Synthesis and Photoconductivity of a Poly(1,6-heptadiyne) Derivative Containing a Carbazole Moiety

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Photoconductive polymers containing a carbazole (Cvz) and related groups, e.g., poly(vinylcarbazole)–TNF complex systems, have been of great interest because of their useful applications, especially in the field of electrophotography.[1,2] In recent years, several attempts[3-6] have also been focused on the copolymer systems to develop intramolecular charge-transfer complexes. Unfortunately, however, it was not easy to obtain high molecular weight copolymers with good film qualities. Furthermore, to our knowledge there have been no reports on the homopolymer systems even with the conjugated double bonds in the main chain except poly[*N*-(2-propynyl)carbazole].[7]

Previously, we developed several poly(1,6-heptadiyne) derivatives of highly conjugated polymers with potentially useful properties by metathesis polymerization.[8-10] In this paper, we describe the results on the synthesis and properties of a new photoconductive poly[bis(*N*-carbazolyl)-*n*-hexyl dipropargylmalonate], poly(BCHDPH), which is a good example of the homopolymer system with an intramolecular charge-transfer complex.

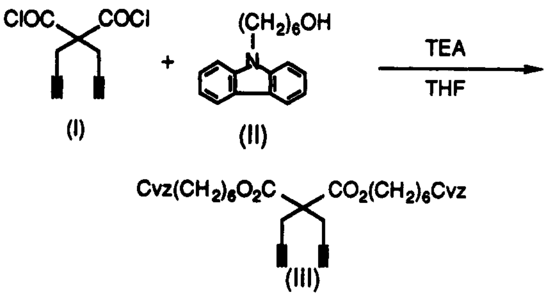
Monomer. As shown in Scheme I, the monomer, bis(*N*-carbazolyl)-*n*-hexyl dipropargylmalonate (III), was synthesized by the reaction of dipropargylmalonyl dichloride (I)[10] with *N*-(6-hydroxy-*n*-hexyl)carbazole (II) in the presence of triethylamine (TEA) using THF as a solvent: yield 80%.

The structure of the product was identified by elemental analysis, IR, ^{1}H- and ^{13}C-NMR, and UV. Elem anal. Calcd for $C_{45}H_{46}O_4N_2$: C, 79.62; H, 6.83; N, 4.13. Found: C, 79.58; H, 6.77; N, 4.29. IR: 1730 ($\nu_{C=O}$), 3290, 2140 cm^{-1} ($\nu_{\equiv CH}$). ^{1}H-NMR (CDCl$_3$): δ 1.3–1.9 [m, 16 H, $-(CH_2)_4-$], 2.0 (t, 2 H, $\equiv CH$), 2.5 (d, 4 H, $-CH_2C\equiv C$), 4.0 (t, 4 H, $-CO_2CH_2-$), 4.2 (t, 4 H, $-CH_2N$), 7.1–8.0 (m, 16 H, aromatic). ^{13}C-NMR (CDCl$_3$): δ 20 ($-CH_2C\equiv$), 56 (>C<), 70 ($\equiv CH$), 170 (CO$_2$). UV (THF): λ_{max} 262.2, 294.2, 346 nm.

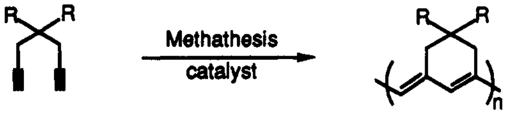
Polymer. Scheme II outlines the cyclopolymerization of the monomer with various transition metal catalyst systems. The polymerizations of the monomer[11] were carried out with $MoCl_5$- and WCl_6-based catalysts, and their results are summarized in Table I. The catalytic activity of $MoCl_5$ was found to be greater than that of WCl_6. As shown in Table I, $(n\text{-Bu})_4Sn$ exhibited better cocatalytic activity than $EtAlCl_2$ for the polymerization of the monomer. These results are similar to those reported for the polymerization of dipropargylmalonate.[8-10]

The resulting polymers exhibited good solubility in common organic solvents such as chloroform, tetrahydrofuran (THF), dimethylformamide (DMF), etc., and were easily cast on glass plates to give violet, shiny thin films. In addition, these spin-coatable conjugated polymers had good stability in air.

Scheme I



Scheme II



R= $-CO_2(CH_2)_6Cvz$

Catalyst : $MoCl_5$, WCl_6

Cocatalyst : $(n\text{-Bu})_4Sn$, $EtAlCl_2$

Table I
Polymerization of Bis(*N*-carbazolyl)-*n*-hexyl Dipropargylmalonate by $MoCl_5$- and WCl_6-Based Catalysts[a]

exp no.	catalyst syst (mole ratio)	M/C[b]	polymer[c] yield (%)	$\bar{M}_n/10^3$ [d]	$\bar{M}_w/\bar{M}_n$
1	$MoCl_5$	50	90	89	3.2
2	$MoCl_5$–$Sn(n\text{-Bu})_4$ (1:1)	50	95	68	2.1
3	$MoCl_5$–$EtAlCl_2$ (1:1)	50	60	32	2.5
4	WCl_6–$EtAlCl_2$ (1:1)	50	trace		

[a] Polymerization was carried out at 60 °C for 24 h in chlorobenzene. $[M]_0$ (initial monomer concentration) = 0.25. [b] Monomer to catalyst mole ratio. [c] Methanol-insoluble polymer. [d] Values were obtained by GPC analysis with polystyrene standards calibration (Waters high-pressure GPC assembly Model M590 pump, μ-Styragel columns of 10^5, 10^4, 10^3, 500, and 100 Å, refractive index detectors, solvent, THF).

The number-average molecular weight ($\bar{M}_n$) values of the polymers obtained here were in the range of (3.2–8.9) × 10^4, relative to the polystyrene standards in GPC. The structure and properties of the polymers obtained were analyzed by NMR, IR, and UV–vis spectroscopic techniques. The ^{1}H-NMR spectra of both the monomer and the polymer are shown in Figure 1. As the polymerization proceeded, the acetylenic proton peak around 2.0 ppm disappeared and a new vinylic proton peak appeared in the aromatic region. In ^{13}C-NMR data, the olefinic carbon peaks of the polymer backbone were observed around 122 and 140 ppm while the monomer gave just the acetylenic carbon peaks at 71 and 81 ppm. Furthermore, it was found that the peak of the two methylene carbons, adjacent to the polymer backbone, shifted from 20 ppm in the monomer to 45 ppm in the polymer. Also, the IR spectrum of the polymer showed no absorption peaks at 3290 and 2140 cm^{-1}, which are expected to be present for the acetylenic carbon–hydrogen bond stretching and carbon–carbon triple-bond stretching in the monomer, respectively.

Figure 2 exhibits the UV–visible spectra of poly(BCHDPM) including poly(diethyl dipropargylmalonate), poly(DEDPM),[9] and photocurrent values[12] of poly(BCHDPM) as a function of wavelength. As shown in Figure 2, these two polymers have the characteristic broad peaks at the longer wavelength regions of above 350 nm, which should be due to the π–π* transition of the conjugated

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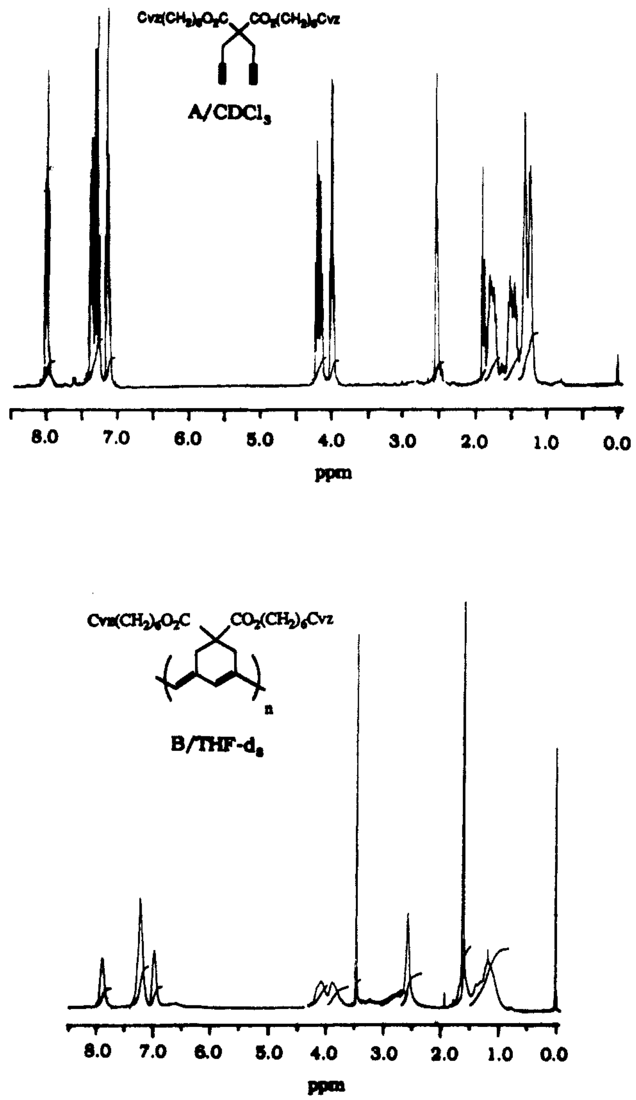

Figure 1. ^1H NMR spectra of the monomer (A) and the polymer (B) [sample: exp no. 1 in Table I].

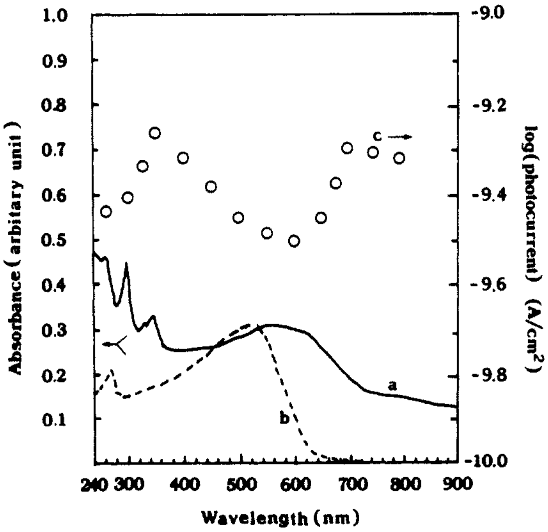

Figure 2. Absorbance and photoconductivity action spectra of the polymers: (a) poly(BCHDPM), (b) poly(diethyl dipropargylmalonate), poly(DEDPM), and (c) photocurrent with wavelength in poly(BCHDPM).

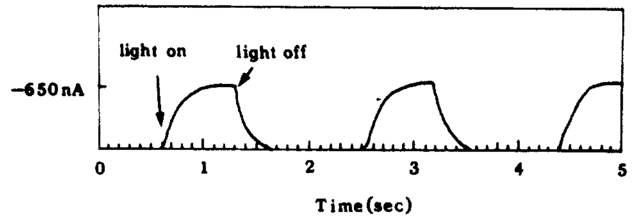

Figure 3. Time-dependent photocurrent response for an ITO/polymer/Au cell with a Hg–Xe lamp (4.5 mW/cm^2, 0-V bias).

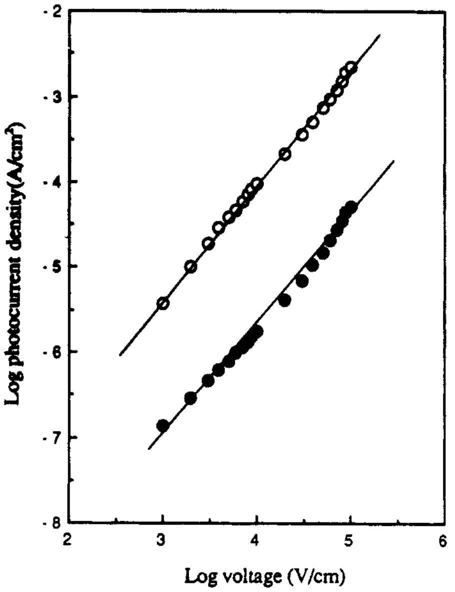

Figure 4. Photocurrent density vs electric field for poly(BCHDPM).

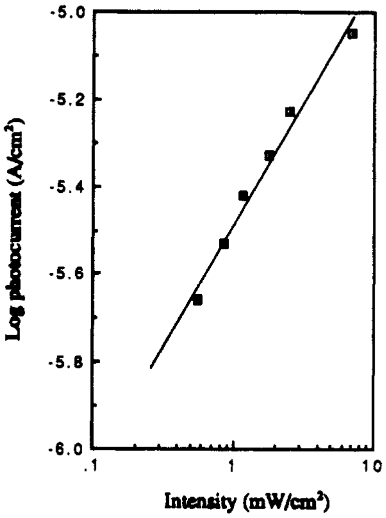

Figure 5. Photocurrent density vs light intensity for poly(BCHDPM).

polyenes. As compared with DEDPM, however, only poly(BCHDPM) has a long tail band at above 700 nm, suggesting intramolecular charge-transfer complexes between the carbazole groups and the conjugated double bonds in the polymer backbone. Consequently, poly(BCHDPM) shows two maximum values of photocurrent around 350 and 700 nm. The former value might be due to the carbazole groups. The latter one might be based on the photodetrapping in shallow electron traps and charge carrier generation in the charge-transfer band.[13] The photocurrent response curves depending on time by oscilloscope without applying electric field are shown in Figure 3. It was found that, under white light, the polymer had both a photovoltaic responce -640 nA and a curvature due to trapping and recombination process.[14] Relations between the photocurrent density (J_{ph}) and the electric field (E) are shown in Figure 4. The photoconductivity to dark-conductivity ratio without doping agent was found to be in the range of 30–50 at the 10^3–10^5 (V/cm). It is also shown that the current value increases in both dark and photo states as the electric field (E) increased, and their slopes are greater than 1. This indicates that the space charge perturbed photocurrents were associated with a large population of trapped charge.[15] Figure 5 shows the dependence of the photocurrent density on the light intensity (I). It is almost a linear relationship, and the slope was about 0.5. Further studies in these directions including copolymer systems are under way.

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References and Notes

(1) Haarer, D.; Mayer, H.; Strohriegl, P.; Naegele, D. *Makromol. Chem.* **1991**, *192*, 617.

(2) Ohkawa, H.; Furuichi, T.; Oshima, R.; Uryu, T. *Macromolecules* **1989**, *22*, 2266.

(3) Hu, C. J.; Oshima, R.; Seno, M. *Macromolecules* **1988**, *21*, 1536.

(4) Chang, D. M.; Gromelski, S.; Rupp, R.; Mulvaney, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 571.

(5) Turner, S. R. *Macromolecules* **1980**, *13*, 782.

(6) Natansohn, A.; Flaisher, H. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, *22*, 579.

(7) Kminek, I.; Cimrova, V.; Nespurek, S.; Vohlidal, J. *Makromol. Chem.* **1989**, *190*, 1025.

(8) Jin, S. H.; Kim, S. H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1991**, *24*, 6050.

(9) Ryoo, M. S.; Lee, W. C.; Choi, S. K. *Macromolecules* **1990**, *23*, 3029.

(10) Han, S. H.; Kim, U. Y.; Kang, Y. S.; Choi, S. K. *Macromolecules* **1991**, *24*, 973.

(11) Polymerization: catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition-metal halides and organometallic compounds were dissolved in each solvent to make 0.2 M solutions prior to use. A typical polymerization procedure was as follows: solvent, catalyst solution, and, when needed, cocatalyst solution were injected into a 20-mL ampule equipped with a rubber septum in the order given. When the cocatalyst was used, the catalyst system was aged at 30 °C for 15 min. Finally, the monomer dissolved in the same solvent was injected into the polymerization ampule. After the reaction mixture was allowed to react at 60 °C for 24 h, the polymerization was terminated by adding a small amount of methanol. The resulting polymer was dissolved in THF and precipitated with a large excess of methanol. The precipitated polymer was filtered from the solution and then dried carefully under vacuum at 40 °C for 24 h. The polymer yield was determined by gravimetry.

(12) The photocurrents were measured on very thin films (0.6–1.5 μm) obtained by spin coating from THF solutions on ITO glass and attached with a semitransparent top gold electrode. The light source was a Hg–Xe lamp. Its power per unit surface was measured with a model radiometer.

(13) Onsager, L. *Phys. Rev.* **1938**, *54*, 554.

(14) Pai, D. M. In *Photoconductivity in Polymer, An Interdisciplinary Approach*; Patsis, A. V., Seanor, D. A., Eds.; Technomic: Westport, CT, 1976; p 28.

(15) Kang, E. T.; Ehrlich, P.; Bhatt, A. P.; Anderson, W. A. *Macromolecules* **1984**, *17*, 1020.