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Synthesis and characterization of poly(1,8-diethynylnaphthalene)

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Summary

The cyclopolymerization of 1,8-diethynylnaphthalene(DEN) and its copolymerization with diethyl dipropargylmalonate(DEDPM) were carried out by various transition metal catalysts. $MoCl_5$-based catalyst was found to be very effective and gave almost a quantitative polymer yield. The resulting dark-brown homopolymer(PDEN) was partially soluble in chloroform, tetrahydrofuran, and dimethyl sulfoxide, whereas copolymer (1:1) with number average molecular weight ($\overline{Mn}$) of 2.1×10^4 by GPC showed good solubility in those solvents. The structure of the polymers was analysed by IR, NMR, and UV-VIS spectroscopies. From the spectral and solubility data, it is proposed that cyclized products with the conjugated system are formed. Room temperature conductivities of the I_2-doped homo and copolymer were found to be about 7.5×10^{-3} and 5.1×10^{-3} S/cm, respectively.

Introduction

Since polyacetylene has been known as a highly conducting polymer (1), numerous π-conjugated organic polymers have been extensively studied because of a variety of interesting optical and electrical properties and their potential in applications (2-5). Many people have developed synthesis routes to polyacetylene derivatives by employing various transition metal catalysts via precursor polymers or direct polymerizations of acetylenes (6-9).

An interesting class of polyacetylenes was prepared by cyclopolymerization between 1,6-heptadiyne derivatives with a number of catalyst systems including metathesis catalysts (10-14). $MoCl_5$- and WCl_6-based catalyst systems and well-defined molybdenum alkylidene complexes are commonly used as metathesis catalysts (13-14). It has been known that the resulting cyclized polymers with conjugated double bonds have both five- and six-membered ring structures with a certain ratio, which should depend on the polymerization conditions and the kinds of catalysts used (14). In our previous work, cyclopolymerization of 1,2-diethynylbenzene (DEB) and its copolymerization with diethyl dipropargylmalonate (DEDPM) were carried out (15) and it was demonstrated that $MoCl_5$-based catalysts were very effective for the polymerizations. The homopolymer having the five-membered ring structure was hardly soluble in common organic solvents, whereas the copolymer with number average molecular weight ($\overline{Mn}$) of 3×10^4 was soluble in the solvents.

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In this article, we report the results of cyclopolymerization of 1,8-diethynylnaphthalene (DEN) and its copolymerization with DEDPM by various transition metal catalysts. Characterization on the structures and physical properties of the polymers are carried out.

Experimental

Materials

Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemical Co, 99.9%) were used without further purification. Palladium(II) chloride (Aldrich Chemical Co, 99.999%) and ethylaluminum dichloride (Aldrich Chemical Co, 25wt % in toluene) were used as received. Tetrabutyltin was purified by distillation under reduced pressure. Tetrabutylammonium perchlolate (TBAClO$_4$) was used after vacuum drying. DEDPM was prepared by the reaction of diethyl malonate and propargyl bromide as described in the literature (13,17). All solvents were used after purification according to the conventional methods.

Preparation of DEN

DEN, a monomer, was prepared through the seven-step synthesis from naphthalic anhydride as a starting material following the procedure described in the literature (17). Yield after purification 27%, mp 72-73°C (lit.(17) : 73-73.5°C). The monomer was stored at -20°C in the dark prior to use. IR (KBr) : 3287, 2113 cm^{-1} (acetylenic C-H and C≡C streching), ^{1}H-NMR (CDCl$_3$) : δ (ppm) 3.4 (s, 2H, acetylenic), 7.3 (t, 2H, aromatic), 7.8 (d, 4H, aromatic), ^{13}C-NMR (CDCl$_3$) : δ (ppm) 83.1, 85.3 (acetylenic), 119.4, 125.4, 130.2, 131.2, 133.8, 135.9 (aromatic). UV-VIS (THF) : λmax; 270, 318, 338nm.

Instruments and Measurement

^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AM-300 spectrometer, and chemical shifts were reported in ppm units with tetramethylsilane as the internal standard. IR spectra were measured as KBr pellets on a Bomem MB-100 spectrometer, and frequencies were given in reciprocal centimeters. A Shimadzu UV-3100S spectrometer was used for UV-VIS spectral data. $\overline{Mn}$ and polydispersity were determined using THF as an eluent by a Waters GPC-150C calibrated with polystyrene standards. Elemental analysis was performed with a Carlo Erba EA 1108 Elemental Analyser.Thermal analyses were carried out on a Dupont TGA 9900 thermogravimetric analyzer in a nitrogen atmosphere at 10°C/min. Electrical conductivities were measured with an Ando AG-4303 LCR meter by the four-point probe method. Cyclic voltammogram was recorded on a Hokuto Denko HA-301 potentiostat/galvanostat.

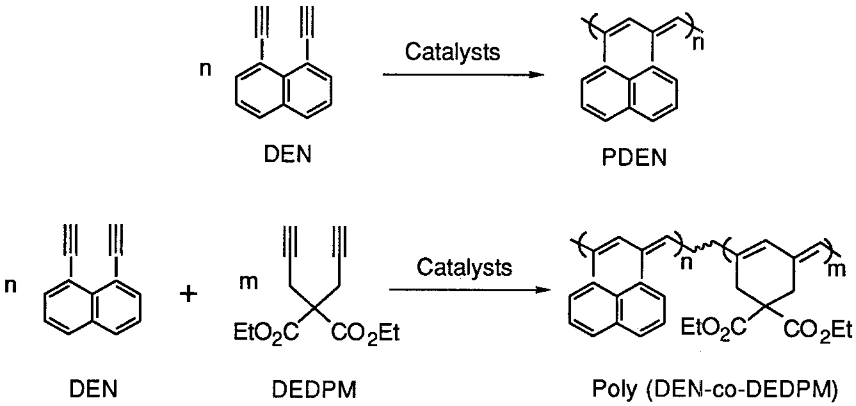
Polymerization

Catalyst preparation and polymerization were carried out under a dry nitrogen atmosphere. Transition metal halides and organometallic compounds were dissolved in appropriate solvents to make 0.2mol/l solutions prior to use. A typical polymerization procedure was as follows : solvent, catalyst solution, and when needed, cocatalyst solution were injected into a 20ml ampoule equipped with a rubber septum according to the order given. When the cocatalyst was used, the catalyst system was aged at 30°C for 15min. Finally, the monomer (DEN) dissolved in the same solvent was injected into the polymerization ampoule. After the reaction mixture was allowed to react at 70°C for 24h, the polymerization was terminated by adding a small amount of methanol. The resulting mixture was poured into THF and precipitated with a large amount of methanol. The precipitated polymer was filtered from the soultion and then dried under vacuum at 40°C for 24h. The polymer yield was determined by gravimetry. Copolymerization was conducted as the same as the above procedure except comonomer (DEDPM) addition in the polymerization ampoule.

Results and Discussion

Scheme I outlines the cyclopolymerization of DEN and its copolymerization with DEDPM with various transition metal catalysts.

Scheme I



Catalyst : $MoCl_5$, WCl_6, or $PdCl_2$
Cocatalyst : $EtAlCl_2$, or $(n\text{-}Bu)_4Sn$

Polymerization yields of DEN with various transition metal catalysts are listed in Table I. The polymerization with $MoCl_5$-$EtAlCl_2$ as the catalyst system gave almost a quantitative yield to show the highest catalytic activity among the catalysts used. Poly (1,8-diethynylnaphthalene) (PDEN) by $MoCl_5$ or WCl_6 as the catalyst was found to be partially soluble in orgarnic solvents such as chloroform, tetrahydrofuran (THF), and dimethyl sulfoxide (DMSO) , and the soluble portion of the polymers was less than 20%. However, PDEN obtained by $PdCl_2$ was quite soluble in such solvents and $\overline{Mn}$ was 2.8×10^3 relative polystyrene standards by GPC.

The IR spectrum of PDEN exhibited no absorptions at 3287 and 2113 cm^{-1} which were expected to be present for the acetylenic carbon-hydrogen streching and carbon-carbon triple bond streching bands of DEN, respectively. Instead, the carbon-carbon double bond streching band in the polymer backbone is observed at 1625 cm^{-1}. The ^1H-NMR spectra

Table 1. Polymerization of DEN with Various Transition Metal Catalysts[a]

Expt. No.	Catalyst System (Mole Ratio)	Solvent	Polym.Yield[c] (%)
1	$MoCl_5$	Chlorobenzene	62
2	$MoCl_5$	Dioxane	56
3	WCl_6	Chlorobenzene	60
4	$MoCl_5/EtAlCl_2$ (1:4)	Chlorobenzene	97
5	$WCl_6/(n\text{-}Bu)_4Sn$ (1:4)	Chlorobenzene	72
6[b]	$PdCl_2$	DMF	87

a : Polymerization was carried out at 70°C for 24h. Initial monomer concentration and monomer to catalyst mole ratio were 0.5 mol/l and 50, respectively.
b : Polymerization was carried out at 90°C for 24h. c : Methanol-insoluble polymer.

of DEN and PDEN are shown in Figure 1. As the polymerization proceeded, the acetylenic proton singlet of DEN at 3.4 ppm disappeared, and new vinylic proton peaks appeared at the region of 6.0 ~ 8.5 ppm together with aromatic naphthalene ring protons. In the ^{13}C-NMR spectra, DEN gave the acetylenic carbon peaks at 83.1 and 85.3 ppm, while PDEN did not show any peak at those positions. Instead, the olefinic carbon peaks

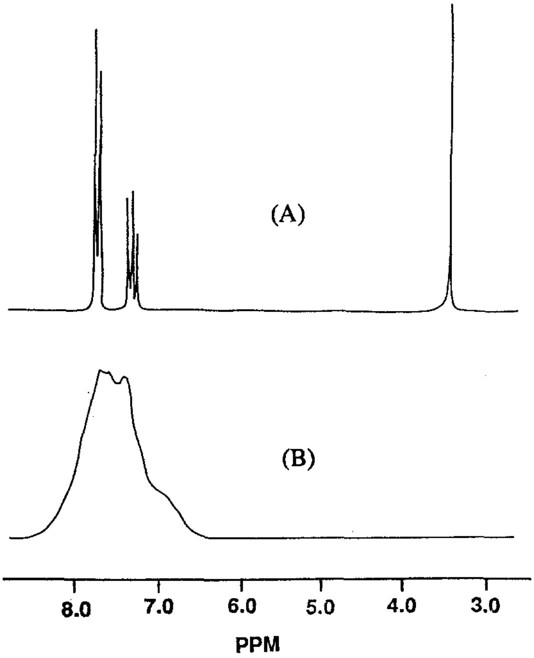


Figure 1. ^{1}H-NMR Spectra of DEN (A) in $CDCl_3$ and PDEN (B) in DMSO

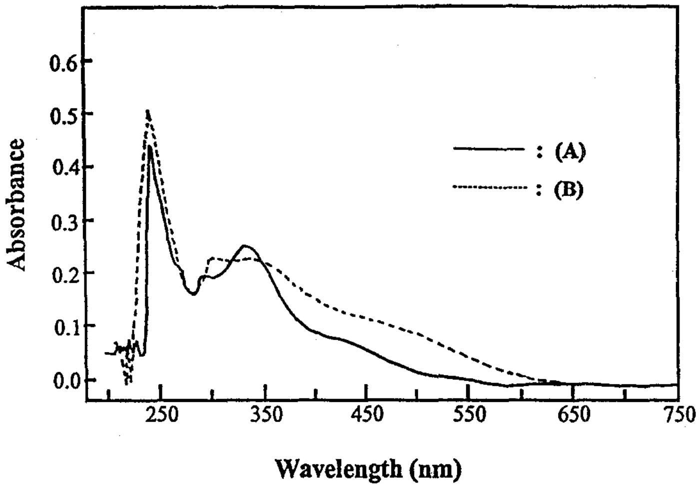


Figure 2. UV-VIS Spectra of PDEN (A) and DEN-DEDPM Copolymer (1:1) (B) in THF

of the polymer backbone appeared at the region of 120~135ppm, although they could not be clearly identified due to the interference with those of naphthalene ring. The UV-VIS spectrum of PDEN (Figure 2) exhibits the characteristic broad peak of 350 ~ 600 nm (λmax= ca.425nm as shoulder) that is due to the π → π* transition of the conjugated polyene (12).

In addition, the elemental analysis data for PDEN agreed well with the theoritical value ; Calculated for $(C_{14}H_8)_n$: C, 95.42% ; H, 4.58% , Found : C, 94.84% ; H, 4.30%. From the above spectral and solubility data, it is proposed that the polymer structure has a cyclized form with six-membered rings as described in Scheme I (12,13), although it has been reported that 1,6-heptadiynes were cyclopolymerized and the polymers had five- as well as six-membered ring structures with a certain ratio, which should depend on the polymerization conditions and the kinds of catalysts used (14).

Table II summarizes the results on the copolymerization of DEN with DEDPM by $MoCl_5$ catalyst varying the DEN content. In general, the catalytic activity of $MoCl_5$ was much greater than that of WCl_6 in the polymerization of DEDPM or its derivatives (12,13). As shown in Table II, the copolymer yields are very high irrespective of the DEN concentration, and the resulting copolymers exibit a good solubility in organic solvents, especially in THF and DMSO. A black-red film was easily obtained by casting the copolymer (1:1) solution in THF on a glass plate. $\overline{Mn}$ of the copolymers were found to be in the range of 0.8 ~ 2.1x 10^4 relative polystyrene standards by GPC. The copolymer structure was also identified by IR, NMR, and UV-VIS spectroscopies. As seen in the homopolymer of DEN, there was no absorption peak at the acetylenic region in the IR spectrum of the copolymer while streching bands of the carbon-carbon double bond and

Table 2. Copolymerization of DEN with DEDPM by $MoCl_5$ Catalyst[a]

Expt. No.	DEN Content (%)	Polym.Yield[b] (%)	$\overline{Mn}$ [c] ($\times 10^{-4}$)	$\overline{Mw}$ / $\overline{Mn}$ [c]
1	10	92	0.8	3.5
2	30	95	1.0	3.4
3	50	97	2.1	2.6
4	70	92	1.2	2.9
5	90	87	0.9	3.1

a : Polymerization was carried out at 70°C for 24h in chlorobenzene. Initial monomer concentration and monomer to catalyst mole ratio were 0.5 mol/l and 50, respectively. b : Methanol-insoluble polymer. c : Values were obtained by GPC analysis with polystyrene standard calibration.

carbonyl bond appeared at 1630 and 1732 cm^{-1}, respectively. Figure 3 represents the ^{1}H-NMR spectrum of the copolymer. The broad peak at 5.5 ~ 8.5 ppm is assigned to the protons of the conjugated double bond and naphthalene ring, and the peaks at 1.2 and 2.5 ~ 4.5 ppm are attributed to the methyl and methylene protons. In addition, carbonyl carbon peak was shown at 174 ppm, and olefinic carbon peak and naphthalene ring carbon peak were shown at 120~140ppm in the ^{13}C-NMR spectrum. The UV-VIS spectrum

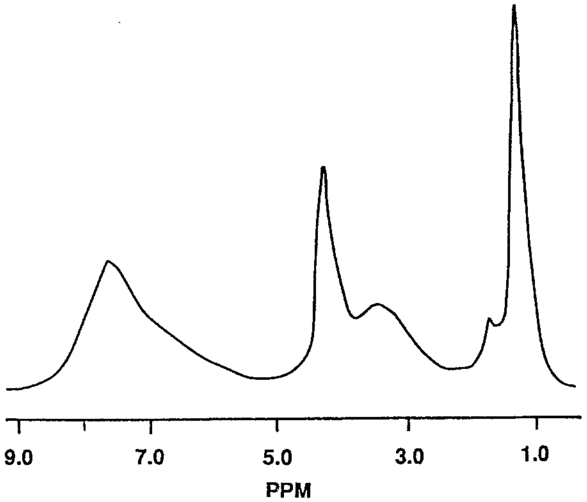


Figure 3. ^{1}H-NMR Spectrum of DEN-DEDPM Copolymer (1:1) in $CDCl_3$

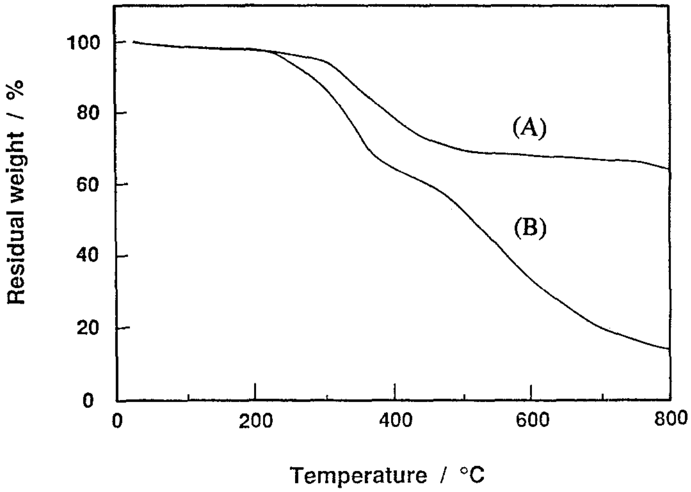


Figure 4. TGA Thermograms of PDEN (A) and DEN-DEDPM Copolymer (1:1) (B)

(Figure 2) of the copolymer exibits a characteristic broad absorption peak of 350 ~ 640 nm (λmax= ca.500nm as shoulder) that is also due to the $\pi \rightarrow \pi^*$ transition of the conjugated polyene as seen in the homopolymer. However, it was clearly observed that λmax shifted to near 550 nm as the content of DEN decreased (12). The TGA thermograms (Figure 4) under a nitrogen atmosphere show that PDEN and the copolymer are

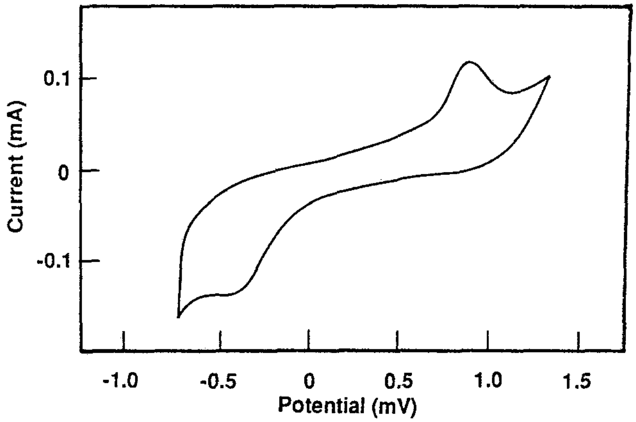


Figure 5. Cyclic Voltammogram of DEN-DEDPM Copolymer (1:1)
Scan Rate : 50 mV/sec. (0.1M TBAClO$_4$/Acetonitrile, Ag/AgCl)

thermally stable up to 300 and 220°C with 63 and 17% residual weight at 800°C, respectively. When the pressed pellets of PDEN and the copolymer were doped with I_2 for 24h at room temperature, the electrical conductivities were found to be about 7.5×10^{-3} and 5.1×10^{-3} S/cm, respectively.

The cyclic voltammogram of the copolymer film which was coated onto platinum foil as a working electrode with the area of $1 cm^2$ is shown in Figure 5. At the potential range of -0.7~1.4V, the copolymer showed a well-defined redox process with oxidation and reduction potentials at 0.9 and -0.4V, respectively.

Conclusions

Cyclopolymerization of DEN and its copolymerization with DEDPM were carried out by various transition metal catalysts. $MoCl_5$-based catalyst was found to be very effective and gave almost a quantitative polymer yield. PDEN obtained by $PdCl_2$ as the catalyst was soluble in chloroform, THF and DMSO, and $\overline{Mn}$ was 2.8×10^3 relative polystyrene standards by GPC. Also, the copolymer yields were very high irrespective of DEN concentration, and the resulting copolymers exibited a good solubility, especially in THF and DMSO. A black-red film was easily obtained by casting the copolymer solution in THF on a glass plate. $\overline{Mn}$ of copolymers were found to be in the range of $0.8 \sim 2.1 \times 10^4$. From the spectral and solubility data, it is proposed that the polymer structure has a cyclized form with six-membered rings. Room temperature conductivities of the I_2-doped homo and copolymer were found to be about 7.5×10^{-3} and 5.1×10^{-3} S/cm, respectively.

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References

1. Shirakawa H, Louis EJ, MacDiarmid AG, Chiang CK, Heeger AJ (1977) J Chem Soc Chem Commun 578
2. Chien JCW (1984) Polyacetylene Academic Press New York
3. Skotheim TA (1986) Handbook of Conducting Polymers Marcel Dekker New York Vol. 1 & 2
4. Patil AO, Heeger AJ, Wudl F (1988) Chem Rev 88: 183
5. Miller JS (1993) Adv Mater 5: 671
6. Edwards JH, Feast WJ (1980) Polymer 21: 595
7. Swager TM, Grubbs RH (1989) J Am Chem Soc 111: 4413
8. Masuda T, Higashimura T (1986) Adv Polym Sci 81: 122
9. Knoll K, Krouse SA, Schrock RR (1988) J Am Chem Soc 110: 4424
10. Stille JK, Frey DA (1961) J Am Chem Soc 83: 1697
11. Gibson HW, Bailey FC, Epstein AJ, Rommelmann H, Kaplan S, Harbour J, Yang XQ, Tanner DB, Pochan JM (1983) J Am Chem Soc 105: 4417
12. Ryoo MS, Lee WC, Choi SK (1990) Macromolcules 23: 92
13. Jin SH, Choi SJ, Ahn W, Cho HN, Choi SK (1993) Macromolecules 26: 1487
14. Fox HH, Wolf MO, O'Dell R, Lin BL, Schrock RR, Wrighton MS (1994) J Am Chem Soc 116: 2827
15. Kim DJ, Kim KL, Cho HN, Kim CY (1994) Polymer (Korea) 18: 297
16. Eglinton G, Galbraith AR (1959) J Chem Soc 889
17. Mitchell RH, Sondheimer F (1968) Tetrahedron 24: 1397