

Sequential Distribution of Main Chain Phosphorus-Containing Copolyesters Characterized by ^1H NMR

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Abstract: A series of main chain phosphorus-containing copolyesters were synthesized by polycondensation of terephthalic acid (TPA), ethylene glycol (EG) and phenyl phosphonic acid (PPA). Chemical structures of these main chain phosphorus-containing copolyesters were characterized by ^1H NMR. Experimental results show that the resonance intensity of PPA aromatic protons increases with increase of the phosphorus content. The chemical shifts of the ethylene protons in the ethylene glycol units vary with different sequences. The resonance chemical shift of the ethylene protons of the T-E-T unit is higher than those of P-E-T (T-E-P) and P-E-P units. The monomer molar fraction, sequential distribution and degree of randomness of the phosphorus-containing copolyesters were determined through analyses of the ethylene protons in the ethylene glycol units. The molar fractions of the PPA comonomer determined by ^1H NMR analyses are close to the values determined by a UV method. The degree of randomness for the copolyesters was found to be in the range 0.66–0.83. © 1998 SCI.

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Key words: ^1H NMR; phosphorus-containing copolyester; sequential distribution; phosphorus content

INTRODUCTION

Phosphorus-containing compounds are known to have a flame-retardant property.¹ Flame retardation of organic polymers using phosphorus compounds has been well established.^{2,3} Organophosphorus flame retardants primarily function as a char promoter of carbonates in the condensed phase,^{4–8} which can provide excellent flame retardation, less volatiles, low smoke and low toxicity. If phosphorus moieties are inserted into the polymer main chain, the phosphorus will not migrate to the surface and maintains its good flame retardation and physical properties.

The flame retardation of a phosphorus-containing polymer and the correlation with its phosphorus content have been studied previously.^{7,9} The phosphorus content was usually determined by a UV

method,¹⁰ or by the charge value. The chemical structure of a copolymer is also known to affect its flame retardation.^{11–15}

The chemical structure of a copolymer (i.e. random, alternating or block) is important in determining its final properties. For a copolyester, nuclear magnetic resonance spectroscopy (NMR) is a powerful technique for qualitative and quantitative analyses of its chemical structure.^{16–22} Yamadera and Murano¹⁶ showed that the degrees of randomness of the same copolyesters can be determined by NMR. These analyses can be effective provided that the resonance signals of the given proton(s) or carbon(s) with different sequences have different chemical shifts. It has also been shown that the aromatic protons of the terephthalate units of copolyesters with different aromatic and aliphatic diol sequences have different resonance signals.^{17–19} The resonance signals of the aromatic carbons of terephthalic acid, the aliphatic carbons of ethylene glycol and 1,4-butanediol

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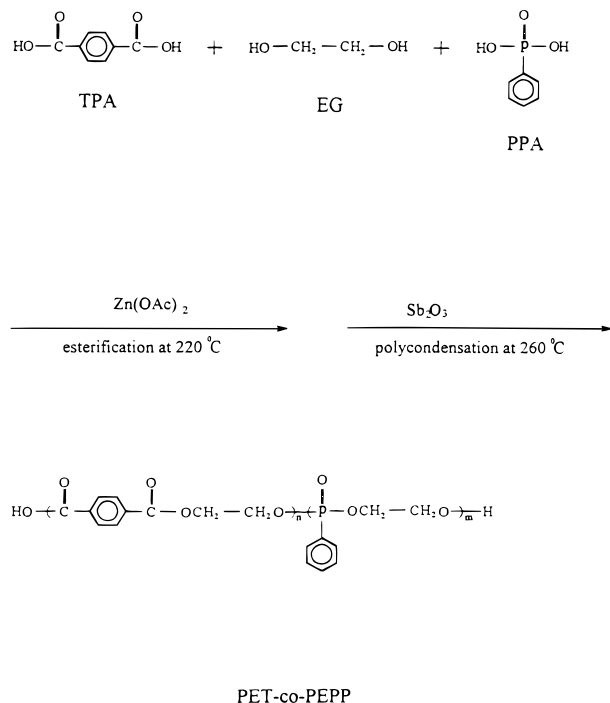
were found to give a quartet.²⁰ Additionally, the resonance signals from the proton(s) or carbon(s) of the glycol units of copolyesters with different diacid sequences also resulted in different chemical shifts, and thus the sequential distributions could be determined.^{16,21-30}

Very few previous studies have been devoted to understanding the sequential distribution of a phosphorus-containing polyester. In this paper, a series of phosphorus-containing copolyesters, poly(ethylene terephthalate)-*co*-poly(ethylene phenyl phosphonate)s (PET-*co*-PEPP)s, were synthesized by polycondensation of terephthalic acid, ethylene glycol and a phosphorus-containing comonomer (phenyl phosphonic acid, hereinafter referred to as PPA). We attempted to analyse the sequential distribution of these phosphorus-containing copolyesters and determine their phosphorus content by using proton nuclear magnetic resonance (¹H NMR).

EXPERIMENTAL

Terephthalic acid (TPA) and ethylene glycol (EG) were obtained from Tokyo Kasei Ltd., Japan. Zinc acetate and diantimony trioxide were purchased from Merck Schuchardt Ltd, Germany.

Scheme 1 illustrates the two-step preparation of phosphorus-containing copolyesters (PET-*co*-PEPP)s. The copolyesters with various phosphorus contents, ranging from 0.79 to 5.00 wt%, were synthesized through co-condensation of phosphonic acid with TPA and EG catalysed by zinc acetate as esterification catalyst and diantimony trioxide as polycondensation cata-



Scheme 1. Preparation of PET-*co*-PEPP polymer.

lyst. The preparation was carried out according to a previously described method.^{31,32} The copolyester with phosphorus content of 0.79 wt% is denoted as P079, 1.19 wt% is denoted as P119 and so on. The intrinsic viscosities of all the copolyesters measured at 30°C in phenol/1,1,2,2-tetrachloroethane (60/40 wt/wt) were greater than 0.50 dl g⁻¹.

¹H NMR spectra of copolyesters in CF₃COOD were measured with a Bruker Am 400 NMR instrument using tetramethylsilane as an internal standard. A Metertek SP-830 UV spectrophotometer was employed to determine the phosphorus content of the copolyesters.

For phosphorus content determination, the following four reagents A, B, C and D were prepared:

Reagent A. Solution 1: 50.0 g ammonium molybdate ((NH₄)₂MoO₄) dissolved in 500 ml of H₂O. Solution 2: 125 ml conc. H₂SO₄ diluted with 350 ml H₂O. Solution 3: Solution 1 and solution 2 were mixed together and diluted to 1 l.

Reagent B. 4 N H₂SO₄.

Reagent C. 10 g ammonium ferrous sulphate ((NH₄)₂SO₄·FeSO₄·6H₂O) added to 2 ml of reagent B, and then diluted to 100 ml.

Reagent D. Blank solution (25 ml reagent A + 10 ml reagent B + 8 ml reagent C). The mixed solution was diluted to 100 ml.

A phosphorus-containing copolyester sample of about 10 mg was accurately weighed into a 100 ml Kjeldahl flask, and 1 ml 18 M H₂SO₄ together with 8 drops of HClO₄ added. The concentrated solution was first heated at 81°C for 1 h; then the temperature was raised to 186°C for another hour to decompose the copolyester completely. The flask was cooled to room temperature and flushed out with 20 ml distilled water. The flushed solution, 25 ml reagent A and 10 ml reagent C were added to a 100 ml volumetric flask, and then diluted with distilled water to 100 ml. The colour of the solution containing phosphorus was navy blue after 10 min. The phosphorus content of the navy blue sample solution was determined with a UV spectrophotometer at 700 nm wavelength using triphenyl phosphine (P content = 11.83%) as a standard.¹⁰

RESULTS AND DISCUSSION

¹H NMR spectra of PET, poly(ethylene phenyl phosphonate) (PEP) and copolyester P079 are shown in Fig. 1. The chemical structure and resonance peak assignments for each polyester are shown in Table 1^{33,34} and Scheme 2. The chemical shifts of the ethylene protons from the ethylene glycol units are 3.8 to 4.8 ppm and those for the aromatic protons are 7.1 to 8.0 ppm. The resonance peaks of the ethylene protons from the PET-*co*-PEPPs are interesting. By comparison with the

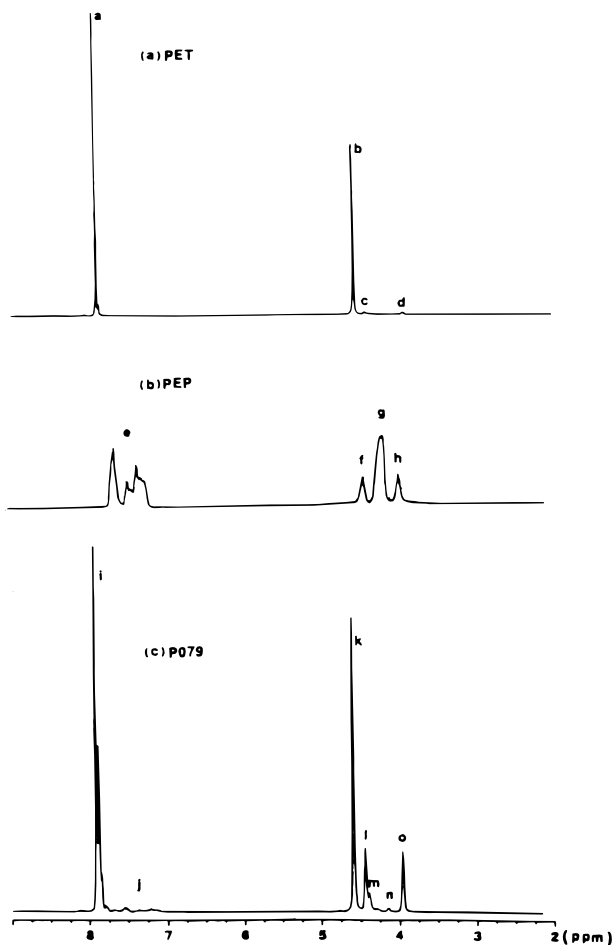
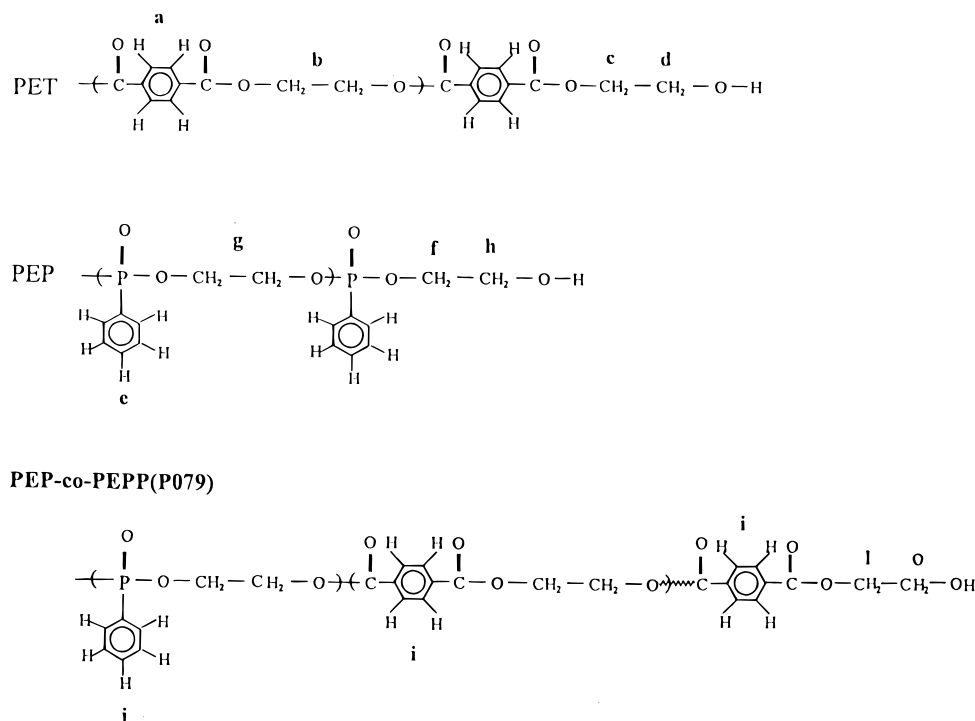


Fig. 1. ^1H NMR spectra of PET, PEP and copolyester P079.

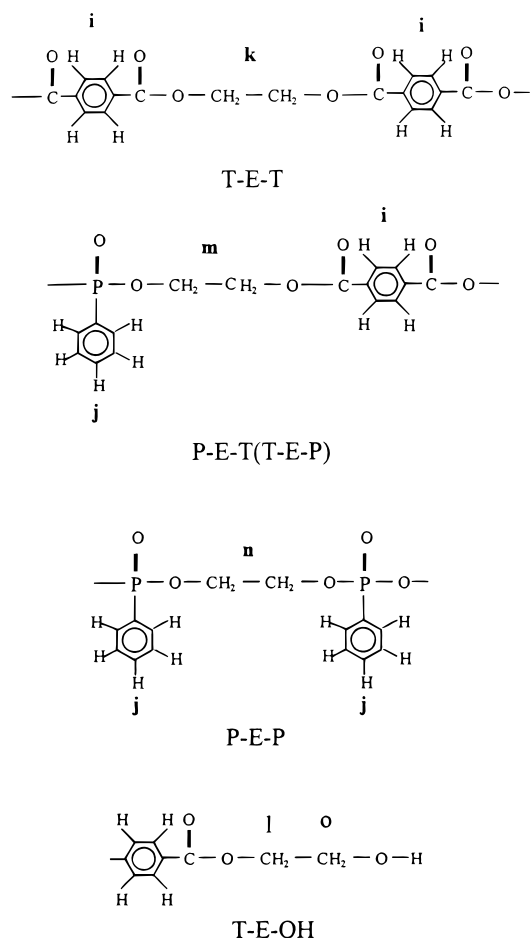
TABLE 1. Assignments for resonance peaks of PET, PEP and P079

Sequence	Proton	Chemical shift (ppm)
T-E-T	a	8.00-7.72
	b	4.56
	c	4.42
	d	3.93
P-E-P	e	7.54-7.13
	f	4.37
	g	4.16
	h	3.89
P079	i	8.00-7.72
	j	7.54-7.13
	k	4.56
	l	4.42
	m	4.40
	n	4.16
	o	3.93

resonance peaks of PET and PEP, the resonance of the ethylene protons from the ethylene glycol units of the copolyester can be from four possible sequences as shown in Scheme 3. The sequences of the ethylene protons of T-E-T, T-E-P (P-E-T) and P-E-P resonate at 4.56 (proton k), 4.40 (proton m) and 4.16 (proton n) ppm, respectively. The β -methylene protons (proton l) and α -methylene protons (proton o) of the hydroxyl terminal units (T-E-OH) in the ethylene glycol units resonate at 4.42 and 3.93 ppm, respectively;³⁴ where T is the



Scheme 2. Sequences of PET-co-PEPP polymer.



Scheme 3. Sequences of PET-co-PEPP polymer.

terephthalate unit, E is the ethylene glycol unit, P is the phenylphosphonate unit and OH is the hydroxyl group. Figure 2 shows the expanded NMR resonance peaks of the ethylene protons in ethylene glycol units of the phosphorus-containing copolyesters with chemical shifts ranging from 3.8 to 4.8 ppm.

Table 2 summarizes the intensities of the ethylene protons resonating at 4.56, 4.40, 4.16, 4.42 and 3.93 for each copolyester. These chemical shifts are in the range

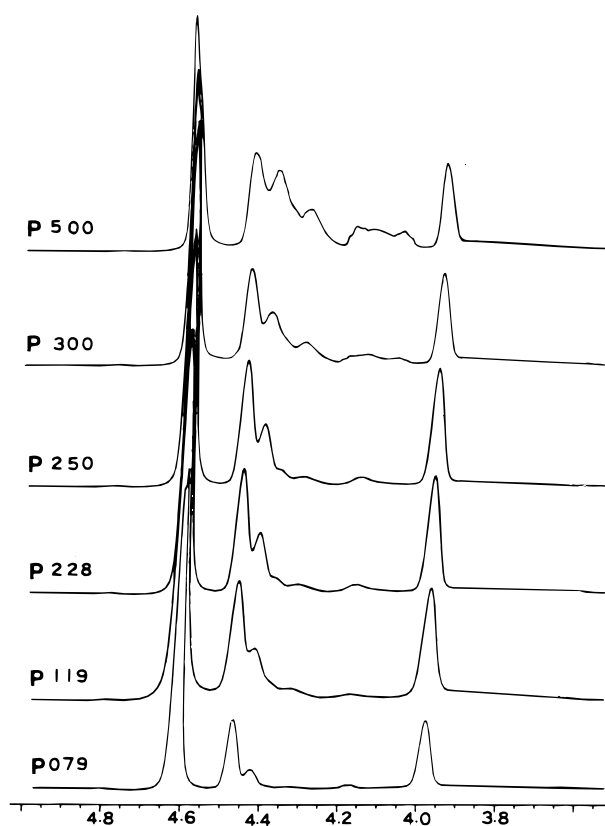


Fig. 2. Expanded ^1H NMR spectra of copolyesters with chemical shifts ranging from 3.8 to 4.8 ppm.

for aliphatic protons of ethylene groups. The resonance chemical shift of the ethylene protons of the T-E-T units (protons k) is higher than that of P-E-T (T-E-P) units (protons m) and P-E-P units (protons n), because the electronegativity of the P unit (phosphorus atom) is weaker than that of the T unit (carbon atom). Comparisons of the resonance peaks of the ethylene protons from samples of P079, P119, P228, P250, P300 and P500 reveal that the resonance intensity of proton k at 4.56 ppm decreases with increase of the phosphorus

TABLE 2. Resonance intensities of ethylene protons of ethylene glycol unit and molar percentages of PPA

Sample	Intensity of chemical shifts					$X_P(\%)^a$
	k	m	n	l	o	
P079	0.735	0.081	0.014	0.194	0.194	4.48
P119	0.635	0.146	0.026	0.223	0.223	7.89
P228	0.616	0.182	0.069	0.237	0.237	11.98
P250	0.596	0.192	0.069	0.246	0.246	12.22
P300	0.528	0.309	0.083	0.209	0.209	17.75
P500	0.405	0.497	0.176	0.178	0.178	29.60

^a Molar percentage of PPA equal to $(I_m/2 + I_n)/S \times 100\%$, where S is the integrated intensities of resonance peaks of ethylene proton ($S = I_k + I_m + I_n + I_l + I_o$).

content. Higher phosphorus content implies a higher content of P-E-T (T-E-P) and P-E-P units. Thus, molar fractions of terephthalate (X_T) and PPA (X_P) of a phosphorus-containing copolyester can be calculated from the intensities of the peaks from the respective methylene protons (k, m, n, l, o):

$$\begin{aligned} X_T &= (I_{\text{TET}} + I_{\text{TEP}}/2 + I_{\text{TEOH}})/S \\ &= (I_k + I_m/2 + I_l + I_o)/S \end{aligned} \quad (1)$$

$$\begin{aligned} X_P &= (I_{\text{PET}}/2 + I_{\text{PEP}})/S \\ &= (I_n/2 + I_p)/S \end{aligned} \quad (2)$$

where I_{TET} , I_{TEP} (where $I_{\text{TEP}} \equiv I_{\text{PET}}$), I_{PEP} and I_{TEOH} represent the integrated intensities of the ethylene proton's resonance signals of T-E-T, T-E-P, PEP sequences and the T-E-OH terminal unit, respectively, and S is the total integrated intensities of all resonance peaks of these ethylene protons. The results calculated by eqn (2) are listed in Table 2.

Figure 3 shows that the intensity of the PPA aromatic proton (proton j) resonance increases with increase of the phosphorus content because of higher PPA molar fractions. Thus, the resonance intensity can also be used to quantify the PPA molar fraction of copolyesters. Table 3 lists the proton resonance intensities and peak assignments for TPA and PPA aromatic protons of each copolyester. Figure 3 reveals that the TPA aromatic protons (proton i) resonate with chemical shifts ranging from 7.72 to 8.00 ppm while the PPA aromatic protons (proton j) resonate with chemical shifts ranging from 7.54 to 7.13 ppm for each copolyester.

The molar fractions of terephthalate (X_T) and PPA (X_P) can also be obtained from the resonance intensities

TABLE 3. Resonance intensities of phenyl protons of the aromatic unit and molar percentages of phenyl phosphonic acid (PPA)

Sample	Intensity of chemical shifts		$X_P(\%)^a$
	i	j	
P079	1.000	0.064	4.88
P119	0.980	0.106	7.93
P228	1.000	0.202	13.91
P250	1.000	0.267	17.60
P300	0.950	0.262	18.05
P500	0.900	0.586	34.25

^a Molar fraction of PPA is equal to $\{(I_j/5)/[(I_i/4) + (I_j/5)]\} \times 100$.

of the aromatic protons by eqns (3) and (4):

$$X_P = (I_j/5)/[(I_i/4) + (I_j/5)] \quad (3)$$

$$X_T = (I_i/4)/[(I_i/4) + (I_j/5)] = 1 - X_P \quad (4)$$

where I_j and I_i represent the integrated intensities of the PPA and TPA aromatic protons, respectively. The results calculated by eqn (3) are listed in Table 3. For comparison, the PPA molar fractions of the phosphorus-containing copolyesters determined by a UV method are listed in Table 4. The molar fractions of PPA obtained by ^1H NMR analyses are close to those from the UV method. The use of the ^1H NMR method in calculating monomer molar fractions has the advantages of small sample size, together with fast and non-destructive determination. It is not necessary to prepare reagents and to decompose the samples. Thus, the ^1H NMR method is more convenient to determine the PPA molar fractions of the phosphorus-containing copolyesters. By using the monomer molar fractions ($X_{\text{P(E)}}$) and

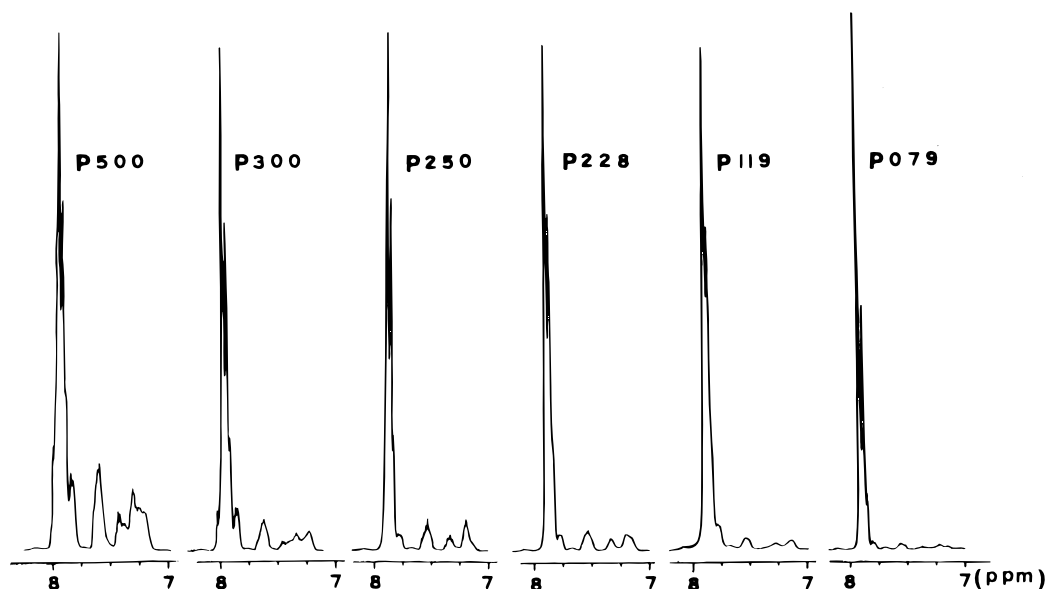


Fig. 3. Expanded ^1H NMR spectra of copolyesters with chemical shifts ranging from 7.1 to 8.2 ppm.

TABLE 4. Molar percentages of PPA obtained by ^1H NMR, UV methods and relative error

Sample	UV ^a	$X_{\text{P(E)}}^b$	$X_{\text{P(Ar)}}^c$
P079	4.88	4.48	3.79
P119	7.34	7.89	6.40
P228	14.03	11.98	11.40
P250	15.37	12.22	14.59
P300	18.42	17.75	14.74
P500	30.50	29.60	27.99

^a Calculated by a UV method.

^b Calculated from the ^1H NMR intensity of the ethylene protons of ethylene glycol units: $X_{\text{P}} = (I_{\text{PET}}/2 + I_{\text{PEP}})/S \times 100\%$.

^c Calculated from the ^1H NMR intensity of the aromatic protons: $X_{\text{P}} = \{(I_{\text{j}}/5)/[(I_{\text{i}}/4) + (I_{\text{j}}/5)]\} \times 100\%$.

$X_{\text{P(Ar)}}$ in Table 4) obtained by the ^1H NMR method to fit a linear least squares equation, the values calculated from the square multiple correlation coefficients are 0.964 and 0.928, respectively. These fittings based on ^1H NMR intensities of the aliphatic protons are considered to be adequate for a linear least squares fitted equation because the square multiple correlation coefficients are all greater than 0.6.³⁵

By taking ethylene glycol units as a reference point, the probability of finding a P unit next to a T unit is as follows:³⁶

$$P_{\text{TP}} = I_{\text{TEP}}/(I_{\text{TEP}} + I_{\text{TET}} + I_{\text{TEOH}}) \quad (5)$$

Similarly, the probability of finding a T unit next to a P unit can be calculated by the following equation:

$$P_{\text{PT}} = I_{\text{PET}}/(I_{\text{PET}} + I_{\text{PEP}}) \quad (6)$$

The probability of a P unit next to a T unit for sample P500 is substantially higher than sample P079, because the former has a significantly higher PPA

molar fraction than the latter. Copolyester containing a higher phosphorus content implies a greater probability of a P unit next to a T unit. The P_{TP} of sample P500 is 24.6%, which is close to X_{P} (29.6%) as shown in Table 5.

The number-average sequential lengths of the T (\bar{L}_{nT}) and P (\bar{L}_{nP}) units are calculated by the following equations:

$$\bar{L}_{\text{nT}} = 1/P_{\text{TP}} \quad (7)$$

$$\bar{L}_{\text{nP}} = 1/P_{\text{PT}} \quad (8)$$

The number average sequential lengths of phosphorus-containing copolyesters are also summarized in Table 5. The sample P500 has a lower sequential length of the T unit (4.06) than that of the sample of P079 (28.73), because the former has a substantially higher phosphorus content than the latter.

The degree of randomness is defined by:

$$B = P_{\text{TP}} + P_{\text{PT}} \quad (9)$$

For total randomness of a copolymer, B is equal to unity. For an alternating copolymer, B is equal to two, and for a block copolymer, B is close to zero.

Table 5 lists the degrees of randomness of the phosphorus-containing copolyesters obtained from the ^1H NMR analyses. The difference in monomer reactivity in the esterification reaction may result in a tendency to block distribution; however, the transesterification reaction results in a tendency to random distribution of the various sequences in the copolyesters. The degree of randomness of these phosphorus-containing copolyesters is in the range 0.64–0.83. The incorporation of the phosphorus linkage into the main chain backbone results in lower thermal stability. The ethylene phosphonate unit (P—O bond) is more readily attacked at high temperature.³³ Therefore,

TABLE 5. Molar percentages of PPA, number average sequential lengths and degree of randomness determined by ^1H NMR analyses

Sample	$X_{\text{P}}(\%)^a$	P_{TP}^b	P_{PT}^c	\bar{L}_{nT}^d	\bar{L}_{nP}^e	B^f
P079	4.48	0.035	0.742	28.73	1.35	0.77
P119	7.89	0.063	0.738	15.83	1.36	0.80
P228	11.98	0.077	0.566	12.97	1.76	0.64
P250	12.75	0.081	0.582	12.34	1.72	0.66
P300	17.75	0.140	0.650	7.13	1.54	0.79
P500	29.60	0.246	0.585	4.06	1.71	0.83

^a Molar percentage calculated from the ^1H NMR intensity of ethylene protons of ethylene glycol units.

^b Probability of finding a T unit next to a P unit.

^c Probability of finding a P unit next to a T unit.

^d Number-average sequential length of T.

^e Number-average sequential length of P.

^f Degree of randomness of the copolyester.

the *B* values obtained from NMR analyses tend to give greater variation.

CONCLUSIONS

A series of main chain phosphorus-containing copolyesters have been characterized by using a 400 MHz ¹H NMR spectrometer. The resonance intensity of the PPA aromatic protons increases with increase of the PPA content. The chemical shifts of ethylene protons of ethylene glycol units vary with different sequences. The resonance chemical shift of ethylene protons of the T-E-T unit is higher than that of P-E-T (T-E-P) and P-E-P units. Molar fractions of phosphorus-containing comonomer (PPA), their sequential distributions and degrees of randomness were determined through analyses of the ethylene protons in the ethylene glycol units. The molar fraction of PPA could also be obtained from the resonance intensities of the aromatic protons. Monomer fractions of the PPA comonomer obtained from ¹H NMR analyses are close to the values determined by a UV method. The copolyesters were found to have a degree of randomness in the range 0.66–0.83.

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