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DOUBLE RING-FORMING CYCLOPOLYMERIZATION OF TRIPROPARGYLAMMONIUM SALTS BY TRANSITION METAL CATALYSTS

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Key Words: Cyclopolymerization, Tripropargylammonium Salts, Conjugated Polymer, Transition Metal Catalyst, Ionic Polymer

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ABSTRACT

Double ring-forming cyclopolymerization of tripropargylammonium monomers having three polymerizable acetylene functionalities in the same monomer was carried out by various transition metal catalysts such as $MoCl_5$-$EtAlCl_2$, WCl_6-$EtAlCl_2$, $PdCl_2$, $PtCl_2$, $RuCl_3$, etc. In general, the polymerization proceeded well to give a relatively high yield of polymers. Poly(tri-propargylammonium tosylate) and poly(tripropargyl-ammonium tetraphenylborate), having bulky counter anions such as tosylate and tetraphenylborate, were generally soluble in such organic solvents as DMF, DMSO, and formic acid, whereas the poly(tripropargylammonium bromide) having Br- as counter anion was insoluble in any organic solvents. The instrumental analyses shows that the resulting poly(tripropargylammonium salt)s have a highly conjugated polymer backbone system having such counter ions as bromide, tosylate, and tetraphenylborate. Thermal and morphological properties of the polymers were also studied by TGA/DSC and X-ray diffraction analytical method.

INTRODUCTION

The polymers obtained from substituted acetylenes are expected to show unique properties in the fields of organic semiconductor [1-5], membrane for the separation of gas and liquid mixture [6-10], side-chain liquid crystal [11-13], electron-beam resist materials [14-16], and nonlinear optical materials [17-19].

In a series of our recent studies, we have succeeded in producing conjugated ionic polyacetylenes by the polymerization of mono- and diacetylenic salt monomers using metathesis catalysts [20-24]. An n-self doped conducting polymer having a similar polymer backbone was prepared by treatment of poly(n-hexyldipropargylamine) with methyl trifluoromethanesulfonate in methylene chloride [25].

In recent years, we reported the synthesis of a highly conjugated ionic polymer having two cyclic recurring units per repeating unit from tripropargylammonium bromide with transition metal catalysts [26]. However, this polymer was insoluble in organic solvents regardless of the polymerization catalysts and conditions used. The insolubility of polymer was thought to be due to the rigidity of conjugated polymer chain and/or the crosslinking by the active allyl protons produced via the polymerization.

Now we report the synthesis of highly conjugated ionic polymers by the double ring-forming cyclopolymerization of three tripropargylammonium monomers having bromide, tosylate, and tetraphenylborate as counter anion, and the characterization of the resulting conjugated ionic polymers.

EXPERIMENTAL

Materials

Dipropargylamine (Aldrich Chemicals, 97%) and tripropargylamine (Aldrich Chemicals, 98%) were used as received. Propargyl bromide (Aldrich Chemicals, 80 wt% solution of toluene) was dried over calcium hydride and fractionally distilled. Tetraphenylboron sodium ($NaBPh_4$, Aldrich Chemicals, 99.5+%) and *p*-toluenesulfonyl chloride (Aldrich Chemicals, 98%) were used as received. $MoCl_5$ and WCl_6 (Aldrich Chemicals, resublimed, 99.9+%), and $EtAlCl_2$ (Aldrich Chemicals, 1.8M solution in toluene) were used without further purification. Ph Sn (Aldrich Chemicals, 97%) was purified by recrystallizing twice from carbon tetrachloride. $PdCl_2$ (Aldrich Chemicals, 99.995%), $PtCl_2$ (Strem), $RuCl_3$ (Aldrich Chemicals), and Me_4Sn (Aldrich Chemicals, 99+%) were used without further purification. The polymerization solvents were analytical grade materials. They were dried with appropriate drying agents and fractionally distilled.

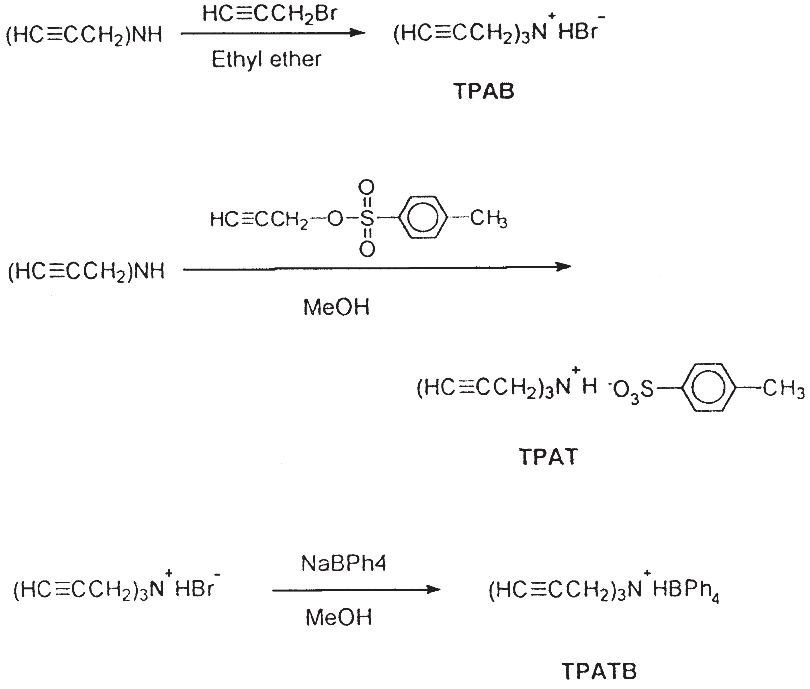
Synthesis of Monomers

The syntheses of tripropargylammonium monomers having three polymerizable functionality were carried out as shown in Scheme 1.

Tripropargylammonium bromide was prepared by the reaction of dipropargylamine and propargyl bromide, and tripropargylammonium tosylate was obtained by the reaction of dipropargylamine and propargyl tosylate under methanol reflux conditions. Finally, tripropargylammonium tetraphenylborate was obtained by the ion exchange reactions of tripropargylammonium bromide using tetraphenylboron sodium in methanol.

Propargyl Tosylate [20]

In a 1000 mL three-neck flask with a thermometer, an ice-water bath, and a 250 mL dropping funnel were placed propargyl alcohol (22.4 g, 0.40 mol) and



Scheme 1. Synthesis of Tripropargylammonium Monomers

p-toluenesulfonyl chloride (40.04 g, 0.21 mol). From the dropping funnel, 65 mL of a 5 N NaOH solution was added dropwise at a rate that did not cause the temperature of the reaction mixture to exceed 15°C. Another portion of *p*-toluenesulfonyl chloride (40.04 g, 0.21 mol) was added and then 65 mL of a 5 N NaOH solution was slowly added. Additional stirring was continued for 4 hours and the oily layer was separated from the water layer by extraction with diethyl ether. The ether layer was washed thoroughly with 150 mL of 10% NaOH solution and dried by stirring overnight over 50 g of anhydrous K_2CO_3. After removal of the solvent, the residue was distilled at reduced pressure. 51.30 g of propargyl tosylate was obtained (61% yield, bp 107-110°C/1mmHg).

^{1}H-NMR (δ, ppm, $CDCl_3$): 2.29 (s, -CH_3), 2.49 (t,≡C-H), 4.56 (O-CH_2-C≡), 7.20-7.67 (phenyl ring). ^{13}C-NMR (δ, ppm, $CDCl_3$): 21.06 (-CH_3), 57.13 (O-CH_2-), 75.01 (≡C-H), 77.34 (-C≡), 126.40-145.03 (aromatic carbons). IR (wavenumbers, cm^{-1}, KBr pellet): 3287, 2137, 1597, 1362, 1101, 1096, 982, 933, 819, 666, 562.

Tripropargylammonium Bromide [TPAB]

To a stirred solution of dipropargylamine (10.0 g, 0.107 mol) in 200 mL of dry ethyl ether was added propargyl bromide (14.0 g, 0.118 mol) at room temperature. After 1 hour, the white precipitates were formed. The reaction mixture was stirred for additional 24 hours. After the solvent was removed, 20.42 g (0.096 mol) of TPAB was obtained (90% yield, mp 50°C). It was recrystallized with a mixed cosolvent of ether and THF.

^{1}H-NMR (δ, ppm, DMSO-d_6): 3.72 (t, ≡C-H), 3.93 (δ, -CH_2-), 9.7 (N-H). ^{13}C-NMR (δ, ppm, DMSO-d_6): 34.76 (C of -CH_2-), 74.27 ≡C-H), 79.88 (-C≡). IR (wavenumbers, cm^{-1}, KBr pellet): 3244, 2962, 2138, 1454, 1014, 721, 690.

Tripropargylammonium Tosylate [TPAT]

To a stirred solution of dipropargylamine (10.0 g, 0.107 mol) in 300 mL of dried methanol was added propargyl tosylate (24.0 g, 0.114 mol) at room temperature. After the reaction mixture was refluxed for 12 hours, the methanol was removed from the reaction mixture under partial vacuum. The crude product (dark-red) was washed several times with ethyl ether. The THF solution of the residual oily product was poured into excess ethyl ether. The precipitate was filtered from the solution and washed with ethyl ether and dried under vacuum at 40°C for 24 hours. 18.9 g (0.070 mol) of TPAT was obtained (65% yield, mp 123-124°C).

^{1}H-NMR (δ, ppm, DMSO-d_6): 3.94 (CH_3 of tosylate), 4.14 (-CH_2-N), 4.37 ≡C-H), 7.33-7.77 (m, phenyl ring). ^{13}C-NMR (δ, ppm, DMSO-$d_{6,}$): 20.66 (CH_3 of tosylate 34.94 (C of -CH_2-), 70.06 (≡C-H), 79.97 (-C≡), 125.56, 128.29, 138.24, 144.89 (aromatic carbons). IR (wavenumbers, cm^{-1}, KBr pellet): 3294, 2102, 1598, 1210, 680.

Tripropargylammonium Tetraphenylborate (TPATB)

A solution of TPAB (6.0 g, 0.028 mol) in 200 mL of methanol was added to a solution of $NaBPh_4$, (10.3 g, 0.030 mol) in 100 mL of methanol with stirring, and the precipitated product was filtered, washed several times with distilled water and methanol, and dried under vacuum. The product was further purified by the recrystallization from a mixed solvent of chloroform and hexane. 11.30 g (0.025 mol) of TPATB was obtained (95% yield, mp 118°C).

^{1}H-NMR (δ, ppm, DMSO-d_6): 3.67 (≡C-H), 3.94 (-CH_2-N), 4.51 (N-H), 6.84-7.30 (m, phenyl ring). ^{13}C-NMR (δ, ppm, DMSO-d_6): 34.9 (C of -CH_2-), 70.46 (≡C-H), 79.71 (-C≡), 121.6, 125.3, 125.4, 135.6 (aromatic carbons). IR (wavenumbers, cm^{-1}, KBr pellet): 3275, 3083, 2137, 1478, 1428, 712, 710, 606.

Preparation of Catalyst Systems

All procedures for catalyst solution preparation and polymerization were carried out under dry nitrogen atmosphere. $MoCl_5$, WCl_6, and $EtAlCl_2$ were dissolved in chlorobenzene as 0.2 or 0.1 M solution before use. $PdCl_2$, $PtCl_2$, $RuCl_3$, and Ph_4Sn were added as powders to the polymerization ampoule.

Polymerization Procedures

A polymerization ampoule equipped rubber septum was flushed with dry nitrogen. Injection of solvent and catalyst solution was done by means of hypodermic syringes from which air and moisture were carefully excluded.

Polymerization of TPAB by $PdCl_2$

$PdCl_2$ (0.014 g, 0.079 mmol) was dissolved in DMF (4.21 mL, $[M]_o$ = 0.5) at 90°C. TPAB (0.5 g, 2.36 mmol) was introduced to the catalyst solution. After a given polymerization time (24 hours) at 90°C, 10 mL of DMF was added and the resulting polymer solution was poured into excess n-hexane. The polymer was filtered from the solution and dried under vacuum at 40°C for 12 hours. The polymer yield was 96%.

Polymerization of TPAT by $MoCl_5$-$EtAlCl_2$ (1:2)

In a 20 mL ampoule containing 0.5 g (1.85 mmol) of TPAT, 2.44 mL chlorobenzene ($[M]_o$: 0.50 M) and a mixture of $MoCl_5$ (0.1 M, 0.37 mL, 0.037 mmol) and $EtAlCl_2$ (0.2 M, 0.37 mL, 0.074 mmol) were injected. The polymerization was carried out at 90°C for 36 hours and terminated by adding a small amount of methanol. The resulting polymer was dissolved in THF and precipitated with a large excess of hexane. The polymer was filtered and dried under vacuum at 40°C for 24 hours. The polymer yield was 94%.

Instruments and Measurement

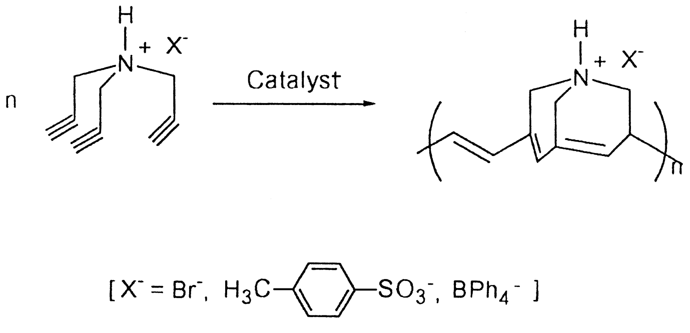
NMR (^{1}H- and ^{13}C-) spectra were recorded on Bruker AM-200 spectrometer in $CDCl_3$ and chemical shifts were reported in ppm units. Infrared spectra were obtained with a BOMEM MB-100 Fournier Transform spectrophotometer using potassium bromide pellets and frequencies were given in reciprocal centimeters. UV-visible spectra were obtained with a Cary 17 spectrometer with Aminco-Y recorder. Inherent viscosities (η_{inh}) of the polymers were measured at a concentration of 0.5g/dL in DMF at 40°C. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere at a heating rate of 10°C/min up to 700°C with a DuPont 9900 thermogravimetric analyzer. DSC thermograms were taken on a DuPont 910 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10°C/min. X-ray diffraction patterns of polymer samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered CuKα radiation at a scan speed of 4°/min.

RESULTS AND DISCUSSION

Polymerization

Double ring-forming cyclopolymerization of three tripropargylammonium monomers was carried out by various transition metal catalysts as shown in Scheme 2.

Table 1 shows the results for the polymerization of TPATB having a highly bulky substituent (BPh_4^-) as counter anion by various transition metal catalysts. The polymerization of TPATB by $MoCl_5$ alone proceeded relatively well to give 64% of polymer yield. Organotin compounds such as Ph_4Sn and Me_4Sn, which have been known as very effective cocatalysts for the polymerization of some acetylene derivatives such as 2-hexyne [27], 2-ethyny-thiophene [28], and



Scheme 2. Polymerization of Tripropargylammonium Monomers

TABLE 1. Polymerization of Tripropargylammonium-tetraphenylborate by Various Transition Metal Catalysts[a]

Experiment	Catalyst system[b] (mole ratio)	M/C[c]	$[M]_0$[d]	Polymer yield (%)
1	$MoCl_5$	50	0.50	64
2	$MoCl_5$-Ph_4Sn(1:1)	50	0.50	58
3	$MoCl_5$-Me_4Sn(1:2)	50	0.50	60
4	$MoCl_5$-$EtAlCl_2$(1:2)	30	0.50	84
5	$MoCl_5$-$EtAlCl_2$(1:2)	50	0.25	81
6	WCl_6	50	0.50	49
7	WCl_6-Ph_4Sn(1:1)	50	0.50	51
8	WCl_6-$EtAlCl_2$(1:2)	50	0.25	73
9	WCl_6-$EtAlCl_2$(1:2)	30	0.50	78
10	WCl_6-$EtAlCl_2$(1:4)	50	0.50	75
11[e]	$PdCl_2$	20	0.50	83
12[e]	$PtCl_2$	20	0.50	65
13[e]	$RuCl_3$	20	0.50	76

[a] Polymerization was carried out for 36 hours in chlorobenzene at 90°C. [b] Mixture of catalyst and cocatalyst was aged at 30°C for 15min before use. [c] Monomer to catalyst mole ratio. [d] Initial monomer concentration. [e] Polymerization solvent was DMF.

phenyl propargyl ethers [29] by WCl_6 and $MoCl_5$, were also used for the present polymerization. However the polymer yields was rather slightly decreased. On the other hand, an organoaluminium compound, $EtAlCl_2$, increased the polymer yield significantly from 64% to 84%. Similar cocatalytic activities of organoaluminium compounds such as $EtAlCl_2$ and Et_2AlCl had been observed for the metathesis polymerization of some acetylene derivatives such as dipropargyl ether [30], propargyl halides (halide: Br, Cl) [31, 32], triethyl α-propargylphosphonoacetate [33], and 4-methoxybiphenyl-oxy-(N,N'-dipropargyl) undecane amide [34] by WCl_6 and $MoCl_5$ catalysts. WCl_6 alone can also polymerized to give the poly(TPATB) in 49% yield. In the polymerization of TPATB by WCl_6, the $EtAlCl_2$ was also found to be an effective cocatalyst. In the present polymerization of TPATB, the catalytic activity of Mo-based catalyst system was found to be similar with those of W-based catalyst system. These polymerization results were found to be similar with those for the polymerization of mono propargyl derivative having a bulky BPh_4^- counter anion, propargyltriphenylphosphonium-tetraphenylborate [$HC{\equiv}CCH_2^+PPh_3^-BPh_4$] [35].

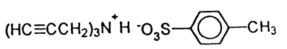
Such transition metal catalysts as $PdCl_2$, $PtCl_2$, and $RuCl_3$, were also effective for the present polymerization of TPATB and gave a relatively high yield of polymers.

Table 2 shows the results for the polymerization of three tripropargylammonium monomers by $MoCl_5$-$EtAlCl_2$ catalyst system. The polymer yield for the polymerization of TPAB having Br^- as counter anion, was quantitative. However, the product, poly(TPAB) was mostly insoluble in any organic solvents. Two other tripropargylammonium monomers such as TPAT and TPATB, were also easily polymerized to show high polymer yield. The resulting two polymers were mostly soluble in organic solvents such as DMF, DMSO, and formic acid, etc. The inherent viscosities of the resulting poly(TPAT) and poly(TPATB) were 0.14 g/dL and 0.07 g/dL, respectively.

Table 3 also shows the results for the polymerization of three tripropargylammonium monomers by WCl_6-$EtAlCl_2$ catalyst system. As mentioned previously, the polymerization behaviors were found to be similar with those of the $MoCl_5$-$EtAlCl_2$ catalyst systems. The inherent viscosities of the resulting poly(TPAT) and poly(TPATB) were found to be slightly lower than those of poly(TPAT) and poly(TPATB) prepared by $MoCl_5$-$EtAlCl_2$ catalyst system. The values were 0.10 g/dL and 0.06 g/dL, respectively.

Table 4 shows the results for the polymerization of tripropargylammonium monomers by $PdCl_2$, $PtCl_2$, and $RuCl_3$ catalysts. The catalytic activity of $PdCl_2$ was generally found to be greater than those of $PtCl_2$ and $RuCl_3$. In the

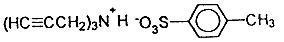
TABLE 2. Polymerization of Tripropargylammonium Monomers by $MoCl_5$-$EtAlCl_2$ Catalyst System[a]

Experiment	Monomer	Polymer yield (%)	η_{inh}[b]
1	$(HC\equiv CCH_2)_3N^+HBr^-$	99	insoluble
2		94	0.14
3	$(HC\equiv CCH_2)_3N^+HBPh_4^-$	84	0.07

[a] Polymerization was carried out for 36 hours in chlorobenzene at 90°C and $EtAlCl_2$ to $MoCl_5$ mole ratio was 2. Initial monomer concentration ($[M]_o$) and monomer to catalyst mole ratio (M/C) were 0.50M and 50, respectively.

[b] Measured at a concentration of 0.5 g/dL in DMF at 40°C.

TABLE 3. Polymerization of Tripropargylammonium Monomers by WCl_6-$EtAlCl_2$ Catalyst System[a]

Experiment	Monomer	Polymer yield (%)	η_{inh}[b]
1	$(HC{\equiv}CCH_2)_3N^+HBr^-$	89	insoluble
2		67	0.10
3	$(HC{\equiv}CCH_2)_3N^+HBPh_4^-$	73	0.06

[a]Polymerization was carried out for 36 hours in chlorobenzene at 90°C and $EtAlCl_2$ to $MoCl_5$ mole ratio was 2. Initial monomer concentration ($[M]_o$) and monomer to catalyst mole ratio (M/C) were 0.50M and 50, respectively.
[b]Measured at a concentration of 0.5 g/dL in DMF at 40°C.

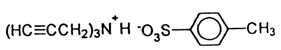
polymerization of tripropargylammonium monomers using $PtCl_2$, similar polymer yields were observed. In the polymerization of TPAB, the polymerization solution seemed to be homogeneous during the polymerization. However the final product, poly(TPAB) after the precipitation and drying process under vacuum, were insoluble. The resulting polymers were mostly black powders. $RuCl_3$ catalyst also showed a high catalytic activity for the present polymerization of tripropargylammonium monomers.

Polymer Structure

The molecular structure of polymers obtained from tripropargylammonium monomers were characterized by various instrumental methods such as NMR (^1H- and ^{13}C-), IR, UV-visible spectroscopies.

Figure 1 shows the ^1H-NMR spectrum of poly(TPAT) prepared by $PdCl_2$ in DMF. It did not show the acetylenic ≡C-H proton peak at 4.37 ppm. Instead, new peaks in the vinyl proton region of conjugated polymer backbone were observed in the 5.0-7.0 ppm region. The aromatic protons of tosylate were also observed in the 7.0-7.7 ppm region. The methyl ($-CH_3$) and methylene ($-CH_2-$) proton peaks were appeared at 2.4 ppm and 3.3 ppm, respectively. Figure 2 shows the ^{13}C-NMR spectrum of poly(TPAT). It shows the disappearance of the acetylenic carbon peaks that were seen at 70.06 ppm and 79.97 ppm. Instead, new peaks due to the olefinic carbons in the polymer backbone were observed at about 140 ppm. The aromatic carbon peaks of tosylate were observed in the 123-136 ppm region.

TABLE 4. Polymerization of Tripropargylammonium Monomers by $PdCl_2$, $PtCl_2$, and $RuCl_2$ Catalyst System[a]

Experiment	Monomer	Polymer yield(%)		
		$PdCl_2$	$PtCl_2$	$RuCl_3$
1	$(HC{\equiv}CCH_2)_3N^+HBr^-$	96	63	85
2		90	67	79
3	$(HC{\equiv}CCH_2)_3N^+HBPh_4^-$	83	65	76

[a] Polymerization was carried out for 24 hours in DMF at 90°C. Initial monomer concentration ($[M]_o$) and monomer to catalyst mole ratio (M/C) were 0.50M and 30, respectively.

Figure 3 shows the magic angle spinning, cross-polarization ^{13}C-NMR spectrum of insoluble poly(TPAB). The broad peak at about 133 ppm is due to the carbons on the conjugated double bond of polymer backbone. And the methyl and methylene carbon peaks were observed broadly in the 10-50 ppm range.

Figure 4 shows the FT-IR spectra of the three polymers from tripropargylammonium monomers in KBr pellets. The FT-IR spectra of these polymers did not show the acetylenic C≡C stretching frequencies at about 2100 cm^{-1} and the acetylenic ≡C-H stretching frequencies at about 3300 cm^{-1}. Instead, more intense peaks around 1620 cm^{-1} due to the C=C stretching frequencies of conjugated polymer backbone were observed. The IR spectrum of poly(TPAT) shows an absorption frequency at 1196 cm^{-1} due to the S=O stretching of sulfonate.

Figure 5 shows the UV-visible spectroscopies of soluble poly(TPAT) and poly(TPATB) in DMSO. A $\pi \rightarrow \pi^*$ absorption peak of conjugated double bonds in the polymer main chain, which are absent in the UV-visible spectra of each monomer, appear up to 650 nm.

From these instrumental analyses, it can be concluded that the present three ionic polymers obtained from tripropargylammonium monomers carrying different counter anions have a highly conjugated polymer backbone system.

Polymer Properties

The solubility test of resulting polymers was performed for powdery samples in excess solvents. Poly(TPAB), which the counter anion is Br^-, was

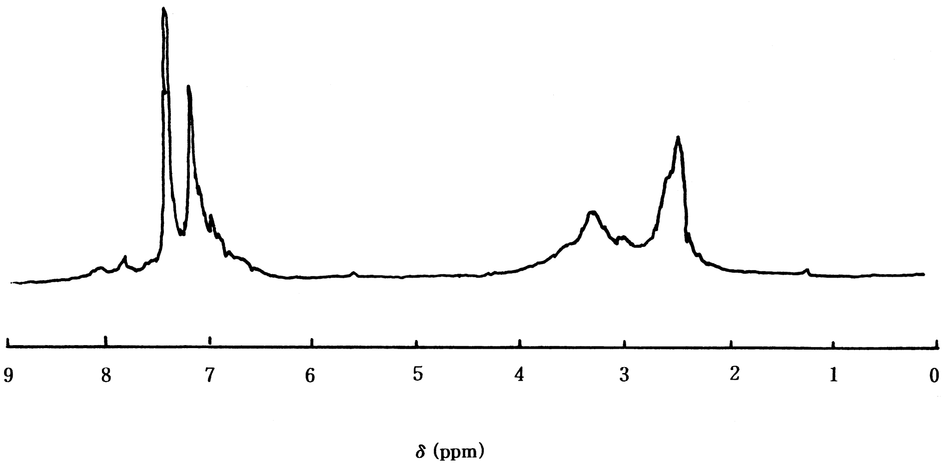


Figure 1. ^{1}H NMR spectrum of poly(TPAT) prepared by $PdCl_2$ in DMF.

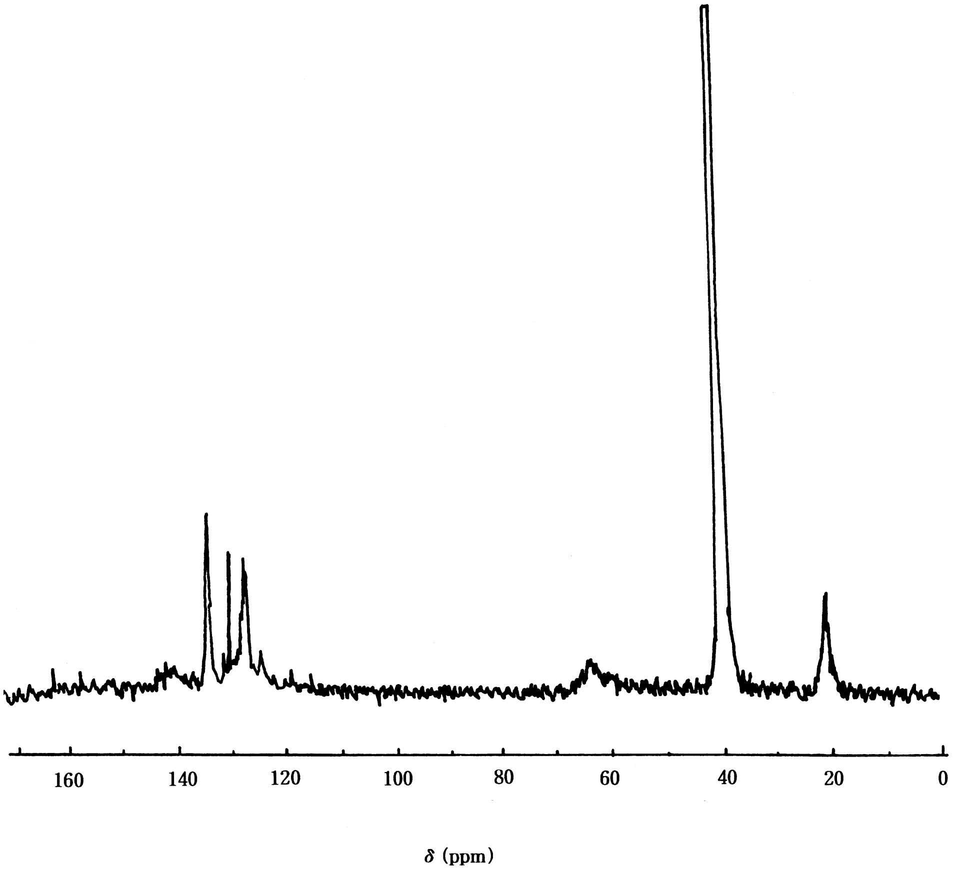


Figure 2. ^{13}C NMR spectrum of poly(TPAT) prepared by $PdCl_2$ in DMF.

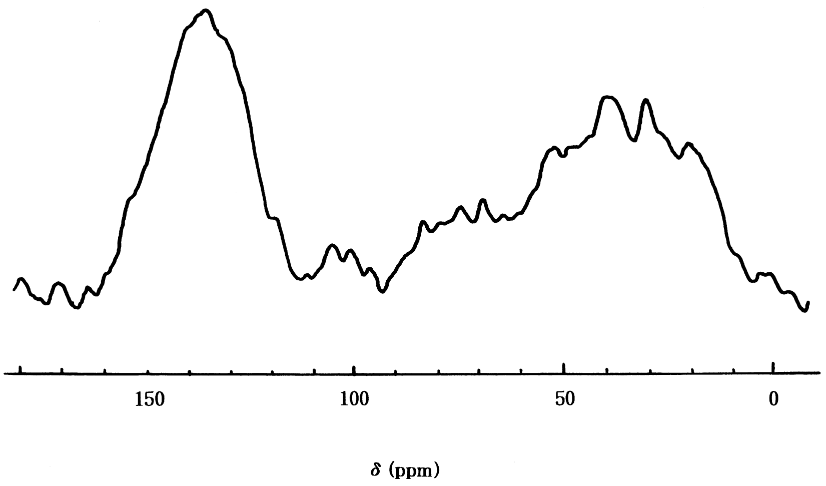


Figure 3. ^{13}C-magic angle spinning-cross polarization NMR spectrum of poly(TPATB) [5-s repetition time, 3.5 ms cross polarization mixing time, 8-W decoupler power, and 3.8-KHz spinning].

found to be insoluble in any organic solvents. The insolubility of poly(TPAB) was attributed to the rigidity of the conjugated polymer and/or the crosslinking by the activated allyl protons of the resulting poly(TPAB). On the other hand, poly(TPAT) and poly(TPATB) having more bulky counter anions such as tosylate and tetraphenylborate were soluble in DMF, DMSO, formic acid, etc.

Thermal properties of these polymers were also studied by the TGA and DSC analytical methods under nitrogen atmosphere. Figure 6 shows the TGA thermograms of three conjugated polymers obtained from tripropargylammonium monomers. The TGA thermograms of poly(TPAB) and poly(TPATB) exhibited some gradual weight losses. The TGA thermogram of poly(TPAB) shows that it retains 92% of its original weight at 200°C, 73% at 300°C, 54% at 400°C, and 32% at 700°C. On the other hand, the TGA thermogram of poly(TPATB) shows that it retains 69% of its original weight at 200°C, 51% at 300°C, 42% at 400°C, and 31% at 700°C. The weight losses at low temperature ≤100°C) seem to be due to the absorbed moisture and residual solvents. The thermograms of 2nd runs for the same samples after 1st heating up to 110°C were essentially similar although the weight loss percentages are slightly lower than those of 1st runs for the same samples. In the TGA thermogram of poly(TPAT) having tosylate as counter anion shows two abrupt weight losses at about 100°C and 280°C. The first weight loss at the temperature range of 100-150°C is assumed to have orig-

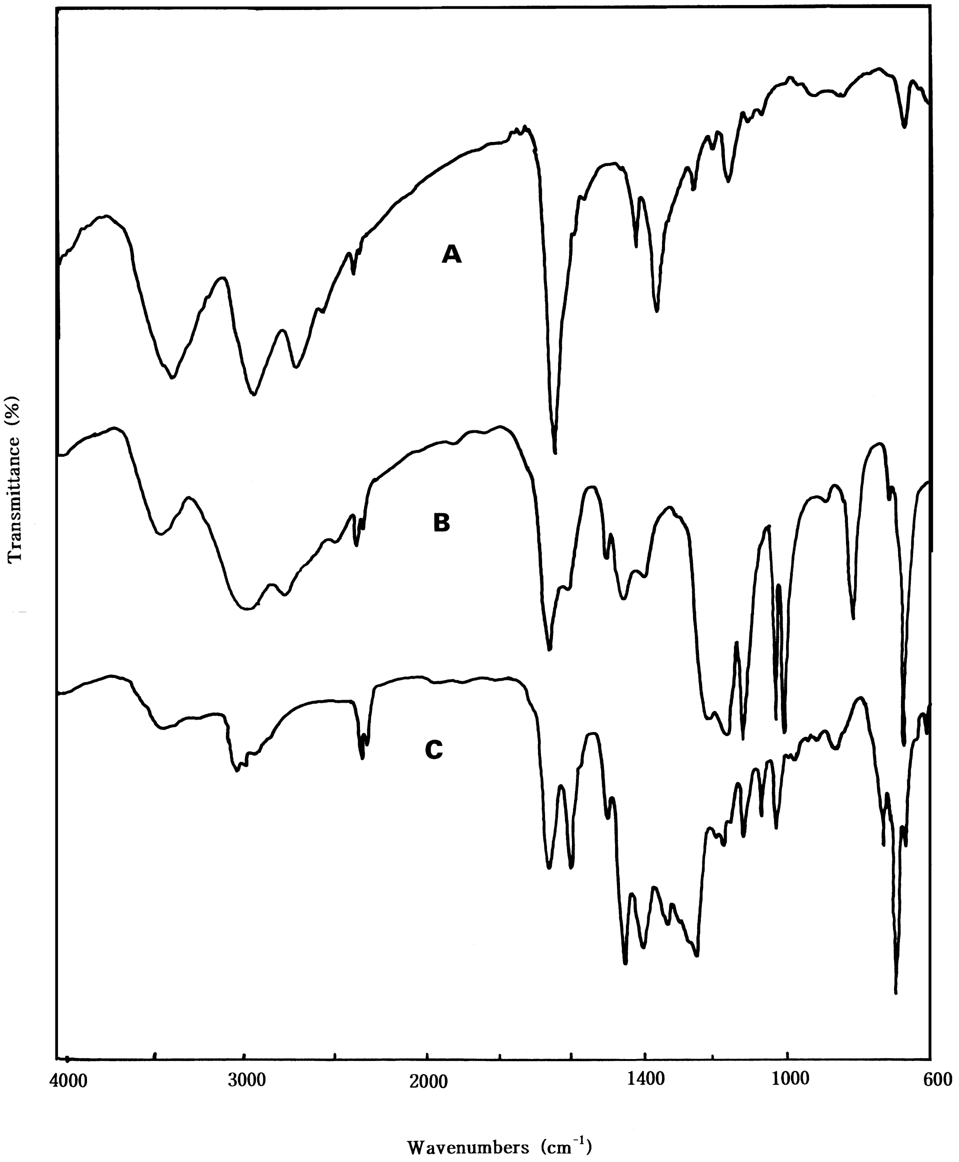


Figure 4. FT-IR spectra of poly(TPAT) [B], and poly(TPAB) [C] in KBr pellet.

inated from the moisture and the thermal decomposition of tosylate functional group of polymer. The second abrupt weight loss starting at about 280°C is due to the thermal decomposition of the polymer main chain system. In addition, poly(TPAT) was found to be more hygroscopic than other two polymers such as

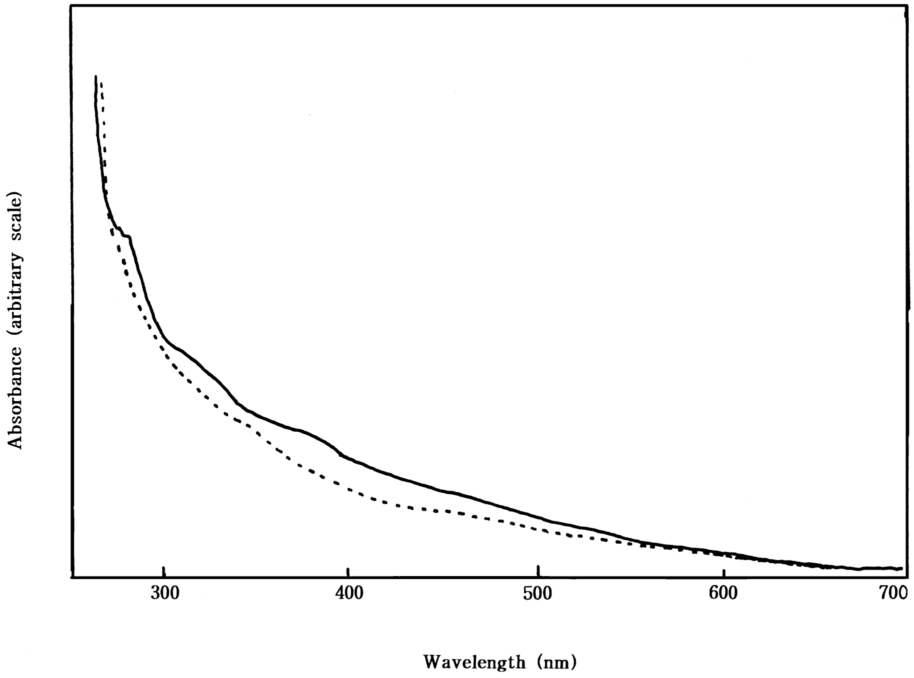


Figure 5. UV visible spectra of poly(TPAT) [——], and poly(TPATB) [...........] in DMSO.

poly(TPAB) and poly(TPATB). The typical DSC thermogram (Figure 7) of poly(TPATB) shows only a featureless exothermic peak starting at about 180°C, which may by originated from the thermal decomposition of polymer system.

The morphological properties of the resulting poly(TPAB) were investigated by X-ray diffraction analysis. Figure 8 shows the X-ray diffractograms of three conjugated polymers prepared from propargylammonium salts. Because the peaks in the diffraction pattern are broad and the ratio of the half-height width to the diffraction angle ($\Delta 2\theta \backslash 2\theta$) are greater than 0.35 [36], the present polymers are mostly amorphous.

CONCLUSION

In this article, we reported the synthesis of novel conjugated polymers having three different counter anions such as Br -, tosylate, and BPh4- from tripropargylammonium monomers. It was concluded that the tripropargyl monomers having three polymerizable acetylenic functionalities in a monomer

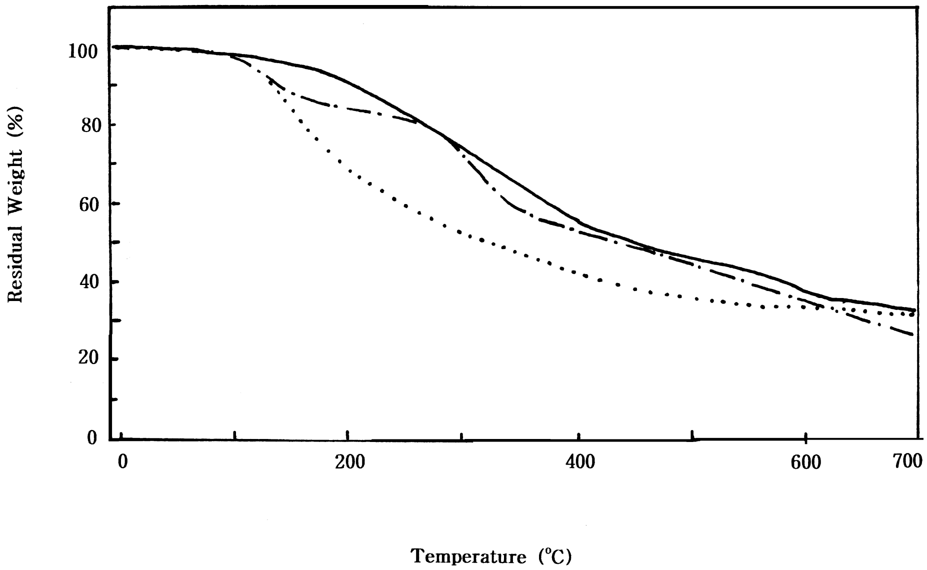


Figure 6. TGA thermogram of poly(TPAB) [———], and poly(TPAT) [–·–·–·], poly(TPATB) [...........].

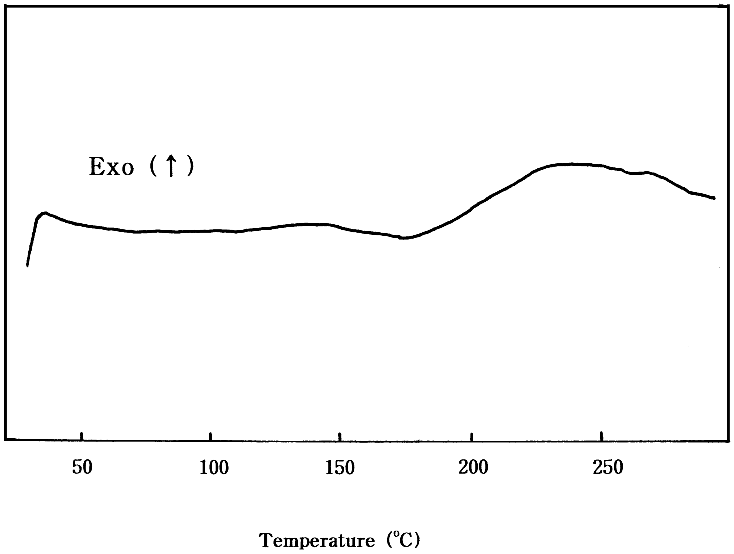


Figure 7. DSC thermogram of poly(TPATB).

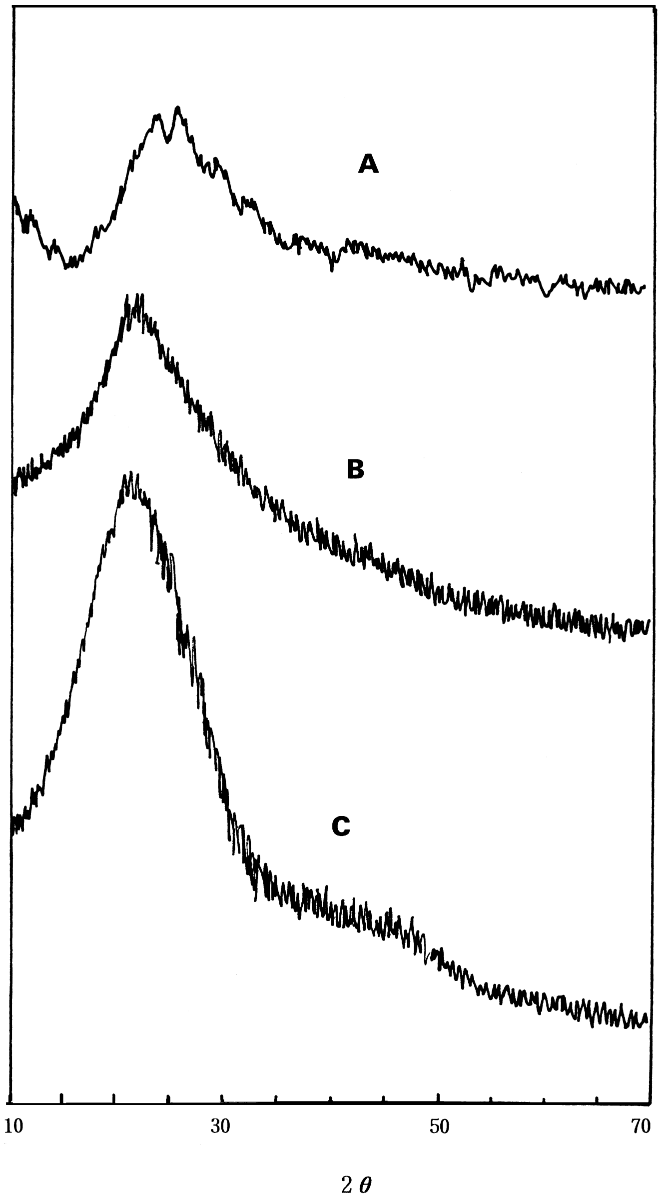


Figure 8. X-ray diffractogram of poly(TPAB) [A], poly(TPAT) [B], poly(TPATB) [C].

are more susceptible to the polymerization reaction, as the results, the polymerization proceed well to give high yield of polymer. The bulky counter anions such as tosylate and tetraphenylborate enhanced the polymer solubility whereas the poly(TPAB) having Br - as counter ion was insoluble in any organic solvents. Various instrumental analyses showed that the present polymers have a highly conjugated polymer backbone system. X-ray diffraction analysis revealed that these conjugated polymers were mostly amorphous.

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