Notes

Synthesis and Characterization of a Novel Electron-Acceptor Polymer Based on a Poly(1,6-heptadiyne) Main Chain

Ji-Hoon Lee, Jong-Wook Park, Jae-Min Oh, and Sam-Kwon Choi*

Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1 Kusung-Dong, Yusung-Gu, Taejeon, Korea

Received April 6, 1994
Revised Manuscript Received October 6, 1994

Introduction

Electron-acceptor polymers have been the subject of considerable interest in the field of electrophotography for at least the last 20 years because of their electron transporting characteristics under an applied electric field.[1-3] However, few examples of these electron-acceptor polymers have been reported to date.[4-9] The reasons are obvious. Most of conventional polymerization methods (such as cationic, anionic, and free-radical polymerization) become problematic in the presence of a strong electron acceptor, e.g., nitro aromatic groups such as a 2,4,7-trinitrofluorenone (TNF) group, a 3,5-dinitrobenzoyl (DNB) group, etc.[10,11] In free-radical polymerization it was difficult to obtain promising results because of electron transfer or other free-radical-inhibition processes resulting from the nitro aromatic groups.[12]

We reported recently the results of work on the synthesis and photoconductive properties of poly[bis(*N*-carbazolyl)-*n*-hexyl dipropargylmalonate] [poly(BCHDPM)] prepared by metathesis catalysts. Poly(BCHDPM) was a good example of a homopolymer system with an intramolecular charge-transfer complex (CTC).[13]

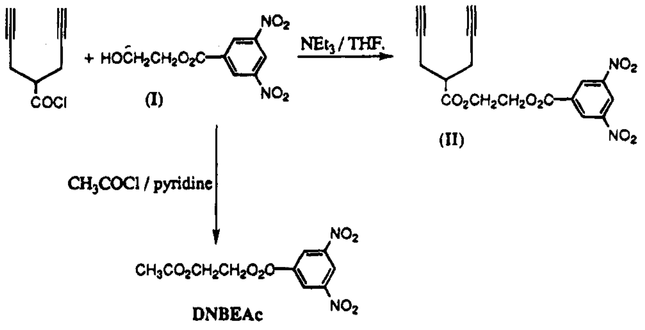
In this study, we report for the first time the synthesis and CTC behavior of a novel electron-acceptor polymer based on a poly(1,6-heptadiyne) main chain by metatheis polymerization with various transition-metal catalysts, poly{2-[(3,5-dinitrobenzoyl)oxy]ethyl dipropargylacetate}.

Experimental Section

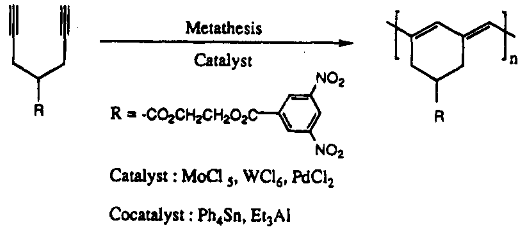
Monomer and Model Compound Synthesis. β-Hydroxyethyl 3,5-Dinitrobenzoate (I) and Acetyl-2-hydroxyethyl 3,5-Dinitrobenzoate (DNBEAc). These compounds were synthesized by the method described in the literature.[14,15]

2-[(3,5-Dinitrobenzoyl)oxy]ethyl Dipropargylacetate (DNBEDPA, II). DNBEDPA was synthesized by reacting β-hydroxyethyl 3,5-dinitrobenzoate with dipropargylacetyl chloride[16] in the presence of triethylamine (TEA) using THF as a solvent: yield 78% (Scheme 1). The structure of the product was identified by elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, and UV spectrometry. Elem. Anal. Calcd for $C_{17}H_{14}N_2O_8$: C, 54.54; H, 3.78; N, 7.49. Found: C, 54.51; H, 3.75; N, 7.52. IR (KBr): 1728 ($\nu_{C=O}$), 3292 ($\nu_{\equiv CH}$), 2140 ($\nu_{C\equiv C}$), 1545 ($\nu_{-NO_2,assym}$), 1349 ($\nu_{NO_2,sym}$), 1630 ($\nu_{Ar,-C=C-}$). ^{1}H-NMR ($CDCl_3$, ppm): δ 1.97 (t, *J* = 2.6 Hz, ≡CH, 2H), 2.62 (dd, $-CH_2C\equiv C-$, 4H), 2.82 (m, >CH, 1H), 4.53 and 4.64 (2t, *J* = 4.6 Hz, 2-CO_2CH_2-, 4H), 9.14–9.23 (m, aromatic, 3H). ^{13}C-NMR ($CDCl_3$, ppm): δ 19.8 (CH_2 of $CH_2C\equiv CH$), 70.6 (≡CH), 80.0 (−C≡), 162.2 ($ArCO_2-$), 172.0 ($-CO_2-$). UV: λ_{max} 296.0, 246.0, 234.5 nm (THF).

Scheme 1. Synthesis of Monomer and Model Compounds



Scheme 2. Cyclopolymerization of the Monomer by Various Transition Metal Catalysts



Polymerization Procedure. 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.

Spectroscopic Measurements. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC-300 spectrometer, and chemical shifts were recorded in ppm units with TMS as the internal standard. FT-IR spectra were measured as KBr pellets on a BOMEM Michelson MB-100 spectrometer, and frequencies are given in reciprocal centimeters. UV spectra were recorded with a Shimadzu UV-3100s. Molecular weights and polydispersities of polymers were determined by gel permeation chromatography (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).

---

* To whom all correspondence should be addressed.

0024-9297/95/2228-0377$09.00/0

Table 1. Polymerization of 2-[(3,5-Dinitrobenzoyl)oxy]ethyl Dipropargylacetate by Various Transition-Metal Catalysts[a]

exptl no.	cat. syst[b] (mole ratio)	M/C[c]	$[M]_0$[d]	temp (°C)	polymer yield (%)	soluble portion[f]	$\bar{M}_w/10^3$ [g]	$\bar{M}_w/\bar{M}_n$
1	$MoCl_5$	50	0.1	60	88	43	21	2.6
2	$MoCl_5$	50	0.2	60	81	27	25	2.3
3	$MoCl_5$–Ph_4Sn (1:1)	50	0.1	60	67	31	31	3.5
4	WCl_6	100	0.2	80				
5	WCl_6–Et_3Al (1:1)	100	0.2	80				
6	$PdCl_2$[h]	30	0.5	90	90	100		

[a] Polymerization was carried out for 24 h in 1,4-dioxane. [b] Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min before use. [c] Monomer to catalyst mole ratio. [d] Initial monomer concentration [mol/L]. [e] Methanol-insoluble polymer. [f] Soluble portion of the obtained polymers in THF. [g] Values were obtained by GPC analysis with polystyrene standards calibration. [h] Polymerization was carried out for 24 h in DMF.

Table 2. Solvent Effect for Polymerization of the Monomer by $MoCl_5$[a]

exptl no.	solvent	temp (°C)	polymer yield (%)[b]	soluble portion[c]
1	THF	60	88	38
2	chlorobenzene	60	90	0
3	benzene	60	87	0
4	chloroform	rt	17	
5	dichloromethane	rt	24	

[a] Polymerization was carried out for 24 h. The monomer to catalyst mole ratio (M/C) and the initial monomer concentration ($[M]_0$) were 100 and 0.1, respectively. [b] Methanol-insoluble polymer. [c] Soluble portion of the obtained polymers in THF.

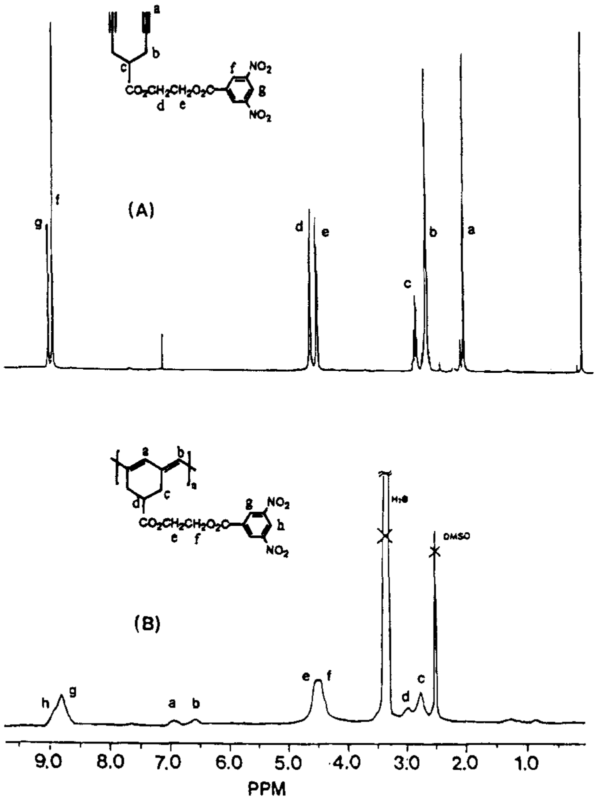


Figure 1. ¹H-NMR spectra of the monomer (A) in $CDCl_3$ and the polymer (B) in DMSO-d_6 [sample: exptl. no. 1 in Table 1].

Results and Discussion

Scheme 2 outlines the cyclopolymerization of DNBEDPA with various transition-metal catalyst systems. The polymerizations of DNBEDPA were carried out with $MoCl_5$-, WCl_6-, and $PdCl_2$-based catalysts, and these results are summarized in Table 1. The $MoCl_5$-based catalysts all showed effective catalytic activity. However, the WCl_6-based catalysts showed no catalytic activity. It seems that the DNB group in the monomer inhibits catalytic activity of WCl_6. The polymers obtained using most catalysts were partially soluble in organic solvents, and the soluble portion of the polymer was less than 43% of the polymer yield. It appears that the polymerization is extremely rapid, producing a cross-linked, insoluble polymer. The polymer obtained from the $PdCl_2$ catalyst was readily soluble in organic solvents. These results are similar to the results for the polymerization of dipropargyl derivatives with polar functional groups.[17] The soluble polymers in common organic solvents such as chloroform, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) can be easily cast on glass plates to give violet-shiny thin films.

Table 2 shows the solvent effect for the polymerization of the monomer by $MoCl_5$. It was found that poly(DNBEDPA) was obtained in good yields in various solvents such as tetrahydrofuran (THF), chlorobenzene, and toluene. Chlorobenzene and toluene solvents, however, gave only insoluble polymers. Chloroform and dichloromethane solvents gave relatively low yields of polymer.

The weight-average molecular weight ($\bar{M}_w$) values of the polymers obtained were in the range of $(3.1-2.1) \times 10^4$, relative to the polystyrene standards in GPC. The structure and properties of the polymers obtained were analyzed by NMR, IR, and UV–vis spectroscopy. The ¹H-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 ¹³C-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 70.6 and 80.0 ppm. Furthermore, it was found that the peak of the two methylene carbons, adjacent to the polymer backbone, shifted from 19.8 ppm in the monomer to 50.7 ppm in the polymer.

The IR spectrum of the polymer showed no absorption peaks at 3292 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. The development of the band characteristic of conjugated –C=C– sequences unfortunately cannot be clearly identified, due to the interference in the region of 1650–1550 cm^{-1} of aromatic –C=C– absorption bands.

Recently, Schrock et al. reported that the poly(1,6-heptadiyne) derivatives, especially from 4,4-disubstituted 1,6-heptadiyne monomers, obtained by the living cyclopolymerization using well-defined alkylidene complexes as initiators have both five- and six-membered ring structures in a certain ratio, which should depend on the polymerization conditions and the kinds of catalysts used, via nominally tail-to-tail and head-to-tail cyclopolymerization of the two acetylenic bonds in

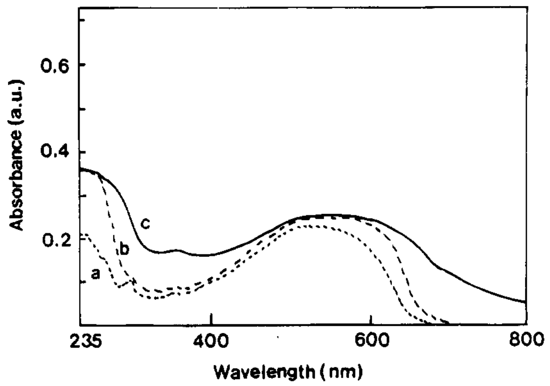


Figure 2. UV–vis spectra of thin films of (a) poly(DEDPM), (b) DNBEAc-doped poly(DEDPM) (1:1 mole ratio), and (c) poly(DNBEDPA).

the monomer.[18,19] In the case of poly(4-monosubstituted 1,6-heptadiyne) derivatives, however, it was difficult to known the exact composition ratio for five- and six-membered rings. Furthermore, when an extremely bulky substituent such as a *tert*-butyldiphenylsiloxymethyl group was introduced at the 4-position, the resulting polymer tended to have mostly one size ring, maybe a five-membered ring.[20]

Figure 2 shows the UV–visible spectra of poly(DNBEDPA), poly(diethyl dipropargylmalonate) [poly(DEDPM)],[21] and DNBEAc-doped poly(DEDPM). As shown in Figure 2, these polymers have characteristic broad peaks at the longer wavelength regions of above 350 nm, which are due to the $\pi-\pi^*$ transition of the conjugated polyenes. The poly(DEDPM) having no DNB group has a $\lambda_{\max}$ at 530 nm. The $\lambda_{\max}$ have shifted to slightly longer wavelengths in both DNBEAc-doped poly(DEDPM) and poly(DNBEDPA), probably due to weak intramolecular charge-transfer complexes (CTC) between the 3,5-dinitrobenzoyl (DNB) groups and the conjugated double bonds in the polymer backbone. Similar CT interactions have also been widely observed in the polyacetylenes/organic acceptor complexes.[22-25] Furthermore, the absorption peak in poly(DNBEDPA) became broader than that in DNBEAc-doped poly(DEDPM). This indicates that the higher order complexes were formed in poly(DNBEDPA), where the electron-acceptor group is linked covalently in the polymer backbone. As compared with DNBEAc-doped poly(DEDPM), however, only poly(DNBEDPA) has a long tail band at above 700 nm. This phenomenon implies that more complicated factors, other than simple quantitative complexation, may be present. Therefore, more studies are obviously necessary to fully characterize the complexing properties of this polymer.

Further studies for copolymer systems containing this monomer and their physical properties are in progress.

Acknowledgment. We gratefully acknowledgement the support of this work by the Korea Science and Engineering Foundation.

References and Notes

(1) Pai, D. M. *Photoconductivity in Polymer, An Interdisciplinary Approach*; Patsis, A. V., Seanor, D. A., Eds.; Technomic: Westport, CT, 1976.
(2) Naarmann, H.; Strohriegel, D. In *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Dekker, Inc.: New York, 1992; p 1404.
(3) Stolka, M.; Pai, D. M. *Advances in Polymer Science*; Cantow, H.-J., et al., Eds.; Springer-Verlag: Berlin, Heidelberg, New York, 1978; Vol. 29, p 1.
(4) Ohkawa, H.; Furuichi, T.; Oshima, R.; Uryu, T. *Macromolecules* **1989**, *22*, 2266.
(5) Schulz, R. C.; Tanaka, H. *Pure Appl. Chem.* **1978**, *38*, 227.
(6) Sulzberg, T.; Cotter, R. J. *Macromolecules* **1968**, *1*, 554; *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 2747.
(7) Simmons, A.; Natansohn, A. *Macromolecules* **1991**, *24*, 3651.
(8) Iwatsuki, S.; Itoh, T.; Takagi, K. *Macromolecules* **1992**, *25*, 4597.
(9) Bengs, H.; Renkel, R.; Ringsdorf, H.; Baehr, C.; Ebert, M.; Wendorff, J. H. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 439.
(10) Turner, S. R.; AuClair, C. *Macromolecules* **1976**, *9*, 868.
(11) Turner, S. R. *Macromolecules* **1980**, *13*, 782.
(12) Bagdasar'ian, K. A.; Sinitsina, Z. A. *J. Polym. Sci.* **1961**, *52*, 31.
(13) Park, J. W.; Lee, J. H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1993**, *26*, 1191.
(14) Chang, D. M.; Gromelski, S.; Rupp, R.; Mulvaney, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 571.
(15) Natansohn, A. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3161.
(16) Jin, S. H.; Kim, S. H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1991**, *24*, 6050.
(17) Jin, S. H.; Cho, H. N.; Choi, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 69.
(18) Fox, H. H.; Schrock, R. R. *Organometallics* **1992**, *11*, 2763.
(19) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.
(20) Kim, S. H.; Kim, Y. H.; Choi, S. K.; Kwon, S. K. *J. Am. Chem. Soc.*, submitted.
(21) (a) Ryoo, M. S.; Lee, W. C.; Choi, S. K. *Macromolecules* **1990**, *23*, 3029. (b) The poly(DEDPM)s prepared by MoCl$_5$ alone in 1,4-dioxane were easily soluble in chloroform, 1,4-dioxane, ethyl acetate, THF, and DMF. The number-average molecular weight (M_n) values of the resulting polymers were in the range of (7.2–12.7) $\times 10^4$, relative to polystyrene standards in GPC.
(22) Kang, E. T.; Neoh, K. G.; Tan, K. L. *Advances in Polymer Science*; Fujita, H., Ed.; Springer-Verlag: Berlin, Heidelberg, New York, 1993; Vol. 106, p 135.
(23) Kang, E. T.; Neoh, K. G.; Tan, K. L. *J. Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 669.
(24) Skotheim, T. A. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986; Vols. 1 and 2.
(25) Kang, E. T.; Ehrlich, P.; Bhatt, A. P.; Anderson, W. A. *Macromolecules* **1984**, *17*, 1020.

MA941049Q