Direct Polycondensation Reaction Using Polymeric Triphenylphosphine as an Initiator

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ABSTRACT: Triphenylphosphine which is known as an effective initiator for direct polycondensation, was immobilized into polymers by polymerizing and copolymerizing with diphenylstyrylphosphine. Copolymerization behavior of diphenylstyrylphosphine with 4-vinylpyridine was analyzed. Polymeric triphenylphosphine could initiate the direct polycondensation to form either polyamide or polyester and a recycling system for the regeneration of triphenylphosphine moiety was proposed.

KEY WORDS Direct polycondensation / Triphenylphosphine / Diphenylstyrylphosphine / Polyamide / Polyester /

Direct polycondensation reactions have been recently developed by using various initiators under mild conditions for synthesis of polyamides or polyesters. Among various initiators, triphenylphosphite¹ and triphenylphosphine² are effective initiators to initiate direct polycondensation under mild conditions.

One of the problems of direct polycondensation is that a stoichiometric amount of initiators to monomers is required to initiate polycondensation reactions, and a recycling system of the initiators has to be established for practical application of direct polycondensation.

Triphenylphosphine which is used for the direct polycondensation reaction, is transformed into triphenylphosphine oxide after reacting with carboxylic acid, and regeneration of the initiator requires the reduction of triphenylphosphine oxide to triphenylphosphine, which is usually difficult. An easy recycling system of the initiator is proposed for the direct polycondensation method by

using triphenylphosphine dichloride³ which was easily obtained by the reaction of triphenylphosphine oxide with oxalyl chloride. Triphenylphosphine dichloride which is pentavalent, was found to be effective for the synthesis of either polyamides or polyesters having high molecular weights and a recycling system was established as shown below:

The recovery and regeneration of the triphenylphosphine moiety becomes much easier when the triphenylphosphine moiety is immobilized into a polymer. Moreover, the direct polycondensation reaction requires the co-existence of pyridine as an acid acceptor. When both triphenylphosphine and pyridine moieties are immobilized into a polymer, it is expected that the direct polycondensation reaction can be carried out as a semi-continuous process, as illustrated in Figure 1.

This paper deals with the direct polyconden-

Figure 1. Recycling system of polymeric TTP for direct polycondensation reactions.

sation method using polymeric triphenylphosphine as an initiator for the synthesis of polyamide or polyester with intention to approach to a semi-continuous process of direct polycondensation.

EXPERIMENTAL

Synthesis of 4-Styryldiphenylphosphine (4-SDP)

4-SDP was synthesized by the method of Relles and Schluez⁴: 14.6 g of powdered magnesium were reacted with 3 cm³ of ethyl bromide in 10 cm³ of tetrahydrofuran (THF) under nitrogen atmosphere and then, 41.4 g of 4-chlorostyrene in 75 cm³ of THF was added into the solution in a period of 1 h, keeping temperatures in the range of 45–50°C. The reacted solution was diluted by 50 cm³ of THF, which was added to a mixture of 55.6 g of chlorodiphenylphosphine and 200 cm³ of THF within 1 h, keeping temperature at 5–10°C.

The reacted solution was poured into 300 cm³ water containing 49.5 g of ammonium chloride and the THF layer was separated. The THF solution was dried over anhydrous sodium sulfate in the presence of 0.37 g of *t*-butyl catechol and then it was concentrated to about

200 cm³, followed by pouring into 700 cm³ of *n*-hexane. A precipitated polymer was filtered off and the filtrate was concentrated by removing THF and *n*-hexane. The residual oily product was recrystallized from ethanol. Yield 22.8 g (32%), mp 76–78°C (lit.⁴ mp 77–78°C). C, 82.86% (calcd 83.32%); H, 5.96% (calcd 5.94%).

Polymerization and Copolymerization

4-SDP was polymerized in benzene and also copolymerized with 4-vinylpyridine (4-VPy) at various molar ratios in *N,N*-dimethylformamide (DMF) at 60°C in the presence of AIBN as a radical initiator. Poly(4-SDP) and poly(4-SDP-*co*-4-VPy)s were recovered by pouring into methanol or ether, respectively.

Poly(4-SDP) was oxidized in methylene chloride in the presence of peracetic acid. Hereafter, the homopolymer from 4-SDP is called Poly-1 and copolymers from 4-SDP and 4-VPy, Poly(1-*co*-2). Synthetic routes are schematically shown in Figure 2.

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(1) *Model Reaction*

Each portion of 0.72 g (0.0025 mol of repeating units) of Poly-1, 0.20 g (0.0021 mol) of aniline and 0.26 g (0.0021 mol) of benzoic acid was dissolved in 5 cm³ of pyridine and then, 0.71 g (0.003 mol) of hexachloroethane (C₂Cl₆) was added to the solution. The solution was stirred at room temperature for 30 min and the resulting product was recovered by pouring the solution into water. The product was recrystallized from benzene, which was identified as benzanilide from elemental and infrared analyses. mp 163–165°C (lit.⁵ mp 163°C). Yield: 91%.

(2) *Poly-1 Oxide and (COCl)₂ (System (1))*

A portion of 9.75 g of Poly-1 oxide (0.032 mol of repeating units) was dissolved in 20 cm³ of solvent such as monochlorobenzene, followed by the addition of 4.10 g (0.032 mol) of oxalyl chloride in 10 cm³ of solvents. After

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Figure 2. Synthetic routes of monomer 1 and poly 1 or poly(1-co-2).

evolution of the gas, 0.015 mol of dicarboxylic acids or 0.03 mol of 4-aminobenzoic acid (4-ABA) was added, followed by heating at refluxing temperature of the solvents for 5 min. After cooling the solution, 0.015 mol of diol or diamine was added to carry out the direct polycondensation except in the case of 4-ABA. To the solution was added 0.06 mol of pyridine or triethylamine as an acid acceptor. The entire solution was heated under reflux for 4 h. Polymers were recovered by pouring the solution into 100 cm³ of methanol so as to precipitate either polyamide or polyester. The precipitated polymers were treated for 24 h in a Soxhlet apparatus with refluxing methanol, followed by water so that the polymeric initiators were eliminated from the resulting polymers.

(3) Poly-1 or Poly(1-co-2) and C₂Cl₆ (System (2))

Poly-1 or poly(1-co-2) and monomers were dissolved in a solvent as in the case of the system (1) and then C₂Cl₆ was added to the solution at a molar ratio of 1.0, 1.2, and 1.5 to

the monomer, respectively. The procedure for the direct polycondensation was the same as the system (1).

RESULTS AND DISCUSSION

Synthesis of Polymeric Triphenylphosphine (TPP)

4-SDP was polymerized and copolymerized with 4-VPy and the structures of polymers were identified by NMR spectra as shown in Figures 3 and 4. The results of the copolymerization are summarized in Table I. Monomer reactivity ratios of the copolymerization were calculated by the Kelen-Tüdös method⁶ as $r_1 = 0.729$ and $r_2 = 0.716$, which were obtained from the copolymer composition curve as shown in Figure 5. The $Q-e$ values of 4-SDP were calculated as $Q = 1.35$ and $e = -1.01$ when the $Q-e$ values of 4-VPy were used as $Q = 0.82$ and $e = -0.20$. From these results, the copolymers were estimated to have a random tendency of sequence distribution as $r_1 r_2 < 1.0$.

Figure 3. ^1H NMR spectra of **1** and poly-**1**.

Table I. Copolymerization of 4-SDP and 4-VPy

4-SDP in feed mol%	Copolymers		
	Yield %	4-SDP mol%	η_{sp}/c^a
100	91	100	0.21
90	26	87	0.26
80	21	77	0.23
60	19	61	0.20
40	4	41	0.27
20	21	21	0.31
10	24	14	0.26

^a Measured at a concentration of $0.1 \text{ g}/10 \text{ cm}^3$ in DMF at 30°C .

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(1) Synthesis of Polyamide

The synthesis of polyamide was carried out by using both initiators of the systems (1) and (2) and results are summarized in Table II. It is seen that these polymeric TPP could initiate

Figure 4. ^1H NMR spectra of poly(**1-co-2**) of various molar ratios of **1** and **2**. Figure 5. Copolymer composition curve of the copolymerization of **1** and **2**.

the direct polycondensation to form polyamide under mild conditions. System (2) which was a combination of Poly-**1** or Poly(**1-co-2**) and C_2Cl_6 was superior to system (1) which was a combination of Poly-**1** oxide and $(\text{COCl})_2$, when solution viscosities of the re-

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Table II. Direct polycondensation using polymeric TPP for the synthesis of polyamides

Initiator		Monomer		Solvent ^d	Acid acceptor	Polymer	
System	Mole fraction of TPP	Kind	Concn. mol dm ⁻³			Yield %	η_{sp}/c^e
(1)	1.0	TPA/APE ^a	0.15	NB	Py	26	0.26
	1.0	TPA/APE ^a	0.15	CB	Py	35	0.31
	1.0	4-ABA ^b	0.15	CB	TEA	16	0.30
	1.0	4-ABA ^b	0.15	NB	Py	> 100	0.38
(2)	1 ^c	4-ABA	0.400	Py	Py	89	2.87
	1.0	4-ABA	0.042	Py	Py	> 100	0.37
	1.0	4-ABA	0.083	Py	Py	> 100	0.46
	1.0	4-ABA	0.160	Py	Py	> 100	0.49
	1.0	4-ABA	0.167	Py	Py	> 100	0.51
	1.0	4-ABA	0.417	Py	Py	> 100	0.71
	1.0	4-ABA	0.833	Py	Py	> 100	0.90
	1.0	4-ABA	0.250	NMP	None	> 100	0.61
	0.877	4-ABA	0.250	NMP	None	> 100	0.78
	0.788	4-ABA	0.250	NMP	None	> 100	0.75
	0.428	4-ABA	0.250	NMP	None	43	0.66
	0.345	4-ABA	0.100	NMP	None	47	0.25
	0.343	4-ABA	0.05	NMP	None	0	—
	0.343	4-ABA	0.400	TMU	None	0	—
	0.154	4-ABA	0.100	NMP	None	Trace	—
	0.154	4-ABA	0.0105	TMU	None	0	—
	0.094	4-ABA	0.0139	NMP	None	Trace	—

^a TPA/APE = terephthalic acid/4,4'-diaminodiphenyl ether.^b 4-ABA = 4-aminobenzoic acid.^c 1 = 4-SDP.^d NB = nitrobenzene; CB = chlorobenzene; Py = pyridine; TEA = triethylamine; NMP = *N*-methylpyrrolidone; TMU = tetramethyl urea.^e Measured at a concentration of 0.1 g/10 cm³ in H₂SO₄ at 30 °C.

sulting polyamide were compared.

When the combination of Poly-1 and C₂Cl₆ was used, pyridine was required for the initiation of the direct polycondensation. On the other hand, system (2) using Poly(1-co-2) and C₂Cl₆ did not require the addition of pyridine for the direct polycondensation since the pyridine moiety was incorporated into the polymeric TPP. System (2) using Poly(1-co-2) and C₂Cl₆ is advantageous from a practical point of view since the direct polycondensation reaction proceeded in aprotic amide solvents such as *N*-methylpyrrolidone (NMP) or tetramethyl urea (TMU) without adding pyridine as an acid acceptor.

The resulting polymers were characterized

as corresponding polyamides from infrared and elemental analyses. However, the yields of the polyamides frequently exceeded 100% and elemental analysis of the resulting polyamide revealed the existence of a small amount of phosphorus atom (1–3%). Therefore, the resulting polyamides contained small amounts of the polymeric TPP initiator. The complete separation of the combined initiator was very difficult by a simple extraction with a solvent and a hydrolytic cleavage of the combined initiator might be required.

As seen in Table II, both yields and solution viscosities of the resulting polyamide decreased with decreasing content of TPP in Poly(1-co-2) and a favorable composition of

Table III. Direct polycondensation using polymeric TPP for the synthesis of polyester

Monomer ^a	Initiator P/N ratio (Poly(1-co-2))	Solvent ^b	Acid acceptor	Polymer	
				Yield	η_{sp}/c^c
				%	
IPA/BPA	1.0/0	Py	Py	25	0.56
	1.0/0	CB	Py	27	0.26
	0.88/0.12	Py	Py	23	0.13
TPA/BPA	0.79/0.21	CB	None	100	0.31
	0.79/0.21	NB	None	94	0.56
	0.79/0.21	TCE	None	95	0.61
	0.79/0.21	CB/NMP (1/1)	None	99	0.61
	0.79/0.21	CB/DMAc (1/1)	None	99	0.40
	0.43/0.57	CB	None	65	0.32
	0.43/0.57	NB	None	50	0.25
	0.43/0.57	TCE	None	45	0.26
	0.43/0.57	NB	None	60	0.45
4-HBA	1.0/0	Py	Py	> 100	Insol.
	1.0/0	Py/ β -Pico (1/1)	Py	16	Insol.
	1.0/0	β -Pico	β -Pico	94	Insol.
	1.0/0	β -Pico/TMU (1/1)	β -Pico	86	Insol.
	1.0/0	NMP	None	10	Insol.
	0.43/0.57	NMP	None	0	—

^a IPA/BPA = isophthalic acid/bisphenol A; TPA/BPA = terephthalic acid/bisphenol A; 4-HBA = 4-hydroxybenzoic acid.

^b Py = pyridine; CB = chlorobenzene; NB = nitrobenzene; TCE = tetrachloroethane; β -pico = β -picoline; TMU = tetramethyl urea; NMP = *N*-methylpyrrolidone.

^c Measured at a concentration of 0.1 g/10 cm³ in phenol/tetrachloroethane = 1/1 at 30°C.

Poly(1-co-2) was in the range of 0.9—0.8/0.1—0.2 of the molar ratio of 4-SDP and 4-VPy in the copolymers. There were no direct relationships between yields and solution viscosities of resulting polymers since the direct polycondensation was not a simple step-wise polycondensation. The decrease in yields and solution viscosities of resulting polymers with decreasing content of TPP might be attributed to less interactions between TPP and pyridine moieties in Poly(1-co-2) owing to an unfavorable conformation of polymer chains to enhance the formation of an active *N*-phosphonium complex.

It was found that Poly(1-co-2) could produce polyamide in a quantitative yield with a solution viscosity of about 0.7 when NMP was used as the solvent.

(2) Synthesis of Polyesters

Table III summarizes the results of the direct polycondensation for the synthesis of various polyesters. It can be seen in Table II that polyesters were produced in good yield from terephthalic acid (TPA)/bisphenol-A (BPA) or 4-hydroxybenzoic acid (4-HBA) when the initiator of system (2) was applied to these monomers in various solvents.

The resulting polyesters were characterized by infrared and elemental analyses which revealed the corresponding structures. However, a small amount of phosphorus atoms was found in the resulting polyesters. Solid-phase polycondensation of the polyesters at 230°C yielded insoluble and infusible polymers which suggest that a cross-linking reaction takes place as soon as they are heated. Therefore, the

polymeric initiator might be attached to the resulting polyester and the complete separation of the initiator is difficult.

Poly(1-*co*-2) which was recovered after the direct polycondensation was applied again for the second run after it was isolated and treated with (COCl)₂ so that the phosphine oxide group was converted to phosphine dichloride which could initiate the polycondensation. Yields and solution viscosities of the resulting polyesters decreased down to about half and the initiator activity of the recovered Poly(1-*co*-2) decreased by regeneration. However, regeneration was much easier than the monomeric initiator and future remodification of

regeneration should make it possible to establish a complete recycling of the initiator.

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