^{31}P-NMR CHARACTERIZATION OF CHAIN ENDS IN POLYMERS AND COPOLYMERS PREPARED USING LUCIRIN TPO AS A PHOTOINITIATOR

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Abstract: ^{31}P-NMR spectra of polymers and copolymers prepared from styrene, substituted styrenes, methyl methacrylate and methyl acrylate using diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (Lucirin TPO) as a photoinitiator are interpreted and analyzed. The spectra provide information about the structures and configurations of phosphorus-containing end groups. The relative amounts of various chain ends present in TPO-initiated copolymers correspond well with the relative amounts of monomers employed in copolymerizations, indicating that photogenerated diphenylphosphine oxide radicals are nonselective in reactions toward the monomers investigated. This result is consistent with the high reactivity reported previously for diphenylphosphine oxide radicals but is not in agreement with the results of time-resolved ESR measurements, which indicate that the diphenylphosphinyl radical is more reactive toward methyl methacrylate than toward styrene by a factor of 1.45.

INTRODUCTION

Acylphosphine oxides and acylphosphonate esters are very effective photoinitiators for vinyl monomer polymerizations, [1-4] but little is known about the chemoselectivity, regioselectivity or stereoselectivity of phosphorus-centered radicals that are de-

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rived from them. Information of this sort can be obtained from the ^{31}P-NMR spectra of polymers and copolymers that are derived from such radicals, in much the same way that ^{13}C-NMR studies on polymers and copolymers derived from ^{13}C-enriched initiators have provided such information. [5-7] In this paper, the ^{31}P-NMR spectra of polymers and copolymers that were prepared using diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (Lucirin TPO) **1** as a photoinitiator are reported and analyzed. This initiator generates a diphenylphosphine oxide radical and a 2,4,6-trimethylbenzoyl radical when irradiated with visible light (Equation 1). Both radicals can initiate polymerization, but based on the

$$\phi_2\overset{\overset{O}{\|}}{P} - \overset{\overset{O}{\|}}{C} - \underset{CH_3}{\overset{CH_3}{\bigcirc}} - CH_3 \xrightarrow{h\nu} \phi_2\overset{\overset{O}{\|}}{P}\bullet \; + \; \bullet\overset{\overset{O}{\|}}{C} - \underset{CH_3}{\overset{CH_3}{\bigcirc}} - CH_3 \tag{1}$$

1
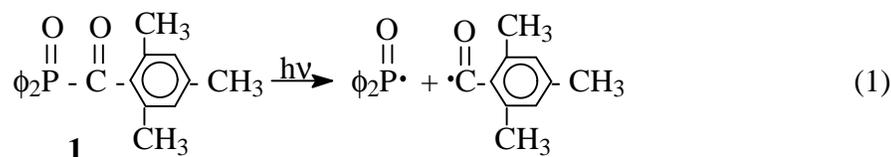
extremely high reactivity of phosphorus-centered radicals, [2,3] compared to carbon-centered radicals, a large proportion of the polymers can be expected to contain diphenylphosphine oxide groups at their chain ends.

If a monomer can be represented by the general structure **2**, many possible chain end structures can be considered. Initiation of polymerization by addition of the unsubstituted or substituted (Equations 2 and 3) ends of the monomer double bond can result in several structures for each mode of addition, if account is taken of the configuration of the monomer-monomer placement that follows the initiation step.

$$\phi_2\overset{\overset{O}{\|}}{P}\bullet \; + \; CH_2 = \overset{A}{\underset{B}{C}} \longrightarrow \phi_2\overset{\overset{O}{\|}}{P} - CH_2 - \underset{B}{\overset{A}{C}} - CH_2 - \underset{B}{\overset{A}{\underset{m}{C}}}\text{\tiny{\textbf{www}}} \tag{2}$$

2

or

$$\phi_2\overset{\overset{O}{\|}}{P} - CH_2 - \underset{B}{\overset{A}{C}} - CH_2 - \underset{A}{\overset{B}{\underset{r}{C}}}\text{\tiny{\textbf{www}}}$$

$$\phi_2 P\cdot \ + \ CH_2 = \underset{\underset{\textbf{2}}{B}}{\overset{A}{C}} \longrightarrow \phi_2 P - \underset{B}{\overset{O \quad A}{C}} - CH_2 - CH_2 - \underset{\underset{m}{B}}{\overset{A}{C}} \sim\!\sim\!\sim \tag{3}$$

$$\text{or}$$

$$\phi_2 P - \underset{B}{\overset{O \quad A}{C}} - CH_2 - CH_2 - \underset{\underset{r}{A}}{\overset{B}{C}} \sim\!\sim\!\sim$$

These various configurations will be termed meso (m) and racemic (r), just as they would be if they occurred in the center of the polymer chain. It should be noted that the second monomer placement in such structures is considered to have resulted from addition of a propagating monomer radical to the unsubstituted end of the second monomer, which is the predominant if not almost exclusive mode of propagation when vinyl monomers are polymerized.

In addition, propagating polymer radicals can be terminated by reaction with the diphenylphosphine oxide radical (primary radical termination) (Equation 4) or perhaps by chain transfer with initiator (induced decomposition of initiator) (Equation 5) to yield other chain ends, as shown below.

$$\phi_2 P\cdot \ + \ \cdot\underset{B}{\overset{A}{C}} - CH_2 \sim\!\sim\!\sim \longrightarrow \phi_2 P - \underset{B}{\overset{O \quad A}{C}} - CH_2 - \underset{\underset{m}{B}}{\overset{A}{C}} - CH_2 \sim\!\sim\!\sim \tag{4}$$

$$\text{or}$$

$$\phi_2 P - \underset{B}{\overset{O \quad A}{C}} - CH_2 - \underset{\underset{r}{A}}{\overset{B}{C}} - CH_2 \sim\!\sim\!\sim$$

$$\phi_2 P\text{-}C\text{-}\underset{CH_3}{\overset{CH_3}{\bigcirc}}\text{-}CH_3 + \cdot\underset{B}{\overset{A}{C}}\text{-}CH_2 \sim\!\sim\!\sim \longrightarrow \phi_2 P\text{-}C\text{-}CH_2\text{-}\underset{\underset{m}{B}}{\overset{A}{C}}\ CH_2 \sim\!\sim\!\sim + \cdot C\text{-}\underset{CH_3}{\overset{CH_3}{\bigcirc}}\text{-}CH_3 \tag{5}$$

$$\text{or}$$

$$\phi_2 P\text{-}C\text{-}CH_2\text{-}\underset{\underset{r}{A}}{\overset{B}{C}}\ CH_2 \sim\!\sim\!\sim + \cdot C\text{-}\underset{CH_3}{\overset{CH_3}{\bigcirc}}\text{-}CH_3$$

It should be noted that the structures of the chain ends that result from Equations 4 and 5 are different than those that result from Equation 3.

When the ^{31}P-NMR spectra of copolymers prepared from TPO-initiated polymerizations are considered, end group structures such as are outlined above must be considered for each monomer. In addition structures involving the two monomers that constitute the terminal monomer-monomer dyad must also be considered. Many different types of phosphorus-containing chain ends may thus be present in polymers and copolymers prepared by TPO-initiated polymerization. The purpose of this paper is to demonstrate that the resonances of many such chain ends can be distinguished by high field ^{31}P-NMR spectroscopy and that useful chemical information can be obtained from their relative intensities.

EXPERIMENTAL

Monomers were obtained from commercial sources and were purified by a two-fold washing with equal volumes of 1 N NaOH followed by a two-fold washing with equal volumes of distilled water. They were then dried over calcium hydride, distilled under reduced pressure and stored in a refrigerator. Prior to use, monomers were tested for the presence of polymer by adding a portion to an excess of a precipitant for the polymer. Only polymer-free monomer was used for polymerization experiments.

Diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide, (Lucirin TPO) was generously supplied by the BASF Corporation and used as received.

TPO-initiated polymerizations and copolymerizations were conducted in bulk in clear one-ounce bottles under nitrogen. Each polymerization mixture contained 3.5 mole percent TPO. The bottles were sealed with rubber septa and were irradiated with light from a tungsten lamp. The lamp was placed sufficiently far from the bottles that the polymerization mixtures did not exceed 30ºC. Homopolymerizations were allowed to proceed to high conversion (~ 3 hr.) but copolymerizations were limited to below 5 percent conversion. The polymerization mixtures were poured into a large volume of methanol to precipitate the polymers. These were then reprecipitated three times from THF solution into methanol. All polymers were then dried at 60º in vacuo.

Polymerization of MMA by Group Transfer Polymerization and Termination with Di-phenylphosphinic Chloride

A mixture containing freshly dried (12 hr. @ 260ºC) zinc chloride (5.5 g), dry toluene (15 ml) and methyl methacrylate was allowed to stir for fifteen minutes and then treated with methyl trimethylsilyl dimethylketene acetal. After being allowed to stir for 45 minutes, a portion of the reaction mixture was added to an excess of diphenylphosphinic chloride. The reaction mixture was poured into methanol to precipitate the polymer. It was then reprecipitated twice from THF solution into methanol. The Mn of this polymer, as measured by GPC, was 18,000 and it contained 0.67 weight percent phosphorus.

Polymerization of MMA Initiated by the Lithium Salt of Diphenylphosphine Oxide

Diphenylphosphine oxide (0.5 g, 0.0025 moles) was treated with a stoichiometric amount (1.5 ml) of a 1.6 M solution of n-butyl lithium in hexane under a nitrogen blanket. [8] The reaction mixture was vigorously stirred at room temperature and a yellow solid rapidly formed. A solution of methyl methacrylate (0.5 g) in dry THF was then added dropwise into the reaction mixture. After 45 minutes, the solution was concentrated by evaporation in vacuo and poured into methanol to precipitate the polymer. The crude polymer (0.27 g, 54% yield) was precipitated twice from THF solution into methanol and then dried at 45ºC in a vacuum oven overnight. Gel permeation chromatography indicated the polymer to have a number average molecular weight of 30,000. The polymer contained 1.14 weight percent phosphorus.

Reaction of Polystyryllithium with Diphenylphosphinic Chloride

A solution of polystyryllithium in benzene (3% v/v, 100 ml), kindly provided by Dr. Thomas J. Lynch, was gradually treated with diphenylphosphinic chloride until the characteristic orange color of the lithiated polymer disappeared. The solution was evaporated to dryness using a rotatory evaporator and the residue was dissolved in THF. The solution was added to methanol to precipitate the polymer, which was then reprecipitated twice from THF solution into methanol and dried in a vacuum oven overnight at 40ºC.

Reaction of Polystyrene with Diphenylphosphinic Chloride

A mixture of polystyrene (0.2 g, 0.0019 moles of repeat groups), diphenylphos-phinic chloride (0.34 g, 0.0026 moles), aluminum chloride (1.0 g, 0.0077 moles) and carbon tetrachloride was stirred at 75ºC for one hour under nitrogen. It was then poured into 40 ml methanol to precipitate the polymer. This was dried overnight in a vacuum oven at room temperature.

Phosphorus NMR Spectroscopy

Phosphorus NMR measurements were performed on samples in CDCl$_3$ using a Varian XL-400 spectrometer operating at a resonance frequency of 161.91 MHz. A 90º pulse, a 0.3 second acquisition time, 30012 data points and a 2 second delay between acquisitions were employed with 15,000 – 20,000 transients being acquired for each spectrum. Polymer solution concentrations were 10 – 15% (w/v). Each sample contained 3 mg of Lucirin TPO which was employed as an internal standard. The chemical shift of Lucirin TPO, relative to 85% ortho phosphoric acid was 11.0 ppm.

Elemental Analyses

Phosphorus analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

RESULTS AND DISCUSSION

TPO-Initiated Poly(Methyl Methacrylate)

Figure 1A shows the ^{31}P-NMR spectrum of a PMMA sample that was prepared by TPO-initiated polymerization. This sample had a Mn of 102,000 as measured by gel permeation chromatography and a phosphorus content of 0.029 weight percent. These values indicate that there is an average of almost exactly one phosphorus-containing chain end group per chain. The spectrum contains two signals having relative intensities of 0.30 and 0.70 in order of increasing field. There is much evidence to indicate that these signals are due to chain ends that result from initiation and not termination proces-ses. For example, this same spectrum is observed for a PMMA sample prepared by TPO-initiated polymerization in the presence of a large amount (10 mole percent) of 1-octylmercaptan. Under such conditions, propagating PMMA radicals can be expected to

terminate almost entirely by chain transfer. There should be almost no opportunity for them to terminate by combining with a diphenylphosphine oxide radical. Similarly, PMMA prepared by AIBN-initiated polymerization in the presence of diphenylphosphine oxide, a powerful transfer agent that is a source of diphenylphosphine oxide radicals, exhibits the same ^{31}P-NMR spectrum as the polymer prepared by TPO-initiated polymerization. In addition, polyMMA prepared anionically using the lithium salt of diphenylphosphine oxide as initiator also exhibits resonances that have the same chemical shift as those in the spectra of the polymers prepared by radical polymerization. However, as can be seen in Figure 1B, the relative intensities of the resonances are different for polymers initiated by diphenylphosphine oxide radicals or anions. Finally, the ^{31}P-NMR spectrum of PMMA prepared by group transfer polymerization and <u>terminated</u> by reaction with diphenylphosphinic chloride (Figure 1C) contained a single resonance at 26.6 ppm, considerably downfield from the resonances (24.3 and 25.0 ppm) of PMMA <u>initiated</u> by diphenylphosphine oxide radicals or anions. Collectively, these results strongly indicate that the resonances at 24.3 and 25.0 ppm are attributable to chain ends that resulted from reaction 2 (A = -CH$_3$, B = -COOCH$_3$). Due to the substantial steric hindrance associated with their formation, chain ends that would result from reaction 3 are not considered likely.
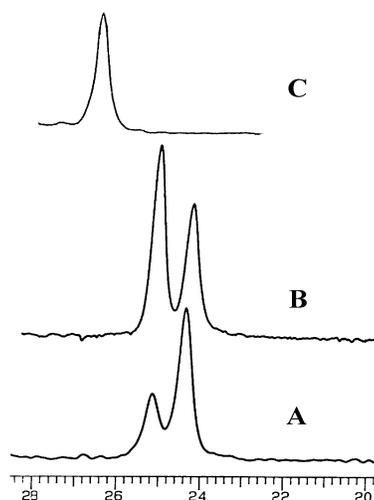
Figure 1. ^{31}P-NMR Spectra of PolyMMA Samples Prepared by TPO-Initiated Polymerization (A), by ϕ_2P(0)Li-Initiated Polymerization (B), and by Group Transfer Polymerization Followed by Termination with ϕ_2P(0)Cl (C).

It seems reasonable to attribute the lower field ^{31}P resonance (25.0 ppm) to ϕ_2P(0)-ends that are connected to MMA units that, in turn, are bound by meso placements to adjacent MMA units. Similarly, the upper field resonance (24.3 ppm) can be attributed to ϕ_2P(0)-ends that are connected to racemic MMA-MMA dyads. These assignments are made because of the similarity of the relative intensities of the resonances to the relative amounts of meso and racemic enchainments in the polymers, as estimated in the classical way [9] from the methyl proton or methyl carbon resonances of the polymers. For example, in the spectra of the ϕ_2P(0)• radical initiated samples, the lower field ^{31}P-resonance accounts for 0.30 of the total ^{31}P-resonance and the meso content of the polymers, as estimated from their methyl proton resonance pattern, is 0.22. In the spectrum of the ϕ_2P(0)Li initiated polymer, the lower field ^{31}P-resonance accounts for 0.55 of the total and the meso content of the polymer, as measured by ^{1}H-NMR is 0.58.

TPO-Initiated Polystyrene

Figure 2A shows the ^{31}P-NMR spectrum of TPO-initiated polystyrene. It contains two major (27.6 and 28.0 ppm) and two minor (30.3 and 30.9 ppm) resonances. The resonance at 27.6 ppm corresponds well with the resonance observed in the spectrum (Figure 2B) of the polymer obtained by terminating polystyryllithium with diphenylphosphinic chloride as shown by Equation (6). This suggests that it can be attributed to chain ends that contain the ϕ_2P(0)-group attached to the head of a styrene unit (resulting from reactions 3, 4 or 5 with A = H and B = C_6H_5). Since the relative intensity of the resonance is the same in Figure 2A as in the spectrum (Figure 2C) of polystyrene prepared using diphenylphosphine oxide as a chain transfer agent, this resonance is attributed to chain ends that resulted from initiation reactions (Equation 3). Resonance at 28.0 ppm is attributed to chain ends that resulted from addition of diphenylphosphinyl radicals to the unsubstituted carbon of styrene (Equation 1, A = H, B = C_6H_5). These assignments are supported by results obtained in a 3D – H,C,P-NMR study of polystyrene prepared using diphenylphosphine oxide as a chain transfer agent. [10]

$$Bu\text{-}(CH_2CH)_nCH_2CHCH_2CHLi \ + \ \phi_2\overset{\overset{\displaystyle O}{\|}}{P}Cl \longrightarrow Bu\text{-}(CH_2CH)\text{-}CH_2CHCH_2CHP\phi_2 \qquad (6)$$
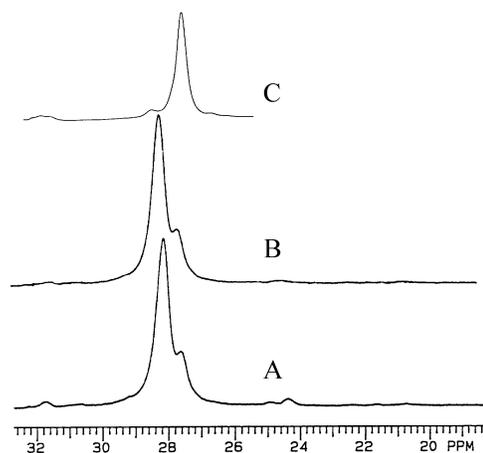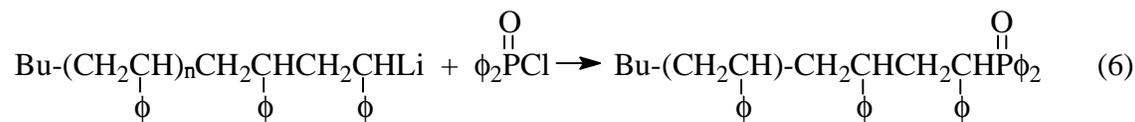
Figure 2. ^{31}P-NMR Spectra of Polystyrene Samples Prepared by TPO-Initiated Polymerization (A), by Using ϕ_2P(0)H as a Chain Transfer Agent (B), and by BuLi-Initiated Polymerization followed by Termination with ϕ_2P(0)Cl (C).

Two of the minor resonances (30.4 and 31.7 ppm) observed in Figure 2A are attributed to ϕ_2P(0)-groups attached to aromatic rings of styrene units, since polystyrene that was diphenylphosphinylated by reaction with diphenylphosphinic chloride and aluminum chloride (Equation 7) also exhibits resonances in those regions. Resonance at 30.4 ppm is attributed to m-substituted rings and that at 31.7 is attributed to p-substituted ones.

$$\wedge\!\wedge\!\wedge CH_2CH \wedge\!\wedge\!\wedge \xrightarrow[\;AlCl_3\;]{\phi_2P(0)Cl} \wedge\!\wedge\!\wedge CH_2CH \wedge\!\wedge\!\wedge \qquad (7)$$
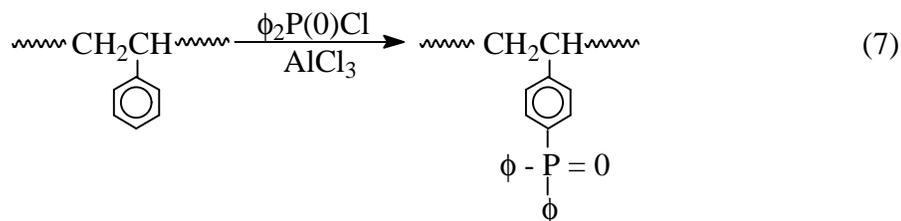
Based on the relative intensities of these resonances, it is estimated that diphenyl-phosphinyl radicals add to the unsubstituted and substituted ends of styrene 85- and 15-percent of the time, respectively. In addition, instead of initiating polymerization, approximately 5 percent of the radicals attack the aromatic rings of styrene or of styrene units. These values are to be compared to results of Solomon et al [11] who reported a 13:1 preference of the benzyloxy radical to add to the tail end of styrene and a relatively strong tendency of this radical to attack the aromatic rings of styrene or styrene units.

The lower selectivity of the diphenylphosphinyl radical compared to the benzyloxy radical with respect to the mode of addition to styrene may reflect the greater reactivity of the former. The ^{31}P-NMR spectra of TPO-initiated poly(p-methoxystyrene) end of poly(p-chlorostyrene) were very similar to that of TPO-initiated polystyrene. These spectra, along with the spectra of TPO-initiated poly(methyl acrylate) are shown in Figures 3, 4 and 5 along with spectra of their copolymers with MMA.
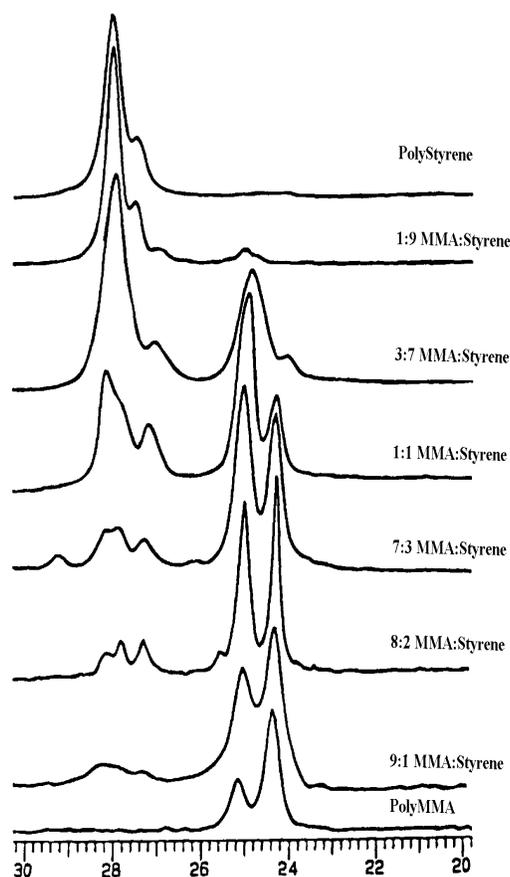
Figure 3. ^{31}P-NMR Spectra of MMA-Styrene Copolymers Prepared by TPO-Initiated Polymerization.

TPO-Initiated Copolymers

Since the chemical shifts of ϕ_2P(0)-groups attached to styrene, substituted styrene or methyl acrylate units (26.4 – 29.0 ppm) and MMA units (23.5 – 26.2 ppm) are appreciably different, it is possible to measure the relative amounts of ϕ_2P(0)-groups attached to styrene, substituted styrene or methyl acrylate and MMA units in copolymers initiated

by diphenylphosphinyl radicals. This will be discussed in detail for copolymers of styrene and MMA.

Figure 3 shows the ^{31}P-NMR spectra of polystyrene, polyMMA and a series of styrene-MMA copolymers that was prepared by TPO-initiated polymerization. The resonance between 26.5 and 29.0 ppm, decreases in relative proportion as the styrene content of the copolymers decreases and is taken as a measure of the $\phi_2P(0)$-groups attached to styrene ends. The resonance between 23.5 and 26.0 ppm increases as the MMA content of the copolymers increases and is taken as a measure of the $\phi_2P(0)$-groups attached to MMA ends. Taking A_S and A_{MMA} as the relative proportions of resonance observed at 26.5 – 29.0 and 23.5 – 26.0 ppm, respectively, the A_S/A_{MMA} ratio can be related to the relative reactivity of styrene and MMA toward the $\phi_2P(0)\bullet$ radical, k_S/k_{MMA}, and the molar ratio of styrene to MMA in the copolymerization mixture, [S]/[MMA], as follows:

$$A_S/A_{MMA} = (k_S/k_{MMA}) \bullet [S]/[MMA] \tag{8}$$

According to this relationship, a plot of A_S/A_{MMA} versus [S]/[MMA] should be a straight line having a slope equal to k_S/k_{MMA}. Figure 4 shows such a plot. The slope of the plot is 1.0, indicating that the $\phi_2P(0)\bullet$ radical shows the same reactivity for styrene and MMA. Similar results were obtained in studies on copolymers of MMA with p-chlorostyrene, p-methoxystyrene and methyl acrylate that were initiated by TPO. The ^{31}P-NMR spectra of the copolymers are shown in Figures 5-7 and the percentages of $\phi_2P(0)$-MMA ends in the copolymers are compared with the percentages of MMA in the polymerization mixtures in Table 1. In all cases, there is excellent correspondence between the two percentages, indicating that the $\phi_2P(0)\bullet$ radical is completely unselective in its reactions with MMA, methyl acrylate and substituted styrenes. This is believed to be a consequence of its high reactivity.
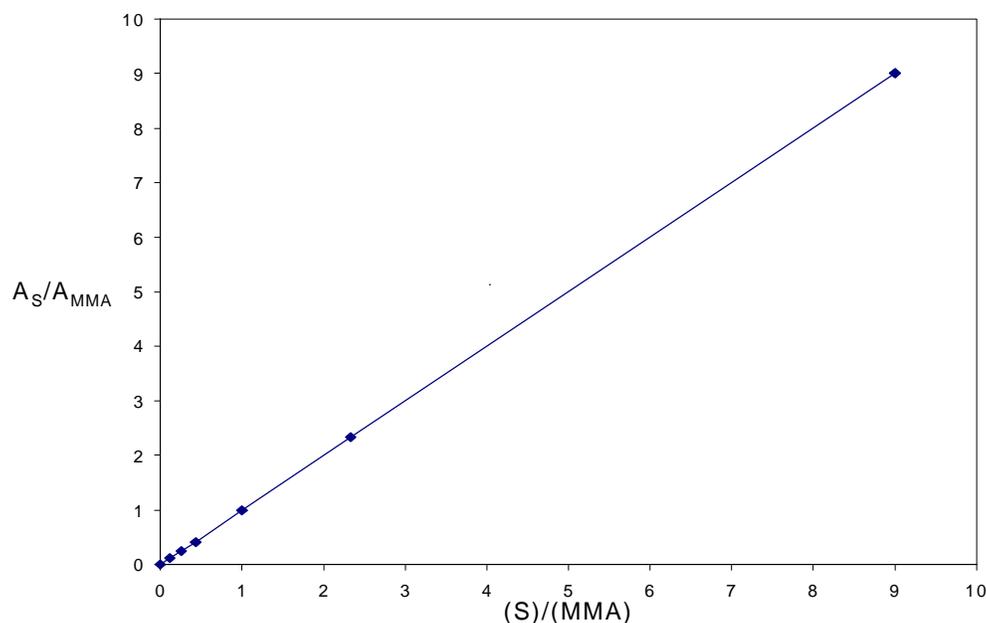
Figure 4. Plot of A_S/A_{MMA} versus $(S)/(MMA)$.

Table 1: Percentage of $\phi_2P(0)$-MMA End Groups in Copolymers Derived from Lucirin TPO-Initiated Polymerizations

Mole % MMA in Monomer Mixture	Mole % $\phi_2P(0)$-MMA End Groups			
	Styrene[a]	4-Chlorostyrene[a]	4-Methoxystyrene[a]	Methyl Acrylate[a]
90	90	90	90	91
80	80	---	80	79
70	71	70	70	69
50	50	50	50	---
30	30	30	30	32
10	10	10	11	---

[a]Comonomer, conversions below 5% in all cases.

Referring back to Figure 3, the resonance of $\phi_2P(0)\bullet$ groups attached to MMA ends (23.5 – 26.0 ppm) consists of two general areas that vary in relative intensity as the MMA content of the copolymers changes. The resonance observed between 24.7 and 26.0 ppm in the spectrum of the MMA homopolymer can be attributed to $\phi_2P(0)$-MMA-

MMA chain ends having meso configurations, as was explained earlier. However, this resonance area increases in intensity relative to that of the resonance observed from 23.5 – 24.7 ppm, as the proportion of styrene in the copolymer increases. In fact, it is the
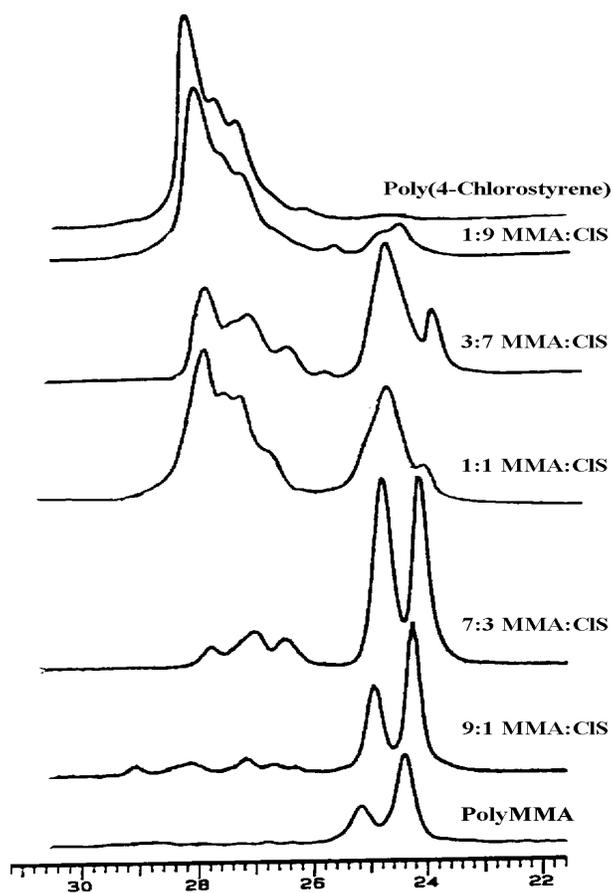
Figure 5. ^{31}P-NMR Spectra of MMA-4-Chlorostyrene Copolymers
Prepared by TPO-Initiated Polymerization.

nly resonance observed from 23.5 – 26.0 ppm in the spectrum of the copolymer prepared from a 90/10 – styrene/MMA mixture. It can be calculated from the reactivity ratio for MMA in the styrene/MMA copolymerization system that 94 percent of the ϕ_2P(0)-MMA chain ends in such a copolymer will be connected to styrene units. On this basis, it was determined that the resonance in the 24.7 – 26.0 region contained contributions from all ϕ_2P(0)-MMA-styrene chain ends, irrespective of stereochemical considerations as well as from ϕ_2P(0)-MMA-MMA chain ends with meso MMA-MMA dyads. Accordingly, the resonance observed in the 23.0 – 26.0 ppm region can be assigned and their relative areas can be calculated as shown in Table 2, where σ is the probability that a MMA-

MMA placement has a meso configuration and P(S/M) is the probability that a styrene unit follows a MMA unit in the copolymer. P(S/M) can be easily calculated by Equation 9, where r_M is the reactivity ratio for MMA in the S/MMA copolymerization system [12] and (M)/(S) is the ratio of monomers in the copolymerization system.

$$P(S/M) = 1/(1 + r_M(M)/(S)) \qquad (9)$$

Table 2: Assignment of Structures Contributing to $\phi_2P(0)$-MMA Resonances in the Spectra of the TPO-Initiated MMA/Styrene Copolymers

CHEMICAL SHIFT	CONTRIBUTING STRUCTURE	RELATIVE PROBABILITY
23.0-24.7 ppm	Racemic	$(1-\sigma_m)(1-P(S/M))$
24.7-26.0 ppm	Meso	$\sigma_m(1-P(S/M))$
	Meso Racemic	P(S/M)
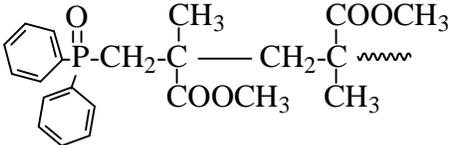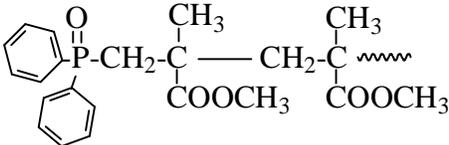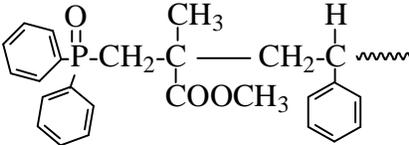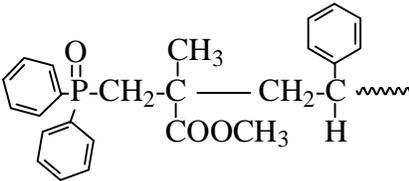
Table 3 compares the relative areas of the resonances observed at 23.0-24.7 ppm in the copolymer spectra with values calculated using the relative probability expressions given in Table 2, a σ value of 0.27 and an r_M of 0.46. The agreement is quite good, indicating

the validity of the assignments given in Table 2. It should be noted that the value
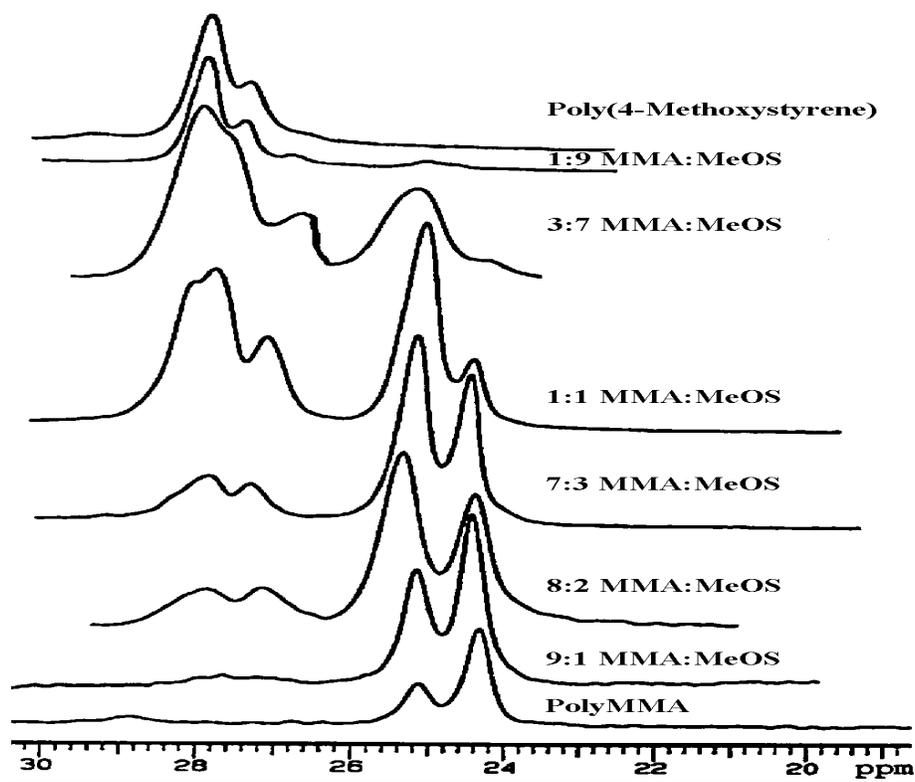
Figure 6. ^{31}P-NMR Spectra of MMA-4-Methoxystyrene Copolymers
Prepared by TPO-Initiated Polymerization.

of r_M that was used for these calculations is the same as that that applies for enchain-ments throughout the polymer chain and that the value of σ, which is based on the ho-mopolymer spectrum is nearly the same as the value (0.23) that prevails for MMA-MMA placements in the main polymer backbone as measured by NMR. The probabilities for the first pair of monomers in the copolymers are apparently very nearly the same as those for monomer pairs more remote from the chain end.

Table 3 compares the relative areas of resonances observed in the 23.0 – 24.7 ppm region for copolymers of MMA with p-chlorostyrene, p-methoxystyrene and methyl acrylate with those calculated as described above for MMA-styrene copolymers. These calculations are based on σ values of 0.27 for all the copolymers and on r_M values of 0.42, 0.29 and 2.15, respectively, for MMA-p-chlorostyrene, [13] MMA-p-methoxysty-rene [14] and MMA-methyl acrylate [15] copolymerizations. The agreement between ob-served and calculated resonance areas is also very good, indicating that these resonances

can be assigned in the same manner as the resonances of MMA-styrene copolymers. The validity of this general interpretation is strengthened by the fact that the r_M values employed from the calculations varied over a wide range.

Table 3: Percentages of $\phi_2P(0)$-MMA Resonance Observed in 24.3 ppm Signal for Copolymers of MMA with Various Monomers

Mole % MMA in Polymerization Mixture	Percentage of Resonance at 24.3 ppm							
	Styrene[*]		4-Chlorostyrene[*]		4-Methoxystyrene[*]		Methyl Acrylate[*]	
	Obs'd	Calc[a]	Obs'd	Calc[b]	Obs'd	Calc[c]	Obs'd	Calc[d]
90	0.61	0.60	0.59	0.59	0.55	0.53	0.72	0.69
80	0.50	0.49	0.37	0.36	0.40	0.39	0.67	0.65
70	0.41	0.39	0.22	0.21	0.29	0.29	-----	-----
60	-----	-----	-----	-----	-----	-----	0.54	0.55
50	0.27	0.25	-----	-----	0.17	0.16	-----	-----
30	0.14	0.13	0.11	0.11	0.10	0.08	0.36	0.35

[*] Comonomer, conversions below 5% in all cases.

[a] $\sigma = 0.27$, $r_M = 0.5$; [b] $\sigma = 0.27$, $r_M = 0.42$; [c] $\sigma = 0.27$, $r_M = 0.29$; [d] $\sigma = 0.27$, $r_M = 2.15$

Fine structure that varies with copolymer composition is also evident in the resonance observed in the 26.0 – 29.0 ppm range in the spectra of the copolymers of MMA and styrene or substituted styrenes. This has not been assigned at present. Undoubtedly these resonance patterns contain information about monomer sequences and stereosequences at the chain ends also.
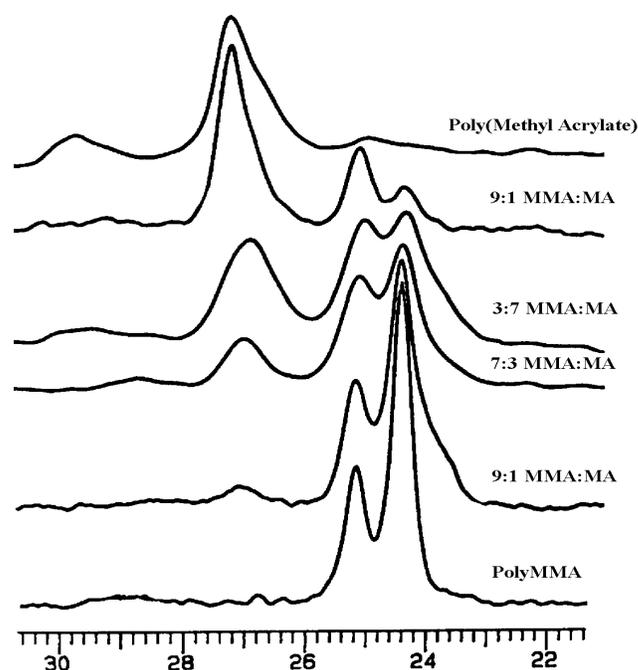
Figure 7.   ^{31}P-NMR Spectra of MMA-Methyl Acrylate Copolymers Prepared by TPO-Initiated Polymerization.

CONCLUSIONS

The ^{31}P-NMR spectra of several copolymers prepared by TPO-initiated polymerizations can provide information about the structures of their chain ends. The diphenylphosphinyl radical shows no selectivity in its reactions toward MMA, styrene, p-chlorostyrene, p-methoxystyrene or methyl acrylate. This appears to be a consequence of its very high reactivity. This finding is in conflict with results obtained in time resolved ESR studies, which report a range of rate constants for the reactions of $\phi_2P(0)\bullet$ radicals with vinyl monomers. [2,3] An explanation for this discrepancy cannot be offered at this time and it needs to be investigated.

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Povzetek

Analizirali in interpretirali smo ^{31}P NMR spektre polimerov in kopolimerov, ki smo jih pripravili iz stirena, substituiranih stirenov, metil metakrilata in metil akrilata z uporabo difenil-(2,4,6-trimetilbenzoil)fosfin oksida (Lucirin TPO) kot fotoiniciatorja.. Iz spektroskopskih podatkov smo izlušèili podatke o strukturi in konfiguraciji fosfor vsebujoèih konènih skupin. Relativna kolièina razliènih konènih skupin ustreza razmerjem uporabljenih kolièin monomerov pri kopolimerizaciji, katalizirani s TPO. To dokazuje neselektivnost fotogeneriranega difenilfosfin oksidnega radikala za promocijo polimerizacije razliènih monomerov. Naši rezultati se ujemajo z že opisano veliko reaktivnostjo difenilfosfin oksidnega radikala, ne pa tudi z rezultati EPR meritev. Le-te kažejo na za faktor 1.45 veèjo reaktivnost omenjenega iniciatorja z metil metakrilatom kot s stirenom.