Synthesis of Polyesters by Emulsion Polycondensation Reaction in Water

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ABSTRACT: Polyesters were prepared from dicarboxylic acids and diols in the presence of a surfactant under mild conditions below 100 °C in water. The results of polycondensation on various conditions in the presence of *p*-dodecylbenzenesulfonic acid (DBSA) show that polyesters were obtained in a good yield from sebacic acid and decanediol in water at 70 °C. The molecular weight of the resulting polyesters were approximately 2000–5000 by gel permeation chromatography (GPC) in a chloroform eluent. The molecular weight distribution from this emulsion polycondensation was below $M_w/M_n = 2.0$. The particle size of these misells from this emulsion polycondensation were *ca.* 4–6 μm. Esterification in water might occur in misells having hydrophobic media from DBSA, which may play a role as the catalyst of esterification and also misell formation for this emulsion polycondensation in a water medium.

KEY WORDS Direct Polycondensation / Polyester / Misell / Surfactant / Emulsion / *p*-Dodecylbenzenesulfonic Acid /

Polycondensation reactions are generally carried out in a molten state of elevated temperature above 200 °C since the reaction are usually accompanied by an equilibrium between esterification and hydrolysis reactions. The enhancement of monomer reactivity can be achieved by using active reagents such as the combination of hexachloroethane and triphenylphosphine or picryl chloride in pyridine so that a polycondensation reaction takes place under mild conditions by direct polycondensation.^{1–10} The synthesis of aliphatic polyesters was performed by a dehydrogenation polycondensation in water using lipase as a catalyst.^{11,12} Recently, it was found that a condensation reaction takes place in water directly between acid and alcohol to form an ester compound in the presence of a surfactant such as *p*-dodecylbenzenesulfonic acid (DBSA) under mild conditions.^{13–15} In this paper, we employ direct polycondensation to prepare polyesters with out the use of reagents for dehydration in organic solvents. This reaction using the surfactant (DBSA) was applied to the polycondensation of dicarboxylic acids and diols and it was found that polyesters could be obtained under mild conditions below 100 °C in water as follows:

EXPERIMENTAL

Materials

Succinic acid, sebacic acid, adipic acid, isophthalic

Figure 1. Illustration of emulsion polycondensation by dehydration in the presence of a surfactant in water.

acid, terephthalic acid, hexanediol, decanediol, and bisphenol-A were used without further purification and deionized water was used.

Polymerization Procedure

A 0.01 mol of sebacic acid, 0.01 mol decanediol, and 0.60 g of *p*-dodecylbenzenesulfonic acid (DBSA) were added to 50 g of deionized water in a 200 mL of Erlenmeyer flask with stirring at 70 °C. After a given period of time, the excess methanol in the reaction mixture was added to remove the unreacted monomers and by-products from the polymer which was then isolated by filtration. The polymers were washed repeatedly with methanol and then dried at 50 °C for 6 h.

Characterization

The number-average (M_n) and weight-average (M_w) molecular weight were determined by GPC using a TOSOH SC-8020 at 40 °C in chloroform as calibrated with polystyrene standards. FT-IR spectra were recorded for film samples cast on an NaCl disk from a chloroform solution, using JASCO FT/IR-300E spec-

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Table I. Polycondensation of sebacic acid and decanediol with DBSA or DBSANA in water

Decanediol Mol	DBSA g	DBSANA g	Condition		Yield %	Molecular weight	
			Temp(°C)	Time(h)		M_w	M_w/M_n
0.01	0.60	—	70	70	81	2400	1.88
0.01	0.33	—	70	70	85	3000	1.73
0.01	0.66	—	15	70	0	—	—
0.02	0.63	—	70	20	83	2800	1.67
0.02	—	0.60	70	20	0	—	—
0.02	—	—	70	70	0	—	—

DBSA; *p*-Dodecylbenzenesulfonic acid. DBSANA; *p*-Dodecylbenzenesulfonic acid sodium salt.

Table II. Polycondensation of various dicarboxylic acid derivatives with DBSA in water

Dicarboxylic acid	Solubility in Water	Acidity		Condition Time(h)	Yield %	Molecular weight	
	g/°C	pK1	pK2			M_w	M_w/M_n
Succinic acid	6.8/20	4.21	5.64	20	17	1300	1.62
Adipic acid	1.4/15	4.43	5.41	19	24	1850	1.36
Sebacic acid	0.1/20	4.60	5.59	20	83	2800	1.67
Isophthalic acid	0.01/25	3.62	4.60	20	0	—	—
Terephthalic acid	0/20	3.54	4.46	19	0	—	—

Polycondensation; monomer concentration : 0.01 mol in 50 g of water at 70°C. Solubility; in 100 g of water.

trometer. The structure of polyesters was determined by NMR using JEOL Lambda 600 MHz. In CDCl_3 as the standard of TMS. The particle sizes of misells from the emulsion polycondensation were determined by Laser particle analyzer LPA-3100 made by Otuka Electronics.

RESULTS AND DISCUSSION

Table I summarizes the results of polycondensation of sebacic acid and decanediol in the presence of DBSA or DBSANA, where it is seen that the resulting polyesters were obtained in a good yield at 70°C at room temperature(15°C) and when of surfactants or DBSANA were used in place of DBSA, no satisfactory results in terms of polymer yield were obtained. Weight average(M_w) molecular weights were determined to be approximately 3000 by GPC analysis and the molecular weight distribution from this condition had a narrow distribution below $M_w/M_n = 2.0$.

Table II shows the results of emulsion polycondensation of various dicarboxylic acids and decanediol in the presence of DBSA in water. Sebacic acid gave polyesters having a high yield and high molecular weight compared with adipic acid or succinic acid in this polycondensation reaction. These results suggest that the solubility and hydrophobic property of acid derivatives in water may be related to this emulsion polycondensation reaction. Aromatic acids such as terephthalic acid or isophthalic acid did not yield polyesters because of poor solubility in water and in the

Figure 2. IR spectrum of polyesters with sebacic acid and decanediol.

misell in this condition. The acidity of acid derivatives were not important in this emulsion polycondensation, as shown in Table II.

The IR spectrum of polyesters with sebacic acid and decanediol is shown Figure 2. Which was identified by an adsorption at 1736 cm^{-1} due to the ester group- ing the polymer chain. The structure of polyesters having straight chains was determined by NMR analysis as shown Figure 3. The spectrum of NMR had proton signals of 2.60 ppm and 4.05 ppm (from polyesters), 2.74 ppm (from sebacic acid), and 3.65 ppm (from decanediol) respectively.

The calculated molecular weight of polyester ($M_w = \text{ca. } 2400$) by NMR value gave approximately the same molecular weight ($M_w = \text{ca. } 2600$) by GPC analysis.

The results of polycondensation with various diols and sebacic acid in the presence of DBSA in water are shown in Table III. Bis-phenol-A having a phenolic hydroxy group, did not yield polyesters under this condi-

Table III. Polycondensation of various diols and sebacic acid in the presence of DBSA in water

Diol	Solubility in Water	Melting point of diols(°C)	Condition Time(h)	Yield %	Molecular weight	
					M_w	M_w/M_n
Hexanediol	soluble	42–43	50	5	—	—
Decanediol	slight soluble	72–73	65	85	3000	1.36
Bis-Phenol-A	insoluble	128	21	0	—	—

Polycondensation; monomer concentration: 0.01 mol in 50 g of water at 70 °C.

Table IV. Results of homogeneous condition of sebacic acid, decanediol, and DBSA in polycondensation

Monomer Condition	Time h	Yield %	Molecular weight	
			M_w	M_w/M_n
Equimolecular	22	91	2400	1.45
5 mol% excess of sebacic acid	19	92	3200	1.54
10 mol% excess of sebacic acid	23	85	2600	1.52
5 mol% excess of decanediol	23	91	3200	1.52
DBSA in water medium	18	86	2800	1.47

Polycondensation; monomer concentration : 0.04 mol in 50 g of water at 80 °C in the presence of 0.60 g of DBSA. Homogeneous Condition; Sebacic acid, decanediol, and DBSA were melted for 5 min at 150 °C, and then poured into water at 70 °C.

Figure 3. NMR spectrum of polyesters with sebacic acid and decanediol.

tion while hexanediol (dissolved in water) gave a small amount of polymers (5% yield). Decanediol having a hydrophobic carbon chain, dissolves slightly in water. Therefore, decanediol dissolved in the misell of DBSA together with dicarboxylic acids in water. This emulsion polycondensation starts in heterogeneous media in water because of the poor solubility of monomers in water. Furthermore, the mole balance in this polycondensation reaction is very important for the preparation of high-molecular-weight polymer.

The results of mole balance of monomers was shown Table IV. Sebacic acid, decanediol, and DBSA were melted to be controlled the mole balance in the misell for 5 min at 150 °C (homogeneous condition) and then the mixture was poured into water at 70 °C. The molecular weight of polymers from a 5 mol% excess of sebacic acid or a 5 mol% excess of decanediol were obtained as $M_w = 3200$ and $M_w/M_n = 1.5$ respectively.

Table V shows the results of the polycondensation of sebacic acid and decanediol in the presence of DB-

Table V. Results of homogeneous condition of sebacic acid and decanediol using 2-naphthalenesulfonic acid in the presence of DBSANA in polycondensation

Monomer Condition	Time h	Yield %	Molecular weight	
			M_w	M_w/M_n
Equimolecular	23	86	2600	1.45
5 mol% excess of sebacic acid	20	84	2400	1.43
5 mol% excess of decanediol	20	83	2400	1.43
Heterogeneous	22	82	1900	1.37
Used of DBSA ^a	22	80	2400	1.40

Polycondensation; monomer concentration: 0.04 mol in 50 g of water at 80 °C. Used 2 g of DBSANA (40% in water) and 0.20 g of NSA. Heterogeneous; all reagents were added to water at the same time. Homogeneous: Sebacic acid, decanediol, and NSA were melted for 5 min at 150 °C, and then poured into water containing DBSANA at 70 °C. ^aUsed 0.20 g of DBSA instead of NSA.

SANA using 2-naphthalenesulfonic acid (NSA) as the catalyst of the esterification. In this case, the molecular weight of the polymers was approximately 2000 under various conditions.

The results of the high-molecular concentrations of DBSA (0.08 mol of monomers in *ca.* 40 g of water) in the polycondensation are shown Table VI. The molecular weight of polyesters increased with an increase in the amount of DBSA. Increasing DBSA (16 wt%) in this emulsion polycondensation yield polyester having high-molecular-weight polyesters (*ca.* $M_w = 5100$). These results show unreacted monomer disperse in water, but they can control the mole balance of diol and dicarboxylic acid in the misell in this polycondensation reaction. The average size of particles of the misells in the emulsion polycondensation were calculated by the laser particle analyzer, as shown Table VI, which

Table VI. Effect for amount of DBSA on the high monomer concentration in polycondensation

Amount of DBSA	Time	Yield	Molecular weight		Average size
wt%	h	%	M_w	M_w/M_n	particle(μ m)
1	17	96	2500	1.43	4.5
2	17	87	2600	1.46	4.5
4	20	95	3300	1.61	5.1
8	23	85	3800	1.65	4.2
16	23	87	5100	1.75	6.0

Polycondensation; monomer concentration : approximate 40 wt% in water at 80 °C. Used 0.08 mol of monomers in *ca.* 40 g of water. Average size of particle; emulsion polymerization medium.

was found to be 4–6 μ m. The esterification in water might occur in the misells having hydrophobic media from DBSA, which may play a role as the catalyst of esterification and also misell formation because DBSANA did not yield polyesters in this polycondensation reaction. A large amount of DBSA might be obtained as a fastened shell structure (surface of misell) and a small of DBSA gives a loose shell structure in this emulsion polycondensation because every misell has approximately same particle size as shown in Table VI. Therefore, the molecular weight of polyesters increases with an increase in the amount of DBSA in this emulsion polycondensation reaction. It was found that there is a good relationship between the amount of DBSA and the molecular weight of polyesters as shown in Table VI.

Table VII shows that the combination of various surfactants with sebacic acid and decanediol in the presence of an acid catalyst took place in this emulsion polycondensation. It was found that only a low yield of polyesters was obtained from non-ion surfactants or phosphate surfactant having a weak acidity with regard to DBSA under this condition. The use of DBSANA and an acid catalyst such as NSA or conc. HCl gave the same results in terms of the yield and molecular weight compared with the polyesters from DBSA surfactants. In the combination of DBSANA and conc. HCl working an ion-exchanging catalyst of DBSANA during this esterification reaction might yield a good yield and the molecular weight of polyester and more conc. hydrochloric acid can control the acidity of the medium in water. The precipitation (aggregation) of polyesters occurred when in storage for 7 d at room temperature because they have bigger-size particles in this emulsion polycondensation reaction and have a sulfonyl group ($-\text{SO}_3\text{H}$ group) on the surface (shell) of the misell as shown in Table VII and Figure 1 of the misell.

It is very important to yield a good emulsion in this polycondensation to control small-size misells below 1 μ m in a water medium. Additional detailed studied on the emulsion polycondensation in polyesters are being carried out so as to determine the optimum reaction

Table VII. Polycondensation of various surfactants with sebacic acid and decanediol in the presence of acid catalysis in water

Surfactant	Acid Catalyst	Time	Yield	Molecular weight	
		h	%	M_w	M_w/M_n
DBSA	–	23	86	2600	1.45
	c.HCl	17	89	2000	1.44
DBSANA	c.HCl	22	85	3100	1.51
	NSA	22	8	1900	1.37
	DBSA	65	82	2100	1.53
DSANA	c.HCl	26	66	2000	1.30
Non-ion	c.HCl	22	23	2700	1.55
	NSA	22	31	2500	1.54
Phosphate	–	22	15	1000	1.08

Polycondensation; monomer concentration: 0.02 mol in 50 g of water at 80 °C. c.HCl; 40% concentrated hydrochloric acid (used 1.0 g). DSANA; Dodecyl sulfate sodium salt. NSA; Naphtharene-sulfonic acid (used 2.0 g). Non-ion; Kao Corporation Emulgen404 (polyoxyethylene alkylether). Phosphate; Di(polyethylene glycol 4-nonylphenyl)phosphate.

condition and the mechanism in the misell involved in this process.

CONCLUSION

The synthesis of polyesters with surfactants such as *p*-dodecylbenzenesulfonic acid (DBSA) was carried out in a water medium under mild conditions. Polyesters having medium molecular weight using aliphatic acids and diols were produced in water under a mild temperatures by this emulsion polycondensation reaction. Such polycondensation with the surfactants in water is environmentally friendly and economical since it is a non-solvent system.

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