Notes

Polymerization of Phosphorus-Containing Acetylenes. 3. Polymerization of Triethyl α-Propargylphosphonoacetate by Transition Metal Catalysts

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1. Introduction

Polymers having a conjugated backbone are expected to show unique properties such as electrical conductivity,[1–3] gas and liquid mixture separation,[4,5] radiation degradation,[6,7] side-chain liquid crystalline,[8–10] and nonlinear optical properties.[11–13]

A large effort in synthetic chemistry has produced a wide range of mono- and disubstituted polyacetylenes with various pendant groups.[1,14] Various mono- and dipropargyl derivatives have been polymerized and characterized as follows: propargyl halides (halide = Br, Cl),[15] propargyl ethers,[16,17] dipropargyl ether,[18] dipropargylsilanes,[19] dipropargyldiphenylmethane,[20] and so on.

The interesting features of phosphorus polymers are flame-retarding characteristics, adhesion to metals, metal ion-binding characteristics, and increased polarity.[21] Phosphorus-containing polyacetylenes are expected to show properties and functions peculiar to their structure. However, to our knowledge, there have been no reports on the polymerization of phosphorus-containing acetylene derivatives. In recent years, we reported the polymerization of a phosphorus-containing ionic monopropargyl salt, propargyltriphenylphosphonium bromide,[22] and the cyclopolymerization of triethyl dipropargylphosphonoacetate and tetraethyl dipropargylmethylene diphosphonate.[23]

The present paper describes the polymerization of a monopropargyl phosphorus compound, triethyl α-propargylphosphonoacetate (TPPA), by transition metal catalysts and the characterization of the resulting poly(TPPA).

2. Experimental Section

TPPA (Aldrich, 97%) was fractionally distilled after drying with anhydrous $MgSO_4$. $MoCl_5$ and WCl_6 (Aldrich, resublimed, 99+%) and $EtAlCl_2$ (Aldrich, 1.8 M solution in toluene) were used as received. $PdCl_2$ (Aldrich Chemical, 99.995%) and $PtCl_2$ (Strem) were used without further purification. Ph_4Sn (Aldrich, 97%) was purified by recrystallization twice from carbon tetrachloride. The polymerization solvents were analytical grade materials. They were dried with an appropriate drying agent and fractionally distilled.

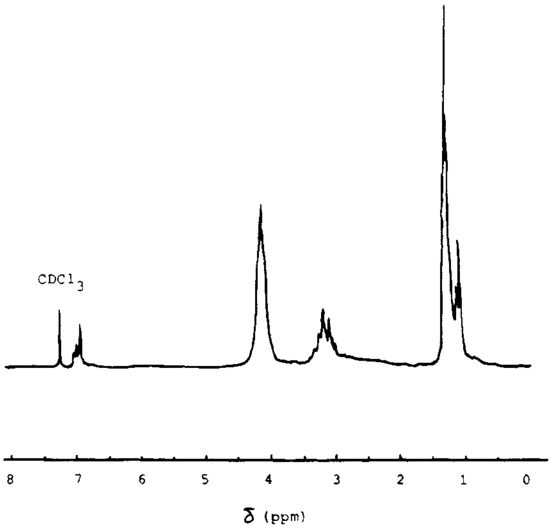

Figure 1. ^{1}H-NMR spectrum of poly(TPPA) in $CDCl_3$.

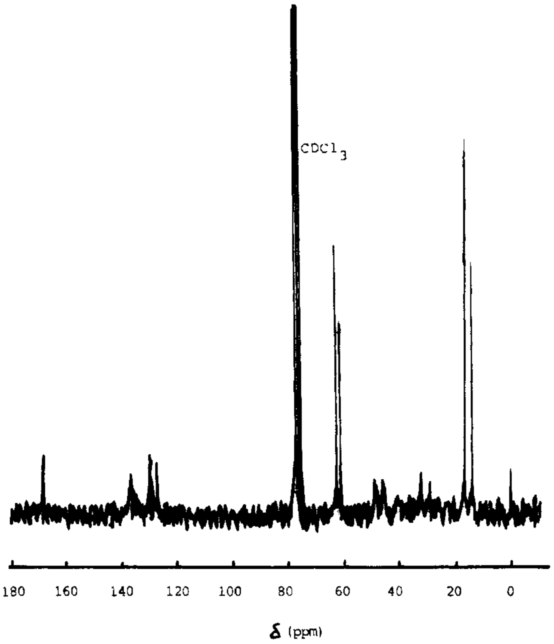

Figure 2. ^{13}C-NMR spectrum of poly(TPPA) in $CDCl_3$.

A polymerization ampule equipped with a rubber septum was flushed with dry nitrogen. Injections of catalyst solution and monomer were done by means of hypodermic syringes. A typical polymerization procedure is as follows: In a 20 mL ampule containing 1.44 mL of chlorobenzene ($[M]_0$ = 0.5 M) were injected the mixture of $MoCl_5$ (0.1 M, 0.381 mL, 0.0381 mmol) and $EtAlCl_2$ (0.4 M, 0.191 mL, 0.0762 mmol) and 0.5 g (1.144 mmol) of TPPA. After standing at 80 °C for 24 h, 10 mL of methanol was added, and the resulting polymer solution was precipitated into excess *n*-hexane. The precipitated polymer was filtered from the solution and dried under vacuum at 40 °C for 24 h.

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Table 1. Polymerization of Triethyl α-Propargylphosphonoacetate by Transition Metal Catalysts[a]

exp no.	cat. system[b] (mole ratio)	M/C[c]	[M]$_0$[d] (M)	solvent	polymer yield[e] (%)	M_n[f]	color
1	WCl_6	30	0.5	chlorobenzene	0		
2	$WCl_6-EtAlCl_2$ (1:2)	30	0.5	chlorobenzene	72	8500	yellow
3	WCl_6-Ph_4Sn (1:1)	30	0.5	chlorobenzene	43	7300	yellow
4	$MoCl_5$	30	0.5	chlorobenzene	trace		
5	$MoCl_5-EtAlCl_2$ (1:2)	15	0.5	chlorobenzene	58	6900	yellow
6	$MoCl_5-EtAlCl_2$ (1:2)	30	0.5	chlorobenzene	45	7400	yellow
7	$MoCl_5-Ph_4Sn$ (1:1)	30	0.5	chlorobenzene	40	6700	yellow
8	$PdCl_2$	15	0.25	DMF	31	4500	brown
9	$PdCl_2$	15	0.25	DMSO	38	5100	brown
10	$PtCl_2$	15	0.25	DMF	17	3300	brown

[a] Polymerization was carried out at 80 °C for 24 h. [b] The mixture of catalyst and cocatalyst in chlorobenzene was aged at 30 °C for 15 min before use. [c] Monomer to catalyst mole ratio. [d] Initial monomer concentration ([M]$_0$). [e] n-Hexane-insoluble polymer yield. [f] Determined by GPC in DMF solution using polystyrene calibration curve.

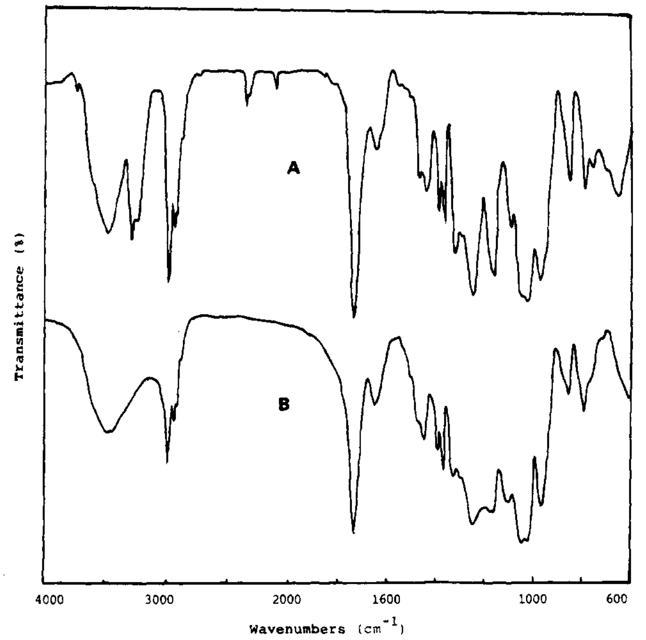


Figure 3. IR spectra of TPPA (A) and poly(TPPA) (B) in KBr pellet.

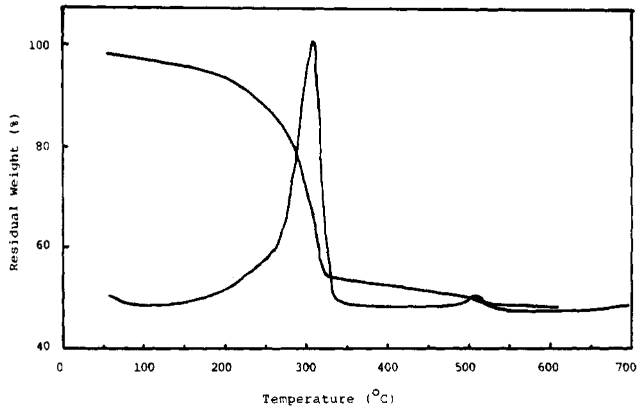
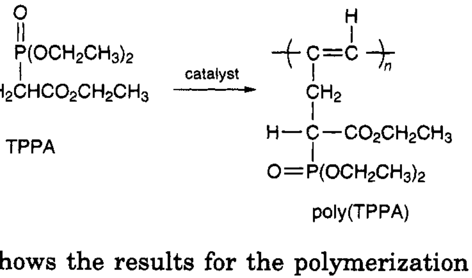


Figure 4. TGA thermogram of poly(TPPA).

NMR (^{1}H and ^{13}C) spectra were recorded on a Bruker AM-200 spectrometer in DMSO-d_6. UV–visible absorption spectra were obtained in methanol on a Shimadzu UV-3100S spectrophotometer. Infrared spectra were obtained with a Bio-Rad Digilab FTS-60 spectrometer using KBr pellets. Thermogravimetic analyses (TGA) were performed with a DuPont 1090 analyzer under a nitrogen atmosphere at a heating rate of 10 °C/min up to 700 °C. X-ray diffraction patterns of the polymer samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a Wahrus flat-plate camera using Ni-filtered Cu Kα radiation at a scan speed of 4°/min.

3. Results and Discussion

The polymerization of TPPA was carried out by various transition metal catalysts.



$$nHC{\equiv}CCH_2CH(P(O)(OCH_2CH_3)_2)CO_2CH_2CH_3 \xrightarrow{\text{catalyst}} -\!\!\left[C(H){=}C(CH_2CH(CO_2CH_2CH_3)P(O)(OCH_2CH_3)_2)\right]_n\!\!-$$

Table 1 shows the results for the polymerization of TPPA by various transition metal catalysts. WCl_6 and $MoCl_5$ alone gave no polymer. The catalytic activity of WCl_6 and $MoCl_5$ was increased by using cocatalysts such as $EtAlCl_2$ and Ph_4Sn. The highest polymer yield (72%) was obtained when the $WCl_6-EtAlCl_2$ catalyst system was used. From these experimental results using W- and Mo-based catalysts, it was found that the phosphonoacetate functional group did not poison the catalysts. Classical $PdCl_2$ and $PtCl_2$ were also used for the present polymerization. In general, the polymerization by $PdCl_2$ and $PtCl_2$ proceeded slowly to give a moderate yield of polymer (17–38%).

Poly(TPPA)s obtained with W- and Mo-based catalysts were yellow whereas the poly(TPPA)s obtained with $PdCl_2$ and $PtCl_2$ were mostly brown. The average molecular weights ($\bar{M}_n$) of the poly(TPPA)s were in the range of 6700–8500, whereas the $\bar{M}_n$'s of the poly(TPPA)s prepared with $PdCl_2$ and $PtCl_2$ were in the range of 3300–5100. The resulting poly(TPPA)s were completely soluble in chlorobenzene, pyridine, methanol, DMF, and DMSO but insoluble in benzene, tetrahydrofuran, hexane, methyl ethyl ketone, and formic acid.

The polymer structure was characterized by various instrumental methods. Figure 1 shows the ^{1}H-NMR spectrum of poly(TPPA) prepared with $MoCl_5-EtAlCl_2$. The peaks at 1.0–1.4 and 2.8–3.4 ppm are due to the methyl protons and the methylene protons adjacent to the oxygen atom, respectively. The peaks at 3.1 and 3.2 ppm are due to $C\mathit{H}P{=}O$ and $C\mathit{H}_2CH$, respectively. The peaks at 6.8–7.1 ppm, which were absent in the NMR spectrum of the monomer, are assigned to the vinyl protons of the conjugated polymer backbone. The ^{13}C-NMR spectrum (Figure 2) of poly(TPPA) shows the presence of olefinic carbons in the polymer backbone at 128 and 136 ppm. Figures 3 shows the IR spectra of TPPA and poly(TPPA) (KBr pellet). The IR spectrum of the polymer showed neither the acetylenic hydrogen (3286 cm^{-1}) nor the carbon–carbon triple-bond stretching (2121 cm^{-1}) frequencies presented in the IR spectrum of the monomer. Instead the peak at about 1640 cm^{-1} became more intense than that of the monomer. The UV–visible spectra showed a characteristic absorption peak of the conjugated polymer, the $\pi \rightarrow \pi^*$ absorption at a long wavelength (up to 500 nm). Figure 4 shows the TGA thermogram of poly(TPPA). This polymer shows a slight weight loss from the initial low temperature. This may be due to the absorbed moisture and organic residues in the polymer. The thermogram shows that poly(TPPA) retains 93% of its original weight at 200 °C, 80% at 283 °C, 55% at 320 °C, and 47% at 700 °C. The morphology of poly(TPPA) was also investigated by X-ray diffraction analysis. Because the peaks in the diffraction patterns are all broad and the ratio of the half-height width to the diffraction angle ($\Delta 2\theta/2\theta$) is greater than 0.35, the present poly(TPPA)s are amorphous.

Further works on the electrical and nonlinear optical properties of poly(TPPA) are now in progress.

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