# Preparation of Sulfonyl Aromatic Polyamides and Copolyamides by Means of Di- or Triphenyl Phosphite

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## SYNOPSIS

High molecular-weight aromatic polyamides were obtained by the direct polycondensation reaction of 4,4'-sulfonyldibenzoic acid (SDA) with various aromatic diamines, by means of di- (DPP) or triphenyl phosphite (TPP) in $N$-methyl-2-pyrrolidone (NMP)–pyridine solution containing metal salts such as LiCl and $CaCl_2$. The factors affecting the phosphorylation reaction were investigated, in particular for the reaction of SDA and 4,4'-oxydianiline (ODA). For the polymerization by means of TPP, the optimum conditions are: molar ratio of TPP to diacid, higher than 2.3; concentration of metal salts, 8 wt % LiCl or 6 wt % $CaCl_2$; reaction temperature, 100°C; and monomer concentration, 0.4 mol/ L. For the polymerization by means of DPP, the optimum conditions are: molar ratio of DPP to diacid, higher than 3.8; concentration of metal salts of 8 wt % LiCl or 10 wt % $CaCl_2$; reaction temperature, 110°C; and monomer concentration, 0.4 mol/L. Copolyamides were also prepared from the reaction of ODA with the mixed diacids of SDA and other dicarboxylic acids such as terephthalic acid, isophthalic acid, and 2,6-naphthalene dicarboxylic acid by using TPP and DPP as the condensing agents.
**Keywords:** sulfonyl aromatic polyamides • direct polycondensation • 4,4'-sulfonyldibenzoic acid • diphenyl phosphite • triphenyl phosphite

## INTRODUCTION

Sulfonyl aromatic polyamides have been reported to have potential for commercial utility, because fibers and films of these polymers not only possess excellent physical properties at room temperature, but retain their strength and excellent response to work-loading at elevated temperatures for prolonged periods of time.[1] However, the preparation of polyamides derived from aromatic diamines and 4,4'-sulfonyldibenzoic acid (SDA) was little investigated.[2] This might be due to the fact that there was some difficulty in obtaining the diacid chloride of SDA in high purity and, thus, the attainment of high molecular weight was difficult.

In 1975 Yamazaki et al.[3] demonstrated the direct polycondensation reaction of dicarboxylic acids and aromatic diamines by using di- or triaryl phosphites in $N$-methyl-2-pyrrolidone (NMP)–pyridine con-

taining metal salts. This phosphorylation reaction is certainly a highly useful laboratory method for screening new polyamides[4,5] because relatively small amounts of monomers are required for synthesis.

Our laboratory[6] has successfully applied the phosphorylation reaction for the preparation of some sulfonyl polyamides from SDA and various aromatic diamines by using triphenyl phosphite (TPP) as condensing agent, where the properties of the obtained polymers were also described. In the present work, we intend to prepare several sulfonyl homopolyamides and copolyamides from SDA or its mixed diacids with aromatic diamines by using TPP and DPP as condensing agents, and to compare the effects of these two phosphites on the polymerization.

## EXPERIMENTAL

### Materials

4,4'-Sulfonyldibenzoic acid (SDA) was supplied by New Japan Chemical Co., Ltd. (Kyoto, Japan) and

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was used as received; mp > 300°C. The neutralization equivalent (mg KOH/g) was 367 (calcd 367). $N$-Methyl-2-pyrrolidone (NMP), pyridine, and $N,N$-dimethylacetamide (DMAc) were purified by distillation over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) and diphenyl phosphite (DPP) were purified by distillation under reduced pressure. $p$-Phenylene diamine (Wako) was vacuum-distilled before use. All other aromatic diamines were of high purity when received from the manufacturers and used without any further purification. Commercial anhydrous LiCl and CaCl$_2$ were dried under vacuum at 150°C for 6 h and 180°C for 10 h, respectively. Terephthalic acid (TPA), isophthalic acid (IPA), and 2,6-naphthlene dicarboxylic acid (NDA) were purified by recrystallization before use.

## Polymerization

A typical polymerization procedure is as follows. A mixture of SDA (1.53 g, 5 mmol), 4,4'-oxydianiline (ODA) (1.0 g, 5 mmol), and TPP (3.72 g, 12 mmol) in a mixed solvent of NMP (10 mL) and pyridine (2.5 mL) containing 8 wt % LiCl (1.0 g) was heated at 100°C for 3 h under nitrogen. The resulting reaction mixture was poured into 300 mL of methanol, and the precipitated polymer was separated by filtration, washed well with methanol, and dried. The yield was 2.4 g (100%). Inherent viscosity of the polymer in DMAc containing 5 wt % LiCl was 1.58 dL/g, measured at concentration of 0.5 g/dL at 30°C. The IR spectrum (film) showed absorptions at 3300 (N—H), 1660 (C=O), and 1300 and 1160 (SO$_2$) cm$^{-1}$.

Other polymers were synthesized by analogous procedures.

## RESULTS AND DISCUSSION

### Factors Affecting the Polycondensation of SDA with ODA

#### Phosphites/Monomer Ratio

The reaction promoted by di- or triphenyl phosphite and pyridine has been successfully applied to the direct polycondensation of $p$-aminobenzoic acid and dicarboxylic acids and diamines.[3] These reactions have been proposed to proceed via the $N$-phosphonium salts of pyridine (I and II) followed by aminolysis [eqs. (1) and (2)]. In the reaction promoted by TPP, besides polyamides, DPP and phenol are obtained as a result of the reaction. Hence, we ex-

pected that only half an equivalent of TPP might be enough for the preparation of polymers.



(1)



Py: Pyridine

(2)
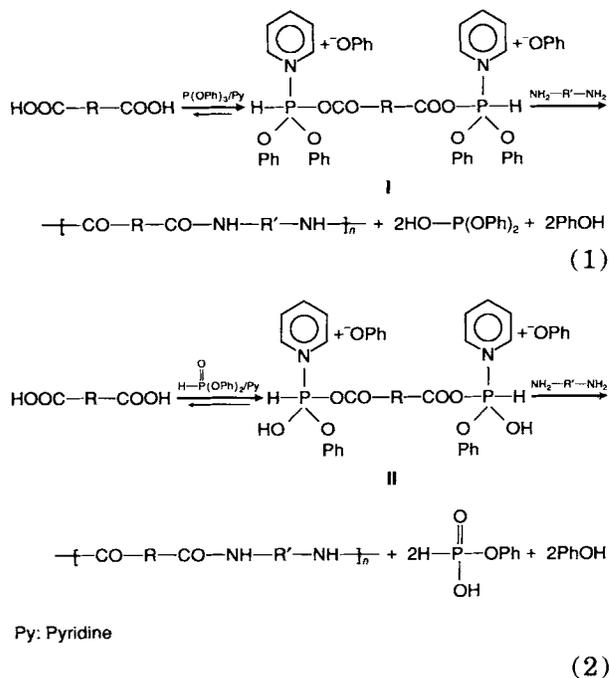
However, no high-molecular-weight polyamides were obtained by using half an equivalent of TPP corresponding to carboxylic groups in the direct polycondensation of 4,4'-sulfonyldibenzoic acid (SDA) with 4,4'-oxydianiline (ODA). As shown in Figure 1, high-molecular-weight polyamide was not obtained unless the molar ratio of TPP to SDA is higher than 2.3. If the TPP/SDA ratio is lower than 2.2 the products had inherent viscosities lower than 0.5 g/dL; however, the yield of polymers was very high. The dramatic drop of inherent viscosity may be related to the equilibrium of phosphonium salt I with dicarboxylic acid and TPP as shown in eq. (1). In the cases of molar ratios lower than 2.2, the polycondensation reaction only remained at the initial stage, and only low-molecular-weight oligomers were produced. Further addition of TPP favored the formation of $N$-phosphonium salt I and thus caused further reactions, leading to an increase of molecular weight in terms of inherent viscosity. Furthermore, more excess of TPP showed no seriously deleterious effect on molecular weight.

In the reaction promoted by DPP, the reaction temperature was increased to 110°C. High molecular-weight polyamides could be obtained at the DPP/SDA molar ratio above 3.8. Lowering the ratio caused a dramatic fall of inherent viscosity. No se-
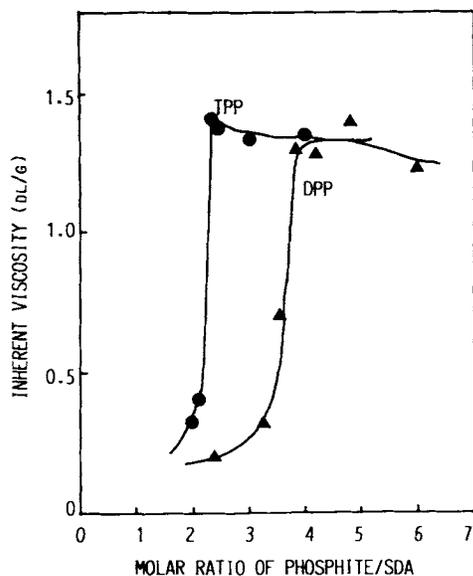
**Figure 1.** Effect of varying the molar ratio of triphenyl phosphite (●) and diphenyl phosphite (▲) to SDA upon the polycondensation of SDA and ODA: SDA = ODA = 5 mmol; NMP = 10 mL; Py = 2.5 mL; temperature = 100°C (TPP), 110°C (DPP); time = 3 h; LiCl = 1.0 g (8 wt %).

riously deleterious effect on inherent viscosity of the resulting polymer was observed with excessive addition of DPP, as found in the case of TPP, indicating that the excessive phosphites did not cause a deleterious side reaction to the polycondensation reaction. Only low molecular-weight polymers were obtained even at a DPP/SDA ratio up to 3.6. This also can be explained by taking into account the equilibrium of $N$-phosphonium salt **II** with dicarboxylic acid and DPP, as discussed in the case of TPP. Only when the concentration of DPP reached a certain value, could the polycondensation reaction proceed smoothly via activated intermediate **II** to give high molecular weight polymers.

### Concentration of Metal Salts

Figure 2 shows the effect of the addition of CaCl₂ and LiCl on the polycondensation of SDA and ODA by using TPP or DPP as the condensing agent. The reaction was carried out on 0.4 mol/L of monomer concentration in NMP–pyridine solution (4 : 1 by volume) at 100°C for the case using TPP and at 110°C for the case using DPP. In the absence of metal salts, less favorable results were obtained due to an early precipitation of polymer in the reaction media.

In the reaction promoted with TPP, the addition of a very wide range of 2–20 wt % of LiCl or CaCl₂

led to satisfactory results. Too high concentrations of metal salts caused reaction mixtures too viscous to stir. The addition of about 8 wt % of LiCl and 6 wt % of CaCl₂ produced the maximum inherent viscosity of 1.58 and 1.41 dL/g, respectively.

In the case promoted with DPP, less favorable results were obtained in the absence of metal salts or in the presence of metal salts lower than 2 wt % due to early precipitation of polymer in the reaction media. Higher amounts of CaCl₂ (4–20 wt %) or LiCl (4–20 wt %) significantly increased the molecular weight of polyamides produced. Too high amounts of metal salts retarded the polycondensation reaction. The inherent viscosity decreased significantly when the amount of LiCl is above 12 wt % or that of CaCl₂ is above 20 wt %.

### Reaction Temperature

The reaction temperature plays a significant role on the achievement of high molecular-weight polymer prepared by the phosphorylation reaction. Figures 3 and 4 show the inherent viscosities of the polymers polycondensed from SDA with ODA at various time intervals and reaction temperatures in the range of 60–120°C by using TPP and DPP as the condensing agents, respectively. In the reaction promoted with TPP, a maximum inherent viscosity was observed
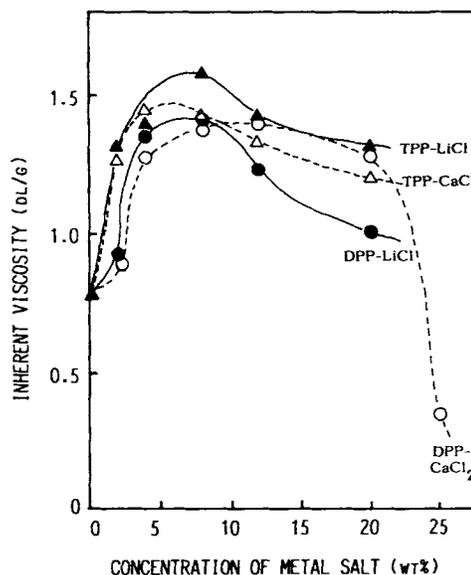


**Figure 2.** Effect of the concentration of metal salts on the polycondensation of SDA with ODA using TPP or DPP as the condensing agent: SDA = ODA = 5 mmol; NMP = 10 mL; Py = 2.5 mL; TPP = 12 mmol, or DPP = 20 mmol; temperature = 100°C (TPP), 110°C (DPP); time = 3 h.
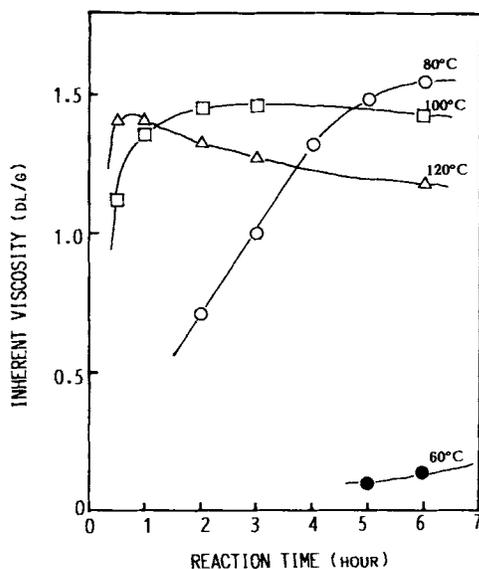
**Figure 3.** Rate of polycondensation of SDA with ODA at various temperatures and times: SDA = ODA = 5 mmol; NMP = 10 mL; Py = 2.5 mL; LiCl = 1.0 g; TPP = 12 mmol.

at a temperature around 80°C. At 80°C, it needs a longer time of about 6 h to achieve high molecular weight. At the higher temperature of 100°C, the formation of high molecular weight takes place within 3 h. Almost no polymer was obtained at the lower temperature of 60°C.
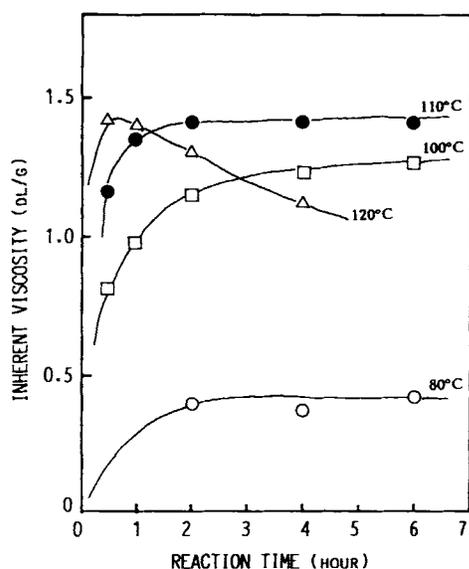


**Figure 4.** Rate of the polycondensation of SDA with ODA at various temperatures and times: SDA = ODA = 5 mmol; NMP = 10 mL; Py = 2.5 mL; LiCl = 1.0 g; DPP = 20 mmol.

In the case promoted with DPP, a maximum inherent viscosity was observed at the temperature of 110°C. At the lower temperature of 80°C, only low molecular weight was obtained. At the higher temperature of 120°C, high molecular-weight polymer was formed in 30 min, while the inherent viscosity decreased gradually with prolonged heating. This can be attributed to the fact that undesirable side reaction may be favored, such as the reaction of acyloxy N-phosphonium salt of pyridine with phenol derived from phosphites to yield phenyl ester.[3]

## Monomer Concentration

During the phosphorylation reaction the attainment of high molecular-weight polymer is affected by many factors, and among them the concentration of reactants plays a very important role. A series of experiments were conducted with the view to find the optimal initial monomer concentration for polymers with the highest molecular weight. The effect of monomer concentration on the inherent viscosities of polyamides derived from SDA and ODA is shown in Table I. In both cases of using TPP and DPP as the condensing agents, viscosity passes through a maximum, with concentration of the solution. Too high concentration caused the reaction mixtures too viscous to stir and possible gelation or precipitation, leading to low molecular weights. Polyamides with the highest molecular weights were obtained at the monomer concentration of 0.4 mol/L in both cases. The lower inherent viscosity obtained at lower monomer concentration can be explained by taking into account competitive side reactions as discussed by Yamazaki et al.[3]

**Table I.** Effect of Monomer Concentration on the Preparation of Polyamide from SDA and ODA in NMP-Pyridine Solution in the Presence of 8 wt % LiCl by using TPP and DPP as Condensing Agents[a]

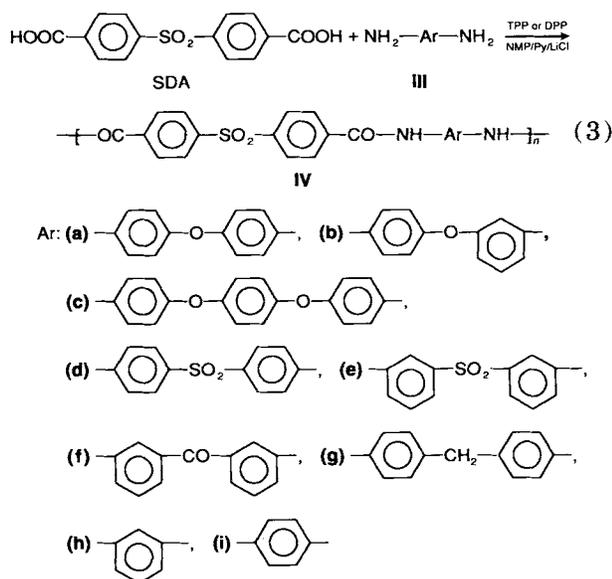| Monomer Concentration (mol/L) | $\eta_{inh}$[b] (dL/g) of Polyamide | |
| --- | --- | --- |
| | By TPP | By DPP |
| 0.1 | 1.15 | 1.07 |
| 0.2 | 1.32 | 1.20 |
| 0.4 | 1.58 | 1.41 |
| 0.6 | 1.41 | 1.23 |

[a] NMP = 10 mL; pyridine = 2.5 mL; TPP = 12 mmol or DPP = 20 mmol; temperature = 100°C (for TPP), 110°C (for DPP); time = 3 h.
[b] Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL concentration.

## Preparation of Various Homopolyamides and Copolyamides

### Homopolyamides

In the previous report,[6] we have applied the phosphorylation reaction to prepare some sulfone-containing polyamides from SDA and various diamines by using TPP as condensing agent. Some properties, such as solubility, crystallinity, glass transition temperature, and thermal stability, of the obtained polymers also have been described in that article. Here, in addition to TPP, we also employ DPP as the condensing agent to prepare polymers from SDA and various diamines [see eq. (3)] by using the optimal conditions for the synthesis of the polyamide of SDA and ODA.



$$\text{HOOC}-\langle\text{O}\rangle-\text{SO}_2-\langle\text{O}\rangle-\text{COOH} + \text{NH}_2-\text{Ar}-\text{NH}_2 \xrightarrow[\text{NMP/Py/LiCl}]{\text{TPP or DPP}}$$

SDA                III

$$-\left[\text{OC}-\langle\text{O}\rangle-\text{SO}_2-\langle\text{O}\rangle-\text{CO}-\text{NH}-\text{Ar}-\text{NH}\right]_n \quad (3)$$

IV

As shown in Table II, DPP showed a comparable efficiency with TPP on the achievement of high molecular weight polyamides when compared to TPP. The polyamides were obtained in quantitative yields except for polymer **IV$_d$**. Except for the polymers derived from 3,3'- and 4,4'-sulfonyl dianiline (**III$_d$** and **III$_e$**), the inherent viscosities of all polymers are higher than 0.8 dL/g. The unsatisfactory results were obtained from diamines **III$_d$** and **III$_e$**, probably because of the lower basicity of the diamines due to the presence of electron-withdrawing sulfonyl group. The more favorable results obtained from ODA (**III$_a$**) and 1,4-bis(p-aminophenoxy)benzene (**III$_c$**) may be due to their high reactivity and the excellent solubility of their resulting polymers.

**Table II.** Preparation of Homopolyamides from SDA and Various Diamines by the Phosphorylation Reaction[a]

| Polymer Code | Diamine | $\eta_{inh}$[b] (dL/g) of Polyamides | |
| --- | --- | --- | --- |
| | | By TPP | By DPP |
| **IV$_a$** | **III$_a$** | 1.65 | 1.41 |
| **IV$_b$** | **III$_b$** | 0.92 | 1.00 |
| **IV$_c$** | **III$_c$** | 1.53 | 1.42 |
| **IV$_d$** | **III$_d$** | 0.42 | 0.35 |
| **IV$_e$** | **III$_e$** | 0.59 | 0.61 |
| **IV$_f$** | **III$_f$** | 0.90 | 0.81 |
| **IV$_g$** | **III$_g$** | 0.95 | 1.00 |
| **IV$_h$** | **III$_h$** | 1.15 | 1.02 |
| **IV$_i$** | **III$_i$** | 1.34 | 1.25 |

[a] SDA = diamine = 5 mmol; TPP = 12 mmol or DPP = 20 mmol; NMP = 10 mL; pyridine = 2.5 mL; LiCl = 1.0 g; temperature = 100°C (for TPP), 110°C (for DPP); time = 3 h.

[b] Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL concentration.

### Copolyamides

Random copolyamides were prepared from the reactions of ODA with various mixed diacids of SDA and TPA, IPA or NDA [eq. (4)], and their inherent viscosities are shown in Table III. Considering the solubility of the resulting polymers, two conditions for the phosphorylation reactions were employed as listed in Table III. In conditions **A**, only LiCl of 8 wt % was added in the reaction media. Conditions **B** are similar to that reported by Higashi,[7] where 5 wt % LiCl and 8 wt % CaCl$_2$ were added into the reaction solution. Moreover, two condensing agents of TPP and DPP were used individually in the preparation of most copolymers.
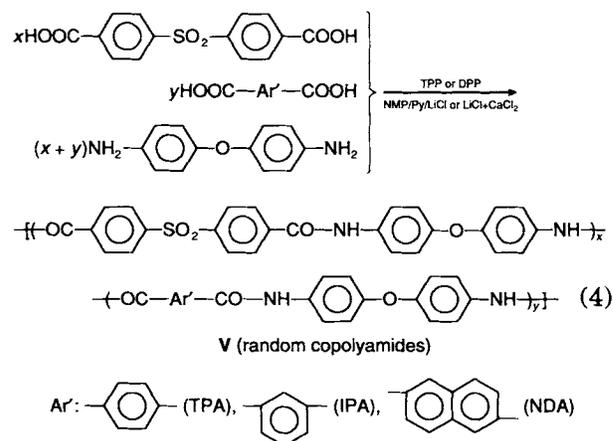


$$(4)$$

V (random copolyamides)

**Table III.**  Random Copolyamides Prepared from SDA and Mixed Diacids with ODA by the Phosphorylation Reaction with TPP and DPP as Condensing Agents

| Polymer Code | Diacid (mol %) | | By TPP | | By DPP | |
|---|---|---|---|---|---|---|
| | | | Conditions[a] | $\eta_{inh}$[b] | Conditions[a] | $\eta_{inh}$[b] |
| | SDA | TPA | | | | |
| V–ST-1 | 10 | 90 | A | 0.52 | A | 0.43 |
| | | | B | 1.97 | B | 1.30 |
| V–ST-2 | 20 | 80 | A | 0.67 | A | 0.61 |
| | | | B | 2.24 | — | — |
| V–ST-3 | 30 | 70 | B | 2.69 | B | 2.37 |
| V–ST-4 | 50 | 50 | A | 2.02 | B | 1.97 |
| V–ST-5 | 70 | 30 | A | 1.83 | B | 1.65 |
| V–ST-6 | 80 | 20 | A | 1.71 | — | — |
| V–ST-7 | 90 | 10 | — | — | B | 1.24 |
| | SDA | IPA | | | | |
| V–SI-1 | 90 | 10 | — | — | A | 1.24 |
| V–SI-2 | 75 | 25 | A | 1.54 | A | 1.39 |
| V–SI-3 | 50 | 50 | A | 1.41 | A | 1.17 |
| V–SI-4 | 25 | 75 | A | 1.38 | A | 1.09 |
| V–SI-5 | 10 | 90 | — | — | A | 1.40 |
| | SDA | NDA | | | | |
| V–SN-1 | 60 | 40 | A | 1.80 | A | 1.78 |
| V–SN-2 | 50 | 50 | A | 1.87 | A | — |
| V–SN-3 | 40 | 60 | A | 2.11 | A | 1.90 |
| V–SN-4 | 20 | 80 | A | 2.42 | A | — |
| V–SN-5 | 10 | 90 | A | 2.48 | A | — |

[a] Conditions **A**: mixed diacids = ODA = 5 mmol; NMP = 10 mL; Py = 2.5 mL; TPP = 12 mmol or DPP = 20 mmol; LiCl = 1.0 g; temperature = 100°C (for TPP) or 110°C (for DPP); time = 3 h. Conditions **B**: mixed diacids = ODA = 5 mmol; NMP = 10 mL; Py = 2.5 mL; TPP = 12 mmol or DPP = 20 mmol; CaCl$_2$ = 1.0 g; LiCl = 0.6 g; temperature = 100°C (for TPP) or 110°C (for DPP); time = 3 h.
[b] Measured in DMAc containing 5 wt % LiCl at 30°C on 0.5 g/dL concentration.

The SDA/TPA series copolymers listed in Table III were prepared in an attempt to overcome the low reactivity of TPA and the poor solubility encountered with the TPA homopolyamides. Under conditions **A**, the inherent viscosity increased with increasing TPA proportion to about 70%, and then decreased sharply for still higher percentage. Copolymers containing more than 80% TPA in the diacid moieties precipitated rapidly from the polymerization medium. Copolymer V–ST-1, containing 90% of TPA units had low inherent viscosity of 0.52 dL/g when prepared by **A** conditions and using TPP as condensing agent. However, high molecular weight of V–ST-1 and V–ST-2 could be obtained by using **B** conditions. A reasonable explanation for

the improved results has been proposed by Higashi and co-workers,[7] i.e., the favorable results can not be explained only by the increased solubility of the polymer by addition of CaCl$_2$; a combination of CaCl$_2$, LiCl, and pyridine might also participate in the reaction through a complexation of the salts with diamines or the phosphites. Replacement of TPA by IPA or NDA leads to an increase in solubility of copolymers. **A** conditions are quite effective in the preparation of copolyamides V–SI-1–5 and V–SN-1–5 by using TPP or DPP as condensing agent. The inherent viscosities of the series copolymers of SDA and NDA increase with increasing NDA proportion may be attributed to the rigid nature of NDA moiety.

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