Polycondensation of Dicarboxylic Acids and Diols in Water Catalyzed by Surfactant-Combined Catalysts and Successive Chain Extension

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Direct dehydration polycondensation of dicarboxylic acids and alcohols was carried out by surfactant-combined Brønsted and Lewis acids. This procedure did not require the removal of water, because the esterification was established at the interface of the emulsion in water. Emulsion polycondensations of 1,9-nonanediol (1,9-ND) and dodecanedioic acid (DDA) (the molar ratio of dicarboxylic acid to diol = 1:1) were carried out at 80 °C for 48 h in the presence of 16 wt % DBSA. The corresponding polyester ($M_w = 10.1 \times 10^3$) was obtained in an excellent yield (99%). Chain extension in the emulsion was carried out using hexamethylene diisocyanate as the chain extender. SEC measurements indicated the expected shift to higher molecular weight region ($M_w = 11.4 \times 10^3$, $M_w/M_n = 3.4$) compared with parent polyester ($M_w = 4.5 \times 10^3$, $M_w/M_n = 2.2$).

Introduction

Remarkable attention has focused on polymers that have potential as biomaterials and environmentally benign materials. Particularly, aliphatic polyesters including poly(alkylene succinate)s could replace many conventional plastics soon because of their biodegradability, acceptable mechanical strength, and softening temperature comparable to low-density polyethylene and polystyrene.[1] In general, they are commercially produced by the polycondensation of aliphatic dicarboxylic acid and diol compounds at temperatures higher than 250 °C under a highly reduced pressure.[2] Recently, we reported the scandium trifluoromethane sulfonate [Sc(OTf)$_3$][3a−c] and scandium trifluoromethane sulfonimide [Sc(NTf)$_3$][3d]-catalyzed room-temperature polycondensation of dicarboxylic acids and diols. This made it possible to synthesize, in one step, a polyester with the number-average molecular weight (M_n) > 10 000.[3] However, the condensation system as well as the conventional system requires removing water under reduced pressure (0.3−30 mm Hg), because the reactions are accompanied by an equilibrium between the condensation of the alcohol with the carboxylic acid and hydrolysis. Recently, it was revealed that esterifications directly took place in water between some alcohols and carboxylic acids in the presence of *p*-dodecylbenzene sulfonic acid (DBSA), in which the condensation was attained at the interface of the emulsion.[4] In this way, the system does not need to remove the water. This report prompted us to explore a new type of polyesterification system of diols and dicarboxylic acids in emulsion without the removal of water. Although two researchers[5] already independently reported the applications of this system for polyester synthesis, the maximum weight-average molecular weight (M_w) was 5100.[5a] Therefore, it is still a challenging research task to develop polyesterification systems using surfactant-combined catalysts. Moreover, to the best of our knowledge, there is no report of a surfactant-combined Lewis acid catalyzed polyesterification system. In this communication, we describe the synthesis of polyesters via the polycondensation of diols and dicarboxylic acids using a surfactant-combined Lewis acid and Brϕnsted acid (Figure 1) and the successive chain extension in the emulsion using diisocyanate as the chain extender.

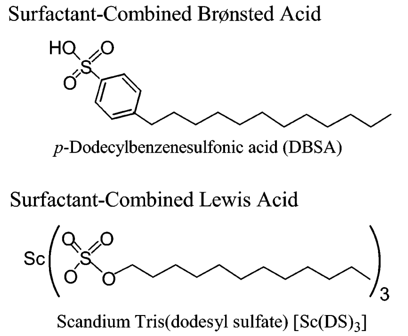

Figure 1. Molecular structure of scandium tris(dodesyl sulfate) [Sc(DS)$_3$] and *p*-dodecylbenzene sulfonic acid (DBSA).

Experimental Section

Materials. Scandium chloride (ScCl$_3$)·6H$_2$O (99.9%) and 12-hydroxydodecanoic acid (97%) were purchased from Sigma Aldrich. Sodium dodecylsulfate (SDS) (99%), *p*-dodecylbenzene sulfonic acid (DBSA) (90%), sebacic acid (SeA) (98%), 1,9-nonanediol (1,9-ND) (98%), 1,10-decanediol (1,10-DD) (98%), and dodecanedioic acid (DDA) (95%) were obtained from the Tokyo Kasei Co. (Tokyo, Japan). Hexamethylene diisocyanate (98%) and adipic acid (ADA) (99%) were purchased from Nacalai Tesque (Kyoto, Japan). Methylsuccinic acid (MSA) (99%) was obtained from the Aldrich Co.

Measurements. The FT/IR spectra were recorded with KBr disks using a JASCO FT/IR-430 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured at 27 °C using a Bruker DPX200 spectrometer (200 MHz for ^{1}H NMR). All chemical shifts were expressed as δ downfield from tetramethylsilane (TMS). The number average molecular weights (M_n) and the polydispersity index (M_w/M_n) of the polymers were

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Scheme 1. Emulsion Dehydration Polycondensation of Dicarboxylic Acids with Diols and Subsequent Chain Extension in Emulsion

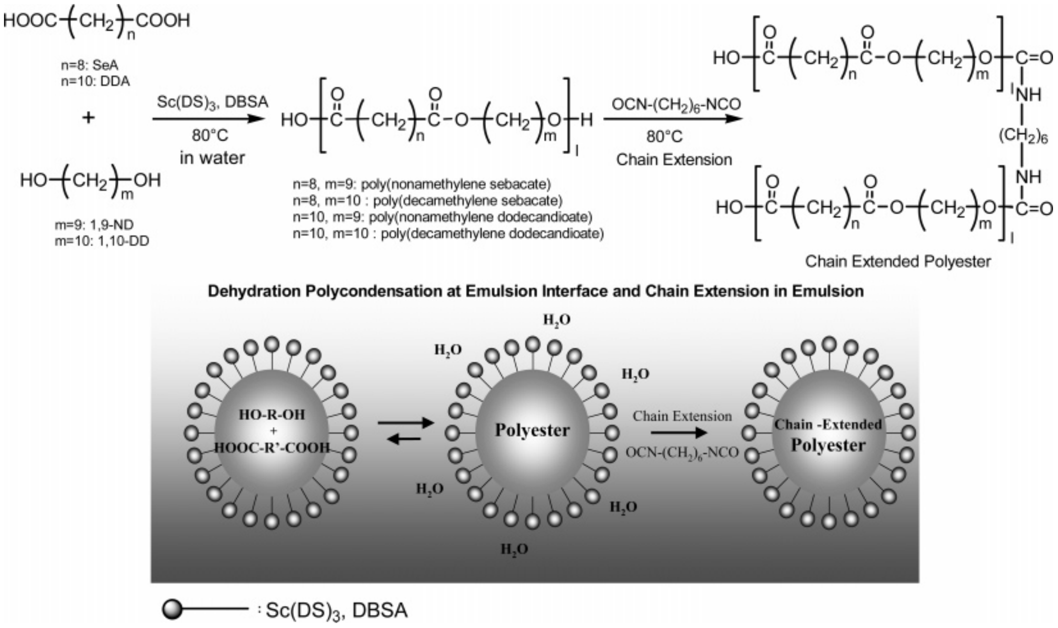
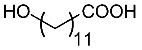


Table 1. Direct Polycondensation of Diols and Dicarboxylic Acids in Water[a]

run	dicarboxylic acid	diol	catalyst (wt%)	yield (%)	M_w[b] $\times 10^{-3}$	M_w/M_n[b]
1	MSA (n=2)	1,9-ND (m=9)	DBSA (16)	28[d]	1.7	1.8
2	ADA (n=4)	1,9-ND (m=9)	DBSA (16)	32[d]	1.4	1.5
3	SeA (n=8)	1,9-ND (m=9)	DBSA (16)	99[d]	7.6	2.1
4	SeA (n=8)	1,10-DD (m=10)	DBSA (16)	99[d]	4.1	1.5
5	SeA (n=8)	1,10-DD (m=10)	DBSA (8)	97[d]	2.7	1.5
6	DDA (n=10)	1,9-ND (m=9)	DBSA (16)	96[d](95[e])	10.1	2.0
7	DDA (n=10)	1,9-ND (m=9)	DBSA (8)	99[d]	4.0	1.5
8	DDA (n=10)	1,10-DD (m=10)	DBSA (16)	96[d]	4.6	1.8
9	DDA (n=10)	1,9-ND (m=9)	none	no polymerization	—	—
10	DDA (n=10)	1,10-DD (m=10)	SDS (16)	96[d]	1.4	1.4
11			DBSA (16)	99[d]	5.4	1.9
12	SeA (n=8)	1,10-DD (m=10)	$Sc(DS)_3$ (16)	97[d]	2.6	1.3
13	SeA (n=8)	1,10-DD (m=10)	$Sc(DS)_3$ (8)	95[d]	2.3	1.5
14	DDA (n=10)	1,9-ND (m=9)	$Sc(DS)_3$ (16)	99[d]	4.0	1.5
15	DDA (n=10)	1,9-ND (m=9)	$Sc(DS)_3$ (8) +DBSA (13)[c]	98[d]	3.3	1.4

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[a] $[\text{Diol}]_0 = [\text{dicarboxylic acid}]_0 = 1.1$ M (in water), at 80 °C for 48 h. [b] Determined by SEC measurement in $CHCl_3$ relative to polystyrene. [c] Mixture of DBSA and $Sc(DS)_3$ (1/1, mol/mol). [d] Without reprecipitation. [e] After washing with methanol.

estimated by size exclusion chromatography (SEC) calibrated with polystyrene standards using a pump system of Tosoh DP8020 with an RI (Tosoh RI-8020) detector and Tosoh G2000, 3000, 4000, and 5000-HXL columns (eluent, chloroform; flow rate, 1.0 mL/min; temperature, 40 °C). The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were measured by a Voyager DE-PRO (Applied Biosystems) using anthracene-1,8,9-triol (dithranol) as the matrix reagent. To generate sodium-cationized ions ($[M + Na]^+$), NaI was used as the cationization salt.

Direct Dehydration Polycondensation of Dicarboxylic Acids and Diols in Water Catalyzed by Surfactant-Combined Catalysts. For poly(nonamethylene dodecandioate): A typical polycondensation procedure is as follows. In a 50 mL flask, DDA (0.46 g, 2.0 mmol), 1,9-ND (0.32 g, 2.0 mmol), and DBSA (0.34 g, 0.98 mmol) were suspended in water (1.0 mL) and stirred at room temperature for a few minutes. The polycondensation started in an oil bath maintained at 80 °C. After 48 h, the reaction mixture was evaporated to yield a polymeric material. The polyester yield was calculated by subtraction of the weight of the catalyst from the isolated material (96% yield, run 6 in Table 1). To remove the DBSA catalyst, the powder was washed several times with 50 mL methanol and then dried to produce the isolated polyester (95% yield). ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.05−1.46 (26H, $-CH_2-$), 1.46−1.79 (4H, $-OCH_2CH_2-$), 2.28 (4H, t, 8 Hz, $-COCH_2-$), 3.01 (s, terminal $-OH$), 3.65 (t, 7 Hz, $-CH_2OH$), 4.05 (4H, t, 7 Hz, $-OCH_2-$). IR (KBr disk, cm^{-1}): 2919 and 2852 (ν_{C-H}), 1734 [$\nu_{C=O}$(ester)], 1249, and 1093 [ν_{C-O}(ester)].

In Situ Chain Extension of Polyester in Emulsion. The chain extension using hexamethylene diisocyanate was carried out as follows. After the polycondensation of 1,9-ND and DDA, into the emulsion of the produced polyester ($M_w = 4.1 \times 10^3$), hexamethylene diisocyanate (95 mg, 0.57 mmol, 2 equiv of terminal hydroxyl groups) was added. The reaction mixture was run at 80 °C for 5 h. During the reaction, any unreacted isocyanate was decomposed to hexamethylenediamine and carbon dioxide. After the reaction, the reaction mixture was evaporated to remove the water and produce the chain-extended polyester ($M_w = 11.4 \times 10^3$) in an excellent yield (98%).

Results and Discussion

As the surfactant-combined Lewis acid, we used scandium(III) alkane sulfate, which is known to be an effective catalyst for some organic reactions of water-labile substances in aqueous media,[6] but there are no examples known for esterification or polyesterification. We prepared scandium tris(dodecyl sulfate) [Sc(DS)$_3$] (99% yield) from ScCl$_3$ and SDS according to a previous report.[6] To evaluate the surfactant properties, the surface tension of the aqueous solution was measured by the drop-weight method.[7] SDS showed a clear inflection point at 0.23 wt % which corresponds to the reported critical micelle concentration (cmc) value (0.23 wt %, 8.1 mM).[8] DBSA and Sc(DS)$_3$ also showed the cmc-like inflection point at 0.01 and 0.05 wt %, respectively, indicating these can act as surfactants similar to SDS.

The emulsion polycondensation of dicarboxylic acids and diols was carried out at 80 °C for 48 h using DBSA as the surfactant-combined catalyst. The initial heterogeneous solution turned into an emulsion after 48 h. These results are summarized in Table 1. In all the runs except the polycondensations using MSA and ADA as the dicarboxylic acids (runs 1 and 2), polymeric solids were quantitatively obtained by evaporation of excess water. It seems that the high solubilities of MSA and ADA in water did not allow them to localize in the emulsion. The obtained polyesters were soluble in chloroform, but insoluble in tetrahydrofuran and ethyl acetate. The structures were confirmed by IR, NMR, and MALDI-TOF mass spectra, and the weight-average molecular weights (M_w's) were estimated by size exclusion chromatography (SEC) using CHCl$_3$ as the eluent (polystyrene standards). To investigate the influence of the vacuum stripping of the excess water on the M_w, SEC measurements were carried out before and after the evaporation of water. However, no remarkable increase in the M_w was observed under this experimental condition. The polycondensation of SeA with 1,9-ND and 1,10-DD are the corresponding polyesters with M_w's of 7.6×10^3 and 4.1×10^3, respectively, (runs 3 and 4) using 16 wt % of DBSA in the aqueous solution (above the cmc: 0.01 wt %). In the MALDI-TOF mass spectrum of the polyester prepared from SeA and 1,10-DD, the peaks are separated by m/z of 340.5 corresponding to the mass of the repeating unit, indicating that the produced polyester had the expected structure. It was also observed that 1,9-ND is more suitable for the polycondensation with SeA than 1,10-DD. When the DBSA content decreased to 8 wt %, the M_w was lower (run 5, 2.7×10^3). The emulsion polycondensations of DDA with 1,9-ND and 1,10-DD were also carried out (runs 6−8). Suprisingly, the polycondensation of DDA with 1,9-ND proceeded to give the corresponding polyester ($M_w = 10.1 \times 10^3$) at 80 °C for 48 h in an excellent yield (99%) (run 6). This is the first report of the synthesis of an aliphatic polyester ($M_w > 10.0 \times 10^3$) by a one-step procedure without removing water. The particle size estimated by the dynamic light scattering (DLS) measurement was 1.5 μm. In the absence of a catalyst, the polyester was not obtained (run 9). With SDS as the surfactant (run 10), the M_n was quite low ($M_w = 1.4 \times 10^3$) compared to that catalyzed by DBSA. The results supported the fact that the polycondensation occurred at the interface of the emulsion. The polycondensation of an ω-hydroxycarboxylic acid, 12-hydroxydodecanoic acid (run 11), took place, but the M_w (5.4×10^3) was lower than that of the polyester from DDA and 1,9-ND (run 6). This indicated that the ratio of the carboxylic acid and alcohol was maintained at 1:1 during the polycondensation of DDA and 1,9-ND as well as that of 12-hydroxydodecanoic acid. The polycondensations of 1,9-ND and DDA at the ratios of 1.2:1 and 1.5:1 were also performed, in which the M_w's were 8.1×10^3 and 5.1×10^3, respectively. These results indicated that the M_w of the obtained polyester was not very sensitive to the stoichiometry of the dicarboxylic acids and diols during this polycondensation.

In the case of Sc(DS)$_3$, the polyesterification of SeA and 1,10-DD for 48 h produced a polyester with $M_w = 2.6 \times 10^3$ (run 12). By using 8 wt % of the catalyst, the M_w was still comparable to that from the polycondensation using 16 wt % of the catalyst (run 13, $M_w = 2.3 \times 10^3$). Another example to illustrate the Lewis acid−surfactant combined catalyst−catalyzed polyesterification is the polycondensation of DDA with 1,9-ND (run 14). The M_w (4.0×10^3) using DDA and 1,9-ND was higher than that using SeA and 1,10-DD (2.6×10^3). This tendency was similar to that using DBSA as the surfactant-type catalyst, indicating that the polymerization rate is dependent on the combination of dicarboxylic acid and diol. In this study, we performed the polycondensation using the mixed catalyst of Sc(DS)$_3$ and DBSA (1/1, mol/mol) (run 15), because the Brϕnsted acid−combined Lewis acids showed an excellent catalytic activity in some organic reactions.[9] However, a remarkable increase in the M_w was not confirmed.

As a challenging trial, a chain extension of the emulsion was carried out using hexamethylene diisocyanate as the chain extender. The diisocyanate (2 equiv of the hydroxyl terminus of the polyester ($M_w = 4.5 \times 10^3$)) was injected into the emulsion after the polycondensation. The chemical structure of the chain-extended polyester was confirmed by ^{1}H NMR and IR measurements. New peaks at 1538 cm^{-1} (δ_{N-H}) and 1684 cm^{-1}($\nu_{N=C=O}$) assigned to the urethane bond appeared in the IR spectrum. Furthermore, peaks ascribed to the hydroxyl terminal at 3.01 ($-CH_2-OH$) and 3.65 ppm ($-CH_2-OH$) decreased and a new peak at 3.15 ppm (t, 7 Hz, $-CH_2-NCO$) appeared in the ^{1}H NMR spectrum (Supporting Information). The SEC measurement indicated the expected shift to a higher molecular weight region ($M_w = 11.4 \times 10^3$, $M_w/M_n = 3.4$) compared to the parent polyester ($M_w = 4.5 \times 10^3$, $M_w/M_n = 2.2$) (Supporting Information). These results indicated that the expected chain extension occurred in the emulsion. The emulsion droplets, although dispersed in water, seemed to be hydrophobic enough to suppress the hydrolytic decomposition of the water−labile diisocyanate (chain extender). With 22 equiv of diisocyanate, the peak at 3.65 ppm completely disappeared in the ^{1}H NMR spectrum, but the shift to a higher molecular weight region of the SEC trace was not confirmed. This may infer that no chain extension, but the chemical modification of terminal hydroxyl groups, occurred. To the best of our knowledge, this is the first report of the chain extension of polyester in water, too.

In this paper, we demonstrated the direct dehydration polycondensation of dicarboxylic acids and diols in water by surfactant-combined catalysts and a subsequent chain extension in the emulsion. This procedure did not require the removal of water, because the esterification reaction occurs at the interface of the emulsion in water. The polyester was obtained at 80 °C in 48 h with an excellent yield ($M_w > 1.0 \times 10^4$). These results may prove to be useful in the area of polymer science based on environmentally benign techniques.

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Supporting Information Available. ^{1}H NMR spectra and SEC traces of poly(nonamethylene dodecanedionate) before and after the chain extension. This material is available free of charge via the Internet at http://pubs.acs.org.

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