Korea Polymer Journal, Vol. 8, No.5, pp 231 – 237 (2000)

Polymerization of 3-Ethynylphenol by Transition Metal Catalysts

Yeong-Soon Gal*

Polymer Chemistry Laboratory, College of General Education, Kyungil University, Hayang 712-701, Kyungsangbuk-Do, Korea

Won-Chul Lee

Department of Textile and Fashion Technology, Kyungil University, Hayang 712-701, Kyungsangbuk-Do, Korea

Sung-Ho Jin

Department of Chemistry Education, Pusan National University, Pusan 609-735, Korea

Hyung-Jong Lee

Zenphotonics, Rm 303, K-MAC BLD., 104-11 Moonji-Dong, Yusong-Gu, Taejon 305-380, Korea

Received August 8, 2000

Abstract : The polymerization of 3-ethynylphenol, phenylacetylene having hydroxy functionality, was carried out by tungsten and molybdenum-based transition metal catalysts. The polymerization proceeded to give a moderate yield of polymer. The effects on the mole ratio of monomer to catalyst (M/C), initial monomer concentration ([M]$_0$), and the polymerization temperature for the polymerization of 3-ethynylphenol were investigated. The catalytic activity of W-based catalysts was found to be greater than that of Mo-based catalysts. The resulting polymers were brown or black powders and mostly insoluble in organic solvents. Structural analysis of the polymer by instrumental methods revealed the conjugated polymer backbone structure carrying hydroxyphenyl moieties. Thermal and morphological properties of the resulting poly(3-ethynylphenol) were also discussed.

Introduction

Conjugated polymers obtained from acetylene derivatives have been applied as organic semiconductors,[1-3] as membranes for gas separation and for liquid-mixture separation,[4-10] as materials for enantioseparation of racemates by high performance liquid chromatograpy,[11,12] as a side-chain liquid crystal,[13-16] as materials for chemical sensors,[17,18] and as materials for nonlinear optical property and for photoluminescence and electroluminescence properties.[19-24]

Various polyacetylenes have been prepared and characterized.[1,2,16,25] In our previous works, the results for the polymerizations of propargyl halides,[26] ethers,[27-30] and amines,[31] and the cyclopolymerization of dipropargyl derivatives such as dipropargyl ether,[32] sulfide,[33] silanes,[34] diethylmalonate,[35,36] dihexylammonium salts,[37,38] etc. have been reported.

The polymerizations of acetylene derivatives having hydroxy functional group are of interest because of their unique structures and facile modification of hydroxy groups with other interesting functional groups. The most simple hydroxy-containing polyacetylene, poly(propargyl alcohol), had been prepared by high pressure with radical initiator,[39] $PdCl_2$,[40] $Ni(CO)_2(PPh_3)_2$,[41] $NiI_2(PPh_3)_2$,[42] $Ni(NCS)(C{\equiv}C\text{-}R)(PPh_3)_2$,[42] γ-ray,[43] plasma,[43] $MoCl_5$,[45-47] and $Pd(C{\equiv}CCH_2OH)_2(PPh_3)_2$.[48,49] In most cases,

*e-mail : ysgal@bear.kyungil.ac.kr

the resulting poly(propargyl alcohol)s were insoluble in any organic solvents.

Various substituents have been introduced into the α-carbon of propargyl alcohol in order to increase the solubility of polyacetylene derivatives having hydroxy functional group.[50-53] Soluble poly (1-ethynyl-1-cyclohexanol),[50,51] poly(ethynylfluorenol),[52] poly(3-butyn-2-ol),[53] poly(1-octyn-3-ol),[53] and poly(2-phenyl-3-butyn-2-ol)[53] were prepared and characterized.

To our knowledge, there has been no report on the polymerization of phenylacetylene having hydroxy functional group. 3-Ethynylphenol have been used for the preparation of acetylene-terminated prepolymer. These acetylene-terminated prepolymers are good candidates for crosslinked optical waveguide materials due to easy synthesis, absence of an aliphatic C-H bond leading to significant optical absorption loss, and absence of catalyst and evolution of any volatile during the curing process.[54,55]

In this article, the results for the polymerization of 3-ethynylphenol using transition metal catalysts and the characterization of the resulting polymers are reported.

Experimental

Materials. 3-Hydroxyphenol (Aldrich Chemicals., 98%) and *tert*-butyldimethylsilyl chloride (Aldrich Chemicals., 98%) were used as received. (Trimethylsilyl)acetylene (Aldrich Chemicals., 98%) was dried with calcium hydride and distilled. WCl_6 (Aldrich Chemicals., 99.9+%) and $MoCl_5$ (Aldrich Chemicals, 99.9+%) were used without further purification. Et_3Al, Et_2AlCl, $EtAlCl_2$(Aldrich Chemicals, 25 wt% (1.8 M) solution in toluene), and Me_4Sn (Aldrich Chemicals, 95%) were used as received. Ph_4Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. The analytical grade solvents were dried with an appropriate drying agent and distilled.

Synthesis of 1-Bromo-3-(*tert*-butyldimethylsiloxy)benzene. 3-Bromophenol (5 g, 28.9 mmol) in 10 mL of N,N-dimethyl formamide (DMF) was added dropwise to 250 mL reaction flask containing *tert*-butyldimethylsilyl chloride (20.9 g, 34.68 mmol) and imidazole (2.36 g, 34.68 mmol) dissolved in 20 mL of DMF under nitrogen. After being stirred at room temperature for 24 h, the mixture was poured into water and extracted three times by 50 mL of ether. The organic layer was dried over anhydrous $MgSO_4$. After removal of the solvent, the mixture was distilled under vacuum to give the product (7.3 g, 88%): bp = 70°C /0.2 mmHg; ^{1}H-NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.97 (s, 9H), 6.76 (m, 1H), 7.00 (m, 1H), 7.08 (m, 2H).

1-(*tert*-Butyldimethylsiloxy)-3-((trimethylsilyl)ethynyl)benzene. A stirred mixture of 1-bromo-3-(*tert*-butyldimethylsiloxy)benzene (5.75 g, 20 mmol) and triphenylphosphine (0.037 g, 0.14 mmol) was dissolved in 12 mL of DMAc under nitrogen. (Trimethylsilyl)acetylene (2.36 g, 24 mmol) was added into the flask through a syringe. $PdCl_2(PPh_3)_2$ (0.02 g, 0.028 mmol) was washed in with 15 mL of triethyl-amine. The mixture was slowly heated to 60°C, and then CuI (0.008 g, 0.04 mmol) was added with 15 mL of triethylamine. The reaction mixture was heated to 80°C and maintained for 6 h with stirring. After cooling, the reaction mixture was filtered to remove inorganic salts and evaporated triethylamine. The reaction mixture was poured into acidic water and extracted with methylene chloride. The organic layer was dried over anhydrous $MgSO_4$, and then the solvent was evaporated. The product, 1-(*tert*-butyldimethylsiloxy)-3-((trimethylsilyl)ethynyl) benzene, was obtained by distillation with 74% yield: bp = 92°C/0.3 mmHg; ^{1}H-NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.25 (s, 9H), 0.98 (s, 9H), 6.80 (m, 1H), 6.94 (s, 1H), 7.11 (m, 2H).

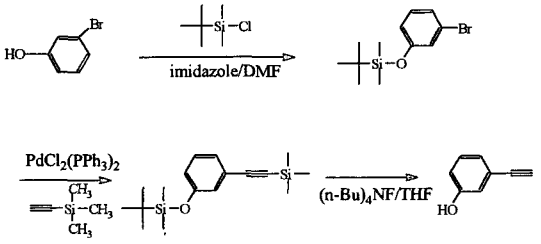
3-Ethynylphenol (EP). Tetrabutylammonium fluoride (45.0 mL, 1.0 M solution in THF, 45.12 mmol) was added dropwise to the solution of 1-(*tert*-butyldimethylsiloxy)-3-((trimethylsilyl)ethynyl) benzene in 15 mL of THF. After being stirred for 4 h, the solution was poured into water. The organic layer was extracted with ether and dried over anhydrous $MgSO_4$. After removal of the solvent, the mixture was distillated under vacuum to provide 3-ethynylphenol: yield = 89%; bp = 46°C/0.3 mmHg; ^{1}H-NMR ($CDCl_3$) δ 3.06 (s, 1H), 4.95 (bs, OH), 6.82 (m, 1H), 6.93 (m, 1H), 7.03 (m, 1H), 7.12 (m, 1H); ^{13}C-NMR ($CDCl_3$) δ 77.3, 83.2 (ethynyl), 116.3, 116.7, 123.3, 124.9, 129.7,

155.1 (phenyl).

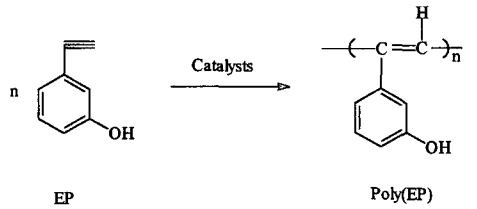
Polymerization of EP by WCl_6. In a 20 mL ampule equipped with rubber septum, chlorobenzene (2.32 mL, $[M]_0$ = 1.0 M), 1.41 mL (1.41 mmol, M/C: 30) of 0.1 M $MoCl_5$ chlorobenzene solution, and 0.5 g (4.23 mmol) of EP were added in that order given. And the polymerization was carried out at 60 °C for 24 h under nitrogen atmosphere. The polymerization proceeded in heterogeneous manner. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The polymer solution was precipitated into an excess of methanol, filtered from the solution, and then dried under vacuum at 40°C for 24 h. The polymer yield was 20%.

Polymerization of EP by WCl_6-$EtAlCl_2$. In a 20 mL ampule equipped with rubber septum, chlorobenzene (1.61 mL, $[M]_0$ = 1.0 M), 1.41 mL (1.41 mmol, M/C: 30) of 0.1 M chlorobenzene solution of $MoCl_5$, and 0.71 mL (2.82 mmol) of 0.4 M chlorobenzene solution of $EtAlCl_2$ were added in that order given. After shaking the catalyst solution at 30°C for 15 min, 0.5 g EP (4.23 mmol) was injected. The polymerization also proceeded in heterogeneous manner. After a given time of polymerization, 10 mL of chloroform was added to the polymerization solution. The polymer solution was poured into an excess of methanol, filtered from the solution, and then dried under vacuum at 40°C for 24 h. The polymer yield was 45%.

Instruments and Measurement. ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AM-300 spectrometer. $CDCl_3$ was used as a solvent, and chemical shifts were reported in ppm units, with tetramethylsilane as an internal standard. IR spectra were obtained with a Bruker EQUINOX 55 spectrometer using a KBr pellet. Elemental analyses were performed with FISONS EA1110 Elemental Analyzer. UV-visible spectra of a slightly soluble polymer solution were taken on a JASCO V-530 spectrophotometer. Thermogravimetry (TG) was performed under a nitrogen atmosphere at a heating rate of 10°C/min upto 800°C with a DuPont 2200 thermogravimetric analyzer. X-ray diffractograms were obtained with a PHILIPS X-ray diffractometer (Model: XPert-APD).



Scheme I. Synthesis of 3-ethynylphenol (EP).



EP Poly(EP)

Scheme II. Polymerization of 3-ethynylphenol.

Results and Discussion

Synthesis of EP. 3-Ethynylphenol (EP), phenylacetylene derivative having hydroxy functional group, was synthesized as shown in Scheme I. Silylated 3-bromophenol was reacted with (trimethylsilyl)acetylene in the presence of Pd/Cu catalyst. EP was easily prepared by the desilylation of silylated phenol and acetylene moieties using tetrabutylammonium fluoride in high yield (89%).

Polymerization of EP. The polymerization of EP was attempted with W- and Mo-based transition metal catalysts (Scheme II).

Table I shows a typical result for the polymerization of EP by tungsten-based catalysts. The polymerization of EP monomer with WCl_6 alone gave low yield of polymer (20%). WCl_6 catalyst had been known to be very effective for the polymerization of phenylacetylene, a similar acetylene derivative without hydroxy groups. A high yield (80%) of soluble poly(phenylacetylene) having a relatively high molecular weight ($M_n \approx 15{,}000$) were obtained.[56] However, only low yield of polymer was obtained in the polymerization of EP bearing a hydroxy group. The reason for this low activity of WCl_6 catalyst may be attributed to be due to the poisoning effect of the hydroxy group of EP and/or the poor solubility of the resulting poly(EP).

It has been known that the addition of a small

Table I. Polymerization of 3-Ethynylphenol by WCl_6-Based Catalysts[a]

Exp. No	Catalyst System[b]	M/C[c]	$[M]_0$[d]	Temp. (°C)	P. Y. (%)[e]
1	WCl_6	30	1.0	60	20
2	WCl_6 /Me_4Sn(1:2)	30	1.0	60	23
3	WCl_6 /Ph_4Sn(1:2)	30	1.0	60	27
4	WCl_6 /Et_3Al(1:2)	30	1.0	60	15
5	WCl_6 /Et_2AlCl(1:2)	30	1.0	60	32
6	WCl_6 /$EtAlCl_2$ (1:2)	30	1.0	60	45
7	WCl_6 /$EtAlCl_2$ (1:2)	50	1.0	60	21
8	WCl_6 /$EtAlCl_2$ (1:2)	100	1.0	60	trace
9	WCl_6 /$EtAlCl_2$ (1:2)	30	0.5	60	21
10	WCl_6 /$EtAlCl_2$ (1:2)	30	2.0	60	40
11	WCl_6 /$EtAlCl_2$ (1:2)	30	1.0	20	5
12	WCl_6 /$EtAlCl_2$ (1:2)	30	1.0	40	17
13	WCl_6 /$EtAlCl_2$ (1:2)	30	1.0	80	46

[a]Polymerization was carried out for 24 h in chlorobenzene.
[b]Mixture of catalyst and cocatalyst solution was aged for 15 min at 30 °C before use.
[c]Monomer to catalyst mole ratio.
[d]Initial monomer concentration.
[e]Methanol-insoluble polymer yield.

amount of reducing agents such as Ph_4Sn and n-Bu_4Sn increases the polymer yield and molecular weight in the WCl_6-catalyzed polymerization of 2-ethynylthiophene[57] and 1-butyl-2-trimethylsilylacetylene.[58] And also the organoaluminum compounds such as $EtAlCl_2$ and Et_2AlCl were very effective cocatalyst in the polymerization of 1-ethynylcyclohexene.[59] In this work, the organotin and organoaluminum compounds besides Et_3Al also increased the catalytic activities of WCl_6. The best result was obtained when $EtAlCl_2$ was used as a cocatalyst.

As shown in Table I (Exp. No, 6-8), the polymer yield was significantly decreased with increasing the M/C ratio. The decreasing extent of polymer yield according to the M/C value was higher than that of the polymerization of phenylacetylene bearing no hydroxy group, probably because the poisoning effect of the hydroxy group of phenyl substituents to WCl_6.

The effect of initial monomer concentration ($[M]_0$) was also tested (Exp. No: 6,9,10). At the low initial monomer concentration ($[M]_0$: 0.5), the polymerization proceed in homogeneous manner, but the polymer yield was low (21%). At the elevated temperature (80°C, Exp. No: 13), the polymerization proceeded vigorously, and then the black polymeric powders were adhered to the bottom and wall of reactor. However, the polymer yield was similar to that of the polymerization at 60 °C.

Table II. Polymerization of 3-Ethynylphenol by $MoCl_5$-Based Catalysts[a]

Exp. No.	Catalyst System[b]	M/C[c]	P. Y. (%)[d]
1	$MoCl_5$	30	trace
2	$MoCl_5$ /Ph_4Sn(1:2)	30	7
3	$MoCl_5$ /Et_2AlCl(1:2)	30	12
4	$MoCl_5$ /$EtAlCl_2$ (1:2)	30	15
5	$MoCl_5$ /$EtAlCl_2$ (1:2)	50	5

[a]Polymerization was carried out at 60 °C for 24 h in chlorobenzene. Initial monomer concentration was 1.0 M.
[b]Mixture of catalyst and cocatalyst solution was aged for 15 min at 30 °C before use.
[c]Monomer to catalyst mole ratio.
[d]Methanol-insoluble polymer yield.

Table II shows the polymerization results of EP by Mo-based catalysts. In general, the $MoCl_5$-based catalysts showed relatively low catalytic activity in this polymerization. The higher catalytic activity of W-based catalysts than that of Mo-based catalysts was similar to the polymerization of phenylacetylene using W- and Mo-based catalysts.[56]

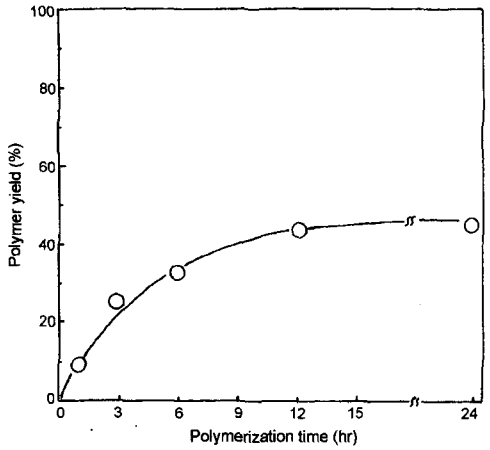


Figure 1. The time dependence curve of polymer yield for the polymerization of EP by WCl_6-$EtAlCl_2$ catalyst system.

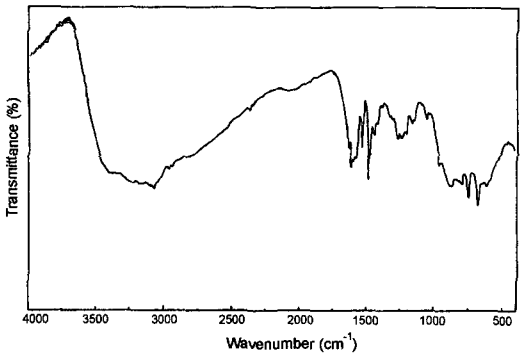


Figure 2. FT-IR spectrum of poly(EP) prepared by WCl_6-$EtAlCl_2$ in KBr pellet.

Figure 1 shows the typical time dependence curve of polymer yield for the polymerization of EP by WCl_6-$EtAlCl_2$ in chlorobenzene (M/C: 30, $[M]_0$: 1.0 M, polymerization time: 24 h). As shown in this figure, the polymerization of EP by WCl_6-$EtAlCl_2$ catalyst system proceeded more slowly to give a low yield of polymer.

Structure and Properties. The resulting poly(EP)s were mostly insoluble in common organic solvents regardless of the polymerization conditions and catalysts used. Thus it was very difficult to identify the exact polymer structure in solution state.

The IR spectrum (Figure 2) of poly(EP) did not show the acetylenic C≡C bond stretching frequency at 2107 cm^{-1} and the acetylenic ≡C-H stretching frequency at about 3292 cm^{-1}. Instead, the C=C double bond stretching frequency peak of conjugated polymer backbone at 1610 cm^{-1} was clearly observed. A small peak at 3018 and 3066 cm^{-1} is originated from the vinylic =C-H stretching frequencies of the conjugated polymer backbone and the phenyl substituents.

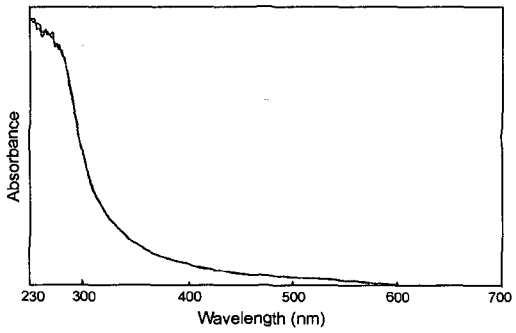


Figure 3. UV-visible spectrum of poly(EP) (in $CHCl_3$).

Figure 3 shows the UV-visible spectra of poly (EP) solution soluble slightly in chloroform (only color change). The UV-visible spectrum exhibits the characteristic broad absorption peak at the visible region was originated from the $\pi \rightarrow \pi^*$ conjugation band transition of the polyene main chain, which had not been observed at the UV-visible spectrum of monomer.

The elemental analysis data of poly(EP) agreed with the theoretical value though it has a slight deviation: Calcd for $(C_8H_6O)_n$: C, 81.34%; H, 5.12%; O, 13.54%, Found: C, 80.12%; H, 5.01 %; O, 12.95%. Inspite of exhaustive washing procedures, ash due to the catalyst residues was always present because of its insolubility to the washing solvents. The Mo and Al catalyst residues were detected by energy dispersive X-ray analysis.

Structural analysis of the polymer by various instrumental methods revealed the conjugated polymer backbone structure with 3-hydroxyphenyl substituents although the exact molecular structure of polymer was not clear due to its poor solubility.

The poly(EP)s were generally dark-brown or black powders. The final poly(EP)s were insoluble in any organic solvents regardless of the catalysts and the polymerization methods. The reason for the insolubility was assumed to be due to the

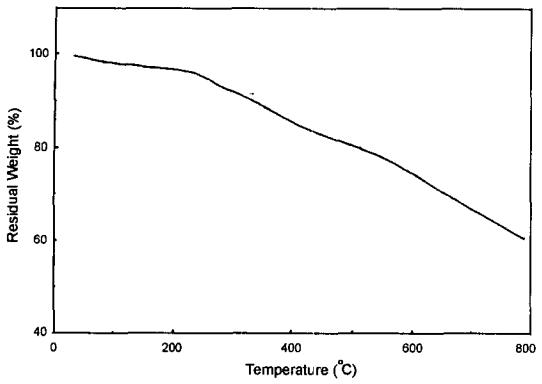


Figure 4. TGA thermogram of poly(EP) prepared by WCl_6-$EtAlCl_2$.

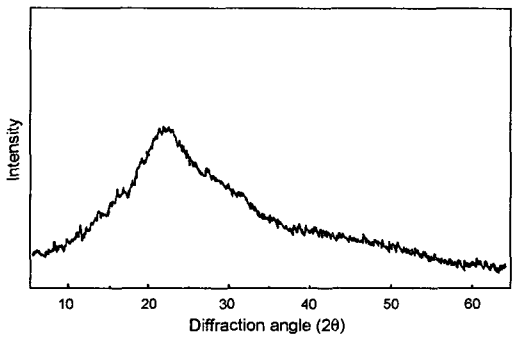


Figure 5. X-ray diffractogram of poly(EP) prepared by WCl_6-$EtAlCl_2$.

increased crosslinking reaction of polymer by the hydroxy group of phenyl substituents during the polymerization.

The poly(EP) was also found to be stable to air oxidation. Even after standing at air for 1 month, the IR spectrum of poly(EP) did not showed any carbonyl carbon absorption peak around 1710 cm^{-1}, which is usually observed with conjugated polymers due to the spontaneous air-oxidation.

Figure 4 is the typical TGA thermogram of poly(EP) prepared by WCl_6-$EtAlCl_2$ catalyst system. It shows that the polymer retains 98% of its original weight at 100°C, 95% at 261°C, 90% at 333°C, 80% at 516°C, and 70% at 665°C. The char yield after heating upto 800°C was 60.5%.

The morphology of poly(EP) was also investigated by X-ray diffraction analysis (Figure 5). The broad diffraction pattern and the ratio of the half-height width to diffraction angle ($\Delta 2\theta/2\theta$) which is greater than 0.35[60] indicated that the poly(EP)s are amorphous.

Conclusions

A conjugated polymer bearing hydroxy-group, poly(EP), was successfully synthesized via the polymerization of the corresponding monomer (EP) with various transition metal catalysts. The catalytic activity of WCl_6-based catalyst system was found to be greater than that of $MoCl_5$-based catalysts. The extent of decrease of polymer yield according to the M/C and $[M]_0$ values was found to be more severe because of the poisoning effect of the phenyl hydroxy group. The resulting poly(EP)s were mostly insoluble in common organic solvents regardless of the catalyst and the reaction conditions. The conjugated polymer backbone structure with 3-hydroxyphenyl substituents was characterized by various instrumental methods. The resulting poly(EP) was found to be stable to air oxidation.

References

(1) Y. S. Gal and S. K. Choi, *Polymer (Korea),* **13**, 188 (1989).
(2) S. K. Choi, Y. S. Gal, S. H. Jin, and H. K. Kim, *Chem. Rev.,* **100**, 1645 (2000).
(3) B. S. Kim, L. Chen, J. P. Gong, and Y. Osada, *Korea Polym. J.,* **8**, 116 (2000).
(4) K. Tanaka, H. Matsuya, T. Masuda, and T. Higashimura, *J. Appl. Polym. Sci.,* **30**, 1605 (1985).
(5) T. Masuda, Y. Iguchi, B-Z. Tang, and T. Higashimura, *Polymer,* **29**, 2041 (1988).
(6) Y. Nagase, K. Sugimoto, Y. Takamura, and K. Matsui, *J. Appl. Polym. Sci.,* **43**, 1227 (1991).
(7) H. Nishide, H. Kawakami, Y. Sasame, K. Ishiwata, and E. Tsuchida, *J. Polym. Sci., Polym. Chem. Ed.,* **30**, 77 (1992).
(8) T. Mizumoto, T. Masuda, and T. Higashimura, *J. Polym. Sci., Polym. Chem. Ed.,* **31**, 2555 (1993).
(9) Y. H. Kim and S. K. Kwon, *Korea Polym. J.,* **5**, 100 (1997).
(10) T. G. Toy, K. Nagai, B. D. Freeman, I. Pinnau, Z. He, T. Masuda, M. Teraguchi, and Yu. P. Yampolskii, *Macromolecules,* **33**, 2516 (2000).
(11) E. Yashimura, T. Matsushima, T. Nimura, and Y. Okamoto, *Korea Polym. J.,* **4**, 139 (1996).
(12) T. Aoki, K.-I. Shinohara, T. Kaneko, and E. Oikawa, *Macromolecules,* **29**, 4192 (1996).
(13) S. H. Jin, S. H. Kim, H. N. Cho, and S. K. Choi, *Macromolecules,* **24**, 6050 (1991).

(14) S. J. Choi, S. H. Jin, W. S. Ahn, H. N. Cho, and S. K. Choi, *Macromolecules,* **27**, 309 (1994).
(15) K. Akagi, H. Goto, H. Shirakawa, S. Y. Oh, and K. Araya, *Synth. Met.,* **69**, 13 (1995).
(16) S. K. Choi, J. H. Lee, S. J. Kang, and S. H. Jin, *Prog. Polym. Sci.,* **22**, 693 (1997).
(17) A. Furlani, G. Iucci, M. V. Russo, A. Bearzotti, and A. D'Amico, *Sensors and Actuators B.,* **7**, 447 (1992).
(18) L. S. Hwang, J. M. Ko, H. W. Rhee, and C. Y. Kim, *Synth. Met.,* **55-57**, 3671 (1993).
(19) S. H. Jin, J. W. Park, S. K. Choi, H. N. Cho, S. Y. Park, N. J. Kim, T. Wada, and H. Sasabe, *Mol. Cryst. Liq. Cryst.,* **247**, 129 (1994).
(20) D. W. Samuel, I. Ledoux, C. Dhenaut, J. Zyss, H. H. Fox, R. R. Schrock, and R. J. Silbey, *Science,* **265**, 1070 (1994).
(21) C. Halvorson, A. Hays, B. Kraabel, R. Wu, F. Wudl, and A. J. Heeger, *Science,* **265**, 1215 (1994).
(22) Y. S. Gal, W. C. Lee, S. S. Lee, J. S. Bae, B. S. Kim, S. H. Jang, S.H. Jin, and J. W. Park, *Korea Polym. J.,* **8**, 131 (2000).
(23) S. K. Choi, J. H. Lee, and H. K. Kim, *Macromol. Symp.,* **118**, 67 (1997).
(24) K. Tada, R. Hidayat, M. Hirohata, M. Teraguchi, T. Masuda, and K. Yoshino, *Jpn. J. Appl. Phys.,* **35**, L1138 (1996).
(25) Y. S. Gal, S. S. Lee, J. S. Bae, B. S. Kim, S. H. Jang, and S. H. Jin, *Bull. Korean Chem. Soc.,* **20**, 451 (1999).
(26) W. C. Lee, J. E. Sohn, Y. S. Gal, and S. K. Choi, *Polymer (Korea),* **12**, 720 (1988).
(27) W. C. Lee, M. W. Huh, Y. S. Gal, and S. K. Choi, *Polymer (Korea),* **13**, 520 (1989).
(28) W. C. Lee, Y. S. Gal, M. S. Ryoo, S. H. Han, and S. K. Choi, *Polymer (Korea),* **15**, 283 (1991).
(29) W. C. Lee, J. H. Seo, Y. S. Gal, S. H. Jin, and S. K. Choi, *Bull. Korean Chem. Soc.,* **14**, 708 (1993).
(30) W. C. Lee, Y. S. Gal, S. H. Jin, S. J. Choi, H. J. Lee, and S. K. Choi, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A31**, 737 (1994).
(31) Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *J. Polym. Sci., Polym. Chem. Ed.,* **30**, 2657 (1992).
(32) Y. S. Gal and S. K. Choi, *Polymer (Korea),* **11**, 563 (1987).
(33) Y. S. Gal and S. K. Choi, *J. Polym. Sci., Polym. Lett. Ed.,* **26**, 115 (1988)
(34) Y. H. Kim, Y. S. Gal, and S. K. Choi, *Macromolecules,* **21**, 1991 (1988).
(35) M. S. Ryoo, W. C. Lee, and S. K. Choi, *Macromolecules,* **23**, 4135 (1990).
(36) Y. S. Gal, W. C. Lee, H. J. Lee, S. H. Jang, and S. K. Choi, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A34**, 2251 (1997).
(37) K. L. Kang, S. H. Kim, H. N. Cho, K. Y. Choi, and S. K. Choi, *Macromolecules,* **26**, 4539 (1993).
(38) S. H. Kim, S. J. Choi, J. W. Park, H. N. Cho, and S. K. Choi, *Macromolecules,* **27**, 2339 (1994).
(39) R. K. Bartlett, G. O'Neill, H. S. Turner, and W. F. Wall, *Br. Polym. J.,* **4**, 503 (1972).
(40) L. A. Akopyan, S. G. Grigoryan, G. A. Zhamkochyan, and S. G. Matsoyan, *Vysokomol. Soedin., Ser. A,* **17**, 2517 (1975).
(41) L. S. Meriwether, M. F. Leto, E. C. Colthup, and G. W. Kennerly, *J. Org. Chem.,* **27**, 3930 (1962).
(42) A. Furlani, M. V. Russo, P. Carusi, S. Licoccia, E. Leoni, and G. Valenti, *Gazz. Chim. Ital.,* **113**, 671 (1983).
(43) S. Okamura and K. Hayashi, Japan 7886 (1986); *Chem. Abst.,* **59**, 7671h.
(44) K. Yoshimura, T. Kitade, K. Kitamura, and K. Hozumi, *J. Appl. Polym. Sci.,* **38**, 1011 (1989).
(45) M. G. Voronkov, V. B. Pukhnarevich, S. P. Sushchinskaya, V. Z. Annenkova, V. M. Annenkova, and N. J. Andreeva, *J. Polym. Sci., Polym. Chem. Ed.,* **18**, 53 (1980).
(46) Y. S. Gal, B. Jung, W. C. Lee, and S. K. Choi, *Polymer (Korea),* **16**, 597 (1992).
(47) Y. S. Gal, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A32**, 61 (1995).
(48) M. Yang, M. Zheng, A. Furlani, and M. Russo, *J. Polym. Sci., Polym. Chem. Ed.,* **32**, 2709 (1994).
(49) M. Yang, H. Sun, and W. Chen., *Polymer International,* **27**, 928 (1995).
(50) A. Usanmaz and N. Kizilirmak, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A29**, 1175 (1992).
(51) Y. S. Gal, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A31**, 703 (1994).
(52) M. V. Russo, G. Iucci, G. Polzonetti, and A. Furlani, *Polymer,* **33**, 4401 (1992).
(53) Y. S. Gal, B. Jung, J. H. Kim, W. C. Lee, and S. K. Choi, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A31**, 1177 (1994).
(54) P. M. Hergenrother, R. G. Bryant, B. J. Jensen, and S. J. Havens, *J. Polym. Sci., Polym. Chem. Ed.,* **32**, 3061 (1994).
(55) G. W. Meyer, T. E. Glass, H. J. Grubbs, and J. E. McGrath, *J. Polym. Sci., Polym. Chem. Ed.,* **33**, 2141 (1995).
(56) T. Masuda, K.-I. Hasegawa, and T. Higashimura, *Macromolecules,* **7**, 728 (1974).
(57) Y. S. Gal, H. N. Cho, and S. K. Choi, *J. Polym. Sci., Polym. Chem. Ed.,* **24**, 2021 (1986).
(58) Y. S. Gal and W. C. Lee, *J. Macromol. Sci.-Pure and Appl. Chem.,* **A37**, 133 (2000).
(59) Y. S. Gal, B. Jung, J. H. Kim, W.C. Lee, and S. K. Choi, *J. Polym. Sci., Polym. Chem. Ed.,* **33**, 307 (1995).
(60) T. Masuda and T. Higashimura, *Acc. Chem. Res.,* **17**, 51 (1981).