

Syntheses of Regular Copolyamides Using Triphenyl Phosphite and Pyridine

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Received 12 May 1999; accepted 29 August 1999

ABSTRACT: In this article, a method of preparing of regular copolyamide (co-PA) in a reactor using triphenyl phosphite/pyridine as the activating agent was investigated. In two-step reactions of copolymers prepared from two kinds of dicarboxylic acids and one kind of diamine, oligomer PAs containing amine end groups were first synthesized; then, the second dicarboxylic acid was added to the same reactor to polymerize high molecular weight and regular co-PAs. However, when oligomers having carboxylic acid end groups were first prepared and another kind of diamine was added, the degree of polymerization was low. The reason proposed was that if the oligomer has an amine end group, it would coexist with the activating agent without deactivating; if the end group was the carboxylic acid end group, deactivation would occur. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 116–122, 2000

Key words: direct polycondensation; triphenyl phosphite/pyridine; aromatic copolyamide; block-alternating copolymer

INTRODUCTION

Aromatic polyamide is a kind of polymeric material of high strength and heat resistance.^{1,2} However, the acid chloride monomer is moisture-sensitive and uneasy to keep, and except for TPC and IPC, other aromatic dicarboxylic acids were all difficult to use to prepare high-purity acid chlorides by distillation. Therefore, in the past, except for the series of TPC and IPC, aromatic polyamides of other series were not easy to synthesize in high molecular weights. In 1980, Yamazaki et al. used triphenyl phosphite/pyridine (TPP/Py) as an activating agent and found that dicarboxylic acids and aromatic diamines could be directly polycondensed to synthesize polyamides without activating the acid groups to acid chlorides.^{3,4} This method became the convenient method for

preparing high molecular weight aromatic polyamides in the laboratory.

Concerning the preparations of copolyamides by means of direct polycondensation, if the preparations were carried out only from dicarboxylic acids and diamines, the copolyamides could be synthesized by using more than two kinds of monomers. If the syntheses were carried out though a one-pot one-step (1P1S) method with equivalent quantities of dicarboxylic acids and diamines, then only random copolymers were produced. If the copolymers of regular structures were to be synthesized, monomers must be added stepwise to control their structure. Now suppose that the three monomers including (a) two kinds of dicarboxylic acids and one kind of diamine or (b) two kinds of diamines and one kind of dicarboxylic acid were used to synthesize the regular copolymers. Two kinds of monomers were chosen first to synthesize the oligomers which had amine or carboxylic acid end groups. Then, the third monomer was added via the 1P2S method to synthesize the alternating copolymers or block-alter-

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Journal of Applied Polymer Science, Vol. 77, 116–122 (2000)
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nating copolymers. If two reactors (two pots) were used individually to synthesize the oligomers that had amine or carboxylic acid end groups and then these oligomers were mixed (the so-called 2P2S steps), block copolymers of arbitrarily structures could be synthesized.

Various copolymers can be obtained depending upon the polymerization process, and they would have different characteristics. In this article, the possibility and a suitable synthesis method of preparing copolyamides from dicarboxylic acids and aromatic diamines by Yamazaki direct polycondensation were investigated. All the past literature about the Yamazaki synthesis of polyamides stressed equivalent reactions of dicarboxylic acids and diamines, the reaction mechanisms, and their applications.^{5–9} Concerning copolymerizations (alternating copolymerization or block copolymerization, etc.), the effects in the reaction systems of excess dicarboxylic acids, excess diamines, different reaction processes, and activating agents on the activities of monomers or intermediates have not yet been investigated completely. Therefore, we set out to investigate how regular copolyamides are synthesized from different dicarboxylic acids and diamines by direct polycondensation.

EXPERIMENTAL

Materials

3,4'-Oxydianiline (3,4'-ODA), 4,4'-oxydianiline (4,4'-ODA), 1,4-bis(4-aminophenoxy)benzene (BAPB), terephthalic acid (TPA), and isophthalic acid (IPA) were obtained from TCI and used without further purification. Triphenyl phosphite (TPP; TCI) was purified by vacuum-distillation. Commercially obtained calcium chloride (Wako) and lithium chloride (TCI) were dried under a vacuum at 120°C for 10 h. *N,N*-Dimethylacetamide (DMAc; TCI), pyridine (Py; Wako), and *N*-methyl-2-pyrrolidone (NMP; Fluka) were purified by distillation under reduced pressure over calcium hydride and stored over 4Å molecular sieves.

Polymerization Processes

Effects of TPP/Py Activating Agent in the IPA/4,4'-ODA Stepwise Polycondensation

- (a) *Equivalent Reaction in One Step.* In a 50-mL flask, a mixture of 2.5 mmol of 4,4'-ODA, 2.5 mmol of IPA, 3.5 mL of NMP, 0.3 g of CaCl₂, 1.5 mL of TPP, and 1.0 mL of Py

Table I The IPA/4,4'-ODA Stepwise Polycondensation

Polymer	First Step Monomer Ratio		Second Step Monomer Ratio		η_{inh}^a (dL g ⁻¹)
	IPA	4,4'-ODA	IPA	4,4'-ODA	
I_a	1	1	—	—	0.82
I_b	1	2	1	—	0.75
I_c	2	1	—	1	0.37

^aMeasured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C.

was heated with stirring at 100°C for 3 h. Then, the reaction mixture was poured into excess methanol to give polymer **I_a**.

- (b) *Excess Diamine in the First Step.* A mixture of 2.5 mmol of 4,4'-ODA, 1.25 mmol of IPA, 3.5 mL of NMP, 0.3 g of CaCl₂, 1.5 mL of TPP, and 1.0 mL of Py was heated with stirring at 100°C for 60 min. An additional 1.25 mmol of IPA was then added to react for another 3 h. The reaction mixture was poured into excess methanol to give polymer **I_b**.
- (c) *Excess Dicarboxylic Acid in the First Step.* In a 50-mL flask, a mixture of 1.25 mmol of 4,4'-ODA, 2.5 mmol of IPA, and the same amount of reagents as (b) was heated with stirring at 100°C for 60 min. An additional 1.25 mmol of 4,4'-ODA was then added to react for another 3 h. The reaction mixture was poured into excess methanol to give polymer **I_c**.

The inherent viscosities (η_{inh}) and stepwise used monomers of **I_a**, **I_b**, and **I_c** are listed in Table I.

Syntheses of Copolymers from One Kind of Diamine and Two Kinds of Dicarboxylic Acids

- (a) *Equivalent Reaction of Random Copolymer Synthesis in One Step.* The synthesis of copolymer **II_{1-A}** (TPA/IPA/BAPB = 1/1/2) is described as a typical procedure. In a 50-mL flask, a mixture of 0.625 mmol of TPA, 0.625 mmol of IPA, 1.25 mmol of BAPB, 3 mL of NMP, 0.25 g of CaCl₂, 0.8 mL of TPP, and 0.8 mL of Py was heated with stirring at 100°C for 3 h. The resulting polymer solution was poured into methanol to give polymer **II_{1-A}**. Three other copolymers, **II_{2-A}**, **II_{3-A}**, and **II_{5-A}**, were synthesized in an analogous procedure and their inherent viscosities are shown in Table II.

Table II Synthesis of Copolyamides

Polymer ^a	First Step Monomer Ratio	Second Step Monomer Ratio	Polymer Structure	η_{inh}^b (dL g ⁻¹)
II _{1-A}	1 _{TPA} + 1 _{IPA} + 2 _{BAPB}	—	Random	0.58
II _{1-B}	1 _{IPA} + 2 _{BAPB}	1 _{TPA}	Alternating	0.96
II _{1-C}	1 _{TPA} + 2 _{BAPB}	1 _{IPA}	Alternating	0.49
II _{2-A}	1 _{TPA} + 2 _{IPA} + 3 _{BAPB}	—	Random	1.08
II _{2-B}	2 _{IPA} + 3 _{BAPB}	1 _{TPA}	Block-alternating	1.22
II _{3-A}	1 _{TPA} + 3 _{IPA} + 4 _{BAPB}	—	Random	0.95
II _{3-B}	3 _{IPA} + 4 _{BAPB}	1 _{TPA}	Block-alternating	1.36
II _{3-C}	1 _{TPA} + 2 _{BAPB}	3 _{IPA} + 2 _{BAPB}	Block ^c	0.62
II _{3-D}	3 _{IPA} + 2 _{BAPB}	1 _{TPA} + 2 _{BAPB}	Block ^c	0.23
II _{4-A}	The same as II _{1-A}	—	Random	0.58
II _{4-B}	3 _{IPA} + 4 _{BAPB}	3 _{TPA} + 2 _{BAPB}	Block ^c	0.79
II _{5-A}	1 _{TPA} + 5 _{IPA} + 6 _{BAPB}	—	Random	1.35
II _{5-B}	5 _{IPA} + 6 _{BAPB}	1 _{TPA}	Block-alternating	0.96

^aPolymerization was carried out with a total of 1.25 mmol of dicarboxylic acid or diamine, and all reagents were added in the first step. After reacting at 100°C for 1 h, additional monomers in the second step were added to react for another 3 h.

^bMeasured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C.

^cIncomplete block.

(b) *Alternating Copolymer Synthesis from Two Steps.* The synthesis of copolymer **II**_{1-B} (TPA/IPA/BAPB = 1/1/2) is described as a typical procedure. A mixture of 0.625 mmol of IPA, 1.25 mmol of BAPA, 3 mL of NMP, 0.25 g of CaCl₂, 0.8 mL of TPP, and 0.8 mL of Py was heated with stirring at 100°C for 60 min. An additional 0.625 mmol of TPA was then added to react for another 3 h. The resulting mixture was poured into excess methanol to give polymer **II**_{1-B}. Copolymer **II**_{1-C} was synthesized in a similar procedure, but the addition order of IPA and TPA was exchanged.

(c) *Block-Alternating Copolymer Synthesis from Two Steps.* Synthesis of copolymer **II**_{2-B} (TPA/IPA/BAPB = 1/2/3) is described as a typical procedure. In a 50-mL flask, a mixture of 0.833 mmol of IPA, 1.25 mmol of BAPA, 3 mL of NMP, 0.25 g of CaCl₂, 0.8 mL of TPP, and 0.8 mL of Py was heated with stirring at 100°C for 1 h. An additional 0.417 mmol of TPA was then added to react for another 3 h. The resulting solution was poured into methanol to give polymer **II**_{2-B}. Two other copolymers, **II**_{3-B} and **II**_{5-B}, were synthesized in an analogous procedure and the used monomers' ratio and inherent viscosities of them are shown in Table II.

(d) *Incomplete Block-Alternating Copolymer Synthesis from Two Steps.* The synthesis of copolymer **II**_{4-B} (TPA/IPA/BAPB = 3/3/6) is

described as a typical procedure. A mixture of 0.625 mmol of IPA, 0.834 mmol of BAPA, 3 mL of NMP, 0.25 g of CaCl₂, 0.8 mL of TPP, and 0.8 mL of Py was heated with stirring at 100°C for 60 min. Then, an additional 0.625 mmol of TPA and 0.413 mmol of BAPA were added, and the reaction was continued for 3 h to form polymer **II**_{4-B}. Two other copolymers, **II**_{3-C} and **II**_{3-D}, were synthesized in a similar procedure.

The inherent viscosity and structure of copolymers synthesized from one kind of diamine and two kinds of dicarboxylic acids are listed in Table II.

Syntheses of Copolymers from Two Kinds of Diamines and One Kind of Dicarboxylic Acid

(a) *Alternating and Block-Alternating Copolymer Syntheses by 1P2S.* The synthesis of the alternating copolymer **III**_a (TPA/3,4'-ODA/4,4'-ODA = 2/1/1) is described as a typical procedure. In a 50-mL flask, a mixture of 1.25 mmol of 3,4'-ODA, 2.5 mmol of TPA, 3.5 mL of NMP, 0.3 g of CaCl₂, 1.5 mL of TPP, and 1.0 mL of Py was heated with stirring at 100°C for 60 min. An additional 1.25 mmol of 4,4'-ODA was then added to react for another 3 h. The resulting polymer solution was poured into methanol to give polymer

Table III Copolymers Synthesized from Two Kinds of Diamines and One Kind of Dicarboxylic Acid

Polymer ^a	First Step Monomer Ratio			Second Step Monomer Ratio		Polymer Structure	η_{inh}^b (dL g ⁻¹)
	TPA	3,4'-ODA	4,4'-ODA	TPA	4,4'-ODA		
III_a	2	1	—	—	1	Alternating	0.74
III_b	3	2	—	—	1	Block-alternating	0.58
III_c	4	3	—	—	1	Block-alternating	0.27
III_d	1	2	—	3	2	Block	1.75
III_e	2	3	—	4	3	Block	1.65
III_f	1	1	—	—	—	Homopolymer	1.62
III_g	1	—	1	—	—	Homopolymer	1.60
III_h	2	1	1	—	—	Random copolymer	1.70

^aPolymerization was carried out with a total of 2.5 mmol of each monomer in two steps, and all reagents were added in the first step. Reaction time of first and second steps is 1 and 3 h, respectively.

^bMeasured at a concentration of 0.5 g dL⁻¹ in DMAc at 30°C.

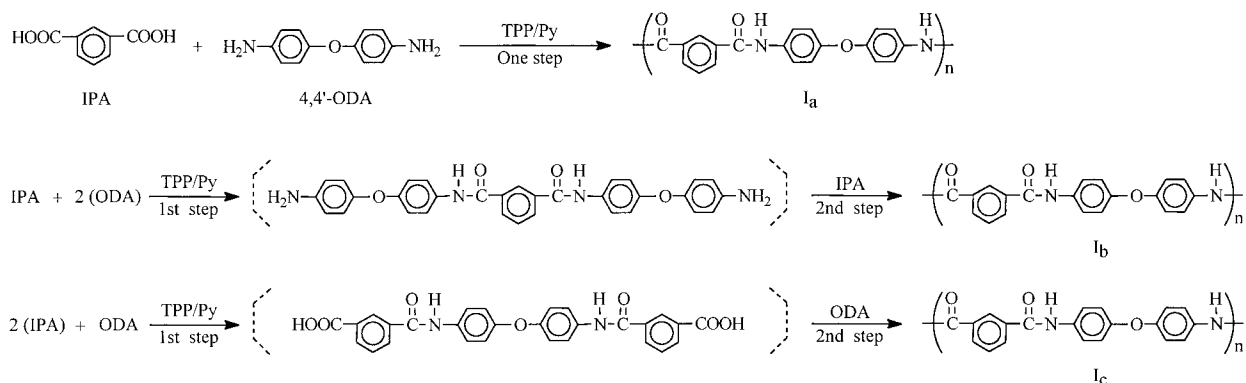
III_a. Copolymers **III_b** and **III_c** were synthesized in an analogous procedure.

(b) *Incomplete Block Copolymer Synthesis by IP2S*. As an example of copolymer **III_d**, a mixture of 1.25 mmol of 3,4'-ODA, 0.625 mmol of TPA, 3.5 mL of NMP, 0.3 g of CaCl₂, 1.5 mL of TPP, and 1.0 mL of Py was heated with stirring at 100°C for 60 min. An additional 1.25 mmol of 4,4'-ODA and 1.875 mmol of TPA were then added to react for another 3 h. The resulting mixture was poured into excess methanol to give polymer **III_d**. Copolymer **III_e** was synthesized in a similar procedure with a different monomer ratio.

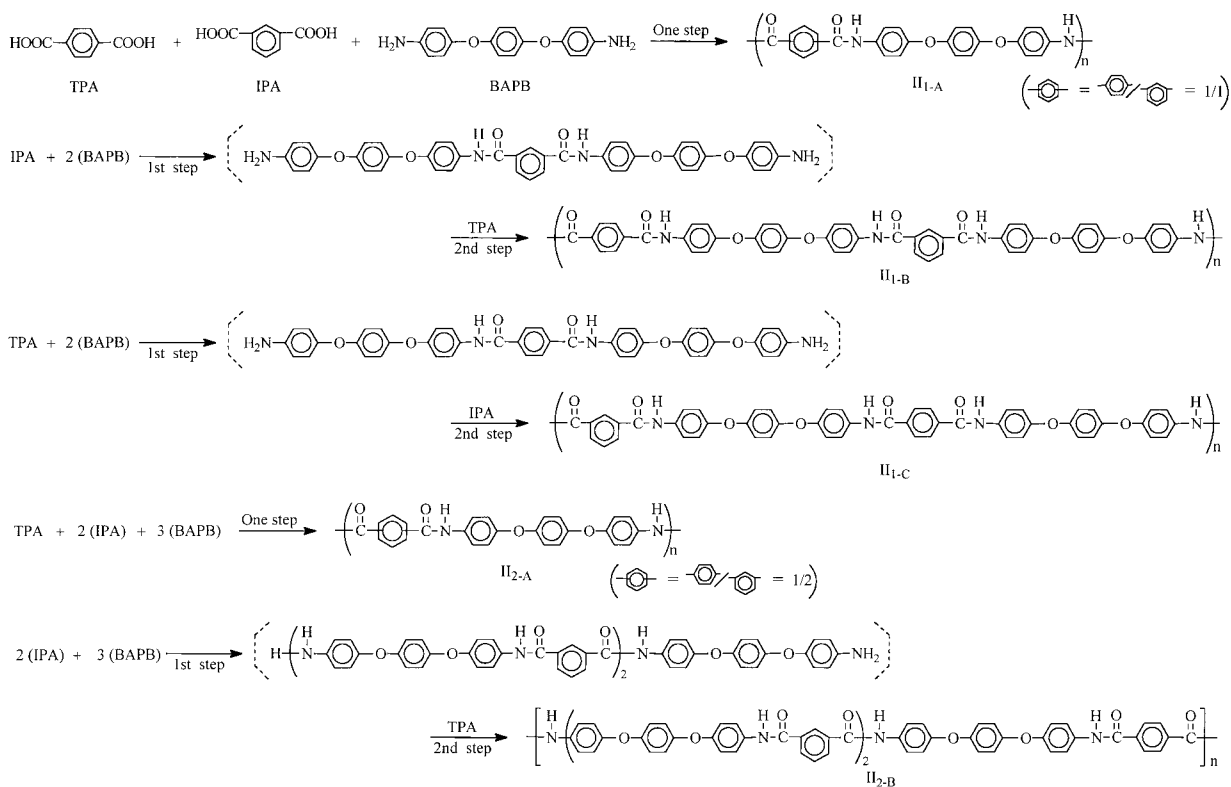
The inherent viscosity and components of the copolymers synthesized from one kind of diamine and two kinds of dicarboxylic acids are shown in Table III.

RESULTS AND DISCUSSION

In this study, three kinds of monomers were reacted to synthesize regular copolyamides in a reactor in two steps, and enough activating agents (TPP/Py) were added in the first step. At first, we investigated the influence of the activating agents (TPP/Py) on the two-step reactions of dicarboxylic acid (IPA) with diamine 4,4'-ODA (as shown in Scheme 1 and Table I). The results showed that TPP/Py did not need to be applied as the theoretical reaction mechanisms; one had to activate the dicarboxylic acid first, then add the diamines to carry out the reactions.³ TPP/Py could be added into the mixture of dicarboxylic acids and diamines at the same time to obtain the best polymerization results. If the dicarboxylic acids or oligomers having carboxylic acid end groups coexisted longer with their activating agents, the reacting activities of them with added diamine were



Scheme 1 Syntheses of aramid (IPA-ODA) by different procedures.



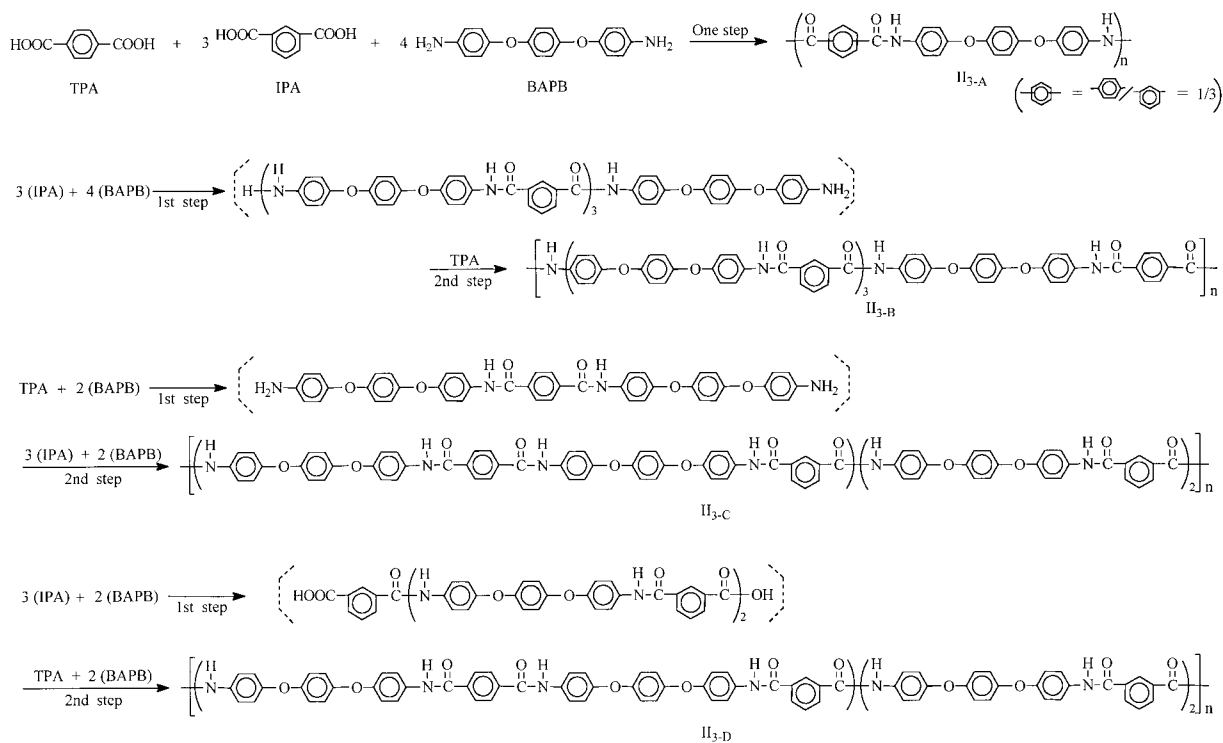
Scheme 2 Syntheses of various co-PTPA (II₁ and II₂) from TPA, IPA, and BAPB (A).

lower and the degrees of polymerization were low (such as I_c). On the contrary, although the amines or oligomers containing amine end groups coexisted with activating agents, their activities would not be lost and they could continue to react with the dicarboxylic acids added further to obtain higher degrees of polymerization (such as I_b).

Next, the syntheses of copolymers with one kind of diamine and two kinds of dicarboxylic acids were investigated (as shown in Scheme 2, Scheme 3, and Table II). The copolymers were formed by combining rigid *para* moieties (TPA/BAPB) with flexible *meta* moieties (IPA/BAPB). The experimental results showed the following: (1) From the random copolymers obtained by the 1P1S method, it was known that if compositions of the rigid moieties were too high insoluble materials would precipitate out during the reaction and, hence, the degree of polymerization would become low. When flexible moieties were enhanced, the degree of polymerization would also be increased (e.g., II_{5-A} > II_{2-A} > II_{1-A}). (2) As regular copolymers were synthesized by the 1P2S method, flexible moieties (IPA/BAPB) were used first to form the diamine oligomer and dicarboxylic acid TPA was added in the second step; then, alternating or block-alternating copolymers (e.g., II_{1-B}, II_{2-B}, II_{3-B}, and II_{5-B}) with a high degree of

polymerization could be obtained. (3) However, if the diamine oligomer formed in the first step was not soluble enough, then the polymerization in the second step would not proceed with ease (e.g., II_{1-C} and II_{3-C}). (4) Also, if the terminal group of the oligomer prepared in the first step was the carboxylic acid group (e.g., II_{3-D}), then the degree of polymerization would be very low.

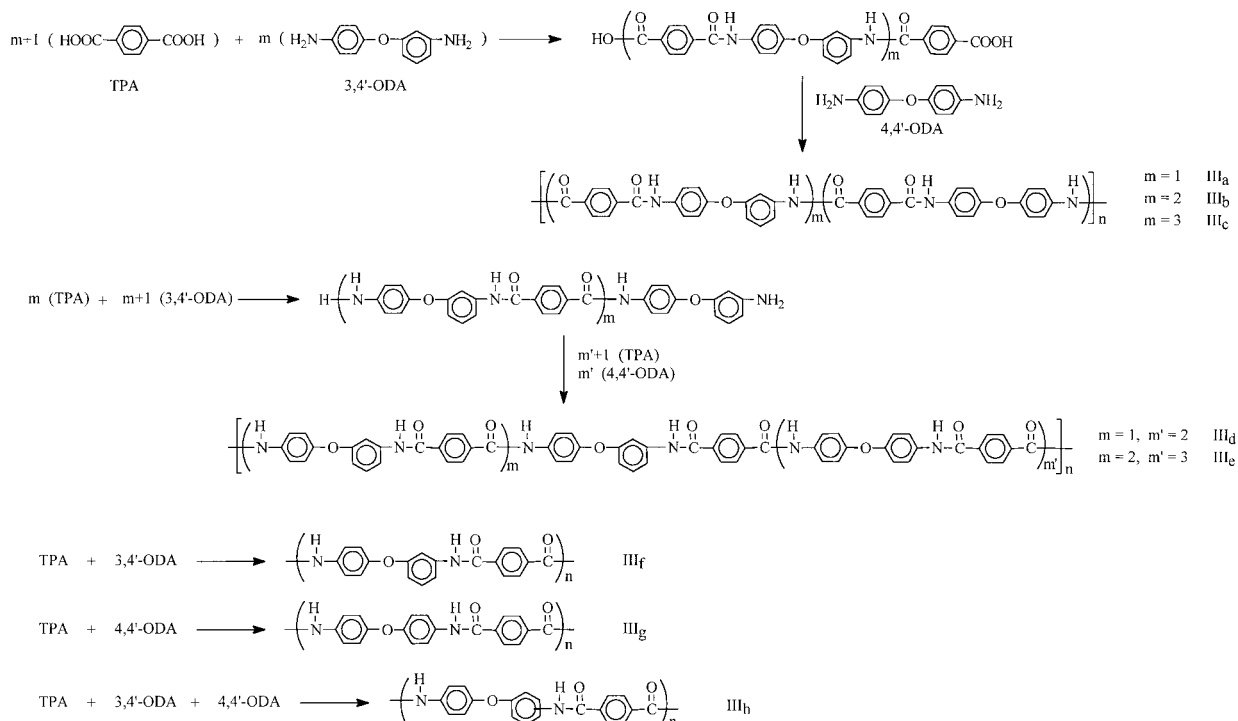
Conditions for the case of synthesizing regular copolyamides from two kinds of diamines and one kind of dicarboxylic acid in two steps were again investigated. Likewise, the combination of a rigid-straight-moiety, TPA/4,4'-ODA, and a flexible moiety, TPA/3,4'-ODA, was chosen (as shown in Scheme 4 and Table III). Polymers of high molecular weights could be obtained from random copolymerization by the 1P1S method (e.g., III_h). By stepwise reactions, when the flexible chain-containing oligomer with a terminal group of carboxylic acid was formed in the first step, copolymers of high molecular weights were all difficult to obtain (e.g., III_{a,b,c}) after the second kind of diamine was added in the second step to carry out the reaction. However, if we ignored some structural regularities by synthesizing the oligomer whose terminal group was the amine group in the first step and then the residual dicarboxylic acid and another kind of diamine were added simulta-



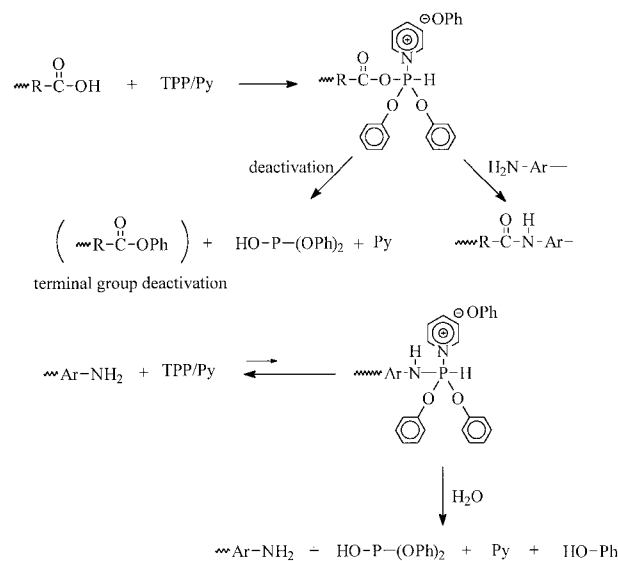
Scheme 3 Syntheses of co-PTPA (II_3) from TPA, IPA, and BAPB (B).

neously in the second step, copolymers of high molecular weights could be obtained (e.g., III_d and III_e).

From these facts, we could determine the feasibility of synthesizing regular copolyamides by direct polycondensation with TPP/Py as an acti-



Scheme 4 Syntheses of PTPA and co-PTPA (III) from TPA, 4,4'-ODA, and 3,4'-ODA.



Scheme 5 Deactivation of the carboxylic acid group.

vating agent: By using more than two kinds of dicarboxylic acids or diamines, copolymers of regular structures could be prepared through the Yamazaki direct polycondensation. No matter whether the one-pot or multipot method was used, the only requirements were that amines were to be kept in excess during the synthesizing process. An oligomer having an amine group at the end was synthesized first; then, they could all continue to polymerize with dicarboxylic acids to form copolymers of high molecular weights.

As for the reason why the oligomers, whose terminal groups were dicarboxylic acids, would deactivate in TPP/Py, it was proposed that an activated dicarboxylic acid–TPP/Py intermediate would form the phenyl ester³ if no aromatic diamine reacted with it at once. Especially, in the coexistence with a greater quantity of a side product, phenol–pyridine, the deactivating rate would be faster. However, if the terminal group of the oligomer was the amine group, then, whether TPP/Py reacted with the amine group or not,⁴ the original reactivity of the diamine could be restored. Thus, added dicarboxylic acids (activated by TPP) could carry out the polycondensation with diamines. The mechanism of the deactivation of the carboxylic acid group is shown in Scheme 5.

CONCLUSIONS

When TPP/Py was used as the activating agent in the direct polycondensation for preparing copoly-

amides, equivalent monomers of various dicarboxylic acids and aromatic diamines reacted by the 1P1S method could synthesize the largest inherent viscosity of the polymers. By the 1P2S method, if diamines were in excess to react with TPP in the first step, high inherent viscosities also could be obtained. However, the analogous procedure for excess diacids in the first step caused the inherent viscosity of the polymers to be very low. Regular copolyamides were prepared from two acids and one amine in two steps, first using diamine/dicarboxylic acid = 2/1 to react and then adding another dicarboxylic acid to obtain the alternating copolymers whose inherent viscosities were close to those of random copolymers obtained by the 1P1S method. In a one acid and two amines system, dicarboxylic acid must be added in both two steps, and the ratio used of the amine/dicarboxylic acid should be greater than 1 in the first step. So, the degree of polymerization could be high; however, the molecular arrangement would also be affected. When the 1P2S method was used to synthesize the block (or alternating-block) copolyamides, using the soft and easily soluble diacid to react in the first step could give better result than using rigid diacid, because the latter would produce insoluble intermediates and, hence, would hinder the polymerization process.

We are grateful to the National Science Council of the Republic of China for the support of this work (Grant NSC 88-2216-E-036-007).

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