

University of Massachusetts Amherst

From the Selected Works of William MacKnight

1977

Phosphonylation of a Polypentenamer and Preparation of its Hydrogenated Derivatives

William MacKnight, *University of Massachusetts Amherst*
C. Azuma



Available at: https://works.bepress.com/william_macknight/55/

467

Phosphonylation of a Polypentenamer and Preparation of its Hydrogenated Derivatives

C. AZUMA and W. J. MACKNIGHT, *Chemistry Department, Polymer Science and Engineering Department and Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01002*

Synopsis

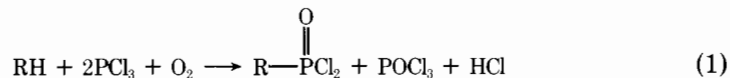
Phosphonylated derivatives of a polypentenamer (PP) containing 82% *trans* and 17% *cis* double bonds have been prepared by the free-radical addition of dimethylphosphite to the double bonds and subsequent hydrogenation of the residual unsaturation. In this way derivatives were prepared containing approximately 5 and 10 mole % dimethylphosphonate side groups. These side groups were further reacted by hydrolysis or neutralization to form phosphonic acid and cesium phosphonate salts. Reaction conditions were so chosen that no backbone degradation occurred, and side reactions leading to crosslinking were avoided. The derivatives were characterized by gel-permeation chromatography (GPC), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), infrared spectroscopy, and nuclear magnetic resonance spectroscopy. It was found that increasing substituent concentration decreases the melting point T_m in the case of the hydrogenated derivatives and increases the glass transition temperature T_g in the case of the unhydrogenated derivatives. The free acid derivatives are the least thermally stable of all those studied and the hydrogenated derivatives are generally more stable than the unhydrogenated derivatives.

INTRODUCTION

We have previously reported chemical modification of a polypentenamer by hydrogenation,¹ addition of thioglycolate side groups,² and hydroformylation.³ The aim of all these studies was the preparation of derivatives containing side groups of differing chemical nature and concentration, but with identical chain backbones. It is thus necessary to carry out the reactions under conditions which prevent backbone modification by scission or crosslinking. Such a restriction drastically limits the number of possibilities. Besides those mentioned above, we have been able to carry out a phosphonylation reaction by reacting dimethylphosphite with the polypentenamer, resulting in the free-radical addition of dimethyl phosphonate ester groups to the double bonds. The residual double bonds in the polypentenamer can be subsequently hydrogenated as was previously done with the other derivatives to yield a crystalline backbone.

It is difficult to incorporate phosphorus into linear polymers by direct polymerization or copolymerization of phosphorus-containing monomers. Therefore most research has been concerned with postpolymerization reactions. Again, the requirements for reactions which form carbon phosphorus bonds but do not degrade the backbone leaves only a small number of reactions to be considered. Sander and Steininger have reviewed a number of such reactions, re-

cently.⁹ The best results seem to have been achieved with polyolefins and polystyrene. In the case of polyolefins, the best method is an oxidative chlorophosphonylation reaction [eq. (1)] with PCl_3 and O_2 .



This method has been previously employed successfully in these laboratories for the modification of low-density polyethylene¹⁰⁻¹³ and appears to proceed without significant backbone degradation up to substituent concentrations of one group per 10 backbone carbons.

For polystyrene, reaction (1) leads to extensive backbone degradation. Phosphonylation of polystyrene may be successfully accomplished by using the Friedel-Crafts reaction with [eq. (2)].



The phosphonylation of several vinyl polymers and cellulose has also been carried out successfully by various routes, and these are described in detail by Sander and Steininger.⁹ The reaction employed in this work, free-radical addition of dimethylphosphite to a double bond, has been applied to natural rubber, and products were obtained containing 5-10% combined phosphorus.¹⁴

In this paper, we report the preparation and characterization of phosphonic ester, acid, and salt derivatives of a polybutadiene (PB) identical to that used in previous studies. These derivatives are directly comparable to the thioglycolate derivatives and carboxylate derivatives and such comparisons are made where appropriate.

In particular, the striking contrast between the properties of the salt derivatives and those of the ester and acid derivatives is evident for all the substituents. Regardless of their chemical nature, the salts uniformly yield elastomeric materials which appear to act as vulcanizates with high tensile strength at room temperature, but are capable of being processed at higher temperatures. In the case of the corresponding hydrogenated derivatives, the salt groups drastically modify the crystal morphology as evidenced by their high degree of optical clarity compared to the hydrogenated esters and acids.

All of these facts are encompassed by a model recently put forward for the structures of such salt-containing polymers which envisages the microphase separation of the salt groups to form domains.⁴

EXPERIMENTAL

Materials

Polybutadiene (PB). This polymer was kindly provided by the Goodyear Tire and Rubber Company and is identical to the polymer used in our previous studies. It consists of 82% *trans* and 17% *cis* double bonds, with less than 1% vinyl side groups. The molecular weight averages are $\bar{M}_n = 94,000$ and $\bar{M}_w = 172,000$.

Reagents. Dimethylphosphite (DMP) and *p*-toluenesulfonyl hydrazide (TSH) (Eastman Kodak Co.) were purified by distillation, and by recrystalli-

zation from ethanol, respectively. Dibenzoyl peroxide (BPO) and cesium hydroxide were used as received.

Solvents. Solvents were purified by standard procedures.

Addition of DMP to PP

A 10-g portion of PP was dissolved in 1000 ml of toluene in a 2-liter, three-necked, round-bottomed flask fitted with a condenser, a thermometer, and a nitrogen gas inlet. A 200-g portion of dimethylphosphite (DMP) was added to the solution. The resulting mixture was heated with stirring at 85–90°C under a nitrogen atmosphere. A 0.35-g portion of BOP in 50 ml of toluene was added dropwise to the mixture through the top of the condenser with a 50-ml syringe. The catalyst was added at the ratio of 35 ml/12 hr. At specified times, the derivatives were recovered by pouring the solution into a 10-volume excess of methanol. The derivative was purified by reprecipitation, dried at room temperature *in vacuo* for 48 hr, and stored under nitrogen with refrigeration.

Hydrogenation of Dimethyl Phosphonate-Substituted PP (PP—PO) with TSH

To a 4-g portion of PP—PO in 300 ml of *p*-xylene, a 20-g portion of TSH was added at 80°C under nitrogen. The resulting mixture was heated with stirring at 135°C for 2 hr. The hydrogenated polymer was isolated by precipitation from methanol. The polymer was purified by reprecipitation from *p*-xylene into methanol.

Hydrolysis of Phosphonyl Groups in PP—PO and Hydrogenated PP—PO (Hy—PP—PO) to Prepare Phosphonic Acid-Substituted PP (PP—POH) and Phosphonic Acid-Substituted Hy—PP (Hy—PP—POH)

The hydrolysis of PP—PO and Hy—PP—PO was carried out using gaseous hydrogen chloride in various solvents. A typical hydrolysis procedure was as follows. A 1-g portion of PP—PO, which contained almost 5 mole % of combined phosphonyl groups, was dissolved in 300 ml of toluene–dioxane (1:1), under nitrogen. Gaseous hydrogen chloride was passed into this polymer solution with stirring at 73–75°C for 3.5 hr. The hydrolyzed polymer was precipitated by pouring the solution into an excess of methanol and dried at room temperature under vacuum for 24 hr. The polymer from PP—PO was immediately dissolved in THF after drying for 3 hr.

The degree of hydrolysis was checked by infrared analysis and was estimated by the titration of residual cesium hydroxide during the preparation of the cesium salt, as described below.

Preparation of the Cesium Salts of PP—PO and Hy—PP—PO (PP—POCs) and (Hy-PP-POCs)

Cesium salts were prepared from PP—POH and Hy—PP—POH by reaction with cesium hydroxide–methanol solution. All of the cesium salts were dried at room temperature under vacuum for 2 days.

Cesium Salts of PP—PO (5%). A 0.2-g portion of PP—POH was dissolved in 100 ml of THF. Cesium hydroxide–methanol solution (0.536 g in 10 ml methanol) was added slowly to the polymer solution with stirring at 72–73°C under nitrogen.

Cesium Salts of PP—PO (10%). A 0.1-g portion of PP—POH was dissolved in 100 ml of THF. To this polymer solution, cesium hydroxide–methanol solution (0.536 g in 20 ml methanol) was slowly added with stirring at room temperature under nitrogen. After 3–4 hr, a half volume of THF solvent in the reaction mixture was removed by vacuum evaporation at room temperature, and the condensed solution was poured into an excess of distilled water. The product was isolated by filtration using a glass filter and washed with sufficient distilled water and a small amount of acetone. The residual cesium hydroxide in the filtrate was titrated with aqueous 0.1*N* hydrochloric acid and methyl red as an indicator.

Cesium Salts of Hy—PP—POH (5%) and Hy—PP—POH (10%). In method I, a 0.4-g portion of Hy—PP—POH (5%) and a 0.2-g portion of Hy—PP—POH (10%) were dissolved in 200 ml of 1,2,4-trichlorobenzene–THF (1:1) with stirring at 72–73°C under nitrogen.

Alternatively (case II), a 0.2-g portion of Hy—PP—POH (5%) and a 0.1-g portion of Hy—PP—POH (10%) were dissolved in 200 ml of *p*-xylene–THF (1:1) with stirring at 72–73°C under nitrogen. To the polymer solution in case I, cesium hydroxide–methanol solution (1.07 g in 10 ml methanol), and to the polymer solution in case II, cesium hydroxide–methanol solution (0.536 g in 10 ml methanol), were added slowly with stirring. After 3 hr, the reaction mixture was poured into 200 ml of methanol. This resulting mixture was adjusted to 500 ml volume of solution with methanol in a 500-ml graduated cylinder. After all of the precipitate settled, a 100-ml portion of the supernatant was pipetted off and titrated with aqueous 0.1*N* hydrochloric acid with the use of methyl red as an indicator. Then, the cesium salt of the polymer was filtered and washed with aqueous methanol and dry methanol.

Characterization

The samples were characterized by elemental, infrared, NMR, and GPC analysis as follows.

Elemental Analysis. Elemental analyses of the samples were performed by the Baron Consulting Co. Analytical Services and the Microanalytical Laboratory, University of Massachusetts. The contents of phosphonyl groups in the polymers were estimated from the results of the elemental analysis.

Infrared Analysis. Film samples of the polymers for infrared measurement were prepared by solvent casting on a NaCl plate and by compression molding at 500 psi at temperatures ranging from 120 to 130°C. Infrared analyses were carried out on a Perkin-Elmer Model 257 grating infrared spectrophotometer. The determination of the contents of phosphonyl groups in the polymers was made on the basis of the absorption band at 820 cm^{-1} (P—O—CH₃) and 1350 cm^{-1} (*trans* C=C) by using standard calibration procedures.

NMR Analysis. NMR measurements of the samples were carried out on a Perkin-Elmer Model R32 NMR spectrometer in carbon tetrachloride using TMS as an internal standard.

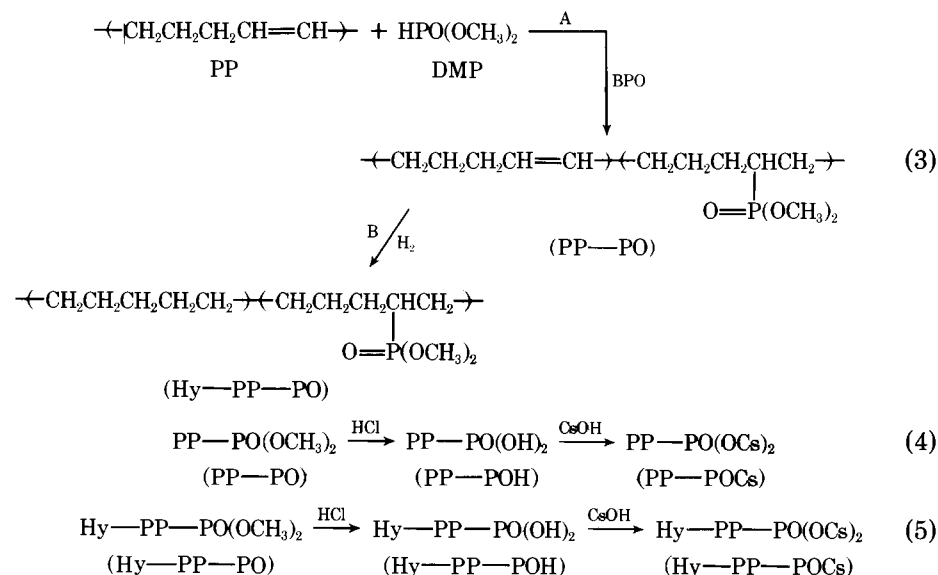
Gel-Permeation Chromatography (GPC). A Waters Associates GPC Model 200 was used for the determination of molecular weight distribution. The experimental conditions were as follows: solvents and temperatures were 25°C in THF and 135°C in trichlorobenzene for the unsaturated and hydrogenated polymers, respectively; columns 10⁶, 10⁵, 10⁴, and 10³ Å; sample concentration, 2 mg/ml; flow rate, 1 ml/min. The columns were calibrated with polystyrene standards of narrow distributions.

Differential Scanning Calorimetry (DSC). DSC measurements were carried out on a Perkin-Elmer Instrument, Model DSC-II. The scanning speed was 10°C/min in all cases, and cyclohexane and indium were used as standards. The temperature range was from -120 to ca. 150°C. The peak temperature of the melting endotherm was taken to be the melting point of the polymers.

Thermogravimetric Analysis (TGA). TGA measurements were carried out in a nitrogen stream on a Perkin-Elmer TGA-1 thermobalance at a scanning speed of 20°C/min in all cases.

RESULTS AND DISCUSSION

Esters, acids, and salts of the phosphonate derivatives of either saturated or unsaturated backbones were prepared by the synthetic routes summarized in eqs. (3)–(5).



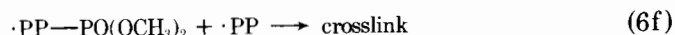
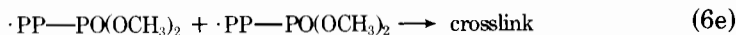
In what follows, we shall discuss each reaction step separately.

Addition of DMP to PP

The reaction of dimethylphosphite (DMP) with an olefin under free-radical conditions results in the addition of dimethyl phosphonate to the double bond.^{5,14} Addition of DMP to PP represented in step A of eq. (3) above was carried out under various conditions as described in Table I, which reveals that by careful control of concentration, temperature, and reaction time it is possible to control

the concentration of combined DMP in amounts ranging from approximately 1 to 20 mole %.

In order to prevent gelation it was necessary to use freshly distilled DMP and to keep the catalyst (BPO) concentration as low as possible. The distilled DMP was used to avoid cationic crosslinking caused by the presence of trace amounts of phosphonic acid in the impure DMP. The BPO concentration must be kept low to avoid free-radical crosslinking reactions. The mole ratio of DMP to PP was greater than or equal to 10 to prevent polymer radical combination and to prevent the addition of BPO radical fragments to the polymer. Some of these undesirable side reactions are summarized in eqs. (6).



The GPC measurements summarized in Table II show minor differences in molecular weights and distributions for the PP—PO derivatives compared to the starting PP. It is doubtful whether the differences noted are significant, inasmuch as problems were encountered with the GPC measurements due to adsorption on the columns. These problems were so severe with the Hy—PP—PO derivatives that it was impossible to obtain meaningful GPC results

TABLE I
Addition of Dimethylphosphite (DMP) To Polypentenamer (PP)

Run	Substrate			Initiator (BPO), mg	Temp., °C	Time, hr	Adduct	
	PP, g	DMP, g	Solvent, ml ^a				IR ratio $\frac{D_{820}}{D_{1350}}$	Combined DMP, mole % ^b
1	2	10	200	400	60	24	0.19	0.9 ^c
2	2	20	200	80	85	24	0.52	2.4 ^c
3	1	20	100 ^d	80	80	3	—	— ^e
4	10	200	1000	476 ^f	90	7	0.35	1.7
						12	0.50	2.3
						27	1.45	6.7
5	1.7	34	170	200 ^f	85	24	1.20	5.6
						48	2.66	12.4
						72	4.42	20.0
6	10	200	1000	848 ^f	85	26	0.76	3.5
						60	2.39	11.1

^a Toluene as solvent unless otherwise noted.

^b Calculated by using a calibration curve made from the result of infrared and carbon analysis.

^c Some fragments of the initiator were seen in the products.

^d Benzene as solvent.

^e Crosslinked.

^f The toluene solution of BPO (70 mg/10 ml toluene) was added dropwise during the reaction.

for these systems, even in trichlorobenzene at 135°C. It is nevertheless evident that the type of branching or crosslinking reactions which could lead to gelation were successfully avoided under the conditions summarized in Table I.

Hydrolysis of Pendant DMP in PP—PO and Hy—PP—PO

Most diesters of phosphonic acid are relatively resistant to alkaline hydrolysis. Thus, the hydrolysis of dimethylphosphite could be carried out only under strongly alkaline conditions at temperatures of 115–125°C.⁶ In contrast, it was found that phosphonates readily undergo hydrolysis with gaseous HCl.⁷ The reaction proceeds as shown in eq. (7).



The reaction scheme in eq. (7) was adapted to the hydrolysis of the PP—PO and Hy—PP—PO derivatives. Various reaction conditions were tried and these

TABLE II
Molecular Weight Averages for PP-PO Derivatives from GPC

Sample	Solvent	Molecular weight		
		$\bar{M}_n \times 10^{-3}$	$\bar{M}_w \times 10^{-3}$	M_w/M_n
PP	THF	82	134	1.63
PP-PO(5)	THF	36	176	4.93
PP-PO(10)	THF	65	135	2.06
Hy-PP-PO(5)	TCB	—	—	—
Hy-PP-PO(10)	TCB	—	—	—

TABLE III
Hydrolysis of Pendant DMP in PP-PO and Hy-PP-PO

	Sub- strate (g)	Reagent		Solvent		Temp, °C	Time, hr	Degree of hydrolysis, %
		Type	Vol, ml	Type	Vol, ml			
PP	0.5	HCl gas		THF	100	65	6	0.5 ^b
	0.5	HCl gas		toluene	100	110	6	0 ^b
PP-PO(5) combined DMP 6.5 mole %	3	5% KOH—MeOH	30	toluene	150	70	5	0
	1	Conc. HCl	2	THF	100	65	5	30 ^c
	1	HCl gas		toluene	150	110	6	100 ^d
	0.5	HCl gas		toluene— dioxane (1:1)	100	95	4	100
PP-PO(10) combined DMP 11.1 mole %	1	HCl gas		toluene— dioxane (1:1)	300	73	3.5	100
	0.5	HCl gas		toluene— dioxane (1:1)	300	73	3.5	100 ^e
	0.5	HCl gas		toluene— dioxane (1:1)	300	73	3.5	100
Hy-PP-PO(5) combined DMP 6.7 mole %	0.3	HCl gas		<i>p</i> -xylene— dioxane (3:1)	200	95	3	100 ^e
	0.1	HCl gas		<i>p</i> -xylene— dioxane (3:1)	100	95	3.5	100
	1	HCl gas		TCB ^e —THF (1:1)	500	73	3.5	100
Hy-PP-PO(10) combined DMP 11.1 mole %	0.5	HCl gas		TCB ^e —THF (1:1)	500	75	3.5	100

^a Calculated from infrared analysis (820 cm⁻¹).

^b Amount of chlorine adduct (mole %).

^c A portion of the product crosslinked.

^d A small portion of the product crosslinked.

^e TCB: 1,2,4-trichlorobenzene.

are summarized in Table III. It was generally found that bubbling HCl gas through solutions of derivatives in polar-nonpolar solvents gave the best results.

Preparation of Salts of PP—PO and Hy—PP—PO

Cesium salts of the derivatives were found to be readily prepared by using methanolic cesium hydroxide in various solvents. The conditions are summarized in Table IV. In general, it was possible to neutralize the derivatives completely, or nearly so.

NMR and Infrared Characterization

Figure 1 shows the NMR spectrum of the 5 mole % methyl ester derivative. Four resonances are discernible in this spectrum. The ($-\text{POCH}_3$) doublet is well resolved in the vicinity of $\delta = 3.7$. This agrees well with literature concerning the chemical shift of the phosphonate ester protons.⁸

The infrared spectra for the methyl ester, acid, and cesium salt derivatives of the PP—PO(5) series are collected in Figure 2, while those for the corresponding hydrogenated derivatives are shown in Figure 3. Some disagreement exists in the literature concerning the assignment of bands in the infrared spectra of phosphonate derivatives. Some of these assignments are collected in Table V. Attention is directed to the band occurring at 820 cm^{-1} in the ester derivatives in Figures 2 and 3, which is not present in the acid and salt forms. It was found that a good correlation exists between the ratio of the peak intensity of this band to the 1350 cm^{-1} (*trans* double bond) band and the concentration of combined phosphonate. This correlation is illustrated in Figure 4. It is seen that both the elemental analysis and NMR results agree quite well with the infrared data. The 820 cm^{-1} band is not present in either the acid or salt forms, indicating that assignment of this band to the P—O—C vibration is indeed plausible. It may be noted that a good correlation also exists between the residual *cis* double-bond concentration and the combined phosphonate concentration. This relationship is exhibited in Figure 5. It was previously found that

TABLE IV
Preparation of Cesium Salts of PP-PO and Hy-PP-PO

Type	Acid combined DMP		Reagent,		Solvent Type	Vol, ml	Temp, °C	Time, hr	Calculated Cation content, %	
	mole %	g	CsOH, g	MeOH, ml					IR ^a	Titration
PP-PO(5)	6.5	0.20	0.536	10	THF	100	72	3	—	95
PP-PO(10)	11.1	0.11	0.536	20	THF	100	room	4	—	105 ^b
Hy-PP-PO(5)	7.5	0.40	0.536	10	TCB— THF (1:1)	200	73	1	90	50 ^b
			1.070	5	TCB— THF (1:1)	200	74	3	100	20 ^b
Hy-PP-PO(10)	11.1	0.10	0.536	10	<i>p</i> -xylene— THF (1:1)	200	72	3	100	95
			0.536	10	<i>p</i> -xylene— THF (1:1)	200	72	4	100	90
			1.070	10	TCB— THF (1:1)	200	73	4	90	35 ^c
			1.070	10	TCB— THF (1:1)	200	73	4	90	35 ^c

^a Calculated from infrared analysis (980 cm^{-1})

^b The value of the titration was used as the difference between that of heated blank solution and that of the reaction mixture.

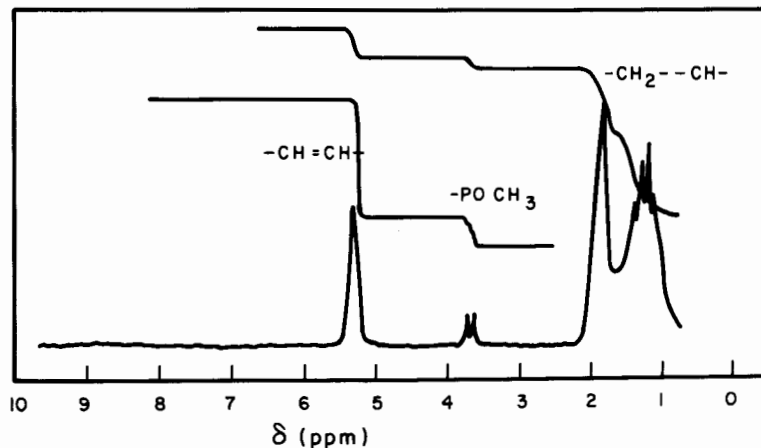


Fig. 1. NMR spectrum of PP—PO(5), 5 wt % carbon tetrachloride solution.

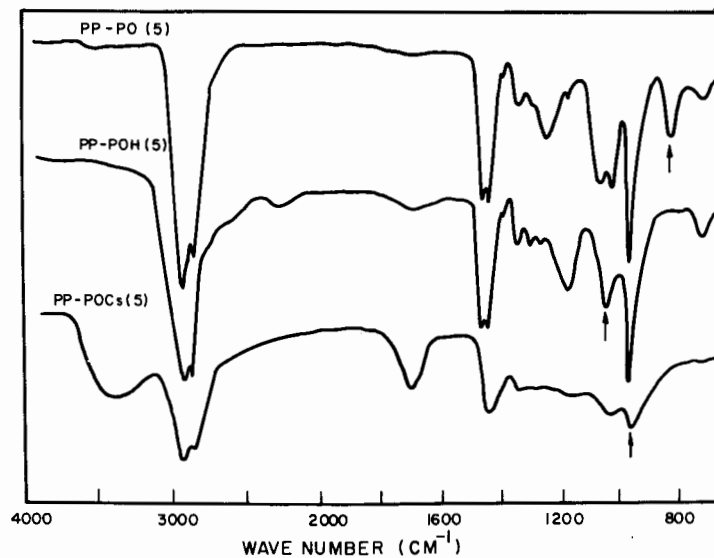


Fig. 2. Infrared spectra of the PP—PO derivatives.

the *cis* double bonds are more reactive to free-radical addition than the *trans* double bonds in the case of the thioglycolate derivatives,² and it is clear that this is also true for the DMP addition reaction.

Properties

The properties of the PP—PO and Hy—PP—PO derivatives are summarized in Table VI. Increasing substituent concentration has the effect of increasing the T_g values of the PP—PO derivatives and decreasing the T_m of the Hy—PP—PO derivatives. The type of substituent, whether ester, acid, or salt, has relatively little effect, however. These observations parallel those made earlier² in the case of the thioglycolate derivatives (PP—S). The magnitude of the ef-

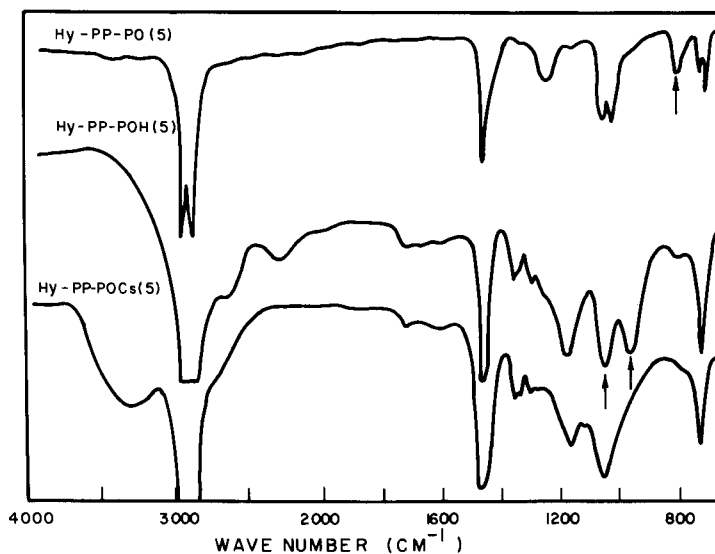


Fig. 3. Infrared spectra of the Hy—PP—PO derivatives.

fects are much greater in the case of the DMP derivatives than the PP—S, however. Figure 6 illustrates the point. The slope of the line in Figure 6 representing the dependence of the T_g of the PP—PO series on pendant group concentration is $4^\circ/\text{mole } \%$, while that of the line representing the dependence of the T_g of the PP—S series on pendant group concentration is $1.2^\circ/\text{mole } \%$. In the case of the hydrogenated derivatives, the slopes of the lines representing the dependence of T_m on pendant group concentration is $-3.4^\circ/\text{mole } \%$ for the Hy—PP—PO series and $-2.2^\circ/\text{mole } \%$ for the Hy—PS series. The T_g effect may be explained at least in part by the suggestion that the T_g of the fully substituted PP—PO polymer must be much greater than that of the fully substituted PP—S polymer. The phosphonyl groups must impart considerably more stiffness to the chain than do the thioglycolate groups. The T_m effect, although less pronounced, is still very considerable. It would appear that the phosphonate groups have a greater disruptive effect on the crystal lattice than do the thioglycolate groups, perhaps by virtue of their greater bulk.

Figures 7 and 8 summarize the results of the TGA analyses for both series of derivatives. In the PP—PO series, the thermal stabilities decrease in the fol-

TABLE V
Infrared Spectral Bands of Phosphonates

Band, cm^{-1}	Assignment ^a	Intensity
2525–2725	—OH (P=O) OH	variable
1150–1362	Free P=O	strong
1087–1261	Hydrogen-bonded P=O	strong
950–1060	P—O—(C) aliphatic	strong
1189	P—O—(CH ₃)	weak
909–1040	P—O—(H)	strong
ca. 800	(P—O)—C	moderate

^a These assignments are based on those of Nakayama¹⁵ and Thomas and Chittenden.¹⁶

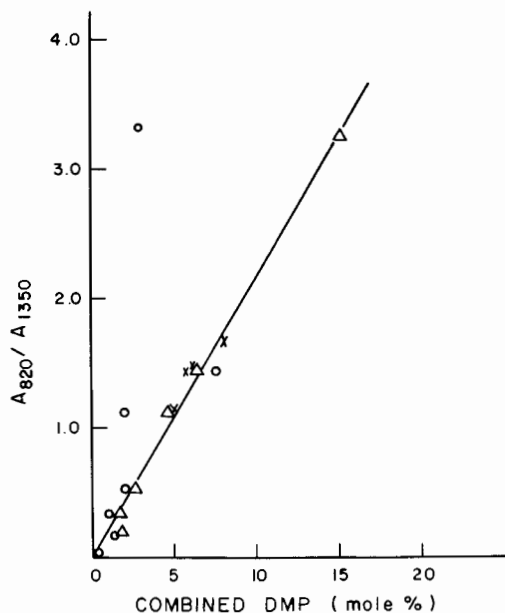


Fig. 4. Dependence of the peak absorbance ratio (A_{820}/A_{1350}) on combined dimethylphosphonate concentration in the PP-PO derivatives: (O) from P analysis; (Δ) from C analysis; (X) from NMR data.

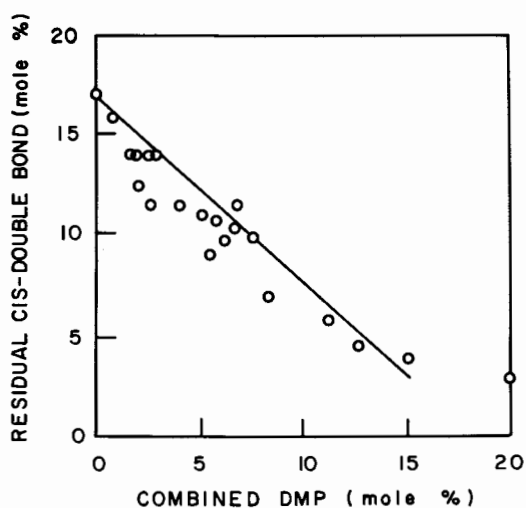


Fig. 5. Dependence of residual *cis* double-bond concentration and combined dimethylphosphonate concentration in the PP-PO derivatives.

lowing order: PP > PP-PO(5) > PP-POCs(5) \geq PP-PO(10) \geq PP-POH(10) \geq PP-POCs(10) > PP-POH(5). In general, the derivatives containing smaller substituent concentrations are more stable than those containing the greater substituent concentrations with the exception of the free acid derivatives.

In the Hy-PP-PO series the thermal stabilities decrease in the following

TABLE VI
 Properties of PP-PO and Hy-PP-PO Derivatives

Sample	Combined DMP, mole % ^a	Ionization, % ^b	T_g , °C ^c	T_m , °C
PP	0		-98	11
PP-PO(5)	6.5		-74	
PP-POH(5)	6.5		-72	
PP-POCs(5)	6.5	95	-70	
PP-PO(10)	11.1		-55	
PP-POH(10)	11.1		-54	
PP-POCs(10)	11.1	100	-53	
Hy-PP	0			131
Hy-PP-PO(5)	6.7			107
Hy-PP-POH(5)	6.7			108
Hy-PP-POCs(5)	6.7	95		103
Hy-PP-PO(10)	11.1			93
Hy-PP-POH(10)	11.1			94
Hy-PP-POCs(10)	11.1	90		95

^a Calculated from infrared analysis and carbon analysis.

^b Percent ionization to pendant content calculated from titration.

^c Determined by DSC.

order: Hy-PP-PO(5) \approx Hy-PP-POH(5) \approx Hy-PP-POH(10) \geq Hy-PP-PO(10) \geq Hy-PP-POCs(5) \geq Hy-PP-POCs(10) \geq Hy-PP.

For the hydrogenated series, it is also true that the derivatives containing small substituent concentrations are more stable than those containing greater substituent concentrations. The hydrogenated series polymers are generally more stable than the unsaturated derivatives as might be expected. In fact, they are at least equal to the unsubstituted hydrogenated derivatives in stability. This is definitely not the case for hydrogenated thioglycolate derivatives, where the Hy-PP polymer is the most stable of the series.²

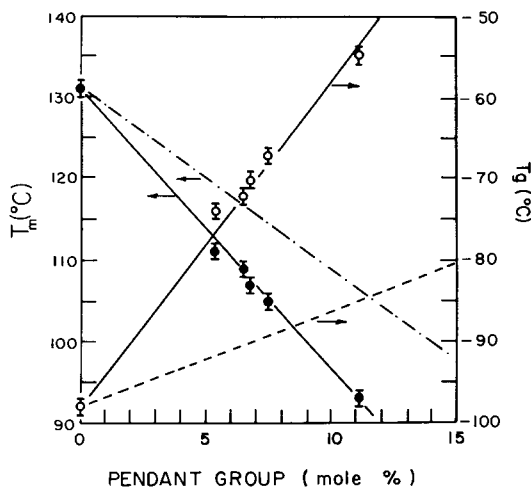


Fig. 6. Dependences of T_m and T_g on substituent content for both phosphonate and thioglycolate substituents: (O) PP-PO; (●) Hy-PP-PO; (- -) PP-S; (- · -) Hy-PP-S.

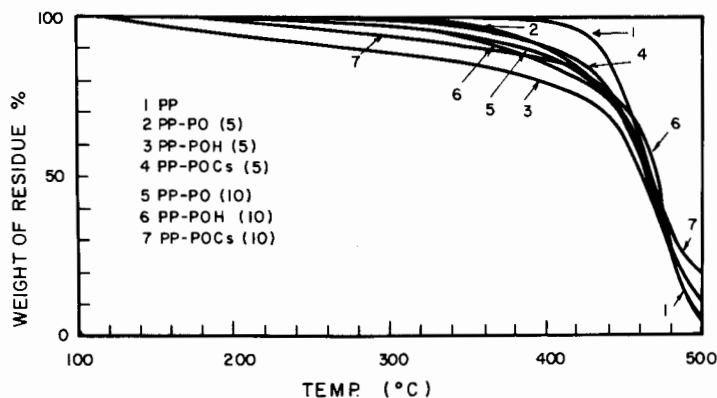


Fig. 7. TGA curves for the PP-PO derivatives.

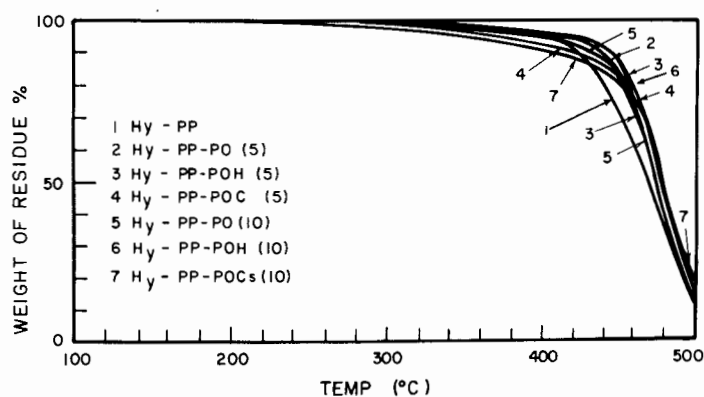


Fig. 8. TGA curves for the Hy-PP-PO derivatives.

In summary, methods have been developed to introduce phosphonate side groups into an unsaturated polymer, polypentenamer, by radical addition of dimethylphosphite. Reaction conditions are elucidated under which substituent concentrations of up to 10 mole % may be obtained without backbone degradation or crosslinking. These polymers are readily hydrogenated with *p*-toluenesulfonyl hydrazide and such hydrogenated derivatives possess excellent thermal stability.

The authors are grateful to the National Science Foundation under Grant DMR 75 06916 for partial support of this research. Acknowledgement is made to the donors of the Petroleum Research Fund administered by the American Chemical Society for partial support of this research. Use of the facilities of the Materials Research Laboratory at the University of Massachusetts is gratefully acknowledged. The assistance of Dr. Robert W. Lenz for many helpful discussions is appreciated.

References

1. K. Sanui, W. J. MacKnight, and R. W. Lenz, *J. Polym. Sci. Polym. Letters Ed.*, **11**, 427 (1973).
2. K. Sanui, R. W. Lenz, and W. J. MacKnight, *J. Polym. Sci. Polym. Chem. Ed.*, **12**, 1965 (1974).
3. K. Sanui, W. J. MacKnight, and R. W. Lenz, *Macromolecules*, **7**, 952 (1974).

4. W. J. MacKnight, W. P. Taggart, and R. S. Stein, in *Ion-Containing Polymers (J. Polym. Sci. Polym. Symp. Ed., 45)*, A. Eisenberg, Ed., Interscience-Wiley, New York, 1974, p. 113.
5. F. W. Stacey and J. F. Harris, Jr., *Organic Reactions*, **13**, 150 (1963).
6. G. M. Kosolapoff, in *Organic Phosphorous Compounds*, Wiley, New York, 1950, Chap. 9.
7. U. F. Coode, *Chem. Ind. (London)*, **1953**, 351.
8. M. Yoshifuji, *J. Syn. Org. Chem. Japan*, **28**, 177 (1970).
9. M. Sander and E. Steininger, *J. Macromol. Sci. Rev.*, **C1**, 1 (1967); *ibid*, **C2**, 1 (1968).
10. P. Phillips and W. J. MacKnight, *J. Polym. Sci. B*, **8**, 87 (1970).
11. P. Phillips, F. A. Emerson, and W. J. MacKnight, *Macromolecules*, **3**, 767 (1970).
12. P. Phillips, F. A. Emerson, and W. J. MacKnight, *Macromolecules*, **3**, 771 (1970).
13. E. Johnson, B. W. Delf and W. J. MacKnight, *J. Polym. Sci. Polym. Phys. Ed.*, **11**, 571 (1973).
14. P. M. Zanlin, M. A. Sokolovskii, and R. S. Tenisheva, *Zh. Prikl. Khim.*, **37**, 928 (1964); *Chem. Abstr.*, **61**, 3275 (1964).
15. J. Nakayama, *J. Syn. Org. Chem. Japan*, **28**, 132 (1970).
16. L. C. Thomas and R. A. Chittenden, *Spectrochim. Acta*, **20**, 489 (1964).

Received March 22, 1976

Revised April 27, 1976