

Electron-Transporting Polymers Having Side-Chain Fluorene Derivatives for Use as N-Type Organic Photoreceptors

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Polymers having a fluorene derivative, a homopolymer of 4-vinylbenzyl-9-dicyanomethylenefluorene-4-carboxylate and its copolymer with butyl acrylate or butyl methacrylate, were prepared as charge transport materials for electrophotography, and their electrical properties were measured. A monomer was prepared from 9-dicyanomethylenefluorene-4-carboxylic acid and 4-chloromethylstyrene. Polymerization was carried out using a radical initiator in a nitrogen atmosphere. These polymers were soluble in organic solvents such as THF, methylene chloride, chloroform, and DMF. All of the polymers showed two reversible redox potentials around -0.59 to -0.61 and -1.15 to -1.17 V versus Ag/AgCl electrode. The copolymers had high light sensitivities with a half-decay exposure of about 0.4 lux-s and a high electron drift mobility of 3.46×10^{-6} cm²/Vs at the electric field of 4.27×10^5 V/cm.

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Introduction

Charge (hole or electron) transport materials are used in many fields, including electrophotography. A layered organic photoreceptor having a high sensitivity and quick photoresponse comparable to those of an inorganic photoreceptor has been developed and put into practical use.^{1–5} Tang et al.⁶ reported on the preparation of an organic electroluminescent device consisting of hole and electron transport materials. Most of the charge transport materials are low-molecular-weight compounds, which are used in cast films with binding polymers for electrophotography. Studies have shown that low-molecular-weight compounds easily crystallize or aggregate when they are dispersed in a polymer matrix.^{7,8} Low-molecular-weight compounds also have poor mechanical and thermal properties. As a consequence, devices using low-molecular-weight compounds have shorter lifetimes and are less durable. Therefore, the need arose for polymeric charge transport materials, because polymers are easily formed into amorphous thin films and are mechanically strong.

Thus far, organic photoreceptors have mainly been constructed using hole transport materials, because of their higher charge mobility. The hole transport materials

should be used for photoreceptors with a negative surface charge, which produces more ozone than does one with a positive surface charge. Therefore, electron transport materials have drawn much interest. Fluorene derivatives have been investigated as electron transport materials in organic photoconductor (OPC) devices and electroluminescent (EL) devices, and their electrical and optical properties have been studied.^{9–16}

Our goal was to synthesize and characterize new electron transport polymeric materials that have 9-dicyanomethylenefluorene units, which are reported to have good electron-transporting abilities.¹⁷ Their electrical and electrochemical properties are discussed in relation to the structure.

Experimental

Chemicals. 9-Fluorenone-4-carboxylic acid (Aldrich Chemicals) was used without further purification. Malononitrile (Kanto Chemicals) and 4-chloromethylstyrene (Seimi Chemicals) were used after distillation under reduced pressure. Tetrahydrofuran for polymerization solvent was used after purification following the conventional method. Other reagents were commercially obtained and used without further purification.

Synthesis of 9-Dicyanomethylenefluorene-4-Carboxylic Acid (DCF). 9-Fluorenone-4-carboxylic acid (18.5 g, 82.8 mmol) and malononitrile (5.47 g, 82.8 mmol) were refluxed by stirring for 4 h in 220 mL methanol in the presence of a few drops of piperidine. After cooling, the precipitate was collected by filtration, recrystallized from methylene chloride and methanol (2:1, v/v), and then dried at 80°C under vacuum. A light yellow powder was obtained with a yield of 84% (15.6 g).

Synthesis of Vinylbenzyl 9-Dicyanomethylene Fluorene-4-Carboxylate (SDCF). 9-Dicyanomethylenefluorene-4-carboxylic acid (15.5 g, 57.2 mmol) and 4-chloromethylstyrene (17.45 g, 114.3 mmol) were stirred in 180 mL *N,N*-dimethyl formamide (DMF) in the presence of sodium bicarbonate (9.61 g, 114 mmol) at 40°C for 48 h. The reaction mixture was poured into cold water to remove the salt and then extracted with methylene chloride. The organic layer was washed with water and dried with anhydrous magnesium sulfate. The solvent was removed by means of a rotatory evaporator, and the crude product was recrystallized from methylene chloride and methanol (2:1, v/v) and then dried at 60°C under vacuum. The yield of this solid was 65% (14.5 g), mp:139°C.

Homopolymerization and Copolymerization of SDCF. Homo- and copolymerizations were carried out in

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Table I. Characteristics of Homopolymer and Copolymers*

Polymer	Molecular weight [†] × 10 ⁻⁴			Yield %	$\lambda_{\max}$ (nm)	Appearance
	M _n	M _w	M _w /M _n			
PSDCF	1.3	3.4	2.6	61	351	Pale yellow powder
PSDCF-BMA (1.79:1) [‡]	3.7	9.7	2.6	61	351	Pale yellow powder
PSDCF-BA (2.18:1) [‡]	6.7	10.2	1.5	43	351	Pale yellow powder

*Polymerization conditions; total monomer concentration = 1 M, [AIBN]=0.01 M, in THF.

[†]Estimated values by GPC (polystyrene standards, using CHCl₃ as an eluent).

[‡]Mole ratio of SDCF to BMA or BA (calculated from ¹H NMR spectra).

a glass ampule in a dry nitrogen atmosphere. 2,2'-Azobis(isobutyronitrile) was used as an initiator and tetrahydrofuran was used as the solvent. Polymers were recovered by pouring the reaction mixture into a large amount of methanol, and they were purified by reprecipitation of methylene chloride solution into methanol, followed by drying under vacuum at 80°C for 12 h.

Measurement. FT infrared spectra were obtained with a spectrometer (JASCO FT/IR-5300). Nuclear magnetic resonance (NMR) spectra were recorded at 50°C, using a 270-MHz spectrometer (JEOL GX-270) and CDCl₃ solutions. Tetramethylsilane (TMS) was used as an internal reference. UV spectra were obtained by a UV-VIS spectrometer (JASCO Ubest-30) and THF solutions. Average molecular weights (M_n, M_w) and polydispersity (M_w/M_n) were estimated by gel permeation chromatography (GPC) with a detector (JASCO, Model 830-RI) and HPLC (Model 880-PU) pump system. Chloroform was used as an eluent, and the molecular weight was calibrated using polystyrene standards. Redox potentials were measured using

cyclic voltammetry (CV) in a one-compartment cell with a polarization unit (TOHO PS-06). The measurements were conducted using dry acetonitrile, which contained the electrolyte tetraethylammonium tetrafluoroborate (Et₄NBF₄, 0.1 mol/L), in an argon atmosphere. Photoinduced surface potential discharge (PID) curves were recorded using an electrostatic paper analyzer (Kawaguchi Electric Works Co., Ltd., Model EPA-8100) irradiating by white light with an intensity of 8.2 lux. The electron drift mobility was measured by the time-of-flight (TOF) technique with a xenon lamp and digitizing oscilloscope.

Results and Discussion

DCF was obtained by the condensation of 9-fluorenone-4-carboxylic acid with malononitrile. DCF was reacted with chloromethyl styrene to give SDCF. SDCF was then homopolymerized or copolymerized with *n*-butyl acrylate (BA) or with butyl methacrylate (BMA) using azobis(isobutyronitrile) as an initiator. Table I shows the yield of polymerization and characteristics of the polymers. The number average molecular weight of the homopolymer was 1.3×10^4 and those of the copolymers were higher than that. All of the polymers were soluble in conventional solvents such as tetrahydrofuran, methylene chloride, chloroform, and *N,N*-dimethyl formamide, but they were insoluble in benzene, toluene, and alcohols. Copolymers had a higher solubility than the homopolymer.

Figure 1 shows ¹H NMR spectra of the monomer and the homopolymer. Each signal in Figs. 1(a) and (b) can be assigned to the protons in the expected structure, as shown in the figure. The NMR spectrum for the homopolymer showed the following signals: 0.7–1.8 ppm from the main chain protons, 5.25 ppm from the methylene proton, and 6.7–8.5 ppm from aromatic protons in Fig. 1(b). Copolymers showed proton signals corresponding to the expected structures. The cyano groups in the polymers were confirmed by the peak at 113 ppm in the ¹³C NMR spectrum and absorption at 2226 cm⁻¹ in the IR spectrum. The chemical compositions of the copolymers were calculated from the ¹H NMR spectra. The mole fractions of SDCF units in copolymers of SDCF with BMA and BA were 0.64 and 0.68, respectively.

The polymers had a UV absorption maximum at 351 nm and a cutoff wavelength of 425–427 nm and were yellow in color. The UV spectra of the polymers were almost equal to those of the corresponding low-molecular-weight compound, *n*-octyl 9-dicyanomethylenefluorene-4-carboxylate (DCF-8).

The chloroform solution of polymers was cast on a platinum electrode and the cyclic voltammograms were measured in acetonitrile containing 0.1 M Et₄NBF₄ at a scan rate of 0.15 Vs⁻¹. Figure 2 shows the cyclic voltammogram of a cast film homopolymer. The redox peaks of the polymer film were symmetrical and well defined. The values of the first and the second reduction potentials of the polymers were observed at -0.6 and -1.15 V versus Ag/AgCl

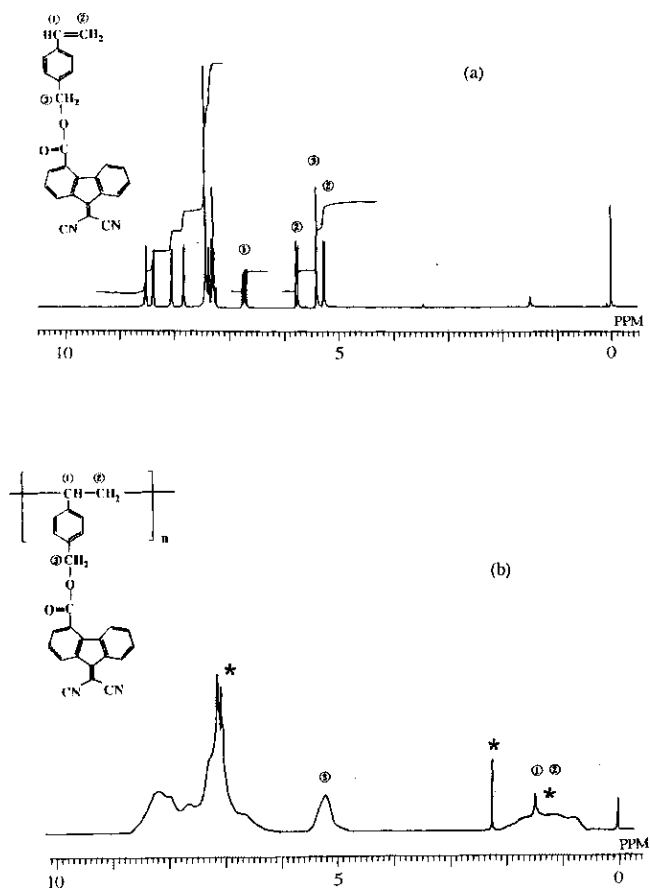


Figure 1. The ¹H NMR spectra of (a) the monomer and (b) the homopolymer. An asterisk (*) represents an impurity.

Table II. Redox Potentials* for Cast Polymer Films on Platinum Electrodes

Polymer	E _{pa} ¹⁺	E _{pa} ²⁺	E _{pc} ¹⁺	E _{pc} ²⁺	ΔE _p ¹	ΔE _p ²
PSDCF	-0.55	-1.08	-0.60	-1.15	0.05	0.07
PSDCF-BMA (1.79:1) [‡]	-0.55	-1.10	-0.61	-1.17	0.06	0.07
PSDCF-BA (2.18:1) [‡]	-0.53	-1.07	-0.59	-1.15	0.06	0.08
(DCF-8)PMMA [§]	-0.44	-1.05	-0.73	-1.34	0.29	0.29

*Redox potentials were measured in CH₃CN containing Et₄NBF₄ (0.1 M); scan rate was 0.15 V/s.

¹Potentials (V) versus Ag/AgCl.

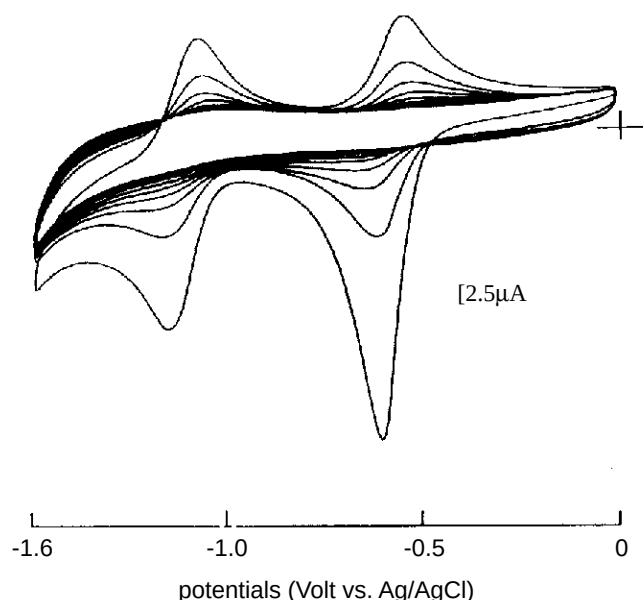
[‡]Mole ratio of SDCF to BMA or BA (calculated from ¹H NMR spectra).

[§]Octyl 9-dicyanomethylene fluorene-4-carboxylate (DCF-8) was dispersed in PMMA (30 wt %).

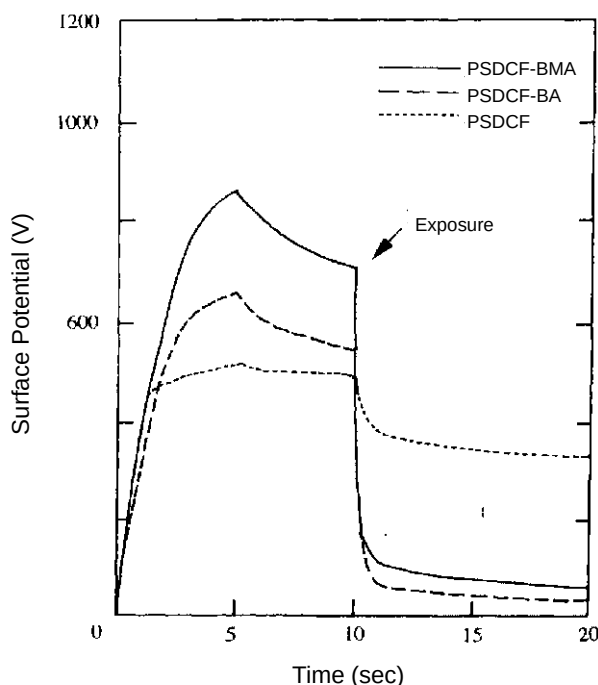
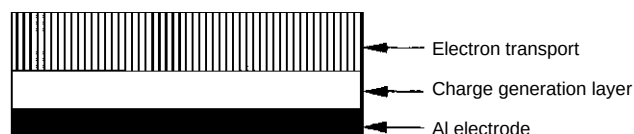
electrode, respectively. The intensity of the redox peak decreased as cycle time increased due to the dissolution of ionized polymer into the solvent. The results of the cyclic voltammograms are summarized in Table II. Note that the redox potentials of the copolymers were almost the same as that of the homopolymer, which indicates that the redox potential is independent of the concentration of the fluorene units. The low-molecular-weight compound, DCF-8, showed almost the same redox potential as the polymers. This finding together with that of UV measurement indicates that the electronic structure of the fluorene unit was not changed by introducing it into the side chain of the polymers. All the polymers had no redox peak in the range of 0 – 1.0 V. The polymers showed reversible electrochromism, with the color change from yellow (neutral) to red (reduction state).

We prepared the photoreceptor, which consisted of aluminum as a substrate, titanyl phthalocyanine as a charge generation layer (CGL; 0.3 μm), and polymers having a fluorene derivative as the charge transport layer (CTL; 13–18 μm). Phthalocyanine has been widely used as a charge generation material. Titanyl phthalocyanine has been reported to be an effective charge generation material for xerographic photoreceptors containing polysilanes as the charge transport layer.⁵ The ionization potentials of our polymers (5.77 and 5.85 eV for PSDCF-BA and PSDCF-BMA, respectively) are almost the same as the values for polysilanes. PID curves were obtained by measuring the surface potential change.

The structure of the organic photoreceptor device and the PID curves in the positive surface charge mode are

**Figure 2.** Cyclic voltammograms of a cast film homopolymer.

presented in Fig. 3. When a corona charge of 6 kV was given to the polymer films, the surface potentials increased to 520–869 V in 5 s. After the corona charging was stopped, the surface potential gradually decreased by 5.3 – 16.6% in 5 s. These results show the stable character of the films. As a result of exposure to light, the surface potential rapidly dropped in less than 1 s and stayed almost constant at 280–53 V after 10 s (residual potential). The residual potential of the homopolymer was 54% of the potential prior to light exposure, so that its half-decay exposure ($E_{1/2}$) could not be obtained. On the other hand, copolymers with BA and BMA showed lower residual potentials and their half-decay exposures were determined to be 0.38 and 0.39 lux-s, respectively. These values are close to those of organic photoconductors used commercially, which indicates that these copolymers could be applied for practical use when the residual surface potential is properly controlled. The small surface potential drop for the homopolymer

**Figure 3.** Structure of an *n*-type photoreceptor and PID curves for polymers.

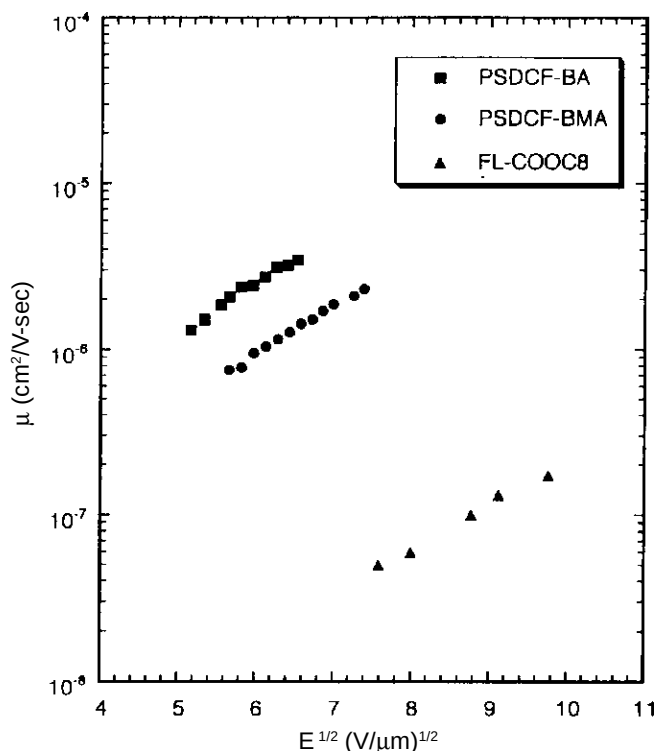


Figure 4. Electron drift mobility of copolymers (PSDCF-BA and PSDCF-BMA) and *n*-octyl-9-dicyanomethylenefluorene-4-carboxylate dispersed in polycarbonate (26 wt %).

can be attributed to the poor adhesion of the polymer to the CGL.

The charge mobility of the polymers was determined by the TOF method, using a cell consisting of an aluminum electrode on the slide glass, CGL, CTL, and a semitransparent gold electrode. The mobility, μ , was calculated according to the following equation:

$$\mu = L^2/t_T V,$$

where L is the sample thickness, t_T the transit time, and V the applied voltage. The homopolymer was so brittle that it did not provide a good cell. Figure 4 shows the electron drift mobility of 10- μm -thick copolymer samples with an electric field of $10^5 - 10^6$ V/cm. The mobility increased with the increase in electric field. The maximum electron drift mobilities of copolymers with BA and BMA were determined to be 3.46×10^{-6} cm²/Vs at 4.27×10^5 V/cm and 2.32×10^{-6} cm²/Vs at 5.04×10^5 V/cm, respectively. For comparison, the mobility of the corresponding low-molecular-weight compound, DCF-8, was measured using a film of 26 wt % in polycarbonate, because higher concentra-

tion provided phase separation. The mobility in an electric field of 4.27×10^5 V/cm was calculated to be 3.46, 1.52, and 0.027×10^{-6} cm²/Vs for copolymers with BA and BMA, and DCF-8, respectively. Therefore, it is clear that the polymeric compound had much greater mobility than the low-molecular-weight compound. This is the first study concerning polymeric materials that show high electron mobility, as far as we know. The electron mobility of these polymers corresponds to the hole mobility of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) dispersed in bisphenol A polycarbonate (40 wt %), where the hole mobility is ca. 4×10^{-6} cm²/Vs at 4×10^5 V/cm.¹⁸ The mobilities of the copolymers were among the highest mobilities seen in electron transport materials.

Conclusions

A novel polymer that has fluorene units on the side chain, poly(4-vinylbenzyl-9-dicyanomethylenefluorene-4-carboxylate), was synthesized by means of radical polymerization. In addition, two copolymers with *n*-butyl (meth)acrylate were also prepared. All the polymers were slightly yellow and soluble in organic solvents such as chloroform and THF. We found from the measurements of cyclic voltammetry that they had a reversible electrochemical activity. PID measurements showed that the copolymers exhibited a good photoresponse with a half-decay exposure of ca. 0.4 lux-s, which is close to the value of the OPC presently used. The electron drift mobility of the copolymer showed a strong electric field dependence. The mobilities of copolymers were $1.5 - 3.5 \times 10^{-6}$ cm²/Vs at 4.27×10^5 V/cm, which correspond to those of hole transport materials dispersed in polymer. ▲

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