

Synthesis of Polymers in Aqueous Solutions. Synthesis of Polyesters by Reactions of Dicarboxylic Acids with Alkylene Dihalides Using 1,8-Diazabicyclo[5.4.0]undec-7-ene in Aqueous Solutions

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ABSTRACT: The polycondensation of adipic acid with *m*-xylylene dibromide was performed using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in mixtures of dimethyl sulfoxide (DMSO) with water or in plain water. The reactions proceeded smoothly even in water to give the corresponding polyesters, although the rate of the reaction decreased gradually with increasing water in the mixture. Polymers prepared in the aqueous solution had higher molecular weights (M_n , 7700—9200) than the polymers synthesized in DMSO (M_n , 6100—6400).

KEY WORDS Water / Aqueous Solution / Polycondensation / Polyester / 1,8-Diazabicyclo[5.4.0]undec-7-ene / Dicarboxylic Acids / Alkylene Dihalides /

The careful removal of water is required in many cases of organic synthesis and polymer synthesis, because these reactions, especially ionic reactions, are strongly hindered or blocked by the presence of water. However, it seems that water and aqueous solution have great possibilities as reaction media from the viewpoint of incombustibility, safety, and economics in the laboratory and industry. Emulsion polymerization and suspension polymerization of hydrophobic monomers such as vinyl chloride, vinyl acetate, styrene, ethyl acrylate, and butadiene with radical initiators in water as a reaction medium have long been carried out for the preparation of polymers in the laboratory and industry.

Recently, phase transfer catalysis between the organic phase and the aqueous phase as well as the solid phase have been used conveniently for various organic reactions¹ such as substitution, elimination, and oxidation reactions. These heterogeneous reaction systems were extended to polymer synthesis² and chemical modification of polymers³ under mild conditions. However, the substitution reaction of pendant nucleophilic groups such as carboxylate and phenolate anions in polymers with low molecular weight alkyl halides does not proceed even in the presence of phase transfer catalysts.^{4,5} Nishikubo *et al.* reported^{4,6} recently that the reaction of pendant carboxyl group in poly(methacrylic acid) with various alkyl halides proceed very smoothly to give the corresponding poly(methacrylic ester)s using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base in dimethyl sulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) under mild reaction conditions. More recently, it was also found⁷ that the esterification reaction of poly(methacrylic acid) with alkyl halides proceeds quantitatively using DBU in aqueous solution or even in water under mild reaction conditions.

Polyesters are usually prepared⁸ by a solution polymerization of dicarboxylic acid chlorides with difunctional alcohols or phenols in anhydrous organic solvent or an interfacial polymerization between dicarboxylic acid chlorides in organic layer and difunctional alcohols or

phenols in aqueous layer. These reactions are carried out under mild conditions. However, the activated dicarboxylic acid chlorides are essentially unstable to the moisture in the air and to water in the solution. Imai *et al.* reported⁹ the synthesis of polyesters by the reaction of potassium salt of dicarboxylic acids with alkylene dihalides using phase-transfer catalysis (PTC), although, the reaction performed at relatively high temperature. The authors reported¹⁰ the synthesis of polyesters by the polycondensation of alkylene dihalides with dicarboxylic acids using DBU method. The reaction with DBU is a very simple and convenient for the synthesis of polyesters because preparation and purification of the activated dicarboxylic acids are not necessary, and the polycondensation proceeds under mild condition.

From these back grounds, it is reasonable to consider for us that aqueous solution and water should be useful for polymer synthesis. This paper reports the synthesis of polyesters by reactions of dicarboxylic acids with alkylene dihalides using DBU as a base in aqueous solution and plain water.

EXPERIMENTAL

Materials

Solvents were purified in the standard way before use. DBU was used after distillation using CaH₂. Sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), 18-crown-6, and 15-crown-5 were used without further purification. *m*-Xylylene dibromide (MXDB) was recrystallized from acetone. *p*-Xylylene dibromide (PXDB) was recrystallized from chloroform. 1,4-Dichlorobutane (DCB), 1,4-dibromobutane (DBB), and 1,4-diiodobutane (DIB) were purified by distillation. Succinic acid (SCA) and adipic acid (AA) were recrystallized from water. Sebacic acid (SBA), phthalic acid (PHA), and isophthalic acid (IPA) were recrystallized from methanol.

Measurements

Infrared (IR) spectra were measured on a JASCO Model IR-700 spectrometer. ¹H NMR spectra were recorded on JEOL Models JNM EX-90 (90 MHz) and

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JNM FX-200 (200 MHz) instruments in DMSO- d_6 or $CDCl_3$ using tetramethylsilane as the standard. Molecular weights of the polymers were estimated by gel permeation chromatography (GPC) using a Tosoh Model HLC-8020 GPC equipped with a refractive index detector using TSKgel GMHKL columns (eluent: DMF, calibrated with narrow molecular weight polystyrene standards).

Typical Procedure for the Polycondensation of Dicarboxylic Acid with Alkylene Dihalide Using DBU

Polycondensation in DMSO. AA (0.365 g; 2.5 mmol) was dissolved in DMSO (2 mL), and DBU (0.761 g; 5 mmol) were added with stirring. To the AA–DBU salt solution, MXDB (0.660 g; 2.5 mmol) dissolved in DMSO (3 mL) was added. The reaction mixture was stirred at 30°C for 12 h and poured into 100 mL of methanol. The resulting polymer (P-1) was purified by reprecipitation from chloroform solution into methanol, and finally dried at 60°C *in vacuo*. The yield of polymer was 0.378 g (61%). The number average molecular weight (M_n) of the polymer determined by GPC was 6300 (M_w/M_n , 1.39). IR (film, cm^{-1}): 1735 ($\nu_{C=O}$), 1238, 1164 (ν_{C-O-C}). 1H NMR (200 MHz, $CDCl_3$, TMS); δ (ppm): 1.55–1.78 (m, 4.0H, $-CH_2-CH_2-$), 2.20–2.50 (m, 4.0H, $-CH_2-CO-$), 5.10 (s, 4.0H, $-CH_2-O-CO-$), 7.10–7.35 (m, 4H, aromatic protons).

Polycondensation in Water. AA (0.365 g; 2.5 mmol) and DBU (0.761 g; 5 mmol) were added to water (5 mL) with stirring. To the AA–DBU salt solution, MXDB (0.660 g; 2.5 mmol) was added. The reaction mixture was stirred at 50°C for 96 h and then poured into methanol (100 mL). The resulting polymer was purified by reprecipitation from chloroform solution into methanol, and finally dried at 60°C *in vacuo*. The yield of polymer was 0.192 g (31%). The M_n of the resulting polymer determined by GPC was 7000 (M_w/M_n , 1.31).

RESULTS AND DISCUSSION

Reaction of AA and MXDB was carried out using DBU as a base in DMSO,⁹ various aqueous solutions of DMSO and water with different volume ratios, and water (Scheme 1). Although the reaction proceeded homogeneously in DMSO, it took place heterogeneously in mixed solvents or plain water. In the heterogeneous reaction system, the resulting polymers precipitated to the bottom of the reaction flask as pasty solids.

As summarized in Table I, polymer P-1 was obtained with 56–61% yields in DMSO at 30°C for 12–72 h. The yields of P-1 were 55–63% when the reactions were carried out in a mixed solvent of DMSO (80 vol%) and water (20 vol%) under the same conditions. It seems that yield of P-1 was not affected by the reaction time when the reaction was performed in DMSO or the mixed solvent containing small amount of water as above conditions.

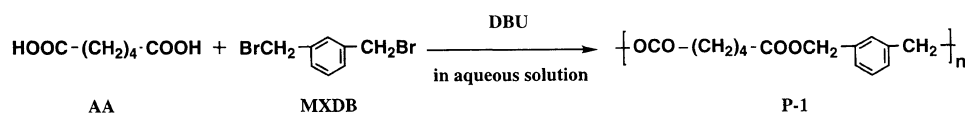
When the reaction was performed in a mixed solvent of DMSO (50 vol%) and water (50 vol%) at 30°C, yields of P-1 were 27, 34, 48, and 45% at 12, 24, 48, and 72 h, respectively. When the reaction was carried out in the plain water at 50°C for 24–96 h, the yield of P-1 increased with reaction time, and P-1 was obtained with 31% yield at 96 h. These results means that the reaction of AA with MXDB thus proceeds using DBU in a mixed solvent of DMSO with water or even water in heterogeneous reaction system, although the reaction rate decreased gradually with increasing water as the reaction medium.

As shown in Table I, M_n s of the resulting polymers P-1 prepared in DMSO were 6100–6400. Polymers P-1 prepared in the mixed solvents of DMSO (80) with water (20), and DMSO (50) with water (50) were 9000–9200, and 7700–8700, respectively. It is clear that the polymers prepared in the mixed solvents have higher M_n than the polymers synthesized in DMSO. Nishikubo *et al.* reported that DMSO is a suitable solvent for the polycondensation of dicarboxylic acids with alkylene dihalides using DBU.¹⁰ However, the oxidation reaction of halomethyl group by DMSO is also known.¹¹ Therefore, it seems that the oxidation reaction occurs slightly as a side reaction, when the reaction is performed homogeneously in DMSO. On the other hand, when the reaction was carried out in the heterogeneous system in the mixed solvents of DMSO with water, the side reaction was blocked by the presence of large amounts of water. The resulting polymers precipitated as pasty solids in the

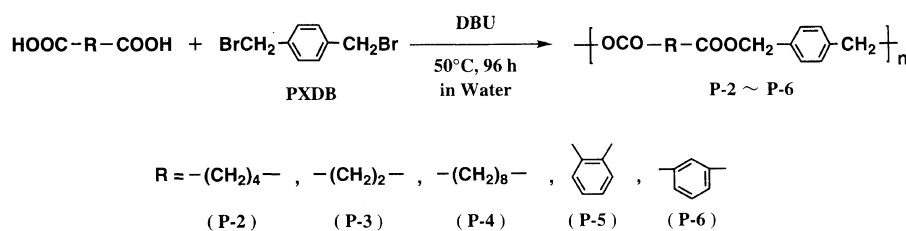
Table I. Synthesis of polymer P-1 by reactions of AA with MXDB using DBU in mixed solvents of DMSO and water^a

Solv.	Time	Yield	M_n	M_w/M_n^c
(DMSO/Water)	h	% ^b	$\times 10^{-3c}$	
(10/0)	12	61	6.3	1.39
(10/0)	24	56	6.2	1.45
(10/0)	48	57	6.4	1.44
(10/0)	72	58	6.1	1.41
(8/2)	12	55	9.1	1.67
(8/2)	24	59	9.0	1.61
(8/2)	48	63	9.2	1.88
(8/2)	72	59	9.2	1.88
(5/5)	12	27	8.0	1.49
(5/5)	24	34	7.7	1.65
(5/5)	48	48	8.7	1.57
(5/5)	72	45	7.8	1.50
(0/10)	72	trace	—	—
(0/10) ^d	24	10	8.8	1.38
(0/10) ^d	48	26	8.5	1.32
(0/10) ^d	96	31	7.0	1.31
(0/10) ^d	168	28	7.3	1.40
(0/10) ^d	240	30	6.4	1.37

^a Reaction was carried out with AA (2.5 mmol) and MXDB (2.5 mmol) using DBU (5 mmol) in solvent (5 mL) at 30°C. ^b Insoluble parts in MeOH. ^c Estimated by GPC based on polystyrene standards. ^d Reaction was carried out at 50°C.



Scheme 1.



Scheme 2.

Table II. Synthesis of polymer P-2 by reactions of AA with PXDB using DBU in mixed solvent of DMSO and water^a

Solv. (DMSO/Water)	Base	Time	Yield	M_n	M_w/M_n^c
		h	% ^b	$\times 10^{-3c}$	
(10/0)	DBU	12	77	7.7	1.66
(10/0)	DBU	24	81	7.9	1.62
(10/0)	DBU	48	86	7.5	1.78
(10/0)	DBU	72	88	9.9	1.78
(8/2)	DBU	12	74	5.1	1.60
(8/2)	DBU	24	72	6.0	1.77
(8/2)	DBU	48	75	6.0	1.75
(8/2)	DBU	72	74	6.0	1.79
(5/5)	DBU	12	13	5.6	1.59
(5/5)	DBU	24	29	5.9	1.56
(5/5)	DBU	48	55	6.0	1.53
(5/5)	DBU	72	61	6.1	1.56
(0/10)	DBU	72	0	—	—
(0/10) ^d	DBU	48	31	8.2	1.63
(0/10) ^d	DBU	96	52	8.6	1.58
(0/10) ^d	DBU	168	55	8.3	1.57
(0/10) ^d	Na ₂ CO ₃ /15-C-5	96	0	—	—
(0/10) ^d	K ₂ CO ₃ /18-C-6	96	0	—	—

^a Reaction was carried out with AA (2.5 mmol) and MXDB (2.5 mmol) using DBU (5 mmol) in solvent (5 mL) at 30°C. ^b Insoluble parts in MeOH. ^c Estimated by GPC based on polystyrene standards. ^d Reaction was carried out at 50°C.

mixed solvents. Therefore, it seems that the concentrations of propagating terminals increase in the precipitated products. However, when the reaction was carried out in plain water, M_n of the obtained polymers decreased gradually with increasing reaction time, although the yield of polymer increased gradually with time. Some hydrolysis of the resulting polyester thus may occur as a side reaction during the polycondensation between AA with MXDB in water for a long reaction time at 50°C.

The polycondensation reaction of AA with PXDB was examined using DBU as a base. When the reaction was performed in DMSO, the reaction system was homogeneous at the initial stage, and then became heterogeneous to precipitate the resulting polymer with increasing reaction time. When the reaction was carried out in mixed solvent or water, the reaction proceeded heterogeneously in a liquid–solid two-phase system from the initial stage. In the reaction of AA with PXDB, the precipitated polymer (P-2) was suspended in solution because it was not a pasty solid such as P-1 but a powdery solid (Scheme 2).

As summarized in Table II, polymers P-2 were obtained in 77–88% yields in DMSO at 30°C for 12–72 h. When the reaction was carried out in the mixed solvent of DMSO (80 vol%) with water (20 vol%), the yields of polymer P-2 were 72–75%. The apparent

correlation between the yield and the reaction time was not found. Polymers P-2 were obtained with 13–61% yields when the reaction was performed in the mixture of DMSO (50 vol%) with water (50 vol%) under the same reaction conditions, and the yield of the polymer increased remarkably with reaction time. The yield of polymer P-2 increased with reaction time when the reaction was carried out in the plain water at 50°C, although polymer P-2 was not obtained at 30°C for 72 h. The rate of the polycondensation of AA with PXDB may thus decrease by with increasing water.

Polymers P-2 prepared in DMSO have relatively higher M_n s than the polymers prepared in the mixed solvents of DMSO with water under the same conditions, although polymers P-1 prepared by the reaction of AA with MXDB in DMSO have lower M_n s than the polymers obtained from the reaction in the mixed solvents of DMSO with water. It seems that the heterogeneous system in the reaction of AA with PXDB blocked effectively the oxidation of halomethyl groups as side reactions even in DMSO, although the oxidation reaction of haloalkyl groups was also blocked by the presence of much water.

When the reaction was carried out in plain water at 50°C for 48–168 h, polymers P-2 with M_n of 8200–8600 were prepared with 31–55% yields, although the polymer was not obtained in water at 30°C for 72 h. Thus although the rate of polycondensation of dicarboxylic acid with alkylene dihalide in plain water is very slow, the reaction was enhanced by heating at appropriate temperature.

When inorganic bases such as Na₂CO₃ and K₂CO₃ with crown ethers were used in water, targeted polymers P-2 were not obtained. This suggests that the carboxylate anion paired with protonated DBU, a hydrophobic residue, has higher reactivity to alkylene dihalide than the carboxylate anion paired with alkaline metal cations which are relatively hydrophilic residues.

The polycondensation reactions of AA with various alkylene dihalides such as MXDB, PXDB, DCB, DBB, and DIB were performed using DBU in plain water at 50°C for 96 h. The reactions of AA with DCB, DBB, and DIB proceeded in a liquid–liquid two-phase system consisting of an aqueous solution of AA and an organic layer based on DCB, DBB, or DIB. As shown in Table III, the corresponding polyesters were not synthesized by reactions of AA with alkylene dihalides such as DCB, DBB, and DIB, although polymers P-1 and P-2 were obtained by reactions of AA with MXDB and with PXDB, respectively, in water. This indicates that the reactivity of DCB, DBB, and DIB to dicarboxylic acid AA is lower than that of MXDB and PXDB.

Table III. Synthesis of polymers by reactions of AA with various alkylene dihalide in water^a

Alkylene dihalides	Yield	M_n	M_w/M_n^c
	% ^b	$\times 10^{-3c}$	
MXDB	31	7.0	1.31
PXDB	52	8.6	1.58
DCB	0	—	—
DBB	0	—	—
DBI	0	—	—

^a Reaction was carried out with AA (2.5 mmol) and alkylene dihalide (2.5 mmol) using DBU (5 mmol) in water at 50°C for 96 h. ^b Insoluble parts in MeOH. ^c Estimated by GPC based on polystyrene standards.

Table IV. Effects of the feed ratio on reactions of AA with PXDB^a

Feed ratio (AA/PXDB/DBU)	Yield % ^b	M_n $\times 10^{-3d}$	M_w/M_n^d
1.00/1.00/2.00	52	8.6	1.58
1.00/1.05/2.00	55	8.5	1.51
1.00/1.00/2.10	56	8.9	1.58
1.00/1.05/2.10	55 (7) ^d	9.4	1.69

^a Reaction was carried out with AA (2.5 mmol) and PXDB using DBU in water (5 mL) at 50°C for 96 h. ^b Insoluble parts in methanol. ^c Estimated by GPC based on polystyrene standards. ^d Insoluble parts in chloroform.



Effects of the feed ratios on the polycondensation of AA with PXDB using DBU as a base in water were examined at 50°C for 96 h (Table IV). Polymer P-2 with the highest molecular weight (M_n : 9400) was obtained in 62% yield using small excess of DBU and PXDB. The product contained 7 wt% of insoluble parts in chloroform. The insoluble parts in chloroform were insoluble in acetone, ethyl acetate, Tetrahydrofuran (THF), DMSO, DMF, 1-methyl-2-pyrrolidinone (NMP), and toluene. The IR spectrum of the product showed the peak of C=O stretching due to ester group at 1731 cm^{-1} . The insoluble parts in the organic solvents were polyester with very high molecular weight.

Polycondensation of some dicarboxylic acids such as succinic acid (SCA), sebacic acid (SBA), phthalic acid (PHA), and isophthalic acid (IPA) with PXDB were performed using a small excess of DBU in water at 50°C for 96 h (Table V).

The polycondensations proceeded smoothly to give the corresponding polymers in 47–74% yields even in water under the mild conditions. When the polycondensation of SCA or IPA with PXDB was performed, the products included 4 or 6 wt% of insoluble parts in organic solvents, respectively. It seems that the insoluble parts in organic solvents were the corresponding polyesters with high molecular weight. The IR and ¹H NMR spectra of resulting polymers (P-1, P-2, P-4, P-5, and soluble parts in chloroform of P-3 and P-6) are summarized in Table VI. These spectral data suggest that the corresponding polyesters were synthesized by the polycondensation of certain dicarboxylic acid with MXDB and PXDB even in water.

From all the results, it may be concluded that both

Table V. Synthesis of various polymers by reactions of certain carboxylic acids with PXDB using DBU in water^a

Polym. No.	R^1	Yield	M_n	M_w/M_n^c
		% ^b	$\times 10^{-3c}$	
P-2	—(CH ₂) ₄ —	56	8.9	1.58
P-3	—(CH ₂) ₂ —	47 (4) ^d	8.8	1.53
P-4	—(CH ₂) ₆ —	74	6.5	1.45
P-5		60	8.2	1.64
P-6		58 (6) ^d	6.6	1.45

^a Reaction was carried out with dicarboxylic acid (2.5 mmol) and PXDB (2.5 mmol) using DBU (5.25 mmol) in water (5 mL) at 50°C for 96 h. ^b Insoluble parts in methanol. ^c Estimated by GPC based on polystyrene standards. ^d Insoluble parts in chloroform.

Table VI. IR and ¹H NMR spectra of polymers

Polym. No.	IR	¹ H NMR
	Film/ cm^{-1}	200 MHz, CDCl ₃ , TMS
P-1	1735 ($\nu_{\text{C=O}}$) 1238, 1164 ($\nu_{\text{C-O-C}}$)	δ (ppm) = 1.55–1.78 (m, 4.0H, —CH ₂ —CH ₂), 2.20–2.50 (m, 4.0H, CH ₂ —CO), 5.10 (s, 4.0H, —CH ₂ —O—), 7.10–7.35 (m, 4H, aromatic protons)
P-2	1736 ($\nu_{\text{C=O}}$) 1259, 1171 ($\nu_{\text{C-O-C}}$)	1.42–1.80 (m, 4.0H, —CH ₂ —CH ₂), 2.20–2.50 (m, 4.0H, CH ₂ —CO), 5.12 (s, 4.0H, —CH ₂ —O—), 7.38 (s, 4H, aromatic protons)
P-3	1730 ($\nu_{\text{C=O}}$) 1267, 1151 ($\nu_{\text{C-O-C}}$)	2.68 (s, 4.0H, —CH ₂ —CO—), 5.10 (s, 4.0H, —CH ₂ —O—), 7.32 (s, 4H, aromatic protons)
P-4	1738 ($\nu_{\text{C=O}}$) 1220, 1176 ($\nu_{\text{C-O-C}}$)	1.05–1.75 (m, 12H, —(CH ₂) ₆ —), 2.20–2.50 (m, 4.0H, CH ₂ CO), 5.10 (s, 4.0H, —CH ₂ —O—), 7.34 (s, 4H, aromatic protons)
P-5	1728 ($\nu_{\text{C=O}}$) 1274, 1121 ($\nu_{\text{C-O-C}}$)	5.05–5.30 (m, 4.0H, —CH ₂ —O—), 7.15–7.80 (m, 8H, aromatic protons)
P-6	1731 ($\nu_{\text{C=O}}$) 1270, 1151 ($\nu_{\text{C-O-C}}$)	5.38 (s, 4.0H, —CH ₂ —O—), 7.10–8.80 (m, 8H, aromatic protons)

water and the mixed solvent of DMSO with water are suitable reaction media for the polycondensation of dicarboxylic acids with alkylene dihalides using DBU as a base to produce the corresponding polyesters with under mild reaction conditions.

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