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Phosphonated poly(1,6-heptadiyne) derivatives prepared by metathesis polymerization for nonlinear optics

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SUMMARY: Poly(triethyldipropargylphosphonoacetate) (TDPA), poly[(tetraethyl dipropargylmethylenediphosphonate) (TDMDP) were prepared by metathesis polymerization using transition-metal catalysts. $MoCl_5$-based catalyst systems were more effective for the polymerization of these monomers than WCl_6-based catalyst systems. Resulting polymers exhibited good solubility in common organic solvents and could be easily cast on glass plates to give thin films. Third-harmonic Maker fringe technique was used to measure third-order nonlinear susceptibility, $\chi^{(3)}$, for thin film of poly(TDPA). The $\chi^{(3)}$ was evaluated to be 3.4 x 10^{-11} esu at incident wavelength of 1.907μm.

Introduction.

Recently increasing interest has been devoted to the electrooptical properties of π-conjugated polymers. These polymers having delocalized π-electron in the main chain are expected to possess extremely large third-order optical susceptibility (1,2) . The highest $\chi^{(3)}$-values ever reported for organic materials were observed for a Shirakawa polyactylene(PA) with a value of 10^{-9} esu and for an oriented PA prepared by Durham method with a value of 2.7 x 10^{-8} esu (3,4) . These highly π-conjugated polyacetylenes, however, are difficult to process because they are rarely fusible and insoluble in solvents. Moigne and co-workors synthesized processable poly(phenylacetylene) derivatives for nonlinear optics (5) . Very recently, we have introduced cyclic polyene main chain with various functional groups which are environmentally stable, and processable (6~8) .

In this paper, we describe the metathesis polymerization and propreties of poly(1,6-heptadiyne)s containing phosphonte group. The phosphoryl group (P=O) provides a stronger coordinating site than the ether or carbonyl group and also improve adhesive properties toward hard tissues (9,10) . Our primary interest in polar phosphonate side group is to modify the chemical and mechanical properties of the conjugated polyene backbone for nonlinear optics.

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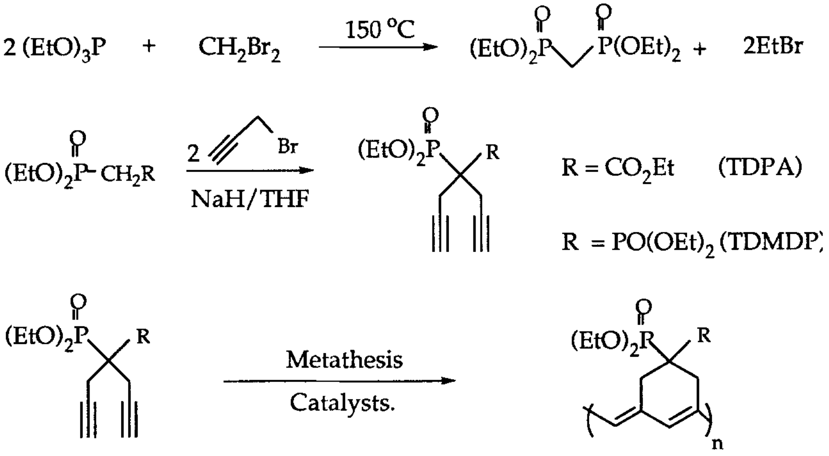
Results and Discussion.

Scheme I outlines the synthesis of the monomers. Tetraethylmethylene diphosphonate was obtained by Michaelis-Arbuzov reaction of triethylphosphite with dibromomethane (11) . α-Dipropargylation of phosphonate with propargyl bromide was carried out successfully using sodium hydride in THF solution.

The cyclopolymerization of dipropargyl derivatives containing mono and diphosphonate group was carried out by metathesis polymerization technique, as show in scheme I.

Scheme I



Catalyst : $MoCl_5$, WCl_6, $PdCl_2$,

Cocatalyst : $(n\text{-}Bu)_4Sn$, $EtAlCl_2$,

Polymerization of TDPA and TDMDP. The results of the polymerization of TDPA and TDMDP by various transition metal catalyst systems are summarized in Table I. In both case, the catalytic activity of $MoCl_5$-based catalyst systems were greater than that of WCl_6-based catalyst system. $EtAlCl_2$ showed more effective activity as cocatalyst than $(n\text{-}Bu)_4Sn$ for the polymerization of TDMDP by $MoCl_5$. The number average molecular weight of poly(TDPA) was in the range of $22 \times 10^3 \sim 46 \times 10^3$, relative to polystyrene standards. The highest number average molecular weight of poly(TDMDP) ($\overline{M}n$=8,200) was obtained with $MoCl_5$ as catalyst. Poly(TDMDP) containing bis-diphosphonate gave only lower molecular weight polymers compared with poly(TDPA) containing phosphonoacetate. It may be due to deactivating effect on catalyst by bis-diphosphonate group.

Table I. Polymerization of Phosphonated Monomers with Various Transition Metal Catalysts[a]

exp no.	monomer system	catalyst system[b] (mole ratio)	M/C[c]	$[M]_o$[d]	polymer yield(%)[e]	$\overline{Mn}$ / 10^3[f]	$\overline{Mw}$/ $\overline{Mn}$[f]
1	TDPA	$MoCl_5$	50	0.25	98	46	3.2
2	TDPA	$MoCl_5$-$EtAlCl_2$(1:4)	50	0.25	83	20	2.6
3	TDPA	$MoCl_5$-$(n\text{-}Bu)_4Sn$(1:4)	50	0.5	76	22	2.3
4	TDPA	WCl_6	50	0.25	trace		
5	TDPA	WCl_6-$EtAlCl_2$	50	0.25	trace		
6	TDPA	$PdCl_2$[g]	50	0.25	30		
7	TDMDP	$MoCl_5$	10	0.5	52	8.2	2.1
8	TDMDP	$MoCl_5$-$EtAlCl_2$(1:4)	25	0.5	78	5.4	2.6
9	TDMDP	$MoCl_5$-$(n\text{-}Bu)_4Sn$(1:4)	10	0.5	44	4.6	1.9
10	TDMDP	WCl_6	10	0.25	trace		
11	TDMDP	WCl_6-$EtAlCl_2$	10	0.25	trace		

[a] Polymerization was carried out at 60°C for 48 hr in dioxane. [b] Mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 min before use. [c]Mole ratio of monomer to catalyst. [d] Initial monomer concentration.
[e] Hexane-insoluble polymer. [f] Values were obtained by GPC analysis.
[g] Polymerization was carried out at 90°C for 48 h in DMF.

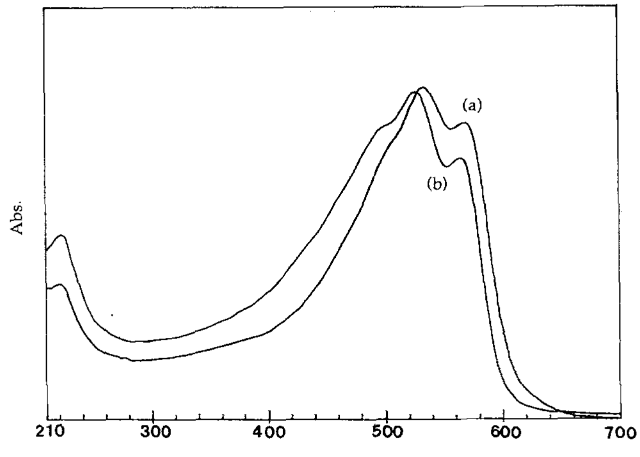


Figure 1. Electronic absorption spectra of poly(TDPA) (a) and poly(TDMDP) (b) in methanol solution. (sample: exp. no.1 and 7 in Table I)

Polymer Structure. The absorption spectra of a polymer solution of poly(TDPA) and poly(TDMDP) are represented in figure 1. The UV-Vis spectra are the same for the solution and for a spin coat film. The absorption spectum of Figure 1(A) shows a large absorption band with a λ_{max} at 534 nm and two shoulder at 565 nm, 500 nm for poly(TDPA). The UV-Vis absorption of polymer depends on degree of π-conjugated system. The UV-Vis absorption of polyene increases with increasing number of consecutive π-conjugated polyenes and shifts longer wavelength (565 nm) for a highly conjugated polymer. A similar trend was reported for conjugation length controled polyene by Schrock et al (12) .

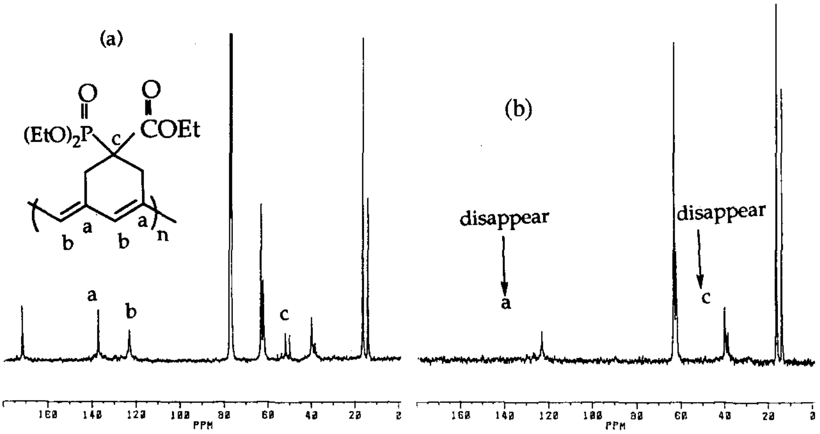


Figure 2. ^{13}C NMR(a) and ^{13}C NMR spectrum obtained by DEPT 45 program (b) of poly(DPPA) (sample: exp. no. 1 in Table I)

Phosphonated polymers are characterized by ^{1}H NMR analysis. As the polymerization proceeded, the acetylenic proton peak at 1.96 ppm disappeared, and new peaks of conjugated cyclic polyene appeared on the region of 6.7-7.3 ppm. Also methylene protons (2.9 ppm, doublet of doublet) which couple with both adjacent phosphorus and acetylene protons shift to the broad peak around 3.4 ppm. The ^{13}C NMR spectra of poly(TDPA) are shown in Figure 2(a). Acetylenic carbon peaks at 71 and 79 ppm disappeared, and new vinylic carbon peaks appeared at 123.2 and 137.2 ppm. Figure 2(b) shows a ^{13}C NMR spectrum obtained by DEPT 45 program. Quaternary carbon atoms give no signal in the DEPT 45 spectrum, but the CH_3, CH_2, and CH peaks are identified as like standard ^{13}C NMR spectrum (13). Quaternary vinylic carbon peak at 137.2 ppm disappeared in Figure 2(b). Two carbon peaks at 50.0 ppm and 51.9 ppm by coupling with adjacent phosphorus (J=570 Hz) also disappeared in Figure 2(b). The IR spectra of polymers showed no absorption at 3275 cm^{-1} and 2150 cm^{-1} which were expected to be present for monosubstituted acetylenic stretching peaks. The characteristic peak of conjugated polyene sequences could be identified in the region of 1660 cm^{-1}.

Polymer Properties. Unlike poly(diethyldipropargyl malonate), phosphonated polymers are good soluble in polar organic solvent such as methanol and acetone, including common organic solvent $CHCl_3$, THF, etc (6) . Poly(TDPA) was ealily film cast for $CHCl_3$ solution at room temperature. These film are farily good mechanical property. But, the poly(TDMDP) film was brittle because of low molecular weight.

The thermal stabilities of polymers were analyzed using thermogravimetry under nitrogen atmosphere. TGA trace indicated that poly(TDPA) was stable up to 270°C. Isothermal pyrolysis showed that at 344°C, 44.3% of the mass which corresponded to a loss of phosphonate group(45.6% mass) was lost. Poly(TDMDP) exhibits an onset of degradation at 133°C, but remains about 57% residue after up to 600°C.

Among nonlinear organic materials, delocalized π -conjugated polymers are expected to possess large third-order optical susceptibility. However, polyacetylene derivatives with processability and large third-order susceptibility have not been reported yet. We studied nonlinear optical properties of the processable phosphonated poly(1,6-heptadiyne) derivative. The third-harmonic generation(THG) measurement was performed using the Maker fringe technique at 1.907μm fundamental wavelength. Since the poly(TDPA) thin film in this experiment has a very week absorption in the third harmonic wavelength region (λ=0.62 - 0.70 μm) (Figure 2), the third-order susceptibility can be estimated. The $\chi^{(3)}$ value of the poly(TDPA) thin film (0.125 μm thickness) was calculated by comparing the measured THG peak intensity of the film with that of the fused quartz substrate using the equation reported elsewhere (14) . From the calculation, the third-order optical susceptibility, $\chi^{(3)}$, was evaluated to be 3.4×10^{-11} esu at 1.907μm wavelength.

Experimental Section

Preparation of monomers. Triethyldipropargylphosphonoacetate (TDPA); Triethylphosphonoacetate (22.4 g, 0.1 mol) was added dropwise to dry THF (200 ml) containing sodium hydride (5.5 g, 0.23 mol) for 1 hr. Propargybromide (32 g, 0.2 mol) was slowly added to the reaction mixture and stirred under room temperature for 12 hrs. After the water was added to quench the reaction, the solution was extracted with ether, then the extracting layer was dried over anhydrous $MgSO_4$. TDPA was obtained by vacuum distillation after evaporating the ether. Yield 72 % (21.6 g), bp 132° C/0.5mmHg. ^1H NMR ($CDCl_3$) d (ppm) 1.2 (q, $-CH_3$), 1.96 (t, $\equiv CH$) 2.9 (d of d, $CH_2C\equiv$), 4.1 (m, $-CH_2-$). ^{13}C NMR ($CDCl_3$) d (ppm), 13 ($-CH_3$ of ester), 16 ($-CH_3$ of phosphonate), 21 ($-CH_2-$ of $CH_2-C\equiv$), 49,5 (C of P-C-), 61.9 ($-OCH_2$ of ester), 63 ($-OCH_2$ of phosphonate), 71 ($\equiv CH$), 79 ($-C\equiv$), 168.7 (carbonyl). ^{31}P NMR ($CDCl_3$) d (ppm) 22.28. IR (neat), 3200 ($\equiv CH$), 1732 (C=O), 1239 (P=O).

Tetraethyl dipropargyl methylene diphosphonate (TDMDP); Dibromomethane (34.8 g 0.2 mol) and triethylphosphite (81.5 g 0.5 mol) were refluxed at 150° C for 2 days, leading to evolution of ethylbromide. The residue was transferred to a microdistillator for removing a byproduct (bromomethyldiethyl phosphonate) or starting materials under vacuum. Tetraethyl methylene diphosphonate was obtained from undistilled colorless liquid and used without further purification (yield, 43.4 %). TDMDP was synthesized in similar method to that of TDPA. But reaction condition was more vigorous e.g. 45° C, 24 hrs. The resulting product was recrystallized from pentane (yield, 53.4 %, mp 77-79°C). ^{1}H NMR ($CDCl_3$) d (ppm), 1.27 (t, $-CH_3$), 2.0 (t, $\equiv CH$), 2.9 (t of d, $-CH_2-C\equiv$). 4.2 (m, $-CH_2-O$). ^{13}C NMR ($CDCl_3$) d (ppm), 16 ($-CH_3$), 20 (t, $-CH_2-C\equiv$), 41,43, 43 (t, PCP), 63 (OCH_2-) 71.5 ($HC\equiv$), 78.7 (t, $-C\equiv$), ^{31}P NMR d (ppm), 23.4. IR (KBr pellet, cm^{-1}) 3200 ($\equiv CH$), 1240 (P=O).

Polymerization. The polymerization was carried out with $MoCl_5$-, WCl_6-, and $PdCl_2$ based catalyst systems as described in the literature (6) .

Instruments for Characterization. ^{1}H-, ^{13}C-NMR spectra were recorded on a Bruker AM-300 spectrometer. FTIR spectra were measured on a BOMEM Michelson using a KBr pellets. UV-visible spectra were obtained with a Cray 17 spectrometer with Aminco-XY recorder. The molecular weights of the polymers were measured by means of GPC 510C Waters using a calibration curve for polystyrene standards. Thermogravimetric analysis(TGA) was performed under nitrogen atmosphere at a heating rate of 10°C/min with TGA Dupont 9900. Nonlinear optical properties was measured by third-harmonic generation method (THG). The poly(TDPA) was dissolved in the casting solvent (5 % dichloromethane) and spun onto a fused quartz plate. A thin-film sample on a fused quartz substrate was mounted on a goniometer and rotated around an axis perpendicular to the direction parallel to the rotational axis. The THG intensities of the poly(TDPA) thin film were measured as a function of laser incident angles.

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