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Direct polymerization of aromatic diacid dimethyl esters with aromatic diamines: I. Analysis of reaction mechanism

Seung Koo Park and Wan Shik Ha
Department of Fiber and Polymer Science, College of Engineering, Seoul National University, Seoul 151-742, Korea

and Chul Joo Lee*
Division of Polymer Research, Korea Institute of Science and Technology, PO Box 131, Cheongryang, Seoul 136-791, Korea

The direct polymerization of aromatic diacid dimethyl esters with aromatic diamines using phosphorus activating agents and tertiary amines was conducted at room temperature. The reaction mechanism was investigated with model compounds. The diacid dimethyl ester of pyromellitic dianhydride was reacted with the activating agent, along with pyridine as a catalyst, or reacted with an N-methylpyrrolidone (NMP)-activating agent complex to form the activated anhydride intermediate. It was characterized with ^{31}P and ^{1}H nuclear magnetic resonance, and ultra-violet–visible spectroscopy. The polymerization proceeded via the nucleophilic substitution reaction between aromatic acid and amine. The amidation reaction proceeded further to afford N-phenylphthalmide with phosphorus oxychloride and phenyl phosphonyl dichloride in the model reactions, but not in the polymerization reaction. As for the degree of polymerization, phenyl phosphonic dichloride and pyridine were superior to any other pairs of activating agent and tertiary amine. The direct polymerization of various diacid dimethyl esters of aromatic dianhydrides with aromatic diamines was successfully performed. © 1997 Elsevier Science Ltd.

(Keywords: direct polymerization; polyamic acid dimethyl ester; activating agent)

INTRODUCTION

Aromatic polyimides have gained a prominent position, due to their excellent thermal stability, along with their good mechanical and electrical properties. However polyamic acid as a polyimide precursor has several disadvantages, including solution instability, an exchange reaction in solution, hydrolytic degradation and a polyelectrolyte effect, which can lead to film thickness changes for microelectronics applications[1,2]. These drawbacks are mainly due to the acid proton and the catalytic effect of the *ortho* carboxylic acid group[3–5]. Polyamic acid esters may be substituted for polyamic acids to alleviate the problems associated with the acid proton.

Polyamic acid esters have been synthesized by the reaction of diester-diacid chloride with diamine. This method is not easy in practice on a large scale, since preparation and purification of acid chloride is complicated. Direct polycondensation, in which carboxylic acid is activated to be readily substituted by nucleophiles, has been developed as a useful method for the synthesis of condensation polymers including polyamides[6,7]. Among activating agents used for direct polycondensation, 3,3′-(phenyl phosphinylidene)bis[2(3H)-benzothiazolone] (1), 3,3′-(phenylphosphinylidene) bis[2(3H)-benzoxazolone]

(2), and diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (3) are useful. Preparation of polyamic acid di-*t*-butyl esters by direct polycondensation of diacid di-*t*-butyl esters of pyromellitic dianhydride with various diamines using activating agents (1) and (3) has been reported[8,9]. In those reports, polymerization was carried out at room temperature and the cleavage of the *t*-butyl ester groups did not occur. Activating agents (1), (2) and (3) are very effective for syntheses of polyamic acid esters, however, they have to be synthesized before use, from their starting materials. A detailed description of the polymerization mechanism has not been reported.

In this study, already commercialized activating agents were used for enhancing the reactivity of aromatic diacid-dimethyl esters with aromatic diamines. Their potential for direct polymerization, and the mechanism of polymerization, were investigated.
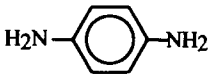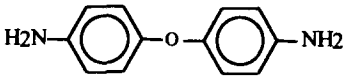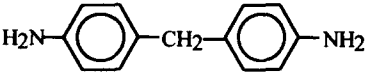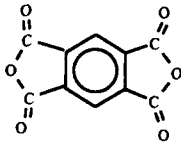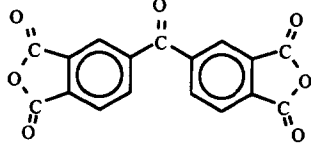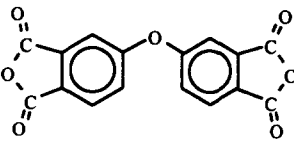
EXPERIMENTAL

Materials

Pyromellitic anhydride (PMDA), 3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA), and 4,4′-oxydiphthalic anhydride (ODPA) were recrystallized from acetic anhydride and sublimed under reduced pressure before use. 4,4′-Oxydianiline (ODA) was also sublimed and *p*-phenylene diamine (PPD) was distilled at 170°C under reduced pressure. *p,p′*-Methylene dianiline

* To whom correspondence should be addressed

Table 1 Monomers, activating agents, and tertiary amines used in this study

Name	Structure	Abbreviation
Diamine		
p-Phenylene diamine		PPD
4,4'-Oxydianiline		ODA
p,p'-Methylene dianiline		MDA
Dianhydride		
Pyromellitic dianhydride		PMDA (PMDE)[a]
3,3',4,4'-Benzophenone tetracarboxylic dianhydride		BTDA (BTDE)[a]
4,4'-Oxydiphthalic dianhydride		ODPA (ODPE)[a]

(MDA) was recrystallized from benzene. All had been kept in a desiccator before use. Phthalic anhydride, used as a model compound, was extracted with chloroform and recrystallized.

N-methyl pyrrolidone (NMP) was distilled over P_2O_5 under reduced pressure, and stored in desiccators. Tertiary amines and phosphorus activating agents were used as received.

Preparation of methyl hydrogen phthalate[10]

A methanol solution (50 ml) of phthalic anhydride (20 g) was heated to reflux, until all the solid was dissolved and the excess methanol was evaporated under reduced pressure. Dry benzene (10 ml) was added to the residue and evaporated thoroughly for removing residual methanol. Benzene was introduced to the white

solid again and heated to reflux and filtered. Ligroin was added to the solution until crystallization started (m.p. 82–82.5°C). Infra-red (i.r.) (KBr, cm^{-1}): 3440 (O–H str., acid); 2953 (C–H) str., methyl); 1743 (C=O str., ester); 1703 (C=O str., ester); 1295 (C–O–C str., ester). ^{1}H nuclear magnetic resonance (n.m.r.) (DMSO-d_6, ppm): 7.57–7.78 (*m*, 4H aromatic); 3.78 (*s*, 3H methyl).

Preparation of dicarbomethoxy terephthaloyl chloride of PMDA and its polymerization[11]

The diacid dimethyl ester of PMDA (PMDE) was prepared in the above manner. PMDE (5 g) was heated to reflux with stirring in thionyl chloride (20 ml) until a clear solution was obtained. Then the excess thionyl chloride was removed by a water aspirator and the residue was recrystallized from benzene/heptane (50/50, v/v).
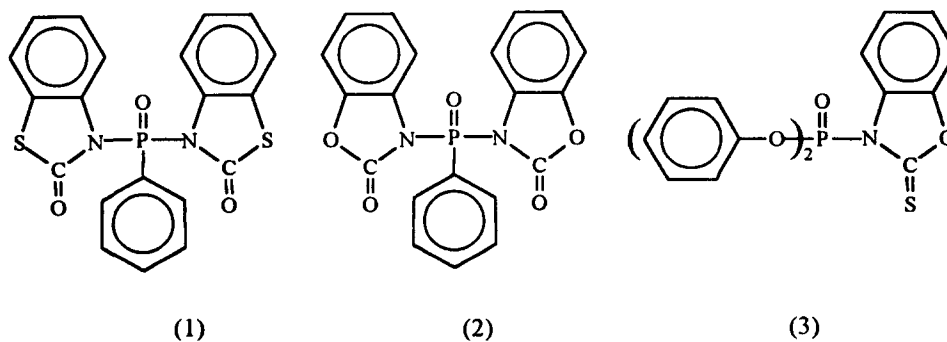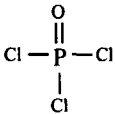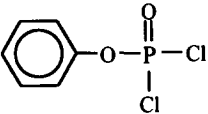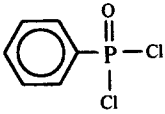

(1)   (2)   (3)
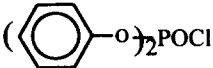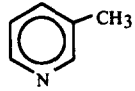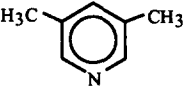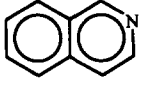
Table 1 (continued)

Name	Structure	Abbreviation
Activating agent		
Phosphorus oxychloride		
Phenyl phosphoryl dichloride		
Phenyl phosphonic dichloride		
Diethyl chlorophosphate	$(C_2H_5)_2POCl$	
Diphenyl phosphoryl chloride		
Tertiary amine		
Pyridine		
α-Picoline		
2,6-Lutidine		
Imidazole		
Isoquinoline		
Triethyl amine	$(C_2H_5)_3N$	

[a] Abbreviations of the corresponding diacid dimethyl ester is in parentheses

Pyridine (0.93 ml, 11.5 mmol) was introduced into the solution after 0.7707 g (3.9 mmol) of ODA was dissolved in NMP (10 ml) under nitrogen. This diacid chloride monomer (1.2293 g, 3.9 mmol) was added all at once at room temperature with vigorous stirring. Polymerization was carried out for 24 h.

Preparation of diacid dimethyl ester and its polymerization

Freshly sublimed dianhydride was introduced into anhydrous methanol and the solution was heated to reflux with stirring until the dianhydride was disappeared. After the solution was cooled to room temperature, the excess methanol was evaporated under reduced pressure to obtain the diacid dimethyl ester of anhydride.

After dissolving this compound (4.1 mmol) in NMP (10 ml) under nitrogen, the tertiary amine (16.4 mmol) and the activating agent (8.2 mmol) were added to the solution carefully. When the exothermic reaction was completed, the aromatic diamine was introduced into the mixture with vigorous stirring for direct polycondensation. It was left with stirring for 24 h at room temperature. The polymer concentration was always adjusted to 20% (w/v). After the reaction, the resulting viscous solution was poured into methanol, and the precipitate was filtered off and dried under vacuum at room temperature.

Table 2 Polymerization of PMDE and 4,4'-oxydianiline with various activating agents in NMP

|		η_{inh}^{a} of polyamic acid ester				
Tertiary amine	(pK_a)	POCl$_3$	PhOPOCl$_2$	PhPOCl$_2$	(PhO)$_2$POCl	(C$_2$H$_5$O)$_2$POCl
Pyridine	(5.23)	0.25	0.20	0.32	d	d
α-Picoline	(5.97)	0.12	0.16	0.16	d	d
2,6-Lutidine	(6.99)	b	b	b	b	b
Imidazole	(7.12)	0.18	0.23	0.24	d	d
Isoquinoline	(8.60)	c	c	c	c	c
Triethyl amine	(11.0)	c	c	c	c	c

^{a} Measured by 0.5 g dl^{-1} in DMAc at 25°C
^{b} Precipitated when tertiary amine was introduced
^{c} Precipitated when activating agent was introduced
^{d} Polymer was not obtained

**Table 3** Polymerization of various diacid–dimethyl esters of aromatic dianhydride and diamine with PhPOCl$_2$ in NMP

Diacid–dimethyl ester	Diamine	η_{inh}^{a}
PMDE	PPD	0.33
	ODA	0.32
	MDA	0.27
ODPE	PPD	Precipitated
	ODA	0.31
BTDE	ODA	0.30

^{a} Measured by 0.5 g dl^{-1} in DMAc at 25°C

Model compound studies

After methyl hydrogen phthalate (3 g, 16.6 mmol) was dissolved in benzene (40 ml) under nitrogen, pyridine (1.34 ml, 16.6 mmol) was added to the solution. The activating agent (16.6 mmol) was added dropwise, to maintain the solution at room temperature. After the hygroscopic white solid was formed, it was filtered off and dried under vacuum. The solid was weighed in a glove-box, and sealed in order to be free from moisture. The filtrate was vacuum-evaporated until benzene was thoroughly removed. A blank test was also conducted.
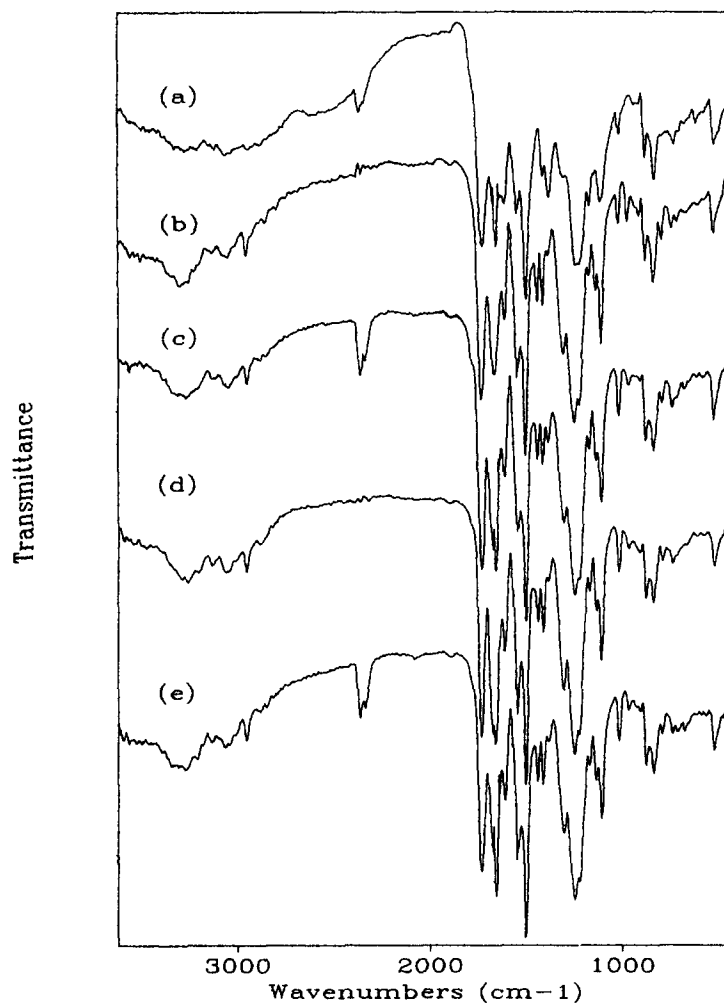
Figure 1 I.r. spectra of PMDA/ODA polyamic acid (a) and polyamic acid dimethyl ester synthesized from (b) dicarbomethoxy terephthaloyl chloride of PMDA/ODA; (c) PMDE/ODA using POCl$_3$ and pyridine; (d) PMDE/ODA using PhOPOCl$_2$ and pyridine; (e) PMDE/ODA using PhPOCl$_2$ and pyridine
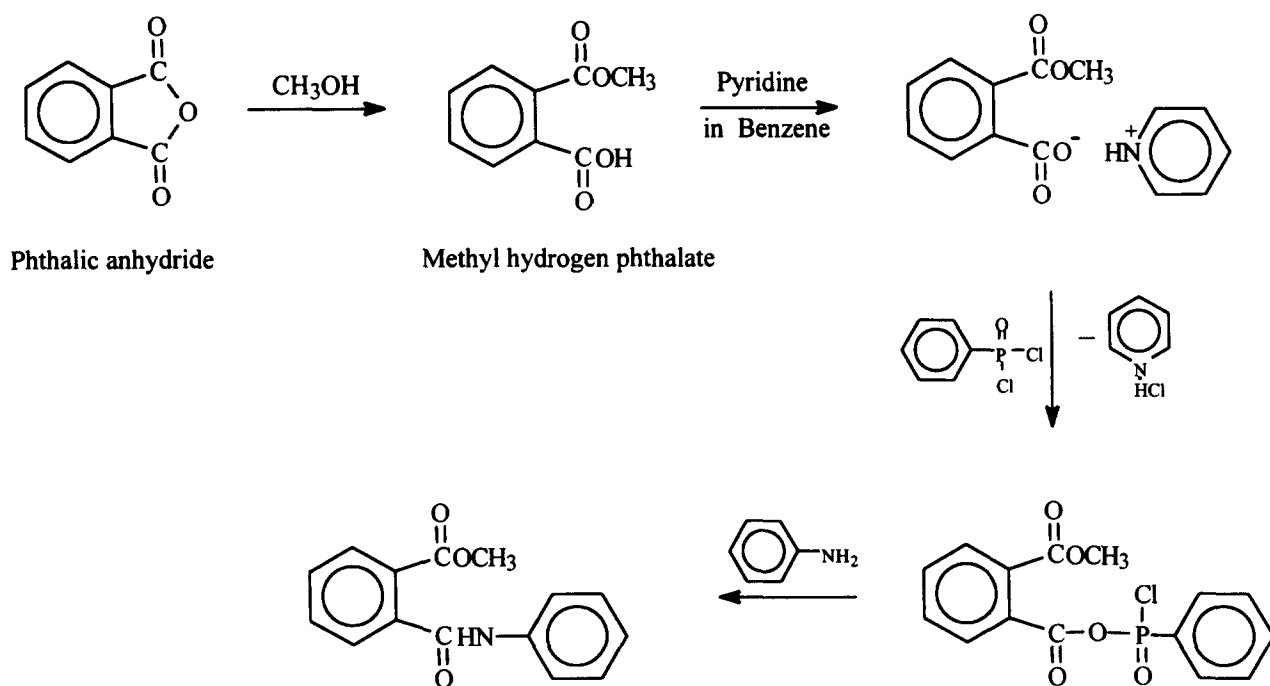
Scheme 1
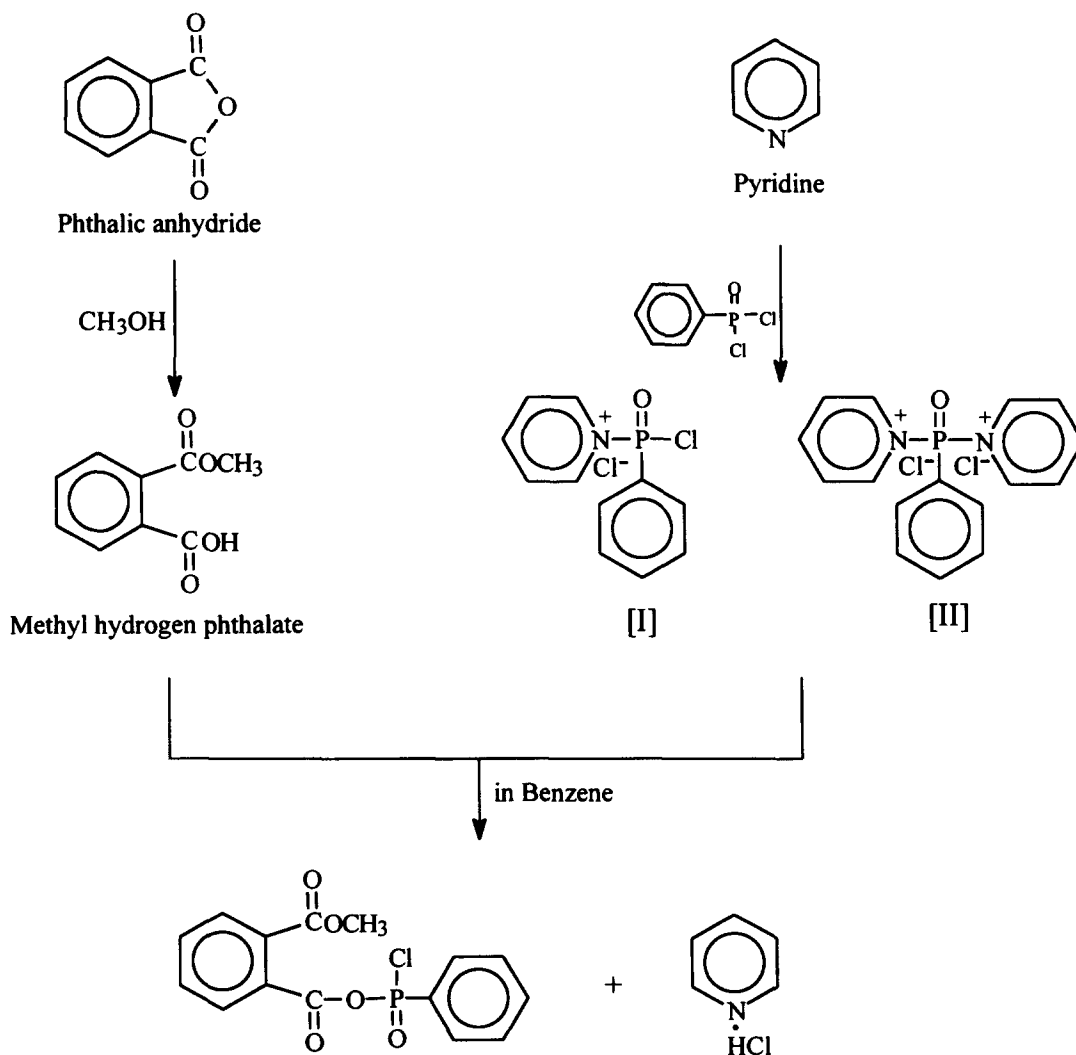
Scheme 2

Instead of benzene, NMP (40 ml), the solvent of the real polymerization system, was used and aniline (2.02 ml, 16.6 mmol) was added without separation of the intermediate. The reaction mixture was stirred for 3 h under nitrogen. The reaction solution was poured into excess water and the precipitate was filtered and dried under reduced pressure at room temperature.

Measurements

I.r. spectra were recorded on a Midac® Fourier transform i.r. spectrophotometer. A Varian® Gemini 200 was used for ^{1}H n.m.r. measurements, and Varian® Gemini 300 for ^{31}P n.m.r. TMS and 85% phosphoric acid were used as standard references, respectively, and acetone-d_6, dimethyl sulfoxide-d_6, benzene-d_6 were used as solvents. For ultraviolet–visible (u.v.–vis) measurements, a Jasco® V-530 spectrophotometer was used, and the concentration was constantly settled to be in absorbance range. Inherent viscosity of all polyamic acid dimethyl esters was determined at 0.5 g dl^{-1} in N,N'-dimethylacetamide (DMAc) at 25°C by an Ubbelohde viscometer.
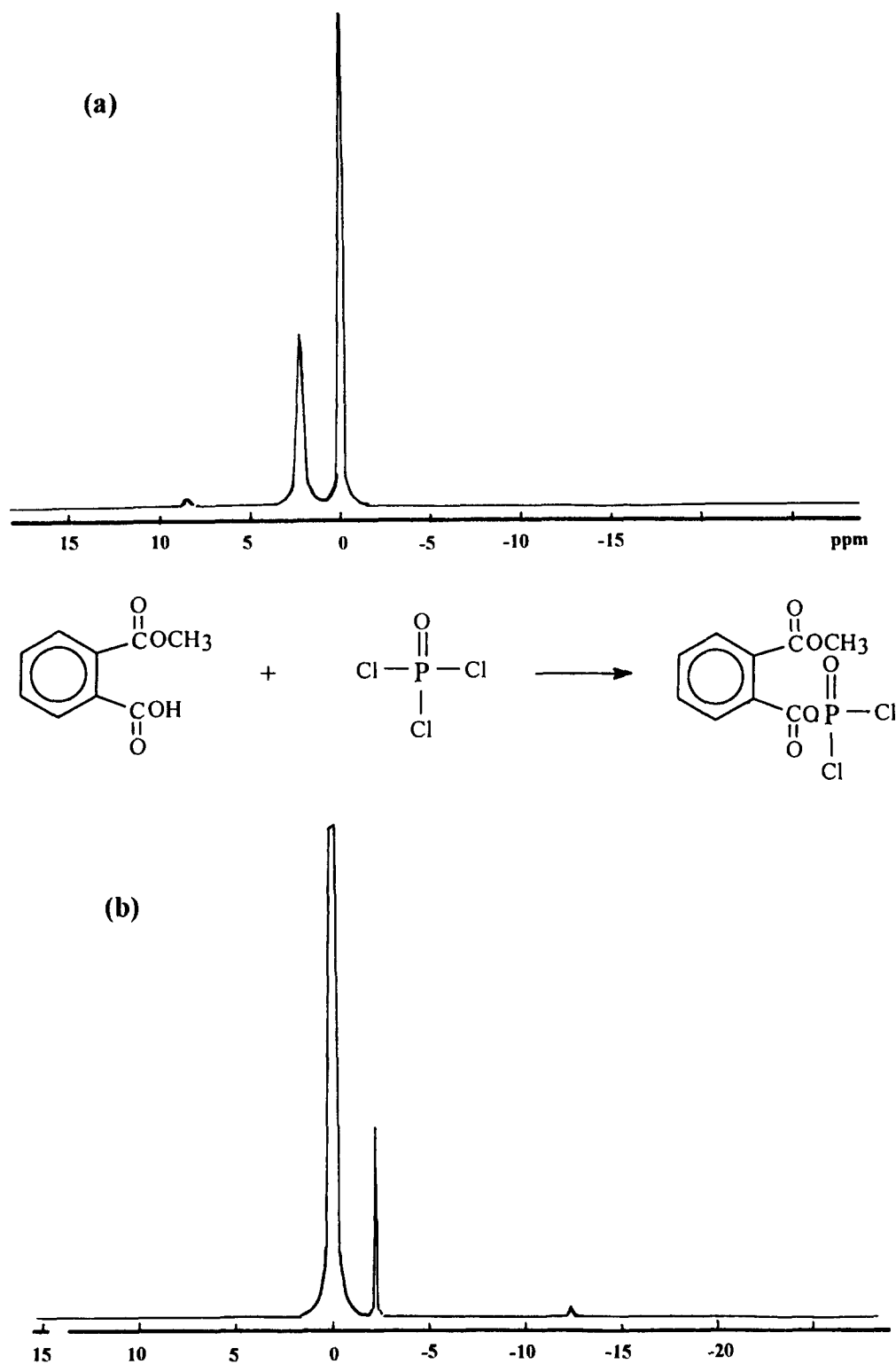
Figure 2 ^{31}P n.m.r. spectra of POCl$_3$ (a) and reaction intermediate of methyl hydrogen phthalate with POCl$_3$ (b)

RESULTS AND DISCUSSION

Monomers, activating agents, and tertiary amines used in this study are summarized in *Table 1*. The diacid dimethyl ester was prepared from the corresponding dianhydride and it was used as a counterpart of diamines. For the subsequent nucleophilic substitution reaction at the carbonyl carbon of the carboxylic acid group of the diacid dimethyl ester, was converted to a mixed anhydride intermediate using a phosphorus activating compound. These phosphorus compounds have been called the activating agent for the condensation reaction of carboxylic acids with thiols, amines, and alcohols[12].

PMDE and 4,4'-oxydianiline were reacted with various activating agents in NMP in the presence of various tertiary amines, and the results are summarized in *Table 2*. When isoquinoline or triethyl amine was used as a tertiary amine, the polymerization solution precipitated after the addition of the activating agent. For 2,6-lutidine, precipitation occurred before addition of the activating agent. Diphenyl phosphoryl chloride and diethyl chloro phosphate activating agents were not successful in any combination with tertiary amines. They seemed to be ineffective for the reaction. The basicity of tertiary amines did not significantly affect the polymerization. From *Table 2*, the combination of pyridine and phenyl phosphonic dichloride gave the best result for the polymerization of PMDE and ODA.
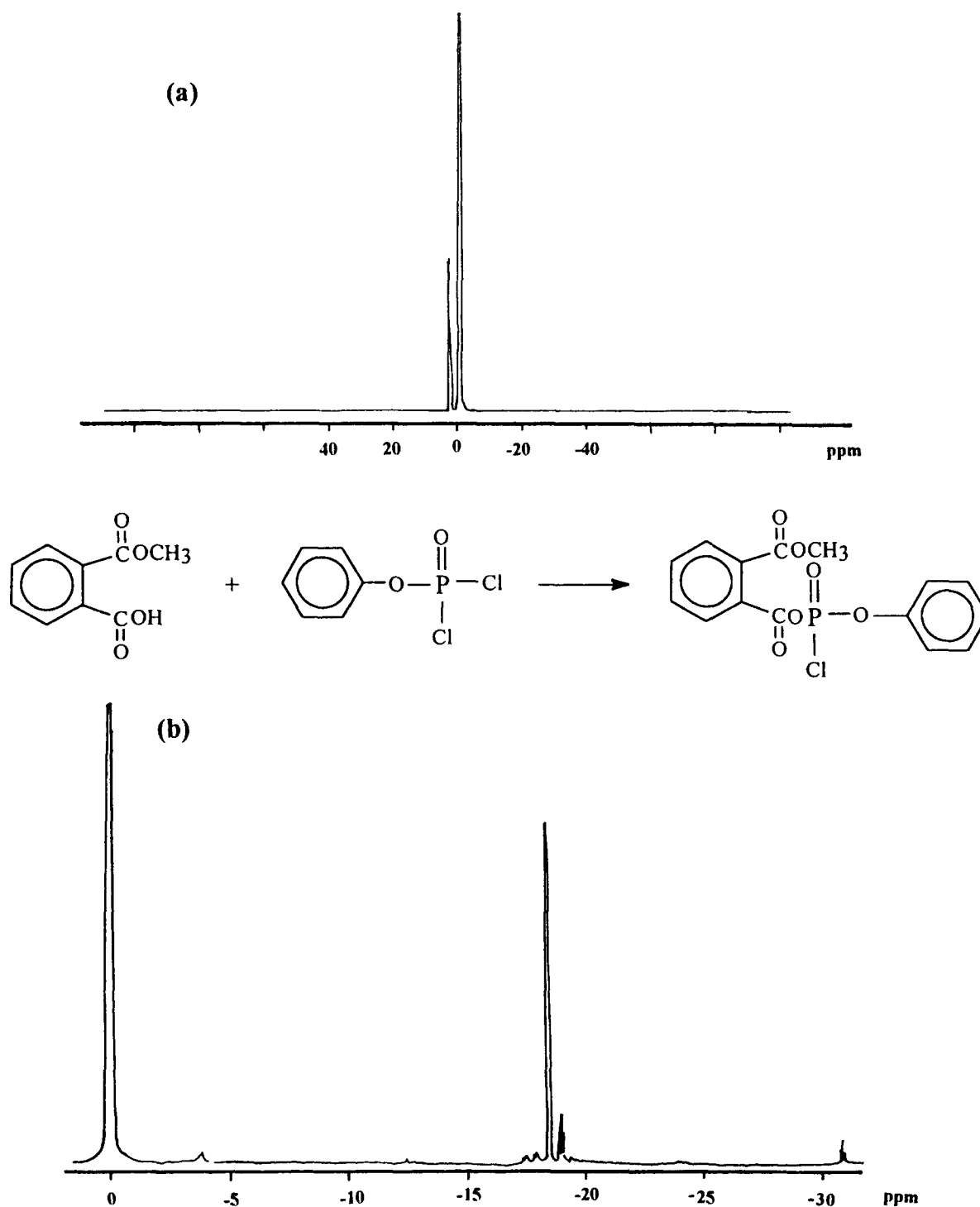

Figure 3 ^{31}P n.m.r. spectra of PhOPOCl₂ (a) and reaction intermediate of methyl hydrogen phthalate with PhOPOCl₂ (b)

Polymerization of various diacid dimethyl esters of aromatic dianhydride and diamine with PhPOCl₂ in NMP in the presence of pyridine was possible (*Table 3*). This means that this polymerization method could be universal. Since anhydride ring opening of an aromatic dianhydride by alcohol decreases its reactivity to diamines, there is no necessity for considering electron affinity of aromatic dianhydride. This means that the reactivity of diamine is more crucial to elevate the degree of polymerization than that of dianhydride. In the case of ODPE/PPD, it was thought that lowering the

solid content would give a homogeneous polymer solution.

The viscous polymerization solution was spread on a glass plate and cast by a doctor-knife. A yellow transparent polyimide film was obtained after thermal curing.

Polymers synthesized in this study were characterized by i.r. spectroscopy in comparison with those synthesized with PMDA and ODA and dicarbomethoxy terephthaloyl chloride of PMDA and ODA. I.r. spectra of polyamic acids and polyamic acid dimethyl esters
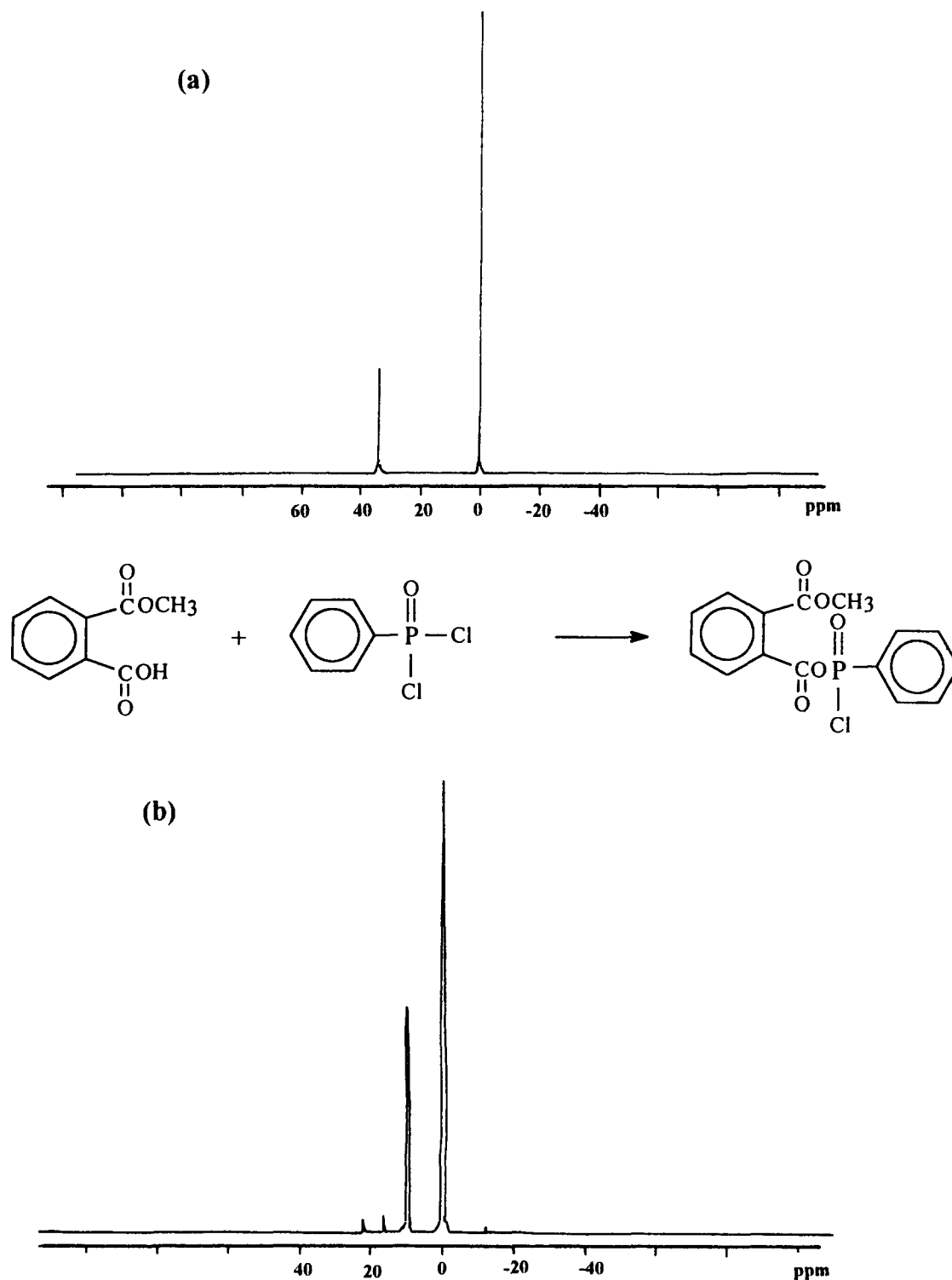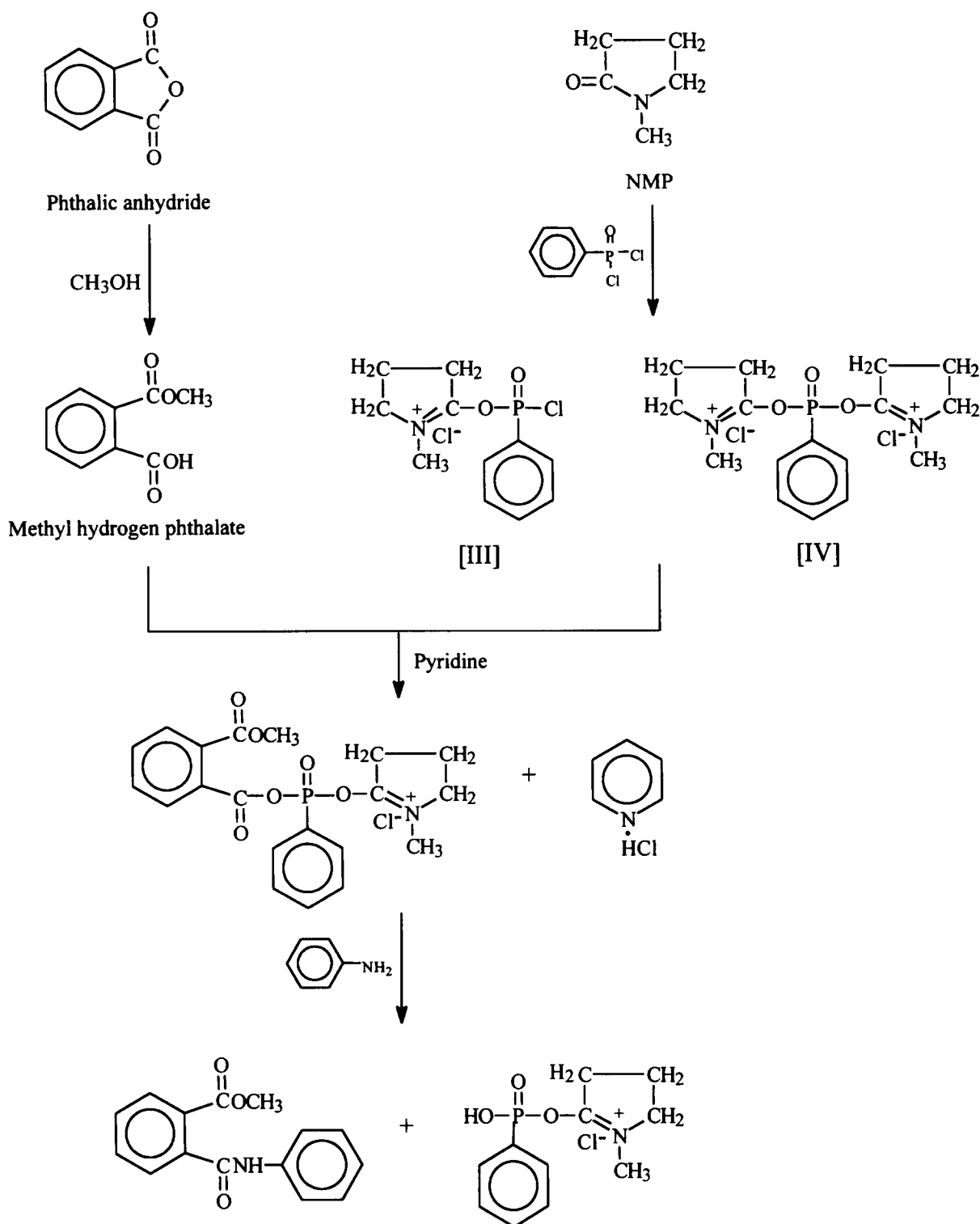
(a)

60   40   20   0   -20   -40   ppm

(b)

40   20   0   -20   -40   ppm

Figure 4   ³¹P n.m.r. spectra of PhPOCl₂ (a) and reaction intermediate of methyl hydrogen phthalate with PhPOCl₂ (b)

Phthalic anhydride

NMP

CH_3OH

Methyl hydrogen phthalate

[III]

[IV]

Pyridine

+

HCl

+

Scheme 3

obtained by these three methods and different activating agents are illustrated in *Figure 1*. Aliphatic C–H stretch peaks in methyl ester appeared at $2950\,cm^{-1}$ in both polymers synthesized from diacid chloride-diamine by this direct method. From the spectra, polyamic acid dimethyl ester seemed to be successfully synthesized in this method.

A model reaction between methyl hydrogen phthalate and phenyl phosphonic dichloride was carried out in benzene. Benzene was chosen due to its non-reactivity and good miscibility with the activating agents and

pyridine. As soon as the activating agents were introduced into the benzene solution of methyl hydrogen phthalate containing pyridine, white pyridine hydrochloride separated out. The role of pyridine is important for the mechanism of activating carboxylic acid. Nucleophilic displacements of phosphorus compounds may be catalysed in one of four ways, i.e. nucleophilic catalysis, general base catalysis, acid catalysis, and electrophilic catalysis. Tertiary amines serve to cause the reaction to proceed by nucleophilic catalysis or by general base catalysis, but it is known that these two

ways are difficult to distinguish from each other[13,14]. In general, they have been distinguished by a kinetic isotope effect, and by sensitivity to steric hindrance.

When pyridine and phenyl phosphonic dichloride were used, the mechanism of activation and amidation
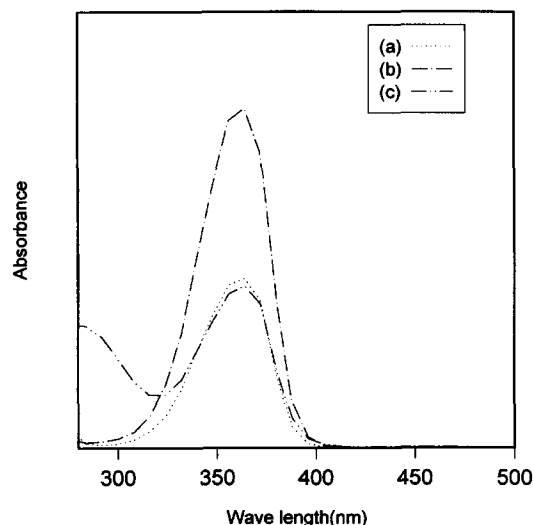

Figure 5 U.v.–vis spectra of reaction complex between phenyl phosphonic dichloride and NMP at: (a) room temperature; (b) 120°C for 30 min; (c) when pyridine was added to the reaction complex at room temperature

reaction between aromatic acid and amine was postulated in *Schemes 1* and *2*. Under benzene, benzoate ion formed by pyridine is reacted with phenyl phosphonic dichloride to give the mixed carboxylic–phosphoric anhydride, the highly activated acylating agent. Then a nucleophilic substitution reaction by diamine occurs at the carbonyl carbon of carboxylic acids to form an amide linkage[15]. Methyl ester in diacid dimethyl ester did not react during the polymerization reaction, because the reaction was carried out below or at room temperature[16].

Pyridine could react with phenyl phosphonic dichloride to give pyridine–phenyl phosphonic dichloride complex [I] or [II], where nucleophilic attack by carboxylic acid occurs[17]. The formation of complex [I] is thought to be dominant, due to the low reaction temperature.

The yield of hygroscopic pyridine hydrochloride was 81.7, 84.0, 91.8, 30.4 and 52.2%, respectively, when phosphorus oxychloride, phenyl phosphoryl dichloride, phenyl phosphonic dichloride, diethyl chlorophosphate, and diphenyl phosphoryl chloride were used as the activating agent. The yields were closely related to the degree of polymerization. Therefore, the extent of polymerization could be checked by the yield of pyridine hydrochloride. From a blank test under the same conditions, the hygroscopic product, complex [I], was also formed, and weighed 0.0979 g, meaning that *ca* 5% of pyridine acted as a nucleophilic catalysis. Hence, pyridine seems to serve as general base catalyst in the polymerization system.
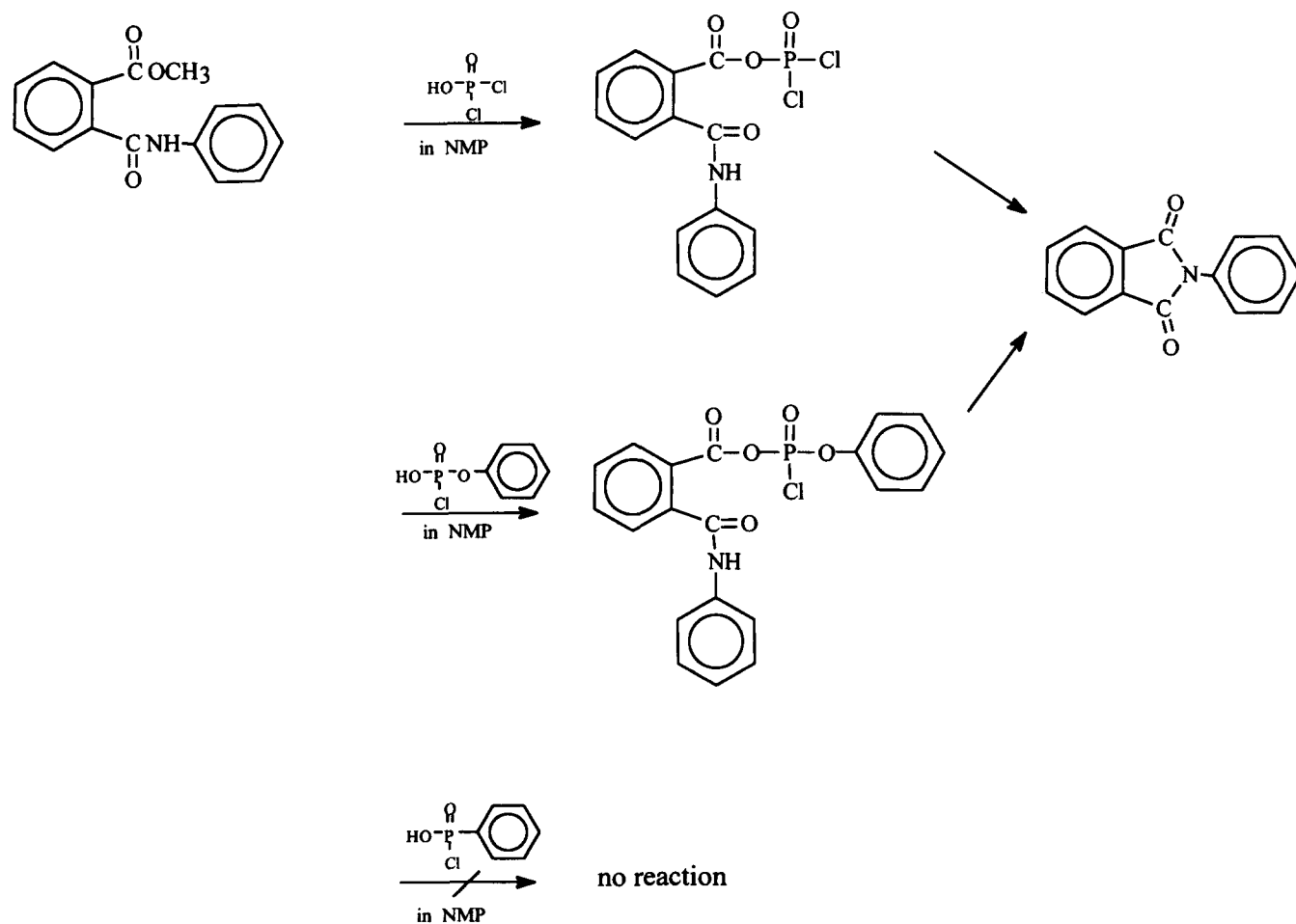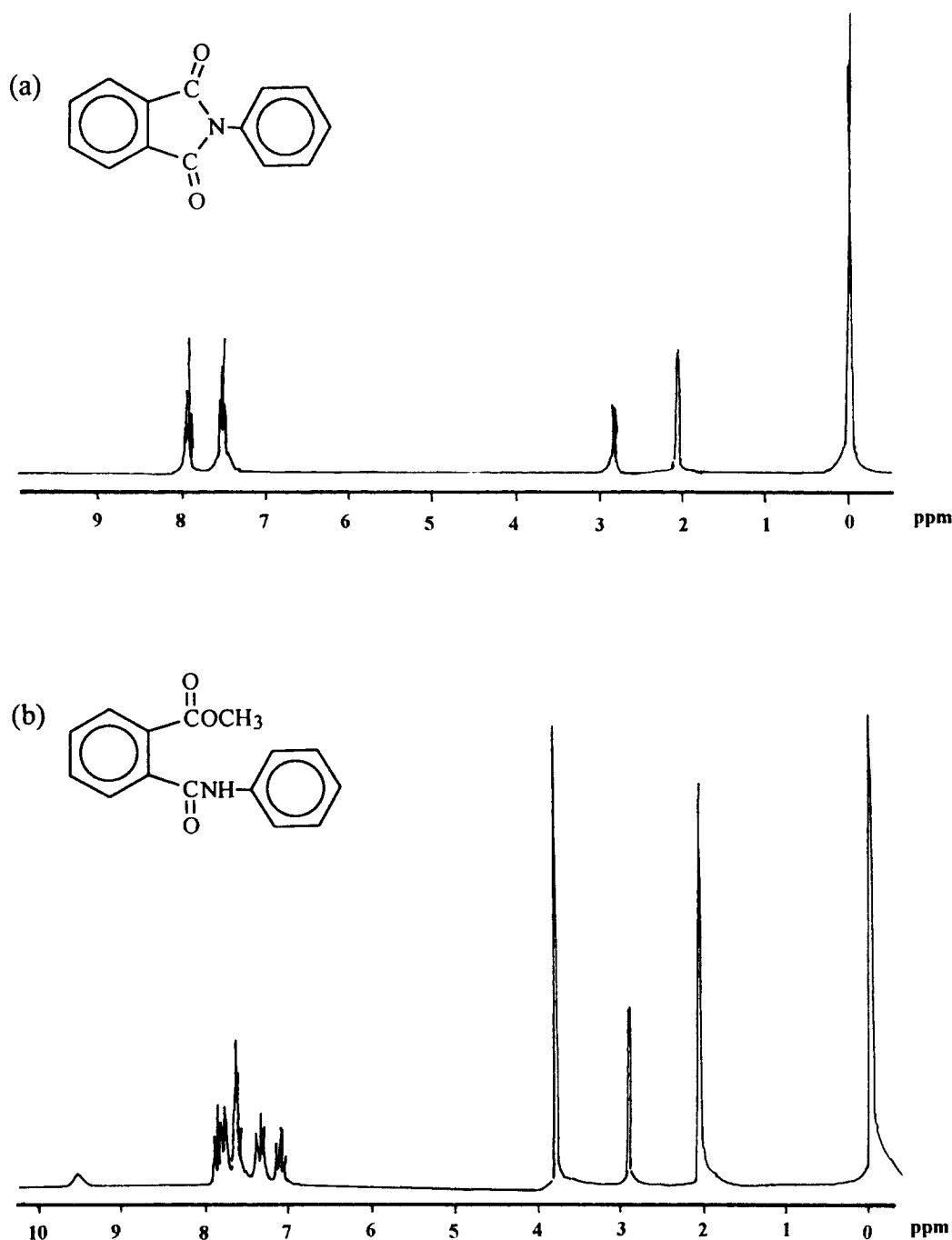

Scheme 4

Figure 6 ^{1}H n.m.r. spectra of the model reaction product using $POCl_3$ or $PhOPOCl_2$ (a) and $PhPOCl_2$ (b)

In order to characterize the reaction intermediate of methyl hydrogen phthalate with activating agents, ^{31}P n.m.r. spectroscopy was used. The excess benzene was evaporated thoroughly after the reaction, and the viscose residue was collected. *Figures 2–4* show ^{31}P n.m.r. spectra of reaction intermediates of methyl hydrogen phthalate with $POCl_3$, $PhOPOCl_2$ and $PhPOCl_2$. ^{31}P chemical shifts of $POCl_3$, $PhOPOCl_2$ and $PhPOCl_2$ were assigned to +2.2, +2.1 and +33.8 ppm, respectively. After reaction, these were changed to −2.3, −18.4 and +9.9 ppm. The reason for these changes can be assumed to be as below. Instead of a chlorine atom, a slightly electron-donating ester group (R–COO) was attached to the phosphorus compound, the phosphorus atom seems to be shielded by the electrons of the ester group, and so the peaks are shifted upward.

A model compound reaction was also conducted in a

polymerization reaction system. NMP reacted with phenyl phosphonic dichloride to form the corresponding complex[17], which had no reactivity to pyridine (*Figure 5*). Its absorption peak in the u.v.-vis spectrum appeared at 364 nm and was not transformed by the addition pyridine or by the reaction temperature. U.v.-vis spectroscopy cannot distinguish complex [III] from [IV] because only the peak intensity changes (hyperchromic or hypochromic effect). As in the pyridine complex, the formation of complex [III] seems dominant.

The mechanism of the amidation reaction between aromatic acid and amine in NMP is shown in *Scheme 3*. In NMP, pyridine is thought to act as an acid captor as well as a catalyst for monomer activation. Phenyl phosphonic dichlorides first react with NMP. Then, the nucleophilic substitution reaction by carboxylic acid occurs at the phosphorus atom in complex [III], with

the help of pyridine, forming the mixed carboxylic–phosphoric anhydride which can be attacked further by nucleophiles. The reaction intermediate of methyl hydrogen phthalate with activating agents is further reacted with aniline in NMP. The corresponding amide compound is obtained using $PhPOCl_2$ (m.p. 108–109°C, i.r. (KBr, cm^{-1}): 3275 (N–H str.); 2955 (C–H str.,
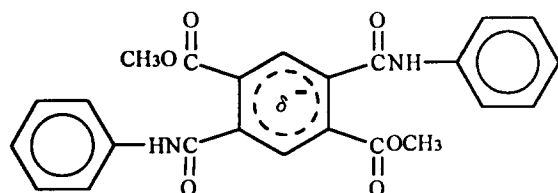
methyl); 1728 (C=O str., ester); 1656 (C=O str., amide); 1599 (N–H ben., amide)). In the case of $POCl_3$ and $PhOPOCl_2$, the reaction goes through to the final imide, so that N-methyl phthalimide is precipitated (m.p. 206–207°C, i.r. (KBr, cm^{-1}): no N–H str.; 1709 (C=O str., ester); 1780 (C=O str., imide); 1496 (C=C str., aromatic)). As shown in *Figure 6a*, N-methyl phthalmide, protons in amide group, 9.54 ppm, and methyl ester, 3.78 ppm, disappear.

As a result, even imidization reaction could occur in the model compound reaction according to the activating agents. After the amidation reaction between aromatic acid and amine is completed, the corresponding phosphorus hydroxide byproduct is formed. Then the nucleophilic substitution reaction by the hydroxyl group of this compound to the carbonyl carbon of methyl ester occurs to form mixed anhydride. Nitrogen in the amide bond can attack this anhydride to form an imide linkage (*Scheme 4*). However, the phosphorus hydroxy compound from $PhPOCl_2$ is not able to react further, because it cannot replace the methoxy group due to the relatively poor electron abundance, compared to the other phosphorus hydroxy compounds.

This result was somewhat different from that in *Figure 1*. Polymers synthesized with $POCl_3$ and $PhOPOCl_2$ had a methyl ester group, i.e. polyamic acid dimethyl ester, not polyimide. It could be explained that the model compound is monofunctional in contrast with

the bifunctional monomer in the real polymerization system. When amide bonds are formed bifunctionally as below, the electron of phenylene ring can be more delocalized by the additional electron-rich amide group. Therefore, the electron density of the carbonyl carbon of the methyl ester would be increased, and this hinders further nucleophilic substitution reaction.
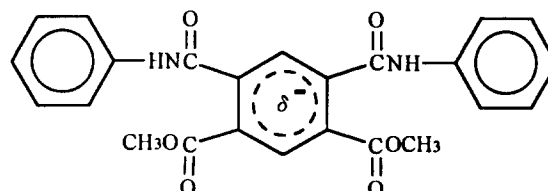

Figure 7 shows the effect of pyridine on the polymerization. Above 4 eq. of pyridine to monomer, the inherent viscosity of polymer was constant, meaning that pyridine mainly serves as an acid captor in this polymerization system.

CONCLUSIONS

Polyamic acid dimethyl ester was synthesized using various commercial phosphorus activating agents and tertiary amines in NMP at room temperature. The combination of phenyl phosphonic dichloride and pyridine were the most effective for polymerization. Benzoate ion, formed by pyridine, in diacid dimethyl ester was reacted with activating agent to form the corresponding mixed carboxylic–phosphoric anhydride as a polymerization intermediate. Otherwise, it would react to the NMP-activating agent complex. In NMP, pyridine seems to serve as an acid captor. It was thought that competitive reaction between benzoate ion and NMP to the activating agent was closely related to the degree of polymerization in the system. The basicity of tertiary amines, revealed in their pK_a values, did not affect the degree of polymerization.

Future studies include the elevation of the degree of polymerization using phenyl phosphonic dichloride and pyridine and synthesis of alternating polyamic acid ester through this direct polymerization. On the other hand, some strong evidence of the other effects of pyridine on the polymerization was revealed very recently.
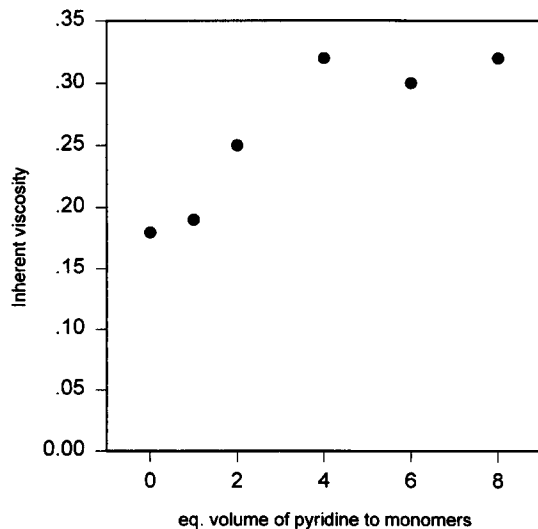

Figure 7 The effect of pyridine on the polymerization

REFERENCES

1. Harris, F. W., in *Polymides*, ed. D. Wilson, H. D. Stenzenberger and P. M. Hergenrother. Blackie & Son, New York, 1990, Chap. 1.
2. Flaim, T. D., Horter, B. L. and Moss, M. G., in *Polyimides: Materials, Chemistry and Characterization*, ed. C. Feger, M. M. Khojasteh and J. E. McGrath. Elsevier, New York, 1989, p. 279.
3. Frost, L. W. and Kesse, I., *J. Appl. Polym. Sci.*, 1964, **8**, 1039.
4. Hasegawa, M., Shindo, Y., Sugimura, T., Horie, K., Yokota, R. and Mita, I., *J. Polym. Sci.,—Polym. Chem. Edn*, 1991, **29**, 1515.
5. Ree, M., Yoon, D. Y. and Volksen, W., *Polym. Mater. Sci. Eng.*, 1989, **60**, 179.
6. Higashi, F., *Yuki Gousei Kagagu Kyokaishi*, 1989, **47**, 994.
7. Ueda, M., *Yuki Gousei Kagagu Kyokaiskhi*, 1990, **48**, 144.
8. Houlihan, F. M., Bachman, B. J., Wilkins, C. W. and Pryde Jr, C. A., *Macromolecules*, 1989, **22**, 4477.
9. Ueda, M. and Mori, H., *Makromol. Chem.*, 1993, **194**, 511.
10. Eliel, E. L. and Burgstahler, A. W., *J. Am. Chem. Soc.*, 1949, **71**, 2251.

11. Bell, V. L. and Jewell, R. A., *J. Polym. Sci., A-1*, 1967, **5**, 3043.
12. Haslam, E., *Tetrahedron*, 1980, **36**, 2409.
13. Emsley, J. and Hall, D., *The Chemistry of Phosphorus*. John Wiley, New York, 1976, Chap. 8.
14. Dudek, G. O. and Westheimer, F. H., *J. Am. Chem. Soc.*, 1959, **81**, 2641.
15. Effenberger, F., König, G. and Klenk, H., *Angew. Chem.*, 1978, **90**, 740.
16. Johnston, J. C., Meador, M. B. and Alston, W. B., *J. Polym. Sci., Part A*, 1987, **25**, 2175.
17. Higashi, F., in *New Methods for Polymer Synthesis*, ed. W. J. Mijs. Plenum Press, New York, 1992, Chap. 7.