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Direct Copolycondensation for the Synthesis of Copolyamides or Copolyesters

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ABSTRACT: Copolycondensation was carried out through synthesis of copolyamides and copolyesters using a direct polycondensation method with triphenylphosphine derivatives under mild conditions. Aromatic copolyamides and copolyesters were easily obtained with the same copolymer compositions as monomer feed ratios. Polyesteramides were also obtained by the direct copolycondensation method which was influenced by solvents in terms of copolymer compositions. When diaminobisphenol was used as a monomer for the direct polycondensation, either polyamide or polyester was selectively obtained using an appropriate solvent.

KEY WORDS Direct Polycondensation / Copolycondensation / Triphenylphosphine Dichloride / Copolyamide / Copolyester / Polyesteramide /

Direct polycondensation method using triphenylphosphine dichloride (TPPCl$_2$) is effective for the synthesis of either polyamides or polyesters under mild conditions and various types of condensation polymers have been obtained by this method.[1,2] Interfacial or solution polycondensations using acid chloride are well-known methods for the synthesis of various condensation polymers under mild conditions. In these methods, however, solvents affect the reactivity of the acid chloride group so that compositions of copolymers are different from monomer feed ratios, owing to the kind of solvents used for the reaction.[3] It is interesting to investigate copolycondensation reactions using the direct polycondensation method because the selectivity of functional groups causes change in copolymer compositions and also in sequence distributions of the resulting copolymers. Particularly, the synthesis of polyesteramide is interesting since a cooporative reaction between diamine and diol takes place during the direct polycondensation to form polyesteramide.

This paper deals with the direct copolycondensation reaction using triphenylphosphine derivatives for the syntheses of copolyamides, copolyesters, and polyesteramide.

EXPERIMENTAL

Monomers and Reagents

Terephthalic acid (TPA), *p*-phenylenediamine (PD), 4,4′-diaminodiphenyl ether (APE), 4-hydroxybenzoic acid (4-HBA), 3,5-dimethyl-4-hydroxybenzoic acid (DM-4-HBA), 6-hydroxy-1-naphthoic acid (HNA), bisphenol A (BPA), and 2,2′-bis(4-hydroxyphenyl)-1,4-di-isopropylbenzene (BDB) were purchased and purified by conventional methods through distillation or recrystallization.

3,3′-Diamino-4,4′-dihydroxybiphenyl (DDB) was synthesized[4] from 4,4′-dihydroxybiphenyl as follows: 15 g of 4,4′-dihydroxybiphenyl was dissolved into 1000 cm^3 of acetic acid and 15 cm^3 of nitric acid were added dropwise to the solution with cooling. 3,3′-Dinitro-4,4′-dihydroxy biphenyl (dinitro DB) was collected by filtration and washed with methanol, followed by drying. Obtained dinitro DB (10 g) was dissolved into a 400 cm^3 aqueous solution containing 4 g of sodium hydroxide and 42 g of sodium hydrosulfite $Na_2S_2O_4$ were added to the solution with stirring at 50°C. The solution was heated at 90°C, followed by adding 25 g of sodium hydrosulfite and the entire solution was refluxed for 30 min. After cooling the solution, 100 cm^3 of hydrochloric acid were added. The resulting salt of DDB was collected by filtration and purified by recrystallization from water. Yield 5.8 g (55%).

Triphenylphosphine (TPP) and triphenylphosphine oxide (TPPO) of special grade were used without purification. Triphenylphosphine dichloride ($TPPCl_2$) was obtained *in situ* from TPPO and oxalyl chloride.[1)] Hexachloroethane and all solvents were purified by distillation before use.

Synthesis of Copolyamides

In a 100 ml flask were dissolved 0.002 mol of terephthalic acid (TPA) and 0.0048 mol of triphenylphosphine (TPP) in 5 ml of pyridine. Three portions of 0.002 mol of *p*-phenylenediamine (PD), 0.002 mol of 4,4′-diaminodiphenyl ether (APE), and 0.006 mol of hexachloroethane (C_2Cl_6) were dissolved in 5 ml) of pyridine. The solution of TPA was added the solution of diamines with stirring at room temperature. Copolycondensation reaction took place within 2 min with the development of a yellowish color and copolymers stated to precipitate out of the mixed solution. After one hour, the reaction product was poured into 100 ml of methanol and copolymers were collected by filtration, followed by washing with methanol and water and by drying in vacuum. This process is the TPP/C_2Cl_6 system.

The same type of copolycondensation was carried out using triphenylphosphine dichloride ($TPPCl_2$) as an initiator which was formed *in situ*, in place of the combination of triphenylphosphine and C_2Cl_6, as described in a previous paper,[1] this process is the $TPPCl_2$ system.

Synthesis of Copolyesters

Copolyesters were synthesized from mixed monomers of 4-hydroxybenzoic acid (4-HBA) and 3,5-dimethyl-4-hydroxy-benzoic acid (DM-4-HBA) or 6-hydroxy-1-naphthoic acid (6-HNA) at various molar rations, using $TPPCl_2$ as an initiator. The experimental procedure was the same as described before.[1] Copolyester from terephthalic acid and BPA/BDB (50/50) was also synthesized using $TPPCl_2$ as an initiator.

Synthesis of Polyesteramide

In a four-necked 100 ml flask were added 5 cm^3 of various solvents as described in Table III and 5.99 g (0.021 mol) of triphenylphosphine oxide (TPPO). To this solution was added dropwise 5 cm^3 of a solvent containing 1.84 cm^3 (0.021 mol) of oxalyl chloride within 10 min. After evolution of gas, 1.66 g (0.01 mol) of TPA were added to the solution which was heated at 130°C. The solution was cooled to room temperature and 0.01 mol of mixture of BPA and AEP at various molar rations in 5 cm^3 of a solvent was added, followed by the addition of 5.60 cm^3 of triethylamine. The entire solution was heated at 130°C for one hour. Then, the solution was poured into excess methanol and the precipitated copolymers were collected by filtration, followed by washing with methanol and water, and then drying in vacuum.

The experimental procedure is schematically shown in Figure 1.

Characterization of Polymers

Polymers were characterized by infrared (IR), NMR and elemental analysis. Copolymer compositions were determined

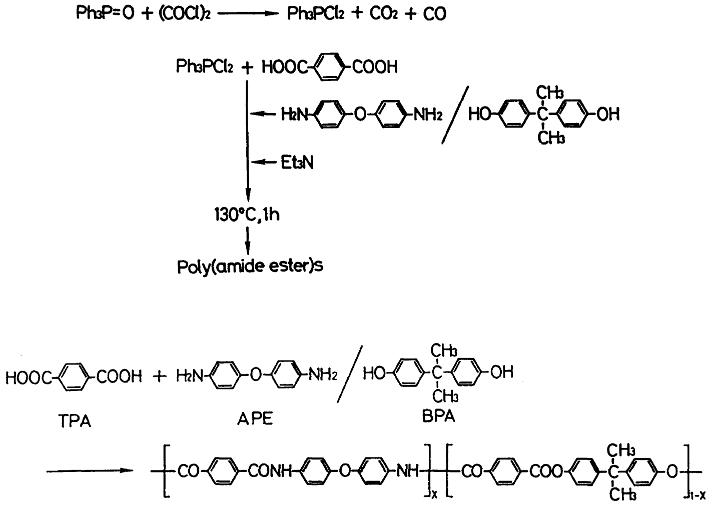

Figure 1. Experimental procedure for the synthesis of polyesteramide.

both by IR and elemental analysis. Thermal properties of the polymers were characterized by DSC analysis.

Solution viscosities were measured in sulfuric acid for copolyamides and in *o*-chlorophenol or monochloroacetic acid for copolyesters at 30°C.

RESULTS AND DISCUSSION

Synthesis of Copolyamides

Copolyamide from TPA and PD/APE (50/50) was obtained at various monomer concentrations in pyridine, using the TPP/C_2Cl_6 system as an initiator and the results are summarized in Table I.

An optimum monomer concentration appeared at 0.21 mol l^{-1} in terms of both yields and solution viscosities of the resulting copolymers. Lower concentrations than 0.21 mol l^{-1} might reduce the rate of the copolycondensation reaction and a higher concentration might cause a rapid growth reaction to precipitate copolymers out of the solution so that further propagation reaction for the growth may stop. The copolymer had a composition of PD/APE = 35/65 and an APE-rich copolyamide was obtained, which was characterized both by IR and elemental analysis.

Table I. Copolycondensation of TPA with PD/APE by the TPP/C_2Cl_6 system[a]

Monomer			Copolymer	
TPA mol l^{-1}	PD mol l^{-1}	APE mol l^{-1}	Yield %	η_{sp}/c[b]
0.10	0.05	0.05	36	0.23
0.14	0.07	0.07	59	0.32
0.21	0.105	0.105	87	0.44
0.24	0.12	0.12	96	0.24
0.30	0.15	0.15	72	0.11
0.40	0.20	0.20	52	0.08

[a] Reaction conditions: pyridine, 10 ml; TPP, 0.0048 mol; C_2Cl_6, 0.006 mol; time, 1 h.

[b] Measured in 96% sulfuric acid at a concentration of 0.1 g/10 ml at 30°C.

The copolycondensation reaction of TPA with PD and APE was carried out at various molar ratios of PD/APE in the feed in pyridine, using the initiator system of TPP/C_2Cl_6 and the results are summarized in Table II.

It is seen in Table II that increasing ratios of PD to APE resulted in decrease in the solution viscosities of the resulting copolyamides. Copolymer compositions are shown in Figure 2 which indicates that copolyamides contained much APE component. APE has more reactive amino groups than PD as two amino groups of APE were independently separated between two benzene rings. Also, solubility of copolyamides rich in the APE component would be superior to that of copolyamides rich in the PD component. As a result, increasing ratios

Table II. Copolycondensation of TPA with PD/APE of various molar rations by the TPP/C_2Cl_5 system[a]

Monomer		Copolymer		
TPA	PD/PD+APE	Yield	η_{sp}/c[b]	PD/PD+APE[c]
$mol\,l^{-1}$	mol/mol	%		
0.21	0	90	0.37	0
0.21	0.2	96	0.49	0.13
0.21	0.4	94	0.40	0.26
0.21	0.6	97	0.35	0.47
0.21	0.8	95	0.28	0.69
0.21	1.0	93	0.14	1.0

[a] Reaction conditions; pyridine, 10 ml; TPP, 0.0048 mol; C_2Cl_6, 0.006 mol; time, 1 h.

[b] Measured in 96% sulfuric acid at a concentration of 0.1 g/10 ml at 30°C.

[c] Elemental analysis.

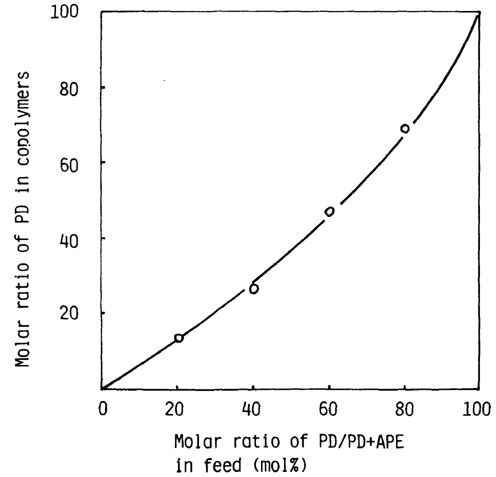

Figure 2. Compositions of copolyamide from TPA and PD/APE.

Table III. Copolycondensation of TPA with PD/APE in various solvents by the $TPPCl_2$ system[a]

Monomer			Copolymer		
TPA	PD/APE	Solvent	Yield	η_{sp}/c[b]	PD/APE[c]
mol	$mol\,l^{-1}$		%		
0.015	0/100	CB[d]	94	0.17	0/100
0.015	20/80	CB	87	0.56	14/86
0.015	40/60	CB	81	0.30	26/74
0.015	60/80	CB	76	0.20	45/55
0.015	80/20	CB	68	0.09	70/30
0.015	100/0	CB	31	0.05	100/0
0.015	0/100	NB[e]	96	0.49	0/100
0.015	20/80	NB	94	0.50	15/85
0.015	40/60	NB	89	0.24	25/75
0.015	60/40	NB	86	0.16	43/57
0.015	80/20	NB	81	0.11	69/31
0.015	100/0	NB	70	0.07	100/0
0.015	20/80	CB/NMP (1/1)	87	1.17	15/85
0.015	20/80	NB/NMP (1/1)	80	0.72	14/86

[a] Reaction conditions: Solvent, 10 ml; $TPPCl_2$, 0.018 mol; PD+APE=0.015 mol; time, 1 h; temp, 30°C.

[b] Measured in 96% sulfuric acid at a concentration of 0.1 g/10 ml at 30°C.

[c] Elemental analysis.

[d] Monochlorobenzene.

[e] Nitrobenzene.

of PD in the feed would cause decrease in solution viscosities of the resulting copolyamides.

Copolycondensation of TPA and PD/APE was carried out in various solvents using the $TPPCl_2$ system as an initiator. The results are summarized in Table III. The same tendency such that increasing ratios of PD in feed caused decrease in solution viscosities of resulting copolyamides, was observed for the $TPPCl_2$ system. A mixed solvent of monochlorobenzene (CB) and *N*-methyl pyrrolidone (NMP) yielded a high solution viscosity of 1.17 when the ratio of PD/APE was 20/80. Presumably, the mixed solvent of CB/NMP might cause favorable swelling of the resulting copolyamide which made the growth reaction to continue even in a solid phase after precipitation out of the solution.

Synthesis of Copolyesters

Table IV summarizes the results of the copolycondensation of 4-HBA and DM-4-HBA at a molar ratio of 50/50 in the feed in various solvents, the $TPPCl_2$ system as an initiator. A mixed solvent of CB/NMP yielded a high solution viscosity of 1.03 of the resulting copolyester. The reactivity of 4-HBA and DM-4-HBA might not be different toward the direct polycondensation reaction, as copolymer compositions were almost identical to monomer feed compositions as shown in Table V.

The copolyesters from 4-HBA and DM-4-HBA in molar ratios of 40/60–60/40 dissolved in monochloroacetic acid or *o*-chlorophenol and the concentrated solution of these copolyesters indicated a liquid crystalline pattern under a cross-polarized microscope and they were liquid crystal polymers in solution.

The copolyesters from 4-HBA and DM-4-HBA did not show clear melting points when DSC analysis was carried out, and they started to decompose at around 450°C by heating in

Table IV. Copolycondensation of 4-HBA and DM-4-HBA (1/1 molar ratio) in various solvents by $TPPCl_2$

Solvent	Acid acceptor	Temp	Time	Polymer	
		°C	hr	Yield %	η_{sp}/c[f]
CB[a]	Py + Et_3N[e]	25	1	95	0.21
CB	Et_3N	25	1	88	0.18
CB	Pyrrole + Et_3N	25	1	90	0.18
CB	Pyrrole	125	2	20	0.18
NB[b]	Py + Et_3N	125	1	87	0.35
NB + NMP[c]	Py + Et_3N	125	1	99	0.25
DMI[d]	Py + Et_3N	125	1	94	0.29
DMI + NMP	Py + Et_3N	125	1	99	0.38
CB + NMP	Py + Et_3N	125	1	89	1.03

[a] Monochlorobenzene.

[b] Nitrobenzene.

[c] Nitrobenzene/*N*-methyl-2-pyrrolidone = 1/1 in volume.

[d] *N*,*N*′-Dimethyl-2-imidazolidinone.

[e] Pyridine/triethylamine = 1/1 in volume.

[f] Measured in *o*-chlorophenol at a concentration of 0.1 g/10 ml at 30°C.

Table V. Copolycondensation of 4-HBA and DM-4-HBA at various molar ratios by $TPPCl_2$[a]

Monomer feed ratios		Copolymers			
4-HBA	DM-4-HBA	Yield %	η_{sp}/c[b]	4-HBA[c]	DM-4-HBA[c]
90	10	95	Insol.	89	11
80	20	90	Insol.	77	23
70	30	94	Swell	71	29
60	40	92	0.54	61	39
50	50	89	1.03	52	48
40	60	90	0.78	38	62
30	70	91	0.25	28	72
20	80	95	0.28	17	83
10	90	89	0.21	8	92
0	100	90	0.35	0	100

[a] Solvent, monochlorobenzene/*N*-methyl-2-pyrrolidone = 1/1 in volume; acid acceptor, pyridine/triethylamine = 1/1 in volume; reaction temperature = 125, reaction time = 1 h.

[b] Measured in *o*-chlorophenol at a concentration of 0.1 g/10 ml at 30°C.

[c] IR analysis.

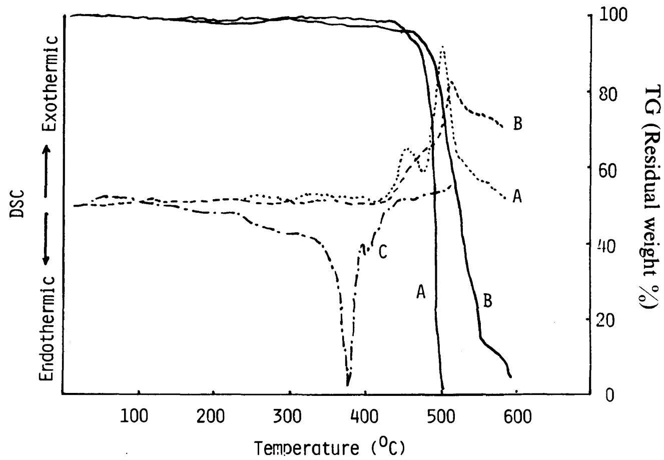

Figure 3. Thermal analysis of copolyesters by TG and DSC: A, copolyester from 4-HBA and DM-4-HBA (50/50); B, copolyester from 4-HBA and 6-HNA (50/50); C, copolyester from TPA and BPA/BDB (50/50).

Table VI. Copolycondensation of 4-HBA/6-HNA or TPA/BPA/BDB by $TPPCl_2$[a]

Monomer type	Monomer feed	Solvent	Acid acceptor	Copolymers	
				Yield/%	η_{sp}/c[d]
4-HBA/6-HNA	90/10	CB[b]	Py + Et_3N	91	Swell
4-HBA/6-HNA	70/30	CB	Py + Et_3N	94	Insol.
4-HBA/6-HNA	50/50	CB	Py + Et_3N	96	Insol.
4-HBA/6-HNA	50/50	NB[c]	Py + Et_3N	89	Insol.
4-HBA/6-HNA	50/50	CB + NB	Py + Et_3N	95	Insol.
4-HBA/6-HNA	30/70	CB	Py + Et_3N	92	0.21
4-HBA/6-HNA	10/90	CB	Py + Et_3N	96	Insol.
TPA/BPA/BDB	100/50/50	CB	Py + Et_3N	94	Insol.
TPA/BPA/BDB	100/50/50	NB	Py + Et_3N	87	Insol.
TPA/BPA/BDB	100/50/50	NB + NMP	Py + Et_3N	98	Insol.

[a] Monomer concentration = 0.5 mol l^{-1}; reaction temperature = 125°C; reaction time = 1 h.
[b] Monochlorobenzene.
[c] Nitrobenzene.
[d] Measured in monochloroacetic acid at a concentration of 0.1 g/10 ml at 30°C.

nitrogen atmosphere as shown in Figure 3.

Copolycondensation of 4-HBA and 6-HNA which was carried out by the $TPPCl_2$ system yielded insoluble and infusible copolymers as summarized in Table VI. These copolyesters started to decompose at around 500°C by heating in nitrogen atmosphere as shown in Figure 3. Copolyester from TPA and BPA/BDB (50/50) obtained by the $TPPCl_2$ system were also insoluble as shown in Table VI. This copolyester melted at 375°C, as can be seen in Figure 3.

Synthesis of Polyesteramide

Copolycondensation of TPA with APE and BPA was carried out at various feed ratios of APE/BPA in either CB or NMP/CP (1/1) solvents of the copolycondensation. Table VII summarizes the results of the copolycondensation, which indicate that copolymers were

Table VII. Copolycondensation of TPA with APE/BPA by TPPCl$_2$[a]

Monomer feed ratios		Solvent	Copolymers			
APE	BPA		Yield/%	η_{sp}/c[e]	APE[f]	BPA[f]
0	100	CB[b]	100	0.31	0	100
20	80	CB	89	0.35	20	80
40	60	CB	78	0.29	35	65
60	40	CB	82	0.32	36	64
80	20	CB	78	0.25	58	42
100	0	CB + DMAc[c]	100	1.45	100	0
20	80	CB + NMP[d]	86	0.45	25	75
40	60	CB + NMP	85	0.35	43	57
60	40	CB + NMP	87	0.31	65	35
80	20	CB + NMP	91	0.29	85	15

[a] Monomer concentration, 1 mol l^{-1}; reaction temperature = 130°C; reaction time = 1 h; acid acceptor = Et$_3$N.

[b] Monochlorobenzene.

[c] Monochlorobenzene/dimethylacetamide = 1/1 in volume.

[d] Monochlorobenzene/*N*-methylpyrrolidone = 1/1 in volume.

[e] Measured in *o*-chlorophenyl at a concentration of 0.1 g/10 ml at 30°C.

[f] Elemental analysis.

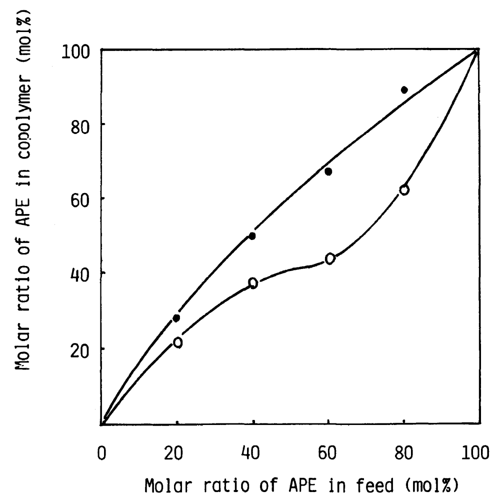

Figure 4. Compositions of copolyesteramide from TPA and APE/BPA: ○, CB solvent; ●, CB/NMP solvent.

Table VIII. Solvent effect on copolycondensation of TPA with APE and BPA in an equimolar ratio (1/1/1) by TPPCl$_2$[a]

Solvent	Polymer		
	Yield[b] %	Amide fraction[c] mol%	η_{sp}/c[d]
CB	100	0.41	0.85
CB/NMP (1/2)	100	1.0	0.85
CB/DMAc	100	1.0	0.86
NB/NMP (1/2)[e]	100	1.0	1.04
NB/DMAc (1/2)	100	1.0	1.24

[a] Monomer concentration = 0.33 mol l^{-1}; reaction temperature = 130°C; time = 1 h.

[b] Based on TPA unit.

[c] IR analysis.

[d] Measured in DMAc containing 7 wt% of LiCl at a concentration of 0.1 g/10 ml at 30°C.

[e] NB = nitrobenzene.

obtained in a good yield when a mixed solvent of NMP/CB was used.

Copolymer compositions as a function of monomer feed ratios (APE/APE + BPA) are shown in Figure 4, which indicates that copolymer compositions were almost identical to the monomer feed ratios when a mixed solvent of NMP/CB (1/1) was used. On the other hand, BPA-rich copolymers were obtained when CB was used as a solvent for the copolycondensation. In other words, amide solvents such as NMP were in favor of the formation for amide linkages, while halogenated solvents such as CB enhanced the formation of ester linkage. The same tendency was observed in terms of solvent effect on the copolymer compositions when a solution polycondensation method was applied for the synthesis of polyesteramide using terephthaloyl chloride as a monomer.[3] The reaction of carboxylic acid with amine or alcohol groups by the TPP/C_2Cl_6 or $TPPCl_2$ system is assumed to pass through the intermediate formation of an active acyl moiety with the TPP group, followed by nucleophilic attack of amine or alcohol groups to form either amide or ester linkages. The selectivity of functional groups caused by these solvents might be ascribed to the change in nucleophilicity of amine or alcohol groups in these solvents.[3]

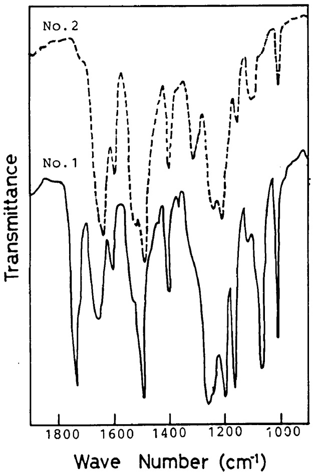

Figure 5. Infrared spectrum of polymers from TPA, APE, and BPA (1/1/1): No. 1, CB solvent; No. 2, CB/DMAc (1/2) solvent.

In order to determine the selectivity of functional groups toward polycondensation reaction, the copolycondensation reaction of terephthalic acid (TPA) with 4,4′-diaminodiphenyl ether (APE) and bisphenol A (BPA) was carried out in an equimolar ratio of TPA, APE, and BPA (1/1/1) in monochlorobenzene (CB) and in mixed solvents containing N-methylpyrrolidone (NMP) and dimethylacetamide (DMAc), using the $TPPCl_2$ system as an initiator. The results are summarized in Table VIII.

Characterization of the resulting polymers by infrared spectrum revealed that the polymer formed in CB showed a strong absorption band of an ester linkage at 1720 cm^{-1}, while the polymer formed in mixed solvents with NMP or DMAc indicated very weak absorption bands of the same linkage on a strong absorption bands of an amide linkage, as seen in Figure 5.

The fraction of amide linkage in the resulting polymers was determined by infrared analysis, as summarized in Table VIII. From these results, it was also confirmed that the ester formation took place in the CB solvent, while the amide formation occurred preferencially in mixed solvents containing amide solvents.

Direct polycondensation of TPA with DDB

Table IX. Direct polycondensation of TPA with DDB by $TPPCl_2$[a]

Monomer type	Concn mol l^{-1}	Solvent	Polymer Yield/%	 Amide/mol%[c]	 η_{sp}/c[d]
TPA	0.50	CB	78	42	0.35
TPA	0.50	CB/NMP (1/1)	100	85	0.65
TPA	0.50	CB/DMAc (1/1)	100	83	0.55
TPC[b]	0.50	CB	59	41	0.21
TPC	0.50	CB/NMP (1/1)	49	38	0.23

[a] Reaction temperature = 130°C; time = 1 h.

[b] Terephthaloyl chloride.

[c] Determined by infrared analysis.

[d] Measured in DMAc containing 7 wt% of LiCl at a concentration of 0.1 g/10 ml at 30°C.

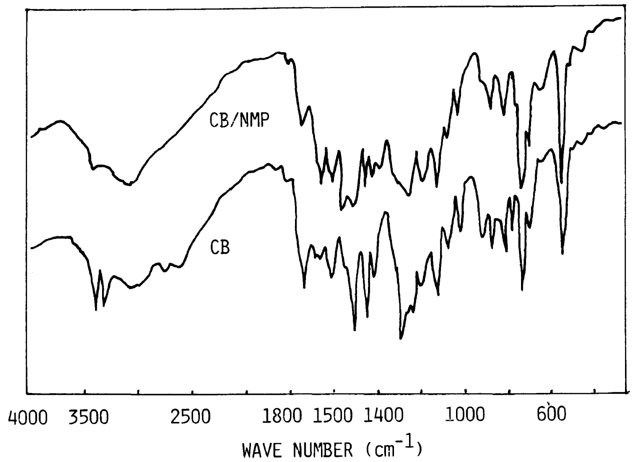

Figure 6. Infrared spectrum of polymers from TPA and DDB obtained in CB or CB/NMP solvents.

was carried out in CB or in a mixed solvent of CB/NMP, using the $TPPCl_2$ system. DDB contained both amino and hydroxyl groups in the same molecules and the selectivity of functional groups toward polycondensation might become clear as there would be no chance of blending of two homopolymers, that is, polyamide and polyester, as shown below:

The results of the polycondensation of TPA with DDB are summarized in Table IX where the polycondensation of terephthaloyl chloride (TPC) with DDB is also compared. It is seen in Table IX that the polymers were obtained in better yields using $TPPCl_2$ as an initiator than those by using TPC.

Figure 6 indicates IR spectra of the polymers obtained in CB or CB/NMP (1/1) as solvents for the direct polycondensation. It is seen in Figure 6 that the polymer obtained in CB had a higher ester group content since the absorption intensity of the ester carbonyl group at 1720 cm^{-1} was stronger in the polymer obtained CB than that in CB/NMP (1/1). This result also supports the previous fact that CB favors formation of the ester linkage and amide solvents such as NMP or DMAC enhanced the formation of the amide linkage. Therefore, solvents could somehow control the direction of the polycondensation owing to the selectivity of the functional groups toward the direct polycondensation by $TPPCl_2$.

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