3 (SRU), 101017-51-0; **4** (homopolymer), 106680-96-0; **4** (SRU), 106681-06-5; **6** (copolymer), 31471-36-0; **7** (homopolymer), 106680-97-1; **7** (SRU), 106681-07-6; **8** (homopolymer), 106680-98-2; **8** (SRU), 106681-08-7; (AA)(TC) (copolymer), 31764-36-0; (AA)(TC) (SRU), 106681-01-0; (SA)(TC) (copolymer), 106680-89-1; (SA)(TC) (SRU), 32031-88-2; (DD)(TC) (copolymer), 106710-14-9; (DD)(TC) (SRU), 106681-02-1; (TA)(TC) (copolymer), 90456-92-1; (TA)(TC) (SRU), 26913-45-1; (SA)(PC) (copolymer), 106680-90-4; (SA)(PC) (SRU), 106681-03-2; (SA)(IC) (copolymer), 106680-91-5; (SA)(IC) (SRU), 106681-04-3; (SA)(FC) (copolymer), 106680-92-6; (SA)(FC) (SRU), 106710-15-0; (GA)(GC) (copolymer), 106680-93-7; (GA)(GC) (SRU), 26968-28-5; (SA)(SC) (copolymer), 106680-94-8; (SA)(SC) (SRU), 26913-47-3; (SA)(1,3,5-benzenetricarboxylic acid) (copolymer), 106680-99-3; $(H_3CCH_2)_3N$, 121-44-8; $(C_6H_5O)_2P(O)Cl$, 2524-64-3; $C_6H_5NHP(O)(Cl)OC_6H_5$, 51766-21-3; pyridine, 110-86-1; *N,N*-bis[2-oxo-3-oxazolidinyl]phosphinic chloride, 68641-49-6; 2,6-lutidine, 108-48-5.

References and Notes

(1) Bucher, J. E.; Slade, W. C. *J. Am. Chem. Soc.* **1909**, *31*, 1319.
(2) Hill, J. *J. Am. Chem. Soc.* **1930**, *52*, 4110.
(3) Hill, J.; Carothers, W. H. *J. Am. Chem. Soc.* **1932**, *54*, 1569.
(4) Conix, A. *Makromol. Chem.* **1957**, *24*, 76.
(5) Conix, A. *J. Polym. Sci.* **1958**, *29*, 343.
(6) Yoda, N.; Miyake, A. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 1120.
(7) Yoda, N. *Makromol. Chem.* **1959**, *32*, 1.
(8) Yoda, N. *Makromol. Chem.* **1962**, *55*, 174.
(9) Yoda, N. *Makromol. Chem.* **1962**, *56*, 10.
(10) Yoda, N. *Makromol. Chem.* **1962**, *56*, 36.
(11) Yoda, N. *J. Polym. Sci., Part A* **1963**, *1*, 1323.
(12) Cottler, R. J.; Matzner, M. *Chem. Weekbl.* **1969**, *63*, 113.
(13) Rosen, H.; Chang, J.; Wnek, G.; Linhardt, R. J.; Langer, R. *Biomaterials* **1983**, *4*, 131.
(14) Leong, K. W.; Brott, B. C.; Langer, R. *J. Biomed. Mater. Res.* **1985**, *19*, 941.
(15) Leong, K. W.; Brott, B. C.; Langer, R. *J. Biomed. Mater. Res.* **1986**, *20*, 51.
(16) Windholz, R. U.S. Patent 3 200 097, 1965.
(17) Chen, F. M. F.; Koroda, K.; Benoiton, N. L. *Synthesis* **1978**, 928.
(18) Cabre-Castellvi, J.; Palomo-Coll, A.; Polomo-Coll, A. L. *Synthesis* **1981**, 616.
(19) Mestres, R.; Palomo, C. *Synthesis* **1981**, 218.
(20) Bodanszky, M.; Klausner, Y. S.; Ondetti, M. A. *Peptide Synthesis*, 2nd ed.; Interscience: New York, 1976; p 115.
(21) Keshavamurthy, K. S.; Vankar, Y. D.; Dhar, D. N. *Synthesis* **1982**, 506.
(22) Conix, A. *Macromol. Synth.* **1966**, *2*, 95.
(23) Gorecka, A.; Leplawy, M.; Zabrocki, J.; Zwierzak, A. *Synthesis* **1978**, 474.
(24) Pouchart, C. J. *The Aldrich Library of Infrared Spectra*, 3rd ed.; Aldrich Chemical Co., Inc.: Milwaukee, 1982; p 415.
(25) Subramanyam, R.; Pinkus, A. G. *J. Macromol. Sci., Chem.* **1985**, *A22*, 23.

Synthesis and High Hole Mobility of Isotactic Poly(2-*N*-carbazolylethyl acrylate)

Toshiyuki Uryu,* Haruki Ohkawa, and Ryuichi Oshima

Institute of Industrial Science, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan.

Received May 8, 1986

ABSTRACT: Isotactic poly(2-*N*-carbazolylethyl acrylate) was synthesized by using ethylmagnesium chloride–benzalacetophenone as catalyst. The polymer showed crystallinity by X-ray diffraction. The temperature and electrical field dependence of hole drift mobility was measured by the time-of-flight method. The room-temperature mobility (1.7×10^{-5} cm^2/(V·s) at 2×10^5 V/cm) was considerably higher than that of both atactic polyacrylate and poly(*N*-vinylcarbazole) and is one of the highest mobility values reported for a photoconductive polymer. The origin of this result is discussed in a model for hopping transport between localized sites.

Introduction

Photoconductive polymers have been extensively studied since they are widely used in electrophotography and are potentially suitable for other electrodevices.[1-3] Most investigations have concentrated on a search for chromophores that are of high efficiency. Few studies have dealt with the effect of polymer structure.[4] There are two kinds of photoconductive polymers. One is a molecularly doped polymer, and the other is a polymer in which the chromophores are attached to the backbone through chemical bonds. In most cases, the former materials exhibit higher carrier mobilities than the latter type polymers.[5,6] One possible reason is that the molecular mobility of the chromophores is depressed due to the linkage between the chromophore and the polymer backbone. High carrier mobility can be expected for linkage-type polymers having higher chromophore contents than for molecularly doped polymers if several drawbacks could be excluded. In fact, poly(*N*-carbazolylpropylene oxide)[7] and poly(2-*N*-carbazolylethyl acrylate),[8] which have relatively low T_g's, exhibited high hole mobilities.

For hopping transport among a set of localized sites, the factors determining the drift mobility are the nature of the chromophore, the concentration, and the energy-state distribution.[9] The site energy distribution in completely disordered materials may be related to the "frozen-in disorder" which is introduced during the course of film formation. Thus, the site energy distribution may be narrower for polymers with lower T_g values, leading to higher drift mobility.

An alternative strategy to average the site energy distribution would be to introduce order by alignment of the chromophores. This can be achieved in stereoregular polymers which may be crystalline. In this investigation, we have succeeded in stereoregular polymerization of 2-*N*-carbazolylethyl acrylate by use of an anionic catalyst, producing the completely isotactic polyacrylate which has good film-forming properties. The hole-transport characteristics of the isotactic polyacrylate were compared with those of the corresponding atactic polymer. It is demonstrated for the first time that the highly controlled stereoregularity of a polymer backbone gives rise to pendant-type photoconductive polymers with high carrier mobility.

Experimental Section

Synthesis of Monomers. *N*-(2-Hydroxyethyl)carbazole (1). A solution of carbazole (10 g, 0.06 mol) in 100 mL of dry dimethylformamide (DMF) was vigorously stirred at 0 °C and treated with 4.32 g (0.072 mol) of sodium hydride oil dispersion

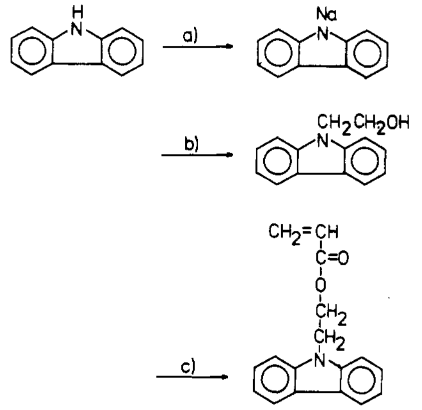
0024-9297/87/2220-0712$01.50/0 © 1987 American Chemical Society

Table I
Polymerization of 2-*N*-Carbazolylethyl Acrylate and Properties of Polymers[a]

polymer	[M],[b] mol/L	cat.[c]	yield, %	$10^{-4}M_n$[d]	M_w/M_n	iso,[e] %
A-1[f]	0.25	B + E	40	5.0	4.8	96
A-2	0.17	B + E	20	0.56	4.4	97
A-3[g]	0.17	B + E	22	0.70	4.2	95
A-4[h]	0.17	*n*-BuLi	40	0.77	4.0	87
A-5[i]	0.17	B + E	20			
R-1[j]	0.38	AIBN	90	5.0	2.3	46

[a] Time, 24 h; temperature, 0 °C; solvent, toluene (5 mL) + diethyl ether (2 mL). [b] Monomer concentration. [c] B + E, benzalacetophenone–ethylmagnesium chloride; *n*-BuLi, *n*-butyllithium; AIBN, α,α'-azobis(isobutyronitrile). [d] Measured by GPC. [e] Isotactic diad tacticity. [f] Monomer concentration, 0.25 mol/L; temperature 30 °C. [g] Time, 72 h. [h] Solvent, toluene (5 mL) + *n*-hexane (2 mL). [i] Monomer, 2-*N*-carbazolylethyl methacrylate; polymer is insoluble. [j] Temperature, 60 °C.

Scheme I
Synthesis of 2-*N*-Carbazolylethyl Acrylate: (a) DMF, NaH; (b) Ethylene Carbonate, H_2O; (c) Acryloyl Chloride, Et_3N, $CHCl_2$



(50%). After 3 h of stirring, ethylene carbonate (6.38 g, 0.072 mol) was slowly added, and the mixture was stirred at 0 °C for 1 h and then at 40 °C for 3 h. To the resulting solution was added 10 mL of water at 0 °C, followed by stirring at 40 °C for 3 h. After evaporation, the residue was poured into 200 mL of water, and the aqueous mixture was extracted with benzene (200 mL × 3). The extract was chromatographed on a silica gel column (50% benzene/ethyl acetate elution). The second fraction was evaporated and recrystallized from toluene to give colorless needles (10.1 g, yield 80%): mp 81–81.5 °C (lit.[10] mp 83–83.5 °C); ^1H NMR (in $CDCl_3$) δ 1.35 (s, 1 H, OH), 3.80–3.82 and 4.20–4.24 (m, 4 H, OCH_2CH_2N), 7.00–7.90 (m, 8 H, aromatic).

2-*N*-Carbazolylethyl Acrylate (2). A solution of acryloyl chloride (5.1 g, 0.057 mol) in 20 mL of dry methylene chloride was added dropwise for 30 min under vigorous stirring to a mixture of **1** (10.0 g, 0.047 mol), a small amount of hydroquinone, and 20 mL of triethylamine in 200 mL of dry methylene chloride. The mixture was stirred overnight at 0 °C. After the Et_3NHCl was filtered off, the solution was evaporated at room temperature. The residue was chromatographed on a silica gel column (50% benzene/methylene chloride elution). The first fraction was evaporated and recrystallized from toluene, yielding colorless needles (8.2 g, yield 65%): mp 76 °C (lit.[11] mp 75–76 °C); ^1H NMR (in $CDCl_3$) δ 4.50–4.60 (m, 4 H, OCH_2CH_2N), 5.80–6.30 (m, 3 H, $CH_2{=}CH-$), 7.00–7.90 (m, 8 H, aromatic).

The monomer was further purified by HPLC (column, Toyo Soda TSK gel ODS-120T, 2.2 × 30 cm; eluent $MeCN/H_2O$ 8/2) to remove a trace amount of fluorescence contaminants.

2-*N*-Carbazolylethyl methacrylate was also synthesized by a similar procedure (Scheme I).

Polymerization. All polymerizations were performed by using the high-vacuum technique at less than 2.5×10^{-4} mmHg. For example, in the case of the polymerization by using ethylmagnesium chloride–benzalacetophenone as anionic catalyst,[12] the monomer solution was made by distillation of toluene into the monomer ampule. The polymerization was started by addition of the catalyst solution in ether and terminated by the addition of methanol.

Polymers were purified by reprecipitation three times from methylene chloride solution into methanol.

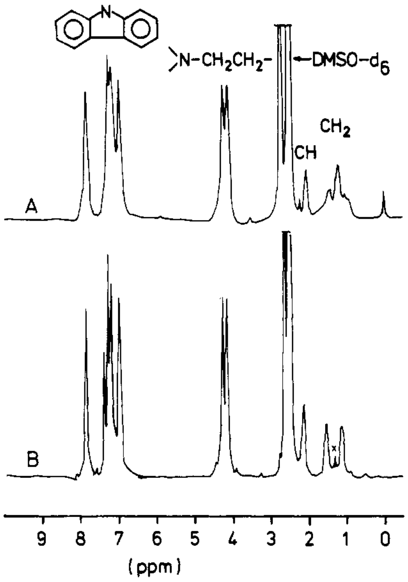


Figure 1. 270-MHz ^1H NMR spectra of poly(2-*N*-carbazolylethyl acrylates): (A) isotactic; (B) atactic.

Measurement. Films for fluorescence measurements were prepared on cover glasses by casting from methylene chloride solution at room temperature and drying overnight under reduced pressure. Films for time-of-flight measurement were similarly prepared on aluminum substrates. Film thickness was determined (5–20 μm) with a Sloan DEKTAK II-A surface profiler.

NMR, fluorescence spectra, and X-ray diffraction patterns were obtained by using a JEOL GX-270 FT-NMR spectrometer, a Hitachi 640-40 fluorescence spectrometer, and a Rigaku Denki geigerflex diffractometer, respectively.

Time-of-flight measurements were carried out by using a 1-μs pulse from a Xe lamp. Transient currents were observed with a digital oscilloscope and analyzed with a microcomputer.[8] Transient time was defined as the time at which the plateau and the tail of the measured current traces intersect.

Results and Discussion

Polymerization and Structure of Polymers. The results of the polymerization of 2-*N*-carbazolylethyl acrylate (**2**) are summarized in Table I. Yields of the anionically polymerized polymers were low, and molecular weight distributions were broad. The reason for these results may be attributed to the poor solubility of poly(2-*N*-carbazolylethyl acrylate) in the polymerization solvent. Precipitation of polymer was observed a few minutes after the polymerization was started.

As shown in Figure 1, polymers with different stereoregularities were obtained. According to the previous investigations,[13] the NMR peaks due to the methylene protons of the polymer backbone at 1.2 and 1.6 ppm can be assigned to isotactic methylene protons and the center peak at 1.35 ppm to syndiotactic ones. The diad tacticity of the polymers was determined from these peaks. Poly-

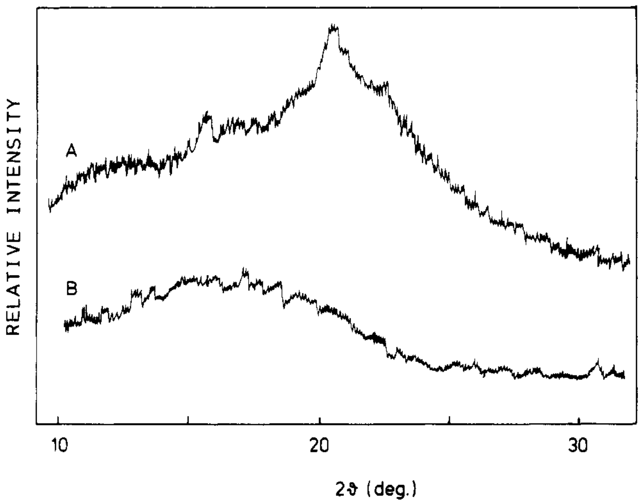


Figure 2. X-ray diffraction patterns of poly(2-*N*-carbazolylethyl acrylates): (A) isotactic; (B) atactic.

mer A-1 obtained from an ethylmagnesium chloride–benzalacetophenone complex catalyst had an almost 100% isotactic configuration. In Figure 1B, a small peak around 1.35 ppm was due to an impurity formed during NMR measurement at the high temperature (150 °C). A radically polymerized polymer (R-1) had an almost random configuration consisting of equal fractions of isotactic and syndiotactic diads. An anionic catalyst, *n*-butyllithium, gave an isotactic-rich polymer composed of 87% isotactic diads. The ethylmagnesium chloride–benzalacetophenone complex has a structure similar to that of the propagating chain-end structure of acrylate polymers, so that little disorder in the tacticity is induced during the early stages of the polymerization. This could be the reason for the high stereoregularity of the polymer obtained by the complex catalyst, as was the case in this polymerization of alkyl α-chloroacrylate.[12] The isotactic polyacrylate was soluble in methylene chloride and 1,2-dichloroethane.

Poly(2-*N*-carbazolylethyl methacrylate) was also prepared by the ethylmagnesium chloride–benzalacetophenone complex catalyst. The polymer initially was soluble in chlorobenzene, but it became insoluble in 1,2-dichloroethane, *o*-dichlorobenzene, and nitrobenzene after reprecipitation probably due to the occurrence of crystallization as in the case of the polymer prepared by using Natta's method.[14]

X-ray diffraction patterns of the polymers (Figure 2) show that the solid-state structure is different for the two kinds of polymers. In contrast to the broad halo observed for the atactic polyacrylate, the isotactic polyacrylate exhibited a diffraction peak at $2\theta = 21.0°$, implying that the isotactic polyacrylate is crystalline. However, the peak is not as distinct as that of the isotactic poly(2-*N*-carbazolylethyl methacrylate) reported by Natta. Since the crystallinity of the isotactic polyacrylate was lower than that of the isotactic polymethacrylate which had almost no solubility,[14] it is assumed that the isotactic polyacrylate has good solubility and film-forming property.

In the fluorescence spectra (Figure 3) of atactic poly(2-*N*-carbazolylethyl acrylate) and atactic poly(2-*N*-carbazolylethyl methacrylate), there are no peaks corresponding to the two excimers, which are known to exist around 410 and 380 nm, respectively, in the spectrum of poly(*N*-vinylcarbazole) (PVK).[15] On the other hand, the isotactic polyacrylate exhibited a broad peak at 500 nm in addition to the peak due to monomer emission at 370 nm. The longer wavelength emission is ascribed to the catalyst fragment bound to the end of the polymer chain, but not to the free catalyst, since a spectrum of the atactic polyacrylate film doped with 20% benzalacetophenone or the alcohol derived therefrom showed no additional peak except the monomer emission.

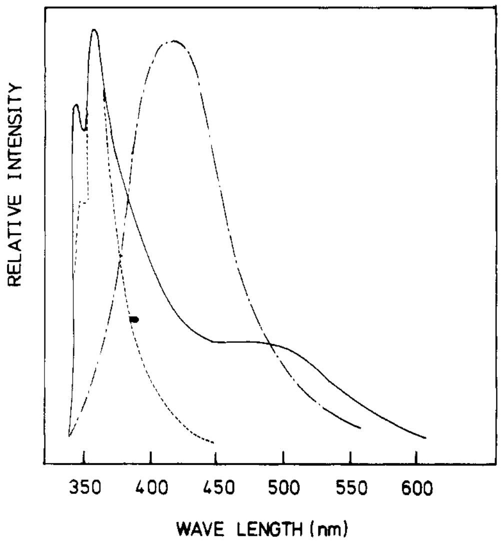


Figure 3. Fluorescence spectra of poly(2-*N*-carbazolylethyl acrylates), poly(2-*N*-carbazolylethyl methacrylate), and poly(*N*-vinylcarbazole (PVK): (—), isotactic polyacrylate; (- - -) atactic polyacrylate; (—·—) PVK.

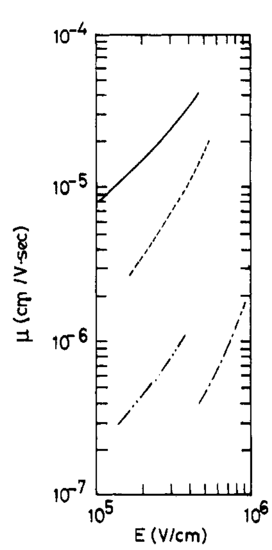


Figure 4. Electric field dependence of the room-temperature mobilities of isotactic poly(2-*N*-carbazolylethyl acrylate) (—), atactic poly(2-*N*-carbazolylethyl acrylate) (- - -), poly(2-*N*-carbazolylethyl methacrylate) (····), and poly(*N*-vinylcarbazole) (PVK) (—··—).

Hole Drift Mobility. The electrical field dependence of the hole drift mobilities of the photoconductive polymers at room temperature is depicted in Figure 4. The carrier mobility of the isotactic poly(2-*N*-carbazolylethyl acrylate) (1.7×10^{-5} cm^2/(V·s)) is about 6 times higher than that (3.0×10^{-6} cm^2/(V·s)) of the atactic polymer at 2.0×10^5 V/cm.[8]

For hopping transport among a set of localized sites, the hole drift mobility μ is expressed according to Mort and Knight[16]

$$\mu \propto \rho^2 \exp(-2\gamma\rho) \tag{1}$$

where ρ is the average separation between sites and γ is the wave-function decay constant. The log (μ/ρ^2) values are plotted against ρ for a number of carbazole-containing polymers, poly(2-*N*-carbazolylethyl acrylates), poly-

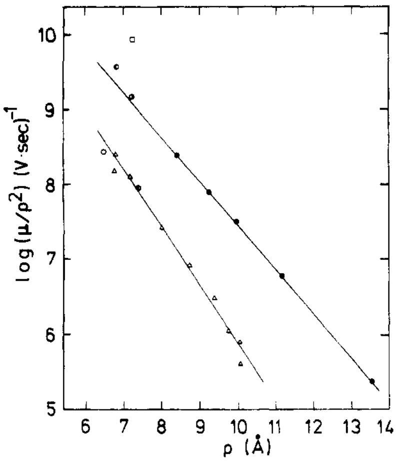


Figure 5. Comparison of room-temperature hole drift mobilities of hopping systems composed of carbazole chromophores at 5 × 10^5 V/cm in the μ/ρ^2 against ρ diagram: (○) PVK; (◐) poly(*N*-carbazolylpropylene oxide); (□) isotactic poly(2-*N*-carbazolylethyl acrylate); (◑) atactic poly(2-*N*-carbazolylethyl acrylate); (⊙) poly(2-*N*-carbazolylethyl methacrylate); (●) *N*-isopropylcarbazole molecularly doped in polycarbonate; (△) PVK-TNF.

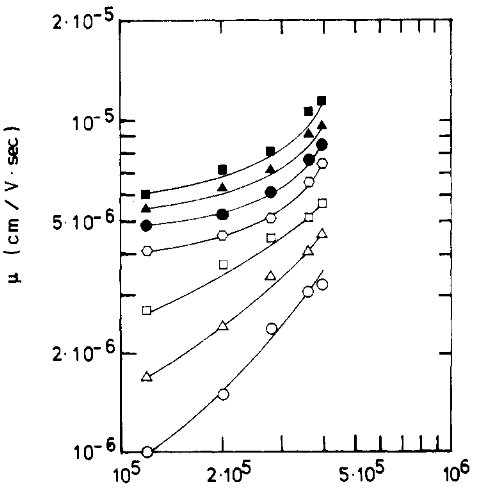


Figure 6. Electric field dependences of hole drift mobilities of isotactic poly(2-*N*-carbazolylethyl acrylate) at different temperatures: (■) 333 K; (▲) 328 K; (●) 323 K; (○) 318 K; (□) 313 K; (△) 309 K; (○) 298 K.

carbonate molecularly doped with *N*-isopropylcarbazole (NIPC/PC),[8] poly(*N*-carbazolylpropylene oxide),[7] PVK, PVK–2,4,7-trinitrofluorenone complexes (PVK–TNF),[17] and poly(2-*N*-carbazolylethyl methacrylate),[18] in Figure 5.

The point for the isotactic polyacrylate is located above the line for NIPC/PC and the atactic polyacrylate. To our knowledge, this may be the first observation that the carrier mobility of a pendant-type polymer is higher than that of the corresponding molecularly doped polymer. This indicates that it is possible to achieve high hole mobility in polymers having chromophores chemically bound to the backbone. As shown in Figure 6, the electrical field dependence of the hole drift mobility of the isotactic polyacrylate was strongly dependent on the applied field, though the dependence was weaker than that for the atactic polymer.[8]

In the μ vs. T^{-2} plot, the data points lie on straight lines, which were calculated by the least-squares method, and the lines converge to one point at infinite temperature (Figure 7). This is in good agreement with Bässler's model for carrier transport by hopping across a Gaussian density-of-states distribution.[19] By use of this model, the temperature and electrical field dependence on the mobility are expressed as

$$\mu = \mu_0 \exp[-(T_0/T)^2] \exp(E/E_0) \tag{2}$$

where

$$T_0 = \kappa\sigma \tag{3}$$

$$E_0 = (\sigma/2Be\rho)(T/T_0) \tag{4}$$

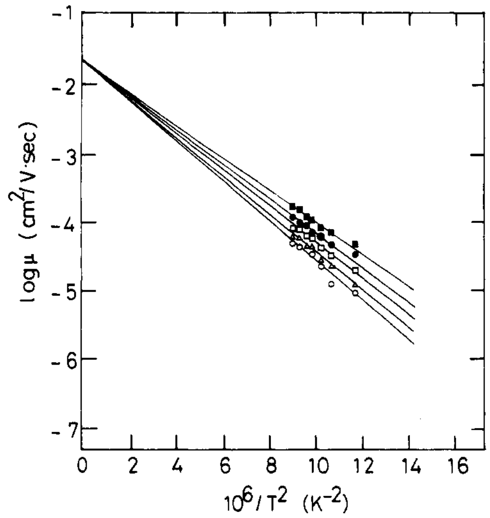


Figure 7. Plot of log μ against T^{-2} for the temperature dependence of the mobility for isotactic poly(2-*N*-carbazolylethyl acrylate) at different electric fields: (■) 4.0 × 10^5 V/cm; (●) 3.6 × 10^5 V/cm; (□) 2.8 × 10^5 V/cm; (△) 2.4 × 10^5 V/cm; (○) 2.0 × 10^5 V/cm.

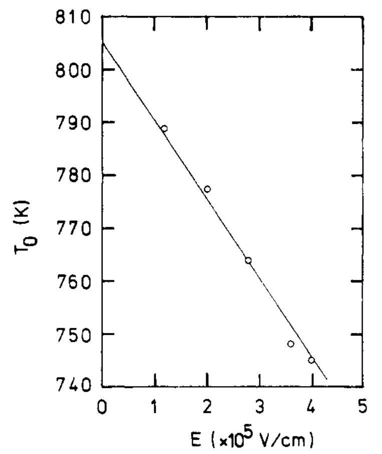


Figure 8. Electric field dependence of apparent T_0. T_0 = 806 K at the infinite temperature.

μ_0 is the mobility in a similar system without disorder, κ = 7400 eV/K, σ is the width of a Gaussian sites-state energy distribution, and $B = {}^1/_6$.[19] From Figure 7, the μ_0 value was determined to be 2 × 10^{-2} cm/V·s) for the isotactic polyacrylate. It is known that the μ_0 value is intrinsic to the nature of site molecules and the intersite distance. ρ for isotactic polyacrylate was measured to be 7.35 Å, which is the same as that for atactic polyacrylate. The above-obtained μ_0 value seems to be realistic, since it has been reported that μ_0 = 0.3 cm²/(V·s) for trap-free PVK (ρ = 6.6 Å),[20] μ_0 = 5 × 10^{-2} cm²/(V·s) for PVK–TNF (1:0.2) (ρ = 7.1 Å),[21] and μ_0 = 1.2 × 10^{-2} cm²/(V·s) for atactic polyacrylate (ρ = 7.35 Å).[8]

From the plot of the T_0 values obtained at different fields against E (Figure 8), the zero-field T_0 value was determined to be 806 K, which corresponds to a Gaussian width σ of 0.109 eV. The T_0 and σ values for the atactic polyacrylate are 949 K and 0.128 eV, respectively. The difference in the hole drift mobility for the isotactic and atactic polyacrylates may be due to the difference in both μ_0 and σ. The Gaussian width σ is determined by the fluctuation of polarization energy between a transient cation center and the neutral molecules surrounding the center. These two polymers have the same T_g (105 °C) and no excimer fluorescence originating from a specific dimeric conformation, which may act as a trapping center for holes in PVK. The small value observed for the isotactic polyacrylate is related to the high stereoregularity of the polymer main chain, which should induce the ordered arrangement of carbazole chromophores. The slightly higher value of μ_0 determined for the isotactic polyacrylate may also be consistent with the ordered alignment of the chromophores, since the wave-function decay constant γ is expected to be smaller in a crystalline or paracrystalline array of hopping site molecules than in the disordered state.

Pendant-type photoconductive polymers, which have high chromophore content and high μ_0 values, have generally also exhibited high σ values, so that the polymers have lower carrier mobilities than the corresponding molecularly doped systems. It was shown in eq 4 that the σ value is more effective on the carrier mobility than the μ_0 value. Therefore, it is concluded that since the highly stereoregular polyacrylate has particularly low σ and high μ_0 values it exhibited a high hole drift mobility.

In conclusion, it has been shown that stereoregular structures enhance the hole drift mobility of pendant-type photoconductive polymers. The present result provides a new insight into the field of photoconductive organic materials.

References and Notes

(1) Pearson, J. M.; Stolka, M. In *Poly(N-vinylcarbazole)*; Huglin, M. B., Ed.; Gordon and Breach: New York, 1981; p 159.
(2) Hughes, R. C. In *Photoconductivity in Polymers, An Interdisciplinary Approach*; Patsis, A. V., Seaner, D. A., Eds.; Technomic: Westport, CT, 1976; p 158.
(3) For example: Yokoyama, M. *Kobunshi* **1985**, *34*, 728–731.
(4) Itaya, A.; Okamoto, K.; Kusabayashi, S. *Polym. J.* (*Tokyo*) **1985**, *17*, 557–565.
(5) Stolka, M.; Pai, D. M.; Renfer, D. S.; Yanus, J. F. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 969–983.
(6) Yamazaki, M.; Tsutsumi, N.; Yamamoto, M.; Nishijima, Y. *Polym. Prepr., Jpn.* **1984**, *33*, 2535–2538.
(7) Gaidelis, V.; Krisščiūnas, V.; Montrimas, E. *Thin Solid Films* **1976**, *38*, 9–14.
(8) Oshima, R.; Uryu, T.; Senō, M. *Macromolecules* **1985**, *18*, 1045–1048.
(9) Günewald, M.; Pohlmann, B.; Movaghar, B.; Würtz, D. *Philos. Mag. B* **1984**, *49*, 341–356.
(10) Flowers, R. G.; Flowers, L. W. *J. Chem. Soc.* **1948**, *70*, 3019–3021.
(11) Kamogawa, H.; Koizumi, H.; Nanasawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *18*, 9–18.
(12) Uryu, T.; Ohaku, K.; Matsuzaki, K. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1723–1734.
(13) Matsuzaki, K.; Uryu, T.; Ishida, A.; Takeuchi, M. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2167–2177.
(14) Natta, G.; Longi, P.; Pellino, E. *Makromol. Chem.* **1964**, *71*, 212–214.
(15) Klöpffer, E. *J. Chem. Phys.* **1969**, *50*, 2337–2343.
(16) Mort, J.; Knight, J. *Nature* (*London*) **1981**, *290*, 659–663.
(17) Gill, W. D. *J. Appl. Phys.* **1972**, *43*, 5033–5040.
(18) Oshima, R.; Biswas, M.; Wada, T.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 151–154.
(19) Bässler, H. *Philos. Mag. B* **1984**, *50*, 347–362.
(20) (a) Fujino, M.; Mikawa, H.; Yokoyama, M. *Photogr. Sci. Eng.* **1982**, 26, 84–8 (b) Lange, J.; Bässler, H. *Phys. Status Solidi B* **1982**, *114*, 561–569.

Donor–Acceptor-Containing Quinodimethanes. Synthesis and Copolyesterification of Highly Dipolar Quinodimethanes

G. David Green, H. K. Hall, Jr.,* and J. E. Mulvaney

C. S. Marvel Laboratories, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

J. Noonan and D. J. Williams

Chemistry Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

Received September 3, 1986

ABSTRACT: Three novel quinodimethane monomers with an electron-acceptor moiety containing an ester group and an electron-donor moiety containing a hydroxyl group were synthesized. These 7,7-[(hydroxyalkanediyl)diamino]-8-carbomethoxy-8-cyanoquinodimethane derivatives are highly crystalline and show a high degree of electron delocalization from the donor moiety to the acceptor moiety. These highly dipolar units are copolymerized by polyesterification with more flexible α-hydroxy-ω-carbomethoxy compounds to yield polymers in which all the dipoles are pointing in the same direction. These copolymers are fusable and are soluble in polar organic solvents.

Introduction

We wished to prepare polyesters containing highly dipolar units, with all dipoles pointing in the same direction. The quinodimethane unit presented itself as the best choice for this purpose.

The polymerization of quinodimethane derivatives bearing only electron-withdrawing groups via a vinyl-type polymerization is well-known,[1,2] and the incorporation of such an acceptor quinodimethane unit itself in the polymer backbone has also been reported.[3] But there are no examples of polymers incorporating a donor–acceptor quinodimethane molecule into the polymer backbone.

We describe the syntheses of donor–acceptor-substituted quinodimethanes that have the appropriate functionalities needed to make condensation polymers. We selected quinodimethane derivatives with an acceptor moiety containing an ester group and with a diamine donor moiety containing a hydroxyl function.

0024-9297/87/2220-0716$01.50/0 © 1987 American Chemical Society