TCPM)·(*m*DMAPM) (copolymer), 93806-50-9; (TCPA)·(*m*DMAPM) (copolymer), 93806-51-0; (TCPM)·(*m*DMAPM)·(MMA) (copolymer), 93806-52-1; 1-bromo-2,4,6-tricyanobenzene, 13520-05-3.

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Analysis of the Mechanism of Copolymerization of Styrene and Maleic Anhydride

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ABSTRACT: The mechanism of copolymerization of styrene and maleic anhydride in bulk at 60 °C has been investigated by measurements of copolymer compositions using ^{13}C NMR and of monomer sequence distributions using DEPT pulse programs to distinguish CH_2 subspectra, which have been attributed to styrene-centered triads. The strong tendency to alternation observed by most previous workers was confirmed. Nonlinear, least-squares analysis of the compositions of copolymers prepared over a wide comonomer composition range showed that the penultimate model gave a better fit to the data than the terminal model with a confidence level >95%. There was only a penultimate effect for styrene-terminated chain radicals. A similar analysis of the composition data of Bamford and Barb for comonomer mixtures with high styrene contents gave reactivity ratios in good agreement with the values derived from our composition data. The complex-participation and complex-dissociation models could also be fitted to the composition data but there was a strong correlation between different reactivity ratios, indicating extensive minima on the hypersurface. The monomer sequence distributions were in good agreement with the predictions of both the penultimate and complex-participation models and could not distinguish between them.

Introduction

The copolymerization of styrene (S) and maleic anhydride (MAn) has been studied extensively over many years. Alfrey and Lavin[1] and subsequent workers[2-5] have used the terminal model to analyze copolymer compositions. However, Barb[6] considered that the terminal model was inadequate and proposed a penultimate effect for styrene-ended radicals to explain the composition data from copolymerizations in acetone and methyl propyl ketone. The penultimate model was also used by Enomoto et al.[7] to explain the copolymerization at high pressure.

Donor–acceptor complexes are known to form between S and MAn and equilibrium constants ranging from 0.34 $dm^3\ mol^{-1}$ at 22 °C to 0.25 $dm^3\ mol^{-1}$ at 60 °C have been reported from UV and ^{1}H NMR measurements.[8-10]

A maximum in the initial rate of copolymerization at a mole fraction, X_S, of styrene in the comonomer feed of *ca.* 0.5 has been suggested as evidence of copolymerization via the comonomer complex.[4,8,11-13] Addition of one monomer following dissociation of the complex during the propagation step has also been suggested.[14]

The position of the initial rate maximum as a function of feed composition can be analyzed for the separate contributions of free monomers and the comonomer complex in propagation.[15] However, Raetzsch et al.[12,16] have shown that variation in the position of the rate maximum can be explained by the terminal model without involvement of complex if termination is taken into account, namely cross-termination and the two homoterminations. Their analyses of the S–MAn copolymerization in acetone and 1,2-dichloroethane are in agreement with reactivity ratios derived from composition analyses using the terminal model and rate constants for homopolymerizations.

The participation of comonomer complexes has been proposed for terpolymerizations involving added donors or acceptors,[14,17,18] although the terpolymer equation derived from the terminal model has also been found adequate to describe some of these systems.[14]

Dodgson and Ebdon[10,19] studied the copolymerization in bulk and in a variety of solvents and also terpolymerizations with methyl methacrylate. They found that the composition data were fitted markedly better by the penultimate and complex-participation models than by the terminal model. They concluded from the effects of (i) dilution on the polymerization in methyl ethyl ketone and (ii) added electron acceptor on both the copolymer composition and initial polymerization rate, that their study did not provide evidence consistent with the complex-participation model which could not be accounted for by the penultimate model. Thus, they suggested that a S–MAn complex was not involved in propagation.

Both monomers form donor–acceptor complexes with the solvents used in their study and the effect of this complexation on monomer reactivity may be important. The dilution studies did show a small dilution effect, less than predicted by the complex model, but not zero as predicted by the penultimate model. The dilution effect may be due to involvement of monomer–solvent complexes or other solvent effects, so that an unequivocal assignment of a model on the basis of this effect is not possible.

We have previously[20] reexamined the composition data of Dodgson and Ebdon for the bulk copolymerization using a nonlinear least-squares (NLLS) analysis and shown that both the complex[21] and penultimate models could adequately describe the data. However, the sequence distributions predicted from the reactivity ratios derived for these models, and for the terminal model, were quite different and their experimental determination should enable the correct model to be distinguished.

We have also developed composition and sequence distribution equations for the complex-dissociation model in its general form.[22] In this model, the comonomer complex competes with free monomers in propagation but dissociates during addition so that only one monomer is

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