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Sequential distribution of copolyesters containing the phosphorus linking pendant groups characterized by ^{1}H-n.m.r.

Shinn-Jen Chang and Feng-Chih Chang*
Institute of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan, ROC
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A series of phosphorus-containing copolyesters were synthesized by polycondensation of terephthalic acid (TPA), ethylene glycol (EG) and 9,10-dihydro-10-[2,3-di(hydroxycarbonyl)propyl]-9-oxa-10-phosphaphenanthrene-10-oxide (DDP). Chemical structures of these phosphorus-containing copolyesters were characterized by ^{1}H-n.m.r.. Experimental results show that these methylene protons of the ethylene glycol unit resonate at lower field than those of the DDP aliphatic protons. The resonance intensity of DDP aliphatic protons increases with the increase of the phosphorus content. The ^{1}H-n.m.r. spectrum of the DDP aliphatic protons contain three peaks since the proton in H–C–P has greater coupling constant than that of H–C–C. The chemical shifts of these methylene protons in the ethylene glycol unit vary with different sequences. The methylene protons in the ethylene glycol of the T–E–T unit resonate at lower field 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 copolyester were determined through analyses of the resonances of methylene protons in the ethylene glycol unit. The molar fractions of the DDP comonomer determined by n.m.r. analyses are close to the charged values in synthetic step and the values determined by an UV method. Moreover, the copolyesters were found to be as random copolymers with a degree of randomness equal to about 1. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ^{1}H-n.m.r.; phosphorus-containing copolyester; sequential distribution)

INTRODUCTION

In recent years, emphasis has been placed on the necessity for various flame-retardant products, and much effort has been directed to this purpose. Phosphorus-containing flame retardants have been developed to replace the conventional halogen-containing flame retardants to meet the requirements of low smoke and low toxicity in view of environmental protection and public security. As the flame retardants are chemically bonded to the polymeric main chains[1-3], they will not migrate to the surfaces of polymers during processing, such as extrusion, injection moulding or spinning, and thus the flame retarding effect and physical properties are not affected.

The flame retardant effect of the phosphorus containing polymer was proposed via a solid-phase mechanism[4-6]. The correlation of the phosphorus content with their flame retardancy has been studied[4,7,8]. The phosphorus content of a phosphorus-containing polymer is usually determined by the UV method[9]. The chemical structure of a phosphorus-containing copolymer is also known to affect the flame retardancy[10-13].

The chemical structure of a copolymer as random, alternative, or block copolymer is an important factor in determining its final properties (comprising flame retardancy). For a copolyester, nuclear magnetic resonance spectroscopy (n.m.r.) is a powerful technique for qualitative and quantitative analyses of its chemical structure[14-28]. Yamadera and Murano[14] showed that the degrees of randomness of some copolyesters can be determined by n.m.r.. These analyses can be effective if 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 unit of copolyesters with different aromatic and aliphatic diol sequences have different resonance signals[15-17]. The resonance signals of carbons of the aromatic carbons of the terephthalic acid, aliphatic carbons of the ethylene glycol and 1,4-butanediol were found to give a quartet[18]. Additionally, the resonance signals from the proton(s) or carbon(s) of the glycol unit of copolyesters with different diacid sequences also result in different chemical shifts and thus the sequential distributions can be determined[14,19-28].

In this paper, the phosphorus-containing copolyesters of various phosphorus contents, poly(ethylene terephthalate)-*co*-poly(ethylene DDP)s (PET-*co*-PEDDP)s, were synthesized by the polycondensation of terephthalic acid, ethylene glycol and phosphorus-containing comonomer (9,10-dihydro-10-[2,3-di(hydroxycarbonyl)-propyl]-9-oxa-10-phosphaphenanthrene-10-oxide, hereinafter referred to as DDP). We attempt to analyze the sequential distribution and the phosphorus content of these phosphorus-containing copolyesters by using the proton nuclear magnetic resonance since the use of the ^{1}H-n.m.r. method has the advantages of small sample size, fastness and non-destructiveness.

EXPERIMENTAL

Terephthalic acid (TPA) and ethylene glycol (EG) were obtained from Tuntex Distinct Corp., Taiwan. 9,10-dihydro-9-oxa-10-phosphaphenanthrere-10-oxide (DOP) and itaconic acid were purchased from the Sanko Ltd., Japan. Tetrabutyl orthotitanate was purchased from Merck Schuchardt Ltd.

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* To whom correspondence should be addressed

DDP (phosphorus-containing comonomer) was prepared by an addition reaction of DOP with itaconic acid[29].

The phosphorus-containing copolyesters of various phosphorus contents, ranging from 0.5 to 4.0 wt%, were synthesized through co-condensation of DDP with TPA and EG catalyzed by tetrabutyl orthotitanate. The preparation was made according to a method previously described by Chang et al.[30] (as shown in Scheme 1). The copolyester with phosphorus content of 0.5 wt% is denoted as P05, 0.7 wt% is denoted as P07 and so on. The intrinsic viscosity at 30°C in phenol/1,1,2,2-tetrachloroethane (60/40 wt/wt) of each copolyester was slightly greater than 0.60 dl/g.

[1]H-n.m.r. spectra of copolyesters in CF_3COOD were carried out by a Bruker Am 400 n.m.r. by using tetramethylsilane (TMS) as an internal standard. The UV method[9] was employed to determine the phosphorus content of the copolyester.

RESULTS AND DISCUSSION

Proton n.m.r. spectra of PET and PET-co-PEDDP P40 (copolyester with phosphorus content of 4.0 wt%) are shown in Figure 1a,b. The chemical structure and resonance peak assignments are shown in Scheme 2 and Scheme 3 and Table 1. The chemical shifts for aliphatic and aromatic protons are in the ranges of 2.0–5.0 and 6.5–8.0 ppm, respectively.

The chemical shifts of aliphatic protons for the methylene protons of the ethylene glycol unit is 3.3 to 5.0 ppm and that for the DDP aliphatic protons is 2.0 to 3.2 ppm as shown in Figure 1b. The inductive effect of the oxygen causes the shifting farther downfield with increasing electronegativity.

Table 1 Assignments of resonance peaks of PET and copolyesters P40

Sequence	Proton	Chemical shift (ppm)
PET[a]	a	7.79
	b	4.48
	c	4.34
	d	3.86
	n'	10.91
P40[b]	e	7.79
	f	7.53–6.81
	g	4.48
	h	4.34
	i	4.25–4.17
	j	3.97
	k	3.86
	l (l_1, l_2)	3.12, 2.34
	m	2.63–2.71
	o'	10.91

[a] PET is poly (ethylene terephthalate)
[b] P40 is phosphorus-containing copolyester with phosphorus-content of 4.0 wt%
[c] n and o are the solvent peak of CF_3COOD

DDP
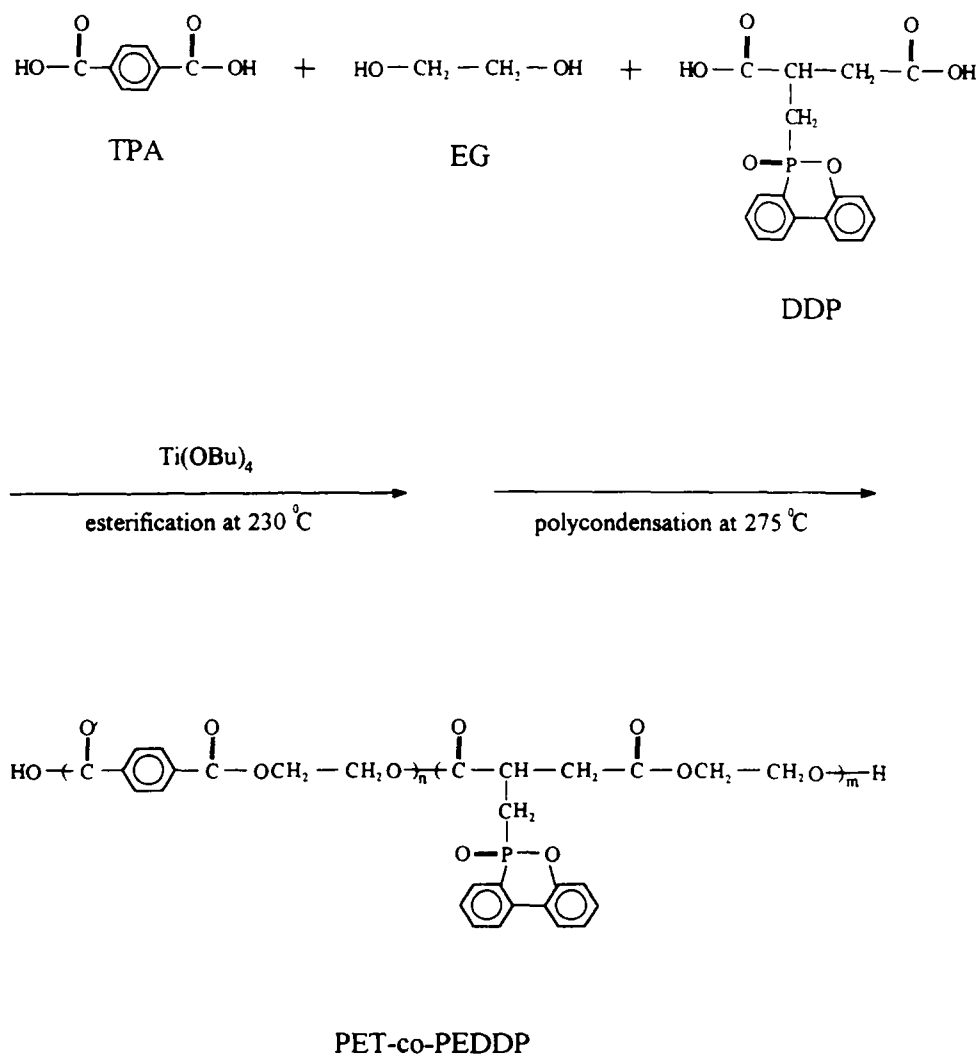
PET-co-PEDDP
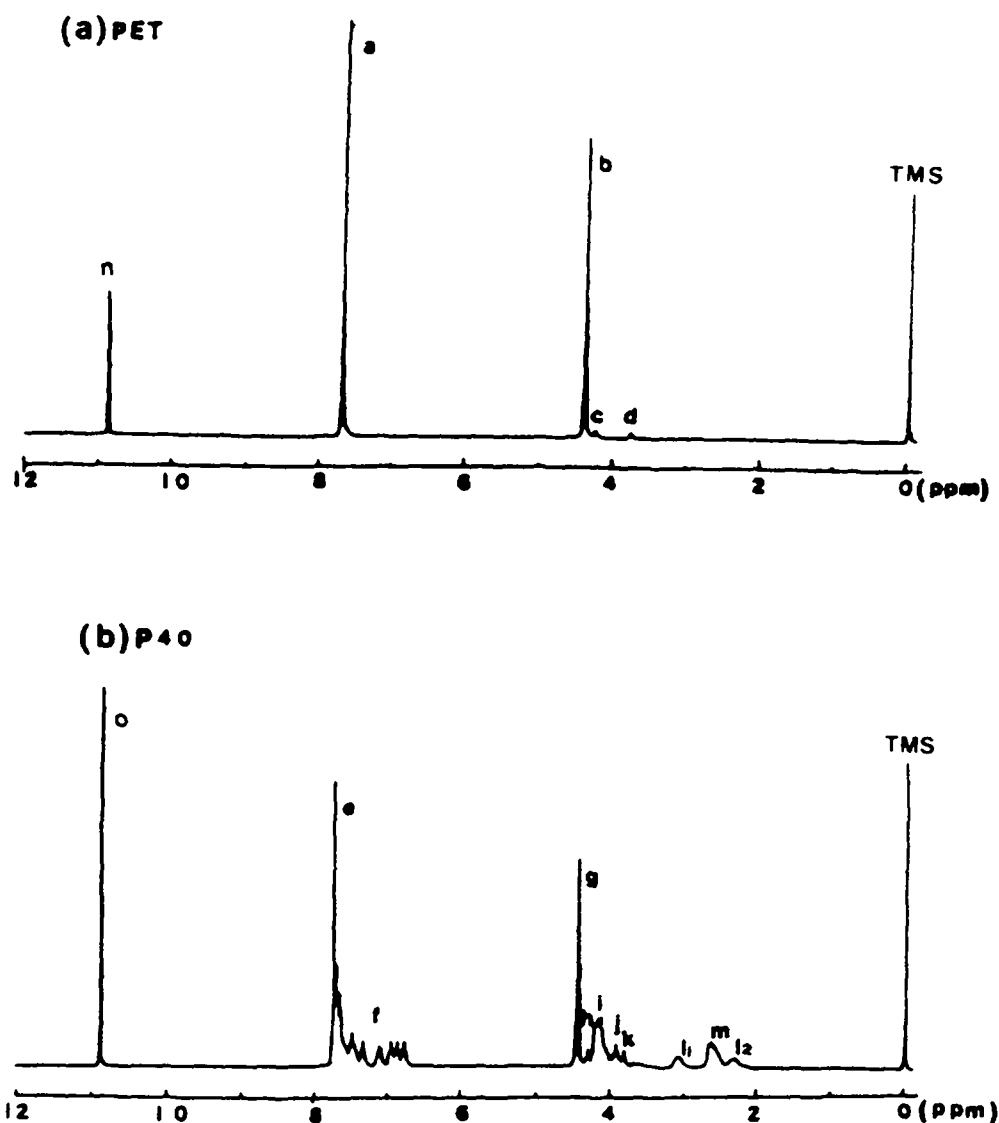
Scheme 1 The preparation of PET-co-PEDDP polymer.

Figure 1 ¹H-n.m.r. spectrum of PET and copolyester P40

Table 2 The chemical shift and intensity of DDP aliphatic protons resonance for each copolyester

| Sample	Intensity at				
	I_1 3.12 (ppm)	m 2.63–2.71 (ppm)	I_2 2.34 (ppm)	I/m^a	$m + I_1 + I_2^b$
P05	0.054	0.181	0.051	0.580	0.286
P07	0.057	0.189	0.055	0.593	0.301
P10	0.045	0.134	0.044	0.664	0.223
P20	0.157	0.513	0.159	0.616	0.829
P30	0.180	0.555	0.184	0.656	0.919
P40	0.286	0.862	0.298	0.677	1.446

$^a I = (I_1 + I_2)$. I/m is the resonance intensity ratio of protons I to protons m
$^b m + I_1 + I_2$ is the total resonance intensity of DDP aliphatic protons

Thus, the methylene protons (g, h, i, j, k) in Figure 1b resonate at lower field than those of the DDP aliphatic protons (m and l). The expanded n.m.r. spectra from 2.0 to 3.2 ppm and 3.3 to 5.0 ppm of various copolyesters are shown in Figures 2 and 3. Figure 2 shows that the intensities of the DDP aliphatic proton resonances increase with the increase of the phosphorus content due to higher DDP molar fraction. Thus, the resonance intensities can be used to quantify the DDP molar fraction in a copolyester. Tables 2 and 3 list the proton resonance intensities and peak

assignments of DDP aliphatic protons and methylene protons of the ethylene glycol unit. Table 2 reveals that the DDP aliphatic protons resonances give three peaks and their relative intensities at chemical shifts of 3.12, 2.63–2.71, and 2.34 ppm are approximately 1:3:1 for each copolyester. Considering the chemical structure in Scheme 3 of a copolyester, the aliphatic protons of DDP should possess only m and l two peaks. However, the ¹H-n.m.r. spectra shown in Figure 2 give three peaks because the proton in H–C–P has greater coupling constant than that of

PET
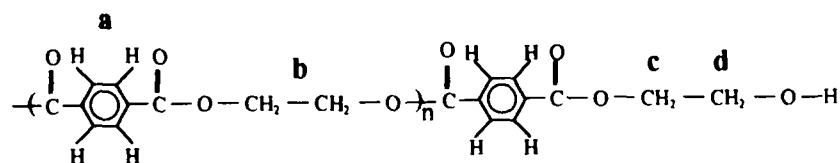
PET-CO-PEDDP
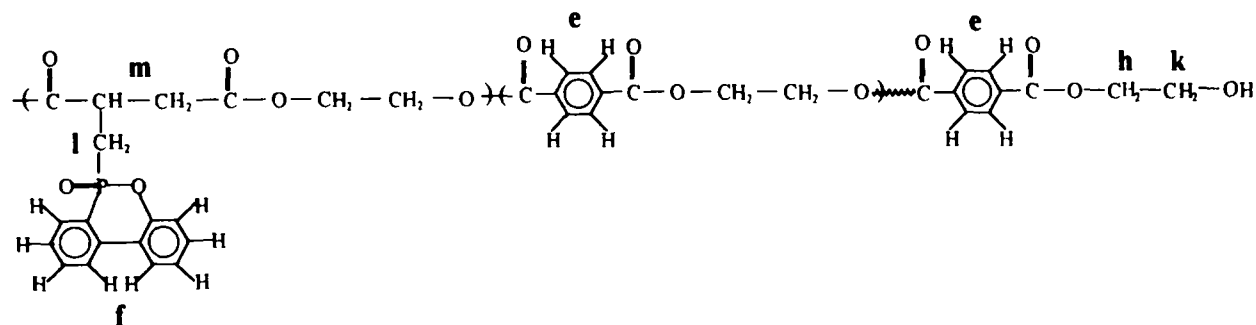
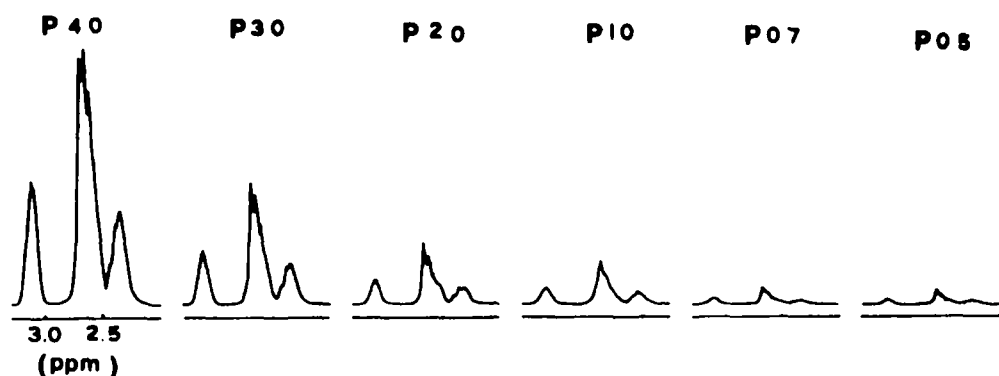**Scheme 2** The sequences of PET-co-PEDDP polymer.

Figure 2 Expanded n.m.r. spectra of copolyesters with chemical shifts ranging from 2.0 to 3.2 ppm

H–C–C. Thus, the resonance peak of P–CH$_2$–C splits into two peaks at 3.12 (I_1) and 2.34 (I_2) ppm, and the total numbers of resonance peaks of aliphatic protons of DDP now become three. The resonance intensity ratios of protons l ($I_{3.12} + I_{2.34}$) to protons m ($I_{2.63-2.71}$) are from 0.580 to 0.677 (about 2:3) as shown in *Table 2* where,

$I_{3.12}$ resonance intensity of ^{1}H-n.m.r. at 3.12 ppm chemical shift;
$I_{2.34}$ resonance intensity of ^{1}H-n.m.r. at 2.34 ppm chemical shift;
$I_{2.63-2.71}$ resonance intensity of ^{1}H-n.m.r. from 2.63 to 2.71 ppm chemical shift.

The resonance intensity ratio of protons l to m shown in *Table 2* represents the proton number ratio of l to m shown in *Scheme 3*.

By comparing with the resonance peaks of a PET, the resonance of the methylene protons in the ethylene glycol unit of the phosphorus-containing copolyester can be from four possible sequences as shown in *Scheme 3*. The resonance signals of methylene protons for the copolyester with TE$_g$T, TE$_i$P(PE$_i$T) and PE$_j$P sequences resonate at 4.48 (proton g), 4.25–4.17 (proton i) and 3.97 (proton j) ppm,

respectively. The β-methylene proton (proton h) and α-$^t\backslash l$ proton (proton k) of the hydroxyl terminal unit (T–E–OH) in the ethylene glycol resonate at 4.34 and 3.86 ppm, respectively[31]. The summarized data are listed in *Table 1* where T is the terephthalate unit, E is the ethylene glycol unit and P is the DDP unit.

Figure 3 shows the resonance peaks of the methylene protons in ethylene glycol unit of the phosphorus-containing copolyesters with chemical shift ranging from 3.3 to 5.0 ppm. The methylene protons of the T–E–T unit (protons i) resonate at lower field than that of P–E–T(T–E–P) (protons i) and P–E–P units (protons j), since the electronegativity of the P unit is weaker than that of the T unit. The wider peak of proton i is given by two non-equivalent CH$_2$ group protons of the EG units present in the T–E–P (and P–E–T) hetrotriads; this is an unresolved multiplet[32]. The intensity of peak h is equal to peak k ($I_h = I_k$) because the hydroxyl terminal unit of T–E–OH possesses both α- and β-methylene protons. The resonance intensities of methylene protons of ethylene glycol unit of each sample are listed in *Table 3*. Comparisons of the resonance peaks of
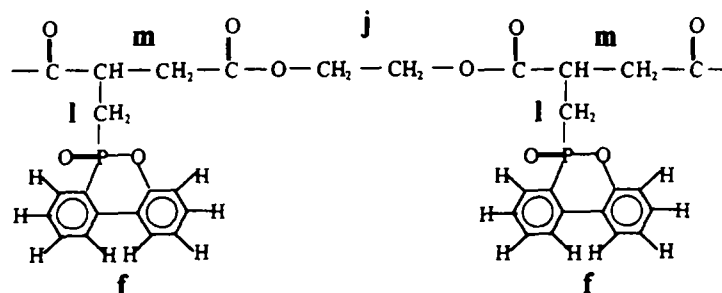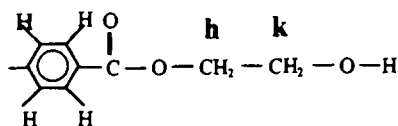
T-E-T
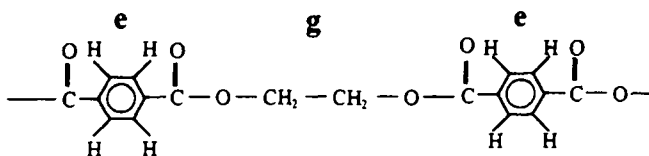
P-E-T(T-E-P)
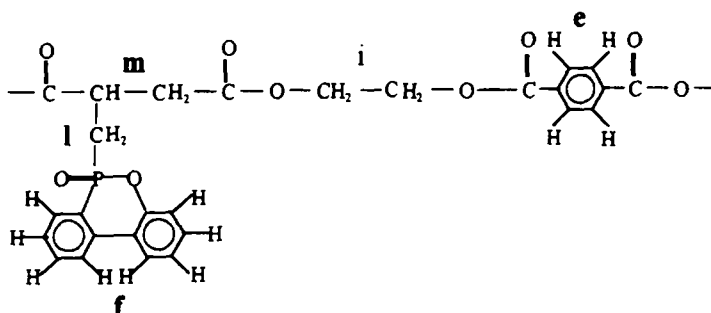
P-E-P

T-E-OH

Scheme 3 The sequences of PET-co-PEDDP polymer.

Table 3 The resonance intensities of methylene protons of ethylene glycol unit and molar fraction percent of DDP

| Sample | Intensity of chemical shifts (%) | | | | | X_P (%)[a] |
	g	i	j	h	k	
P05	86.5	7.9	0	2.8	2.8	3.95
P07	80.4	8.4	0.1	5.5	5.5	4.30
P10	76.4	13.9	0.3	4.7	4.7	7.25
P20	66.3	23.8	1.6	4.1	4.1	13.50
P30	51.9	30.3	4.8	6.5	6.5	19.95
P40	39.6	43.1	9.1	4.1	4.1	30.65

[a] X_P (%) is the molar fraction percent of DDP. $X_P = (I_i/2 + I_j)/S \times 100\%$, where S is the total integrated intensities of resonance peaks of methylene protons of the ethylene glycol ($S = I_g + I_{i+j} \cdot I_h + I_k$)
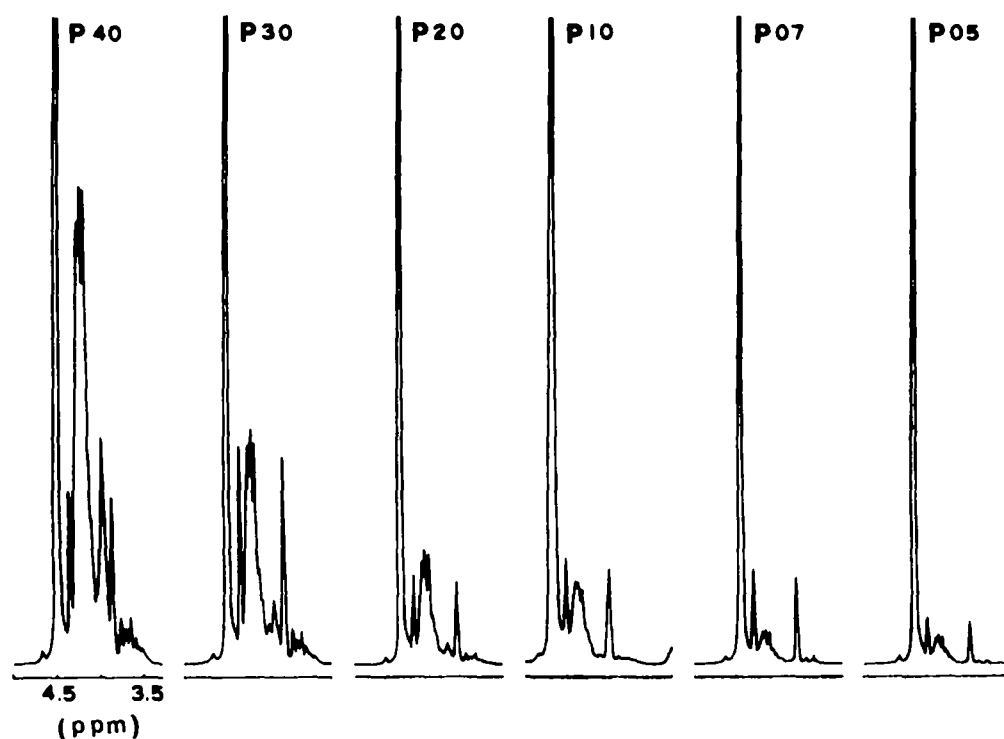
Figure 3 Expanded n.m.r. spectra of copolyesters with chemical shifts ranging from 3.3 to 5.0 ppm

Table 4 The molar fraction percent of DDP by the ^{1}H-n.m.r. method, experimentally charged value, UV methods, and relative error

Sample	Charged[a] (%)	UV[b] (%)	H_{TET}^c (%)	H_{DDP}^d (%)	RE_{TE}^e (%)	RE_{DDP}^f (%)
P05	3.19	3.19	3.95	3.97	23.82	24.45
P07	4.58	4.48	4.30	4.59	−4.02	2.46
P10	6.63	7.21	7.25	8.60	0.55	19.28
P20	14.01	12.92	13.50	15.49	4.49	19.89
P30	22.48	22.38	19.95	23.38	−10.86	4.47
P40	32.25	33.33	30.65	39.29	−8.04	17.88

[a] The charged value in the synthetic step
[b] By UV method
[c] H_{TET} is molar the fraction percent calculated by ^{1}H-n.m.r. intensities of methylene protons of ethylene glycol unit method, $X_P(\%) = (I_{PET}/2 + I_{PEP} + I_{TEOH})/S \times 100\%$
[d] H_{DDP} is the molar fraction percent calculated by ^{1}H-n.m.r. intensities of aliphatic protons of DDP method, $X_P(\%) = I_{DDP}/S \times 100\%$
[e] RE_{TET} is the relative error (%) of H_{TET} *versus* UV
[f] RE_{DDP} is the relative error (%) of H_{DDP} *versus* UV

the methylene protons from samples of P05, P07, P10, P20, P30 and P40 reveal that the resonance intensity of proton *g* at 4.48 ppm decreases with the increase of the phosphorus content. Higher phosphorus content implies higher content of the P–E–T (T–E–P) and P–E–P units. Thus, the molar fractions of terephthalate (X_T) and DDP (X_P) of a phosphorus-containing copolyester can be calculated from the intensities of the five peaks of the methylene protons,

$$X_T = (I_{TET} + I_{TEP}/2 + I_{TEOH})/S$$
$$= (I_g + I_i/2 + I_h + I_k)/S \tag{1}$$

$$X_P = (I_{PET}/2 + I_{PEP})/S$$
$$= (I_i/2 + I_j)/S \tag{2}$$

Where I_{TET} (I_g), I_{TEP} (I_i) (where $I_{TEP} = I_{PET}$), I_{PEP} (I_j) and I_{TEOH} (I_h, I_k) represent the integrated intensities of methylene protons resonance signals of TET, TEP, PEP sequence and TEOH terminal unit, respectively. S is the total integrated intensities of the resonance peaks of methylene protons in

the ethylene glycol (comprising methylene protons of TET, TEP (PET), PEP sequences and α- and β-methylene protons of T–E–OH). The summarized results are listed in *Table 3*.

The molar fractions of terephthalate (X_T) and DDP (X_P) can also be obtained from the total resonance intensities of aliphatic protons of DDP by the equations (3) and (4),

$$X_P = I_{DDP}/S = (I_l + I_m)/S \tag{3}$$

$$X_T = 1 - X_P \tag{4}$$

where I_{DDP} represents the integrated intensity of the DDP aliphatic protons ($I_{DDP} = I_l + I_m = I_{3.12} + I_{2.34} + I_{2.63-2.71}$). The molar fraction of DDP (X_P) and the results calculated by equation (3) are listed in *Table 4*. The DDP molar fraction of the phosphorus-containing copolyesters determined by the UV method and the charged value in the synthetic step are also listed in *Table 4*. The DDP molar fractions obtained from ^{1}H-n.m.r. analyses are fairly close to the charged values in synthetic step and values from the UV spectrum method. The use of the ^{1}H-n.m.r. method in calculating

Table 5 The molar fraction percent of DDP, number-average sequential length, and degree of randomness determined by ^{1}H-n.m.r. analyses

Sample	X_P (%)	P_{TP}^a	P_{PT}^b	$\bar{L}_{nT}{}^c$	$\bar{L}_{nP}{}^d$	B^e
P05	3.95	0.079	1.000	12.658	1.000	1.079
P07	4.30	0.084	0.988	11.881	1.012	1.072
P10	7.25	0.139	0.979	7.173	1.022	1.118
P20	13.50	0.242	0.937	4.130	1.067	1.179
P30	19.95	0.318	0.863	3.142	1.158	1.181
P40	30.65	0.474	0.826	2.109	1.211	1.300

^{a} The probability of finding a T unit next to a P unit
^{b} The probability of finding a P unit next to a T unit
^{c} The number-average sequential length of T
^{d} The number-average sequential length of P
^{e} The degree of randomness of copolyester

monomer molar fraction has the advantages of small sample size, fastness and non-destructiveness. Thus, the ^{1}H-n.m.r. method is convenient to calculate the DDP molar fraction of the phosphorus-containing copolyester. By taking the DDP monomer molar fractions (H_{TET} and H_{DDP}, *Table 4*) obtained from ^{1}H-n.m.r. method to fit a linear least fitted equation, the calculated values from the square multiple correlation coefficient are 0.998 and 0.996, respectively. These fittings based on ^{1}H-n.m.r. intensities of the aliphatic protons are considered to be adequate for the linear least fitted equation because the square multiple correlation coefficients are all greater than 0.6^{32}.

The relative errors of the column HTET *versus* column UV (i.e., the error of comonomer molar fraction calculated from ^{1}H-n.m.r. method by equation (2) relative to that of the UV experimental method) and column H_{DDP} *versus* column UV (i.e., the error of comonomer molar fraction calculated from ^{1}H-n.m.r. method by equation (3) relative to that of the UV method) are listed in *Table 4*. These results reveal that ^{1}H-n.m.r. is an adequate method to analyze monomer molar fraction of a phosphorus-containing copolyester due to relatively smaller error. The relative error of sample P05 are relatively higher because the small S/N ratio which is not unexpected.

By taking ethylene glycol unit as a reference point, the probability of finding a P unit next to a T unit is^{33}

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

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

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

The PTP and PPT of phosphorus-containing copolyesters are summarized in *Table 5*. The probability of P unit next to a T unit for sample P40 is substantially higher than sample P05 because the former has significantly higher DDP molar fraction than the latter. Copolyester containing higher phosphorus content implies greater probability of finding a P unit next to a T unit.

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

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

$$\bar{L}_{nT} = 1/P_{PT} \qquad (8)$$

The average sequential lengths of phosphorus-containing copolyesters are summarized in *Table 5*. The sample P40 has lower sequential length of the T unit than that of the sample of P05 because the former has higher phosphorus content than the latter.

The degree of randomness is defined by^{14}

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

For a total randomness of a copolymer, B is equal to 1. For an alternative copolymer, B is equal to 2 and a block copolymer, B is close to zero.

Table 5 lists the degrees of randomness of the phosphorus-containing copolyesters determined by ^{1}H-n.m.r. analyses. The difference in monomer reactivity may be significant in the melt polycondensation, however, the transesterification reaction renders random distribution of various sequences of copolyesters. The degrees of randomness of these phosphorus-containing copolyesters are close to 1 as shown in *Table 5*. Therefore, these copolyesters are random or nearly random with uniform phosphorus distribution in the polymer chain.

CONCLUSIONS

A series of phosphorus-containing copolyesters have been characterized using a 400 MHz ^{1}H-n.m.r.. Methylene protons of ethylene glycol unit resonate at a lower field than that of the DDP aliphatic protons. The resonance intensity of the DDP aliphatic protons increase with the increase of the DDP content. ^{1}H-n.m.r. spectra of the DDP aliphatic protons possess three peaks because the proton in H–C–P has greater coupling constant than that of H–C–C. The chemical shifts of methylene protons of ethylene glycol unit vary with different sequence. The chemical shift of the methylene protons in the ethylene glycol of the T–E–T unit is higher than those of P–E–T(T–E–P) and P–E–P units. Molar fractions of phosphorus-containing comonomer (DDP), their sequential distributions and degrees of randomness were determined through analyses of the corresponding multiplet of the methylene protons in ethylene glycol unit. Molar fractions of the DDP comonomer obtained from ^{1}H-n.m.r. analyses are close to the experimentally charged values in synthetic step and the values determined by the UV method. These copolyesters are random or nearly copolymers with degree of randomness equal to about 1.

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