

# Preparation of Polyamide-Imides via the Phosphorylation Reaction. II. Synthesis of Wholly Aromatic Polyamide-imides from *N*-[*p*-(or *m*-)Carboxyphenyl]trimellitimides and Various Aromatic Diamines

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## Synopsis

Wholly aromatic polyamide-imides with high molecular weight ( $\eta_{inh}$  up to 1.7 dL/g in DMAc-5%LiCl) were obtained by the direct polycondensation reaction of *N*-[*p*-(or *m*-)carboxyphenyl]trimellitimide [*p*-(or *m*-)CPTMI] and aromatic diamines by means of di- or triphenyl phosphite in *N*-methyl-2-pyrrolidone (NMP)-pyridine solution in the presence of lithium or calcium chloride. The factors affecting the phosphorylation reaction were investigated, in particular for the reaction of *p*-CPTMI and 4,4'-oxydianiline (ODA). Molecular weight of polymers varied with the amount of metal salts and showed maximum values at the concentration of 10–15 wt % in the reaction mixture. Monomer concentration of 0.2 mol/L produced polymer of the highest viscosity. Higher concentrations produced gelation and yielded polymers of low molecular weight. A reaction temperature of about 120°C gave the best results. Among the solvents tested, NMP was significantly the most effective for the reaction. The highest inherent viscosity values,  $\eta_{inh} = 1.35$  and 1.58 dL/g, were obtained with triphenyl phosphite (TPP)/monomer and diphenyl phosphite (DPP)/monomer molar ratios of 2.0. Excessive addition of phosphites did not cause a serious deleterious effect on the molecular weight of polymer. Polycondensations of several combinations of *p*- or *m*-CPTMI and aromatic diamines were carried out with satisfactory results.

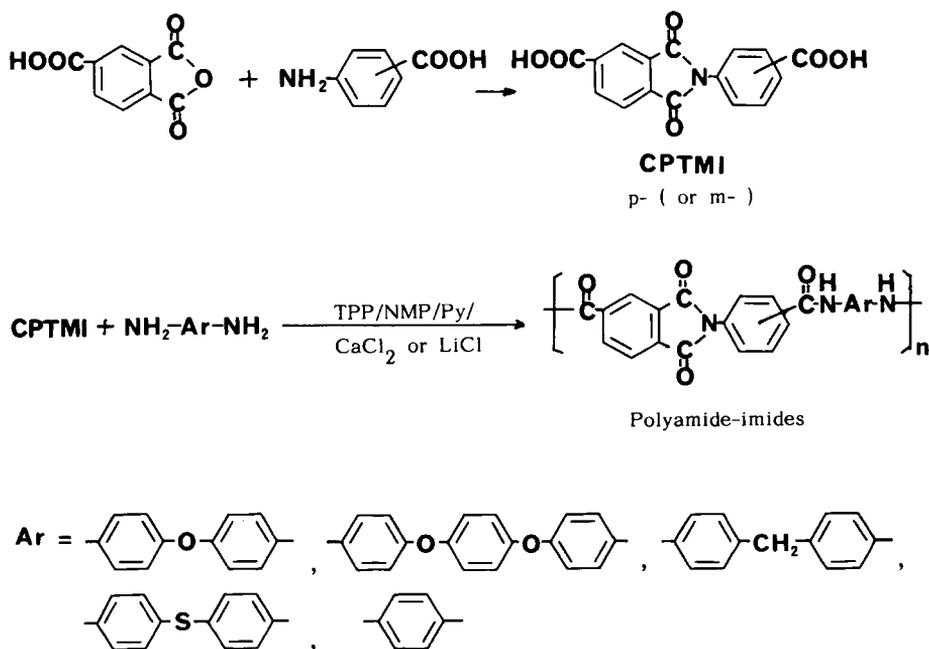
## INTRODUCTION

Aromatic polyamide-imides bridge the property gap between the aromatic polyamides and the aromatic polyimides. Three methods of syntheses based on polyamic-acid intermediates have been employed. In the first, using interfacial conditions, an amine-terminated polymer can be formed from the reaction of a diacid chloride with excess primary diamine. This polymer is then reacted in solution with a dianhydride and the resultant polymer is cyclodehydrated by heat or chemical reagents to form imide rings. In the second, a polymer can be obtained from the reaction of a diamine and the 4-acetyl chloride of trimellitic anhydride. This polymer will contain alternating amide-imide links. Finally, a dianhydride may be reacted with excess diamine to obtain a low molecular weight prepolymer which is further reacted with a diacid chloride, utilizing either solution or interfacial condensation techniques.

Polyamic-acids are hydrolytically unstable and undergo hydrolysis during various steps such as preparation, storage, and the cyclization reaction. They require special storage and handling care. Their synthesis requires highly purified reagents and extremely anhydrous reaction conditions to achieve high molecular weights.<sup>1,2</sup>

Wrasidlo and Augl<sup>3</sup> prepared polyamide-imides from monomers containing preformed imide rings. After them other researchers have followed the same system to obtain copolyimides.<sup>4-6</sup> This method involves the previous obtainment of imide-containing diacyl chlorides, which can be made to react with diamines in solution of polar solvents or under the conditions of interfacial polycondensation. This synthetic approach offers the remarkable advantage of achieving copolyimides in solution without the necessity of a thermal curing to assure the closing of imide rings. However, the diacid chlorides require a troublesome process of purification before use and cannot be stored for a long time.

In an earlier paper,<sup>7</sup> we have successfully applied the phosphorylation reaction to the preparation of various aliphatic-aromatic polyamide-imides. We describe here successful results of the direct synthesis of wholly aromatic polyamide-imides from *p*- or *m*-CPTMI with aromatic diamines by means of phosphites in NMP-pyridine solution in the presence of LiCl or CaCl<sub>2</sub> (Scheme 1). In the present work we also report a study of the factors affecting this phosphorylation reaction system, particularly with regard to the effect on the molecular weight of the polymer derived from *p*-CPTMI and 4,4'-oxydianiline (ODA) with respect to such factors as the concentration of metal salts, the monomer concentration, reaction temperature and time, the type of solvent, and the ratio of phosphites to monomer.



Scheme 1.

## EXPERIMENTAL

### Materials

Trimellitic anhydride (Wako) and aminobenzoic acids (TCI) were used without previous purification. Commercially obtained anhydrous LiCl and CaCl<sub>2</sub> were dried under vacuum at 150°C for 6 h and 180°C for 10 h, respectively. *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), and pyridine were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. *p*-Phenylenediamine (Wako) was vacuum distilled before use. All other aromatic diamines supplied by Tokyo Kasei Kogyo Co. were used as received. Triphenyl phosphite (TPP) and diphenyl phosphite (DPP) were purified by distillation under reduced pressure.

### Synthesis of Imide-Diacids

Imide-dicarboxylic acids were synthesized by condensation of trimellitic anhydride with aminobenzoic acids as follows: 19.2 g (0.1 mol) of trimellitic anhydride and 13.7 g (0.1 mol) of *p*-aminobenzoic acid were dissolved in 100 mL of dried DMAc. The stirred reaction mixture was heated at 60°C for 1 h. Then, 50 mL of toluene was added, and the mixture was heated with reflux for about 5 h until about 1.8 mL of water was distilled off azeotropically. On cooling, a light yellow precipitated product was separated from the final reaction solution, which was recrystallized from DMAc-H<sub>2</sub>O. 22 g (70% yield) of pure *N*-(*p*-carboxyphenyl)trimellitide (*p*-CPTMI) were obtained, mp > 360°C. IR: carboxylic —OH at 2500–3000 cm<sup>-1</sup>, carboxylic C=O at 1705 cm<sup>-1</sup>, imide C=O at 1770 and 1730 cm<sup>-1</sup>, imide ring at 735 cm<sup>-1</sup>.

ANAL. Calcd for C<sub>16</sub>H<sub>9</sub>NO<sub>6</sub>: C, 61.74%; H, 2.91%; N, 4.50%. Found: C, 61.70%; H, 2.88%; N, 4.43%.

*m*-CPTMI was synthesized from trimellitic anhydride and *m*-aminobenzoic acid with a similar procedure.

### Polymerization

As a typical experiment of this study, a mixture of 0.78 g (2.5 mmol) of *p*-CPTMI, 0.5 g (2.5 mmol) of ODA, 1.6 g (12 wt %) of calcium chloride, 1.6 g (5 mmol) of TPP, 2.5 mL of pyridine, and 10 mL of NMP was heated with stirring at 120°C for 3 h under nitrogen. When cooled the reaction mixture was poured into 500 mL of methanol, and the precipitated polymer was washed thoroughly with methanol and water, collected by filtration and dried. The yield was 1.17 g (99%). The inherent viscosity of the polymer in DMAc containing 5 wt % LiCl was 1.35 dL/g, measured at a concentration of 0.5 g/dL at 30°C.

## RESULTS AND DISCUSSION

It is well-known that homogeneity of reaction medium favors the polycondensation of dicarboxylic acids and aromatic diamines in the phosphorylation reaction.<sup>8,9</sup> The polycondensation reaction of CPTMIs and aromatic diamines, such as ODA, by using phosphites as condensing agents could proceed

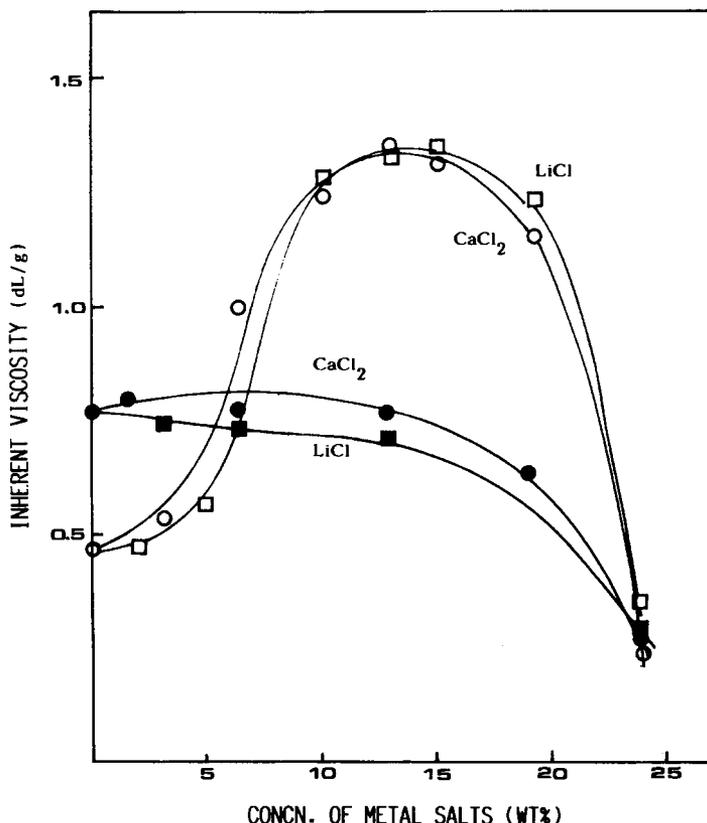


Fig. 1. Effect of the concentration of metal salts on the polycondensation of *p*-CPTMI (open symbol) and *m*-CPTMI (closed symbol) with ODA: CPTMI = ODA = 2.5 mmol; triphenyl phosphite = 5 mmol; pyridine = 5.0 mL (*p*-), 2.5 mL (*m*-); NMP = 20 mL (*p*-), 10 mL (*m*-); temperature = 120°C; time = 3 h.

homogeneously by the choice of proper monomer concentration, reaction temperature, and solvent system.

Results of the polycondensation of *p*-CPTMI and *m*-CPTMI with ODA by using triphenyl phosphite in the presence of various amounts of LiCl or CaCl<sub>2</sub> are shown in Figure 1. CaCl<sub>2</sub> or LiCl is soluble in NMP but the solution of higher wt % of them, especially for CaCl<sub>2</sub>, is difficult to prepare at room temperature. However, when pyridine is present in NMP the solubility of the salt is significantly improved and a solution of more than 10 wt % can easily be obtained, probably due to the formation of a complex like CaCl<sub>2</sub> · *n*Py, which may be readily soluble in NMP.<sup>10</sup> The reaction of *p*-CPTMI and ODA was carried out with 0.2 mol/L of monomer concentration in NMP–pyridine solution at 120°C for 3 h. Less favorable results were obtained when the reaction media were in the absence of metal salts or in the presence of metal salts of less than 5 wt % due to an early precipitation of polymer in the reaction media. The addition of LiCl or CaCl<sub>2</sub> with a higher concentration of 10–20 wt % led to a considerable increase in the molecular weight of the polymers produced. Further addition retarded the reaction, and almost no

polymer was formed in the presence of more than 20 wt % of each metal salt, where the reaction mixtures were deeply colored. In the case of addition of LiCl, the reaction mixture was apt to gel and a supplement of solvent was necessary to redissolve the swollen gel and give smooth stirring. The addition of CaCl<sub>2</sub> evidently produced a more favorable reaction state, and a clear and highly viscous polymer solution could be obtained at 10–15 wt %. Although the effect of metal salts is not understood in detail, a reasonable explanation has been proposed by Yamazaki and co-workers,<sup>9</sup> i.e., the addition of metal salts to the amide-type solvent improves solubility and promotes monomer reactivity and also may depress side reactions owing to the formation of some complexes of metal salts with the phenol derived from di- or triphenyl phosphite. In the reaction of *p*-CPTMI with ODA, the factor of the improvement of the dissolution power of the resulting polymers seems to be more significant.

For the other reaction system of *m*-CPTMI and ODA, the polycondensation could be carried out with a higher monomer concentration of 0.4 mol/L due to the high solubility of the resulting polymer having a more flexible structure. The polycondensation reaction thus could proceed homogeneously even in the absence of metal salts. The addition of metal salts, however, did not increase significantly the molecular weight of polymer. This result is different from that in the case of *p*-CPTMI. The addition of LiCl even caused a decrease of inherent viscosity. Presumably, this is caused by the different reactivities of the diacids under this condition. Moreover, the lower value on inherent viscosity of the polymer derived from *m*-CPTMI and ODA does not necessarily imply a lower molecular weight since this polymer is semiflexible.

To find suitable conditions in which to prepare polyamide-imides with high molecular weights, the effects of monomer concentrations, reaction temperatures, reaction solvents, and the molar ratio of phosphites to monomer on the reaction of *p*-CPTMI with aromatic diamines, particularly with ODA, were investigated in some detail.

The formation of polyamide-imide by mixing equimolar *p*-CPTMI and ODA with 12 wt % CaCl<sub>2</sub> in a mixture of NMP and pyridine at 120°C rapidly

TABLE I  
Effect of Monomer Concentration on the Polycondensation  
of *p*-CPTMI with ODA in the Presence of 12 wt % CaCl<sub>2</sub><sup>a</sup>

Monomer concentration mol/L (wt %)	Appearance of reaction mixture	Polymer	
		Yield (%)	$\eta_{inh}^b$ (dL/g)
0.10 5.1	deeply colored	83	0.43
0.15 6.8	colored	96	0.62
0.20 10.2	highly viscous	99	1.35 (1.16) <sup>c</sup>
0.30 13.6	swollen gel	100	1.15
0.40 20.4	solid-like gel	100	1.01

<sup>a</sup>Solvent = NMP/pyridine = 20/5 (mL/mL); TPP = 2.0 mol/mol of each reactant; temperature = 120°C; time = 3 h.

<sup>b</sup>Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL.

<sup>c</sup>Measured in concentrated H<sub>2</sub>SO<sub>4</sub>.

TABLE II  
Effect of Monomer Concentration on the Polycondensation  
of *p*-CPTMI with *p*-Phenylenediamine in the Presence of 12 wt % CaCl<sub>2</sub><sup>a</sup>

Monomer concentration mol/L (wt %)	Appearance of reaction mixture	Polymer	
		Yield (%)	$\eta_{inh}^b$ (dL/g)
0.05 2.1	colored	85	0.48
0.075 2.8	viscous	99	1.09
0.10 4.2	gelation	100	1.65
0.20 8.4	precipitated	95	0.50

<sup>a</sup>Solvent = NMP/pyridine = 20/5 (mL/mL); TPP = 2.0 mol/mol of each reactant; temperature = 120°C; time = 3 h.

<sup>b</sup>Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL.

proceeds, with stirring, through a highly viscous state to a heavy, thick gel at the moderately high concentrations. The gel presumably has little reactivity and polymerization is nearly complete at this point. The inherent viscosity of the final polymer is dependent upon such factors as the reaction temperature, stirring state, solvent composition, and stoichiometry. When the polymerization of *p*-CPTMI and ODA was carried out in NMP-pyridine (4:1 by volume), the maximum inherent viscosity was obtained when the concentration of the reactants was on the order of 0.20 mol/L as shown in Table I. The lower inherent viscosity obtained at lower monomer concentration can be readily rationalized by taking into account competitive side reactions as discussed by Yamazaki et al.<sup>9</sup> One possible explanation for the decrease of inherent viscosity at higher monomer concentration is reduced reactant mobility due to the onset of gelation before high inherent viscosity could be reached. We would expect, therefore, that as the solvent power of the reaction medium is increased, the maximum inherent viscosity attainable would move to higher concentrations.

A similar result to that above was found in the polycondensation of *p*-CPTMI with *p*-phenylenediamine, as shown in Table II. Thus, a lower reactant concentration should be employed in order to avoid an early precipitation of low molecular weight polymer which has a more rigid structure than that from *p*-CPTMI and ODA. The optimum reactant concentration was found to be 0.1 mol/L, although the appearance of the reaction mixture showed a state of slight gelation under this condition.

The reaction temperature plays a significant role on the attainment of high molecular weight for polymers synthesized by the phosphorylation reaction. The effect of temperature upon the inherent viscosities of the obtained polymers has been studied by several workers.<sup>9, 11-12</sup> Yamazaki and co-workers<sup>9</sup> reported that a maximum inherent viscosity value was observed at a temperature around 80°C in the polycondensation reaction of *p*-aminobenzoic acid. However, Preston and Hofferbert<sup>11</sup> found that reaction at 100°C is more effective than reaction at the 80° temperature suggested by Yamazaki et al. Furthermore, Preston and co-workers<sup>12</sup> described that the inherent viscosity of poly(*p*-phenylene terephthalamide) prepared from *p*-phenylenediamine and terephthalic acid by the phosphorylation under Higashi conditions<sup>10</sup> can

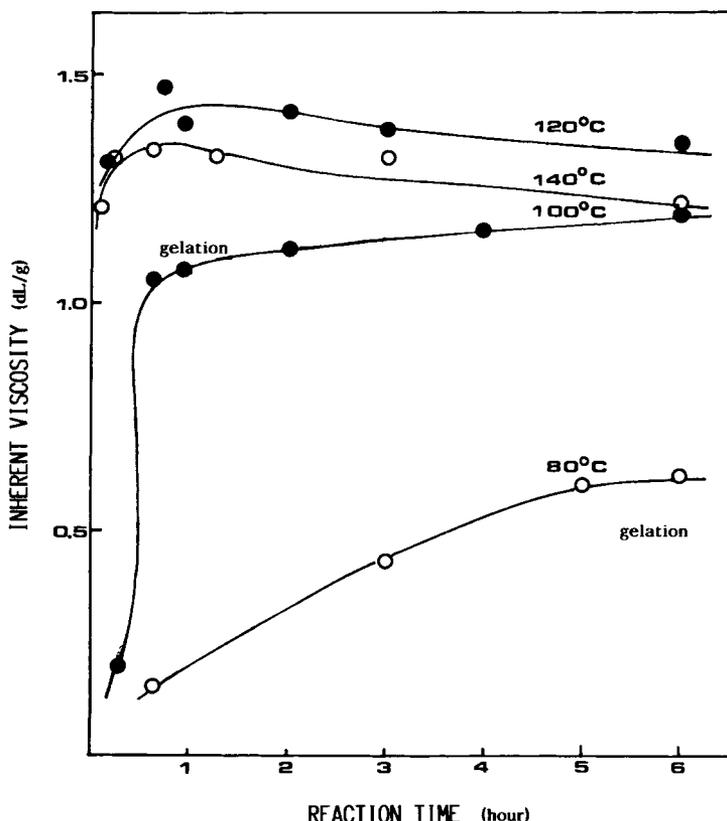


Fig. 2. Rate of the polycondensation of *p*-CPTMI with ODA at various temperatures and times: [monomer] = 0.2 mol/L in NMP/pyridine (4 : 1 by volume) solution; TPP = 2.0 mol/mol of each monomer; [CaCl<sub>2</sub>] = 12 wt %.

be significantly improved by increasing the reaction temperature from 100 to 115°C. In the present work, a higher temperature was adopted for the synthesis of aromatic polyamide-imides because of their lower solubility compared to polyamides.

Figure 2 presents the variation curves of inherent viscosities of the polymers obtained from *p*-CPTMI with ODA at various times by using reaction temperatures in the range of 80–140°C. A maximum inherent viscosity value was observed at a temperature around 120°C. At the higher temperature of 140°C, the formation of high molecular weight takes place in a matter of some minutes. However, the inherent viscosity of the final polymer produced was lower than that obtained at 120°C. This can be attributed to the fact that undesirable side reactions may be favored, such as the reaction of acyloxy *N*-phosphonium salt of pyridine (as suggested by Yamazaki et al.<sup>9</sup>) with phenol derived from phosphite to yield phenyl ester, and the reactions related to the thermal decomposition of the solvent and possible decomposition of obtained polymers in the presence of metal salt at high temperatures, as indicated by slight colorization of the reaction mixture. At the lower temperature of 100°C the reaction mixture formed a gel after about 40 min. Under this condition, the solvating power of this solvent system is not strong enough

TABLE III  
Polycondensation of *p*-CPTMI with ODA in Various  
Solvent Systems Containing CaCl<sub>2</sub><sup>a</sup>

Solvent system	mL/mL	Appearance of reaction mixtures	Polymer	
			Yield (%)	$\eta_{inh}$ (dL/g)
DMF/Py	10/2.5	precipitated	94	0.16
DMAc/Py	10/2.5	clear	98	0.62
NMP/Py	10/2.5	highly viscous	99	1.35
NMP/Py	7.3/4.9	highly viscous	99	1.21
NMP/Py	6.3/6.3	highly viscous	99	1.17
NMP/Py	4.9/7.3	viscous	99	1.00
NMP/Py	2.5/10	precipitated	98	0.60
HMPA/Py	10/2.5	clear	98	0.52
HMPA/NMP/Py	6.8/3.4/2.5	clear	99	0.52
HMPA/NMP/Py	3.4/6.8/2.5	clear	99	0.75
HMPA/DMAc/Py	6.8/3.4/2.5	clear	97	0.49

<sup>a</sup>*p*-CPTMI = ODA = 2.5 mmol, monomer concn = 0.2 mol/L, TPP = 5 mmol, CaCl<sub>2</sub> = 1.6 g, temperature = 120°C, time = 3 h.

<sup>b</sup>Measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30°C.

to dissolve the swollen gel. The polycondensation reaction was retarded by the heavy thick gel and the viscosity of the final polymer increased little after 6 h. At the lower temperature of 80°C, the reaction proceeded very slowly in the initial 3 h and the reaction mixture formed a solid-like gel after the inherent viscosity of the polymer reached 0.6 dL/g (after about 5 h). At this point, polymerization nearly ceased and no increase in inherent viscosity was observed after 12 h.

The polycondensation reaction of *p*-CPTMI with ODA in the presence of 12 wt % CaCl<sub>2</sub> was examined in various solvents or by varying the amounts of pyridine in NMP (Table III). Among the solvents tested, NMP, which can most readily dissolve the salt, was significantly effective. The viscosity of the resulting polymer varied with the amounts of pyridine in NMP, showing higher values at 20–50% (by volume) of pyridine in the NMP–pyridine mixtures. Although pyridine is not a good solvent for polyamide-imides, the reaction can tolerate a relatively high level (60%) of pyridine in an NMP–pyridine mixture. However, the higher proportion of pyridine caused an early precipitation of low molecular weight polymer during polymerization.

DMF did not completely dissolve CaCl<sub>2</sub> and gave only low molecular weight polymer which precipitated at an early stage of polycondensation. Increasing the amount of DMF used as solvent in order to carry out the reaction in a homogeneous phase has met with failure in raising the molecular weight of the polymer.

Although the metal salts were soluble in DMAc, hexamethylphosphoramide (HMPA), and the mixtures of HMPA with NMP or DMAc, unfavorable results were obtained in these solvent systems as shown in Table III. The solvent effects on the polycondensation could not be explained in terms of the insolubility of monomer or of the resulting polymer. These results might be

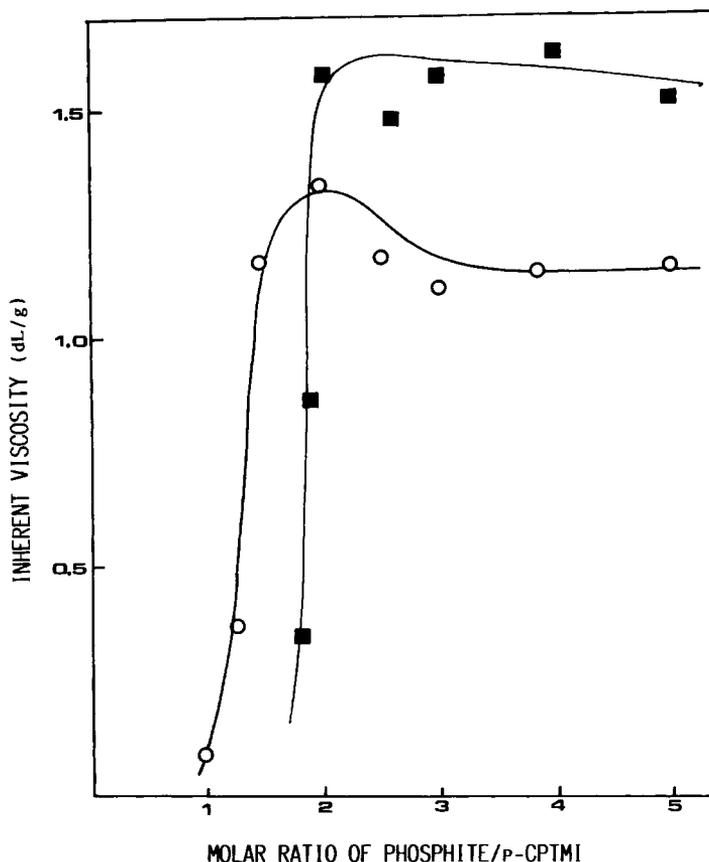


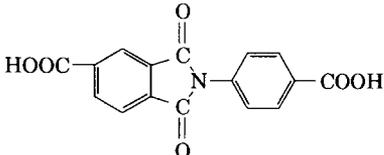
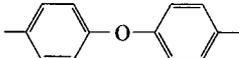
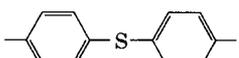
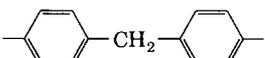
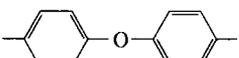
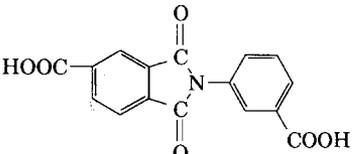
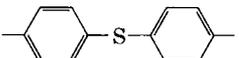
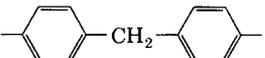
Fig. 3. Effect of varying the molar ratio of triphenyl phosphite (○) and diphenyl phosphite (■) to *p*-CPTMI upon the polycondensation of *p*-CPTMI and ODA at 120°C for 3 h with monomer concentration of 0.2 mol/L in NMP/pyridine (4:1 by volume) solution containing 12 wt % CaCl<sub>2</sub>.

related to the thermal stability of the solvent in the presence of metal salts at high temperature.

We also investigated the effect of variation of the molar ratio of triphenyl phosphite (TPP) or diphenyl phosphite (DPP) to monomer. As shown in Figure 3, the optimum molar ratio of TPP to monomer is 2.0. These conditions produced the polyamide-imide having inherent viscosity of 1.35 dL/g. A moderately high inherent viscosity value still can be obtained at the molar ratios of TPP/*p*-CPTMI ranging 1.5–2.0, indicating the resulting DPP from TPP can bring about further polycondensation reaction. However, at lower ratio such as 1.0 and 1.25 of TPP/*p*-CPTMI, no high molecular weight polymer was produced. The reason is not understood in detail, and requires a more detailed investigation.

By using DPP as condensing agent, it is expected that only low molecular weight product was produced when the equivalent of DPP is less than that of carboxylic groups. No serious effect on inherent viscosity of resulting polymer was observed upon excessive addition of TPP or DPP, indicating that an

TABLE IV  
Preparation of Several Polyamide-Imides in NMP-Pyridine  
Solution Containing  $\text{CaCl}_2$ <sup>a</sup>

Imide-diacid	Diamine $\text{NH}_2\text{—Ar—NH}_2$ (Ar =)	$\eta_{\text{inh}}^b$ (dL/g)
		1.70
		1.35
		1.65 <sup>c</sup>
		1.05
		0.95
		0.85
		0.80
		0.78
		0.72
		0.77

<sup>a</sup>For *p*-CPTMI, monomer concn. = 0.2 mol/L, i.e., imide-diacid = diamine = 1.25 mmol, NMP = 5 mL, Py = 1.25 mL, TPP = 0.8 g,  $\text{CaCl}_2$  = 0.8 g (12 wt %); for *m*-CPTMI, monomer concn = 0.4 mol/L; temperature = 120°C; time = 3 h.

<sup>b</sup>Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL.

<sup>c</sup>For the reaction with *p*-phenylenediamine, monomer concn. = 0.1 mol/L.

excessive use of phosphites did not cause a deleterious side reaction to the polycondensation reaction. The effect of DPP seems to be superior to that of TPP; however, the utilization of the latter is more economic.

Several aromatic polyamide-imides from *p*-CPTMI or *m*-CPTMI with various aromatic diamines were prepared by carrying out the reaction at 120°C for 3 h using TPP in NMP-pyridine (4 : 1 by volume) in the presence of 12 wt %  $\text{CaCl}_2$  (Table IV). All polymers were obtained in quantitative yield. Combination of *p*-CPTMI and aromatic diamines produced polyamide-imides

with higher inherent viscosity in comparison with *m*-CPTMI. In interpreting this observation, one must bear in mind that the inherent viscosity of a semiflexible polymer is much lower than that of a rigid polymer of the same molecular weight.<sup>13</sup> The more satisfactory results obtained from ODA and 1,4-bis(*p*-amino-phenoxy)benzene may be due to their high reactivity and the excellent solubility of their resulting polymers. In the polycondensation of *p*-CPTMI and *p*-phenylenediamine, a suitable reactant concentration is 0.1 mol/L. Above this value the reaction mixture formed a highly swollen gel, leading to lower molecular weights.

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