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Star Polymer Synthesis from ϵ-Caprolactone Utilizing Polyol/Protonic Acid Initiator

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ABSTRACT: Three- and four-armed star-shaped poly(ϵ-caprolactone)s were synthesized from trimethylolpropane and pentaerythritol as initiators using fumaric acid as an activator of the monomer, respectively. Star-shaped poly(ϵ-caprolactone)s could be satisfactorily obtained, which was confirmed by size exclusion chromatography equipped with low-angle laser light scattering and viscometer detectors. Comparing the melting points among the polymers with similar molecular weights, the order was as follows: linear poly(ϵ-caprolactone) > three-armed poly(ϵ-caprolactone) > four-armed poly(ϵ-caprolactone). On the other hand, poly(ϵ-caprolactone)s with similar arm length showed similar melting points irrespective of the arm numbers. Thermal decomposition temperature of poly(ϵ-caprolactone)s increased with the arm number.

Introduction

Branched polymers such as star polymers, dendrimers, and hyperbranched polymers attract much attention, because they exhibit useful rheological and mechanical properties, which are not accessible in conventional linear polymers.[1] Plural polymer end groups of branched polymers contribute the unique properties in addition to the branched backbone structures, which enable branched polymers as reactive materials. Star polymers show melt viscosities lower than those of the corresponding linear polymers, so they can be molded at a temperature lower than that of the linear polymers, which is preferable to polymers with relatively low thermal stability such as polyl(lactone).[2] A wide variety of star polymers are synthesized by living anionic polymerization of styrene derivatives, 1,3-dienes, and (meth)acrylates;[3] living cationic polymerization of vinyl ethers, isobutylene, and styrene derivatives;[4] coordination polymerization of isocyanates;[5] and recently living radical polymerization of styrene and (meth)acrylates.[6] Three methods are employed for star polymer synthesis: (1) core-first method (living polymerization with a multifunctional initiator); (2) arm-first method (coupling of linear living polymers with a multifunctional terminator); and (3) linking of linear living polymers with a divinyl compound. Hedrick et al.[7] and Qiu et al.[8] have reported the synthesis of star-shaped polymers from ϵ-caprolactone (ϵ-CL) using multifunctional alcohols with stannous or aluminum catalysts. Although their work satisfactorily provides star-shaped poly(ϵ-CL) derivatives, it is desirable to develop a metal-free method, because poly(ϵ-CL) finds its application in biomedical and pharmacological fields.[9] We have recently developed controlled ring-opening polymerization of lactones with combination of alcohol and acid, which serve as initiator and activator, respectively.[10] This metal-free initiator system has also enabled us to obtain block copolymers of lactones with cyclic carbonates. If we employ a multifunctional alcohol as the initiator, we may obtain star polymers with controlled arm length. This article deals with star polymer synthesis from ϵ-caprolactone (ϵ-CL) using trimethylolpropane and pentaerythritol as the initiators (Scheme 1).

Experimental Section

Measurements. ^{1}H NMR spectra were measured on a JEOL Lambda-300 spectrometer using tetramethylsilane as an internal standard in chloroform-*d* ($CDCl_3$). Number-average molecular weights (M_n) and polydispersity indexes (M_w/M_n) were estimated by size exclusion chromatography (SEC) on a Tosoh HLC 8120 system equipped with two consecutive polystyrene gel columns (Tosoh TSK gels G4000HXL and G-2500HXL), ultraviolet, refractive index, viscometer, and light scattering (Viscotek model T60) detectors using tetrahydrofuran (THF) as an eluent, with a flow rate of 1.0 mL/min by polystyrene calibration at 30 °C. Thermal analyses were performed on Seiko Instruments DSC6300 and TG/DTA6200. Melting points (T_m's) were determined by differential scanning calorimetry (DSC) at a heating rate of 10 °C/min under a nitrogen atmosphere. Temperatures with 10% weight loss (T_{d10}'s) were determined by thermogravimetric analysis (TGA) at a heating rate of 10 °C/min under a nitrogen atmosphere.

Materials. Unless stated otherwise, all chemicals and reagents were obtained commercially and used without further purification. CH_2Cl_2 was dried over P_2O_5 and then distilled from CaH_2. THF was dried over sodium and distilled. ϵ-CL was distilled from CaH_2. Trimethylolpropane was recrystallized from acetone/ether.

Cationic Polymerization (Typical Procedure). All glass vessels were dried by heating in vacuo and filled with and handled in a dry nitrogen stream. To a mixture of trimethylolpropane (13 mg, 0.1 mmol) and fumaric acid (175 mg, 1.5 mmol) in a glass tube was fed ϵ-CL (1.712 g, 15 mmol) at 90

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Scheme 1

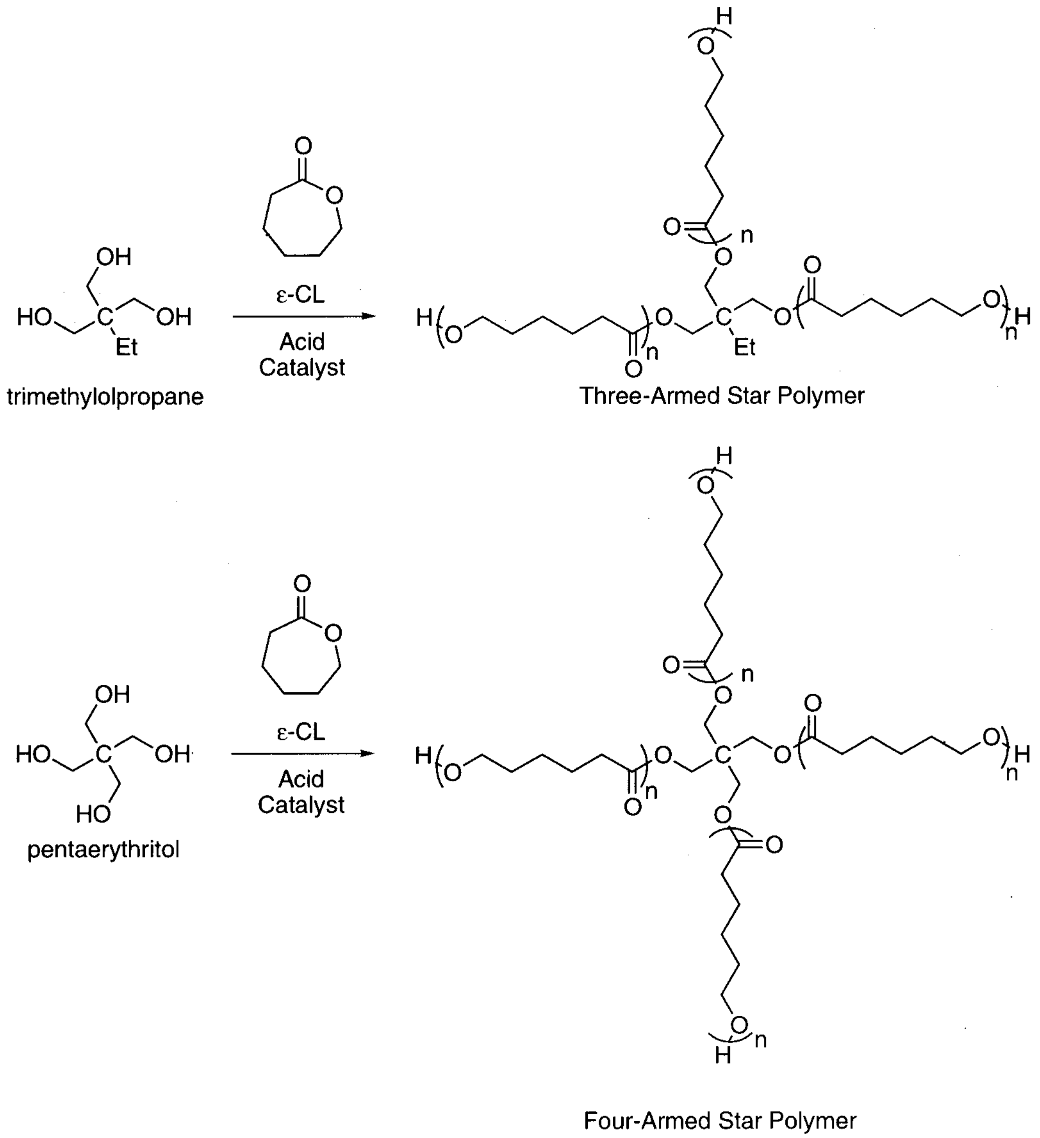

Table 1. Polymerization of ϵ-CL with Pentaerythritol in the Presence of Acid Catalyst

run	acid	solv[a]	[ϵ-CL]$_0$/[alcohol]$_0$	[acid]$_0$/[alcohol]$_0$	temp (°C)	time (h)	yield[b] (%)	M_n[c]	M_w/M_n[c]
1	$HCl \cdot Et_2O$	THF	80	6	20	75	35	7600	1.24
2	$HCl \cdot Et_2O$	CH_2Cl_2	80	12	20	72	43	13300	1.40
3	CF_3CO_2H	none	100	6	70	6	95	8100	1.67
4	CCl_3CO_2H	none	100	20	70	6	73	6000	1.98
5	maleic acid	none	100	6	70	6	79	10300	1.27
6	fumaric acid	none	100	10	90	12	81	9500	1.09

[a] Initial monomer concentration 1 M. [b] *n*-Hexane-insoluble part. [c] Determined by SEC.

°C. After the reaction mixture was stirred at the temperature for 24 h, it was diluted with CH_2Cl_2 (20 mL), and the resulting mixture was poured into *n*-hexane (300 mL). The precipitate formed was filtered off and washed with water and then dried at 25 °C in vacuo for 5 h to isolate a white powdery polymer. ^1H NMR ($CDCl_3$): δ 1.39 (broad s, 2H), 1.65 (broad s, 4H), 2.31 (broad s, 2H), 4.06 ppm (broad s, 2H).

Results and Discussion

Table 1 summarizes the conditions and results of polymerization of ϵ-CL with pentaerythritol as the initiator using several acids as the activator. First, we attempted the polymerization using $HCl \cdot Et_2O$ (2 M solution in ether) as the activator, effective for living ring-opening polymerization of ϵ-CL (runs 1 and 2).[10] The polymerization proceeded heterogeneously. The polymer yields were low (35−43%), and they showed bimodal SEC curves with relatively large M_w/M_n's (1.24−1.40). The low solubility of pentaerythritol in the reaction mixture would be responsible for these unsatisfactory results. Elevation of polymerization temperature is necessary to achieve homogeneous polymerization, but $HCl \cdot Et_2O$ is inappropriate for this purpose. We therefore examined CF_3CO_2H (pK_a 0.23), CCl_3CO_2H (pK_a 0.89), maleic acid (pK_a 1.92), and fumaric acid (pK_a 3.02) instead of $HCl \cdot Et_2O$ (pK_a −3.7) without a solvent at elevated temperatures (70 and 90 °C) to achieve homogeneous polymerization. The polymerization with CF_3CO_2H at 70 °C afforded the polymer in a high yield

Table 2. Polymerization of ϵ-CL with Trimethylolpropane and Pentaerythritol in the Presence of Fumaric Acid at 90 °C

run	alcohol	$[\epsilon\text{-CL}]_0/[\text{alcohol}]_0$	$[\text{fumaric acid}]_0/[\text{alcohol}]_0$	time (h)	conv[a] (%)	yield[b] (%)	$M_{n(cal)}$[c]	M_n[d]	M_w/M_n[d]	$g^{1/2}/g'$[e]
1	trimethylolpropane	50	5	6	90	70	5100	4400	1.07	0.98
2	trimethylolpropane	100	10	15	78	67	8900	7800	1.12	1.04
3	trimethylolpropane	150	15	24	99	91	16900	15400	1.14	0.97
4	pentaerythritol	50	5	8	92	61	5200	3700	1.06	0.96
5	pentaerythritol	100	10	12	95	81	10800	9500	1.09	0.89
6	pentaerythritol	150	15	24	99	76	16900	15800	1.10	1.26

[a] Determined by ^{1}H NMR. [b] *n*-Hexane-insoluble part. [c] Calculated by the following equation: ([consumed ϵ-CL]/[alcohol]$_0$) × 114 (molecular weight of ϵ-CL). [d] Determined by SEC. [e] $g = 6f/[(f + 1)(f + 2)]$, where f represents the number of arms (trimethylolpropane **3**, pentaerythritol **4**). g' was determined by SEC equipped by LALLS and viscosity detectors.

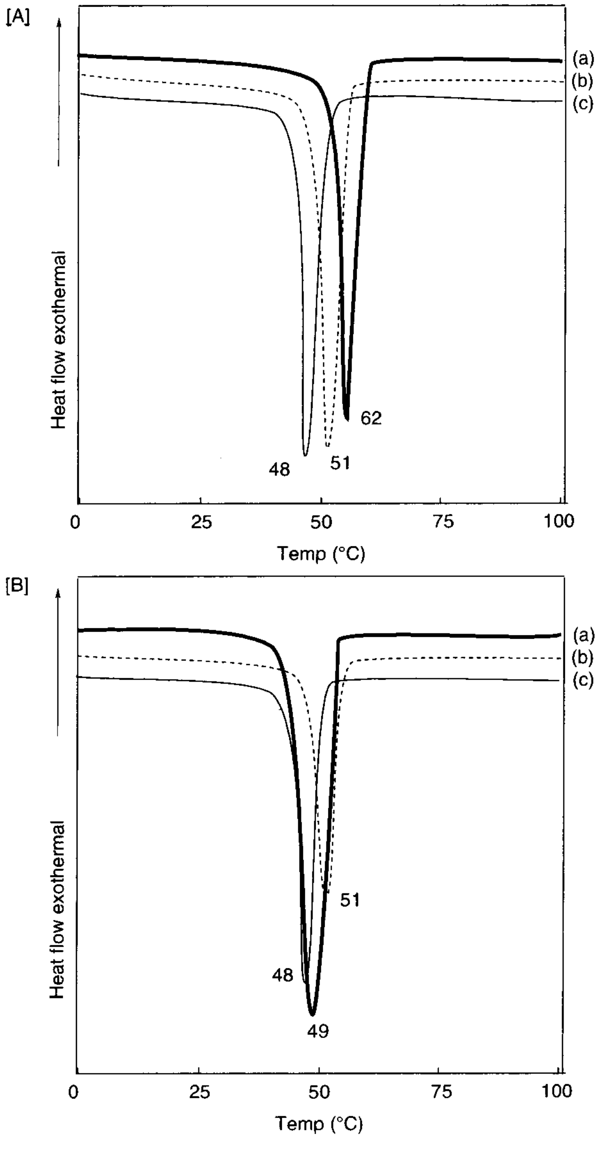

Figure 1. DSC traces of linear and star-shaped poly(ϵ-CL). [A] (a) Linear poly(ϵ-CL) (M_n = 10 300, M_n (per arm) = 10 300, M_w/M_n = 1.15), (b) three-armed star-shaped poly(ϵ-CL) (M_n = 12 500, M_n (per arm) = 4200, M_w/M_n = 1.14), (c) four-armed star-shaped poly(ϵ-CL) (M_n = 12 100, M_n (per arm) = 3000, M_w/M_n = 1.14). [B] (a) Linear poly(ϵ-CL) (M_n = 2700, M_n (per arm) = 2700, M_w/M_n = 1.15), (b) three-armed star-shaped poly(ϵ-CL) (M_n = 12 500, M_n (per arm) = 4200, M_w/M_n = 1.14), (c) four-armed star-shaped poly(ϵ-CL) (M_n = 12 100, M_n (per arm) = 3000, M_w/M_n = 1.14).

(95%, run 3), but the M_w/M_n was large (1.67). It was considered that the activity of CF_3CO_2H was so high at this temperature that conventional cationic polymerization via activated chain end mechanism also took place in addition to the alcohol-initiated activated monomer polymerization desirable to controlled star polymer synthesis. CCl_3CO_2H also afforded the polymer with a large M_w/M_n (1.98, run 4). On the contrary, maleic acid afforded the polymer with a relatively low M_w/M_n (1.27, run 5). Fumaric acid achieved the most satisfactory result in both the polymer yield and M_w/M_n at 90 °C for 12 h (run 6). Consequently, we employed this condition for synthesis of star polymers with several molecular weights by varying the monomer/initiator ratios.

Table 2 summarizes the ϵ-CL polymerization initiated with trimethylolpropane or pentaerythritol using 1/10 equiv of fumaric acid to ϵ-CL as the catalyst with various monomer/initiator ratios at 90 °C. The polymerization time was fixed according to the monomer/initiator ratios to achieve high monomer conversion. In every case, monodispersed poly(ϵ-CL) was obtained in a satisfactory yield. The M_n increased according to the monomer/initiator ratio, keeping a small M_w/M_n, and agreed well with the theoretical M_n [$M_{n(cal)}$], indicating the proceeding of controlled polymerization. The obtained star polymers with the M_n's lower than 5000 were sticky solid (runs 1 and 4), while linear poly(ϵ-CL) with the M_n's in this range was white powder.[10] The star polymers with the M_n's higher than 5000 were white powder (runs 2, 3, 5, and 6).

Degrees of branching of star polymers can be estimated by comparing the mean-square radii with those of linear polymers. The following equation provides a mean-square radius (g) of a star polymer with the number of arms (f).[11]

$$g = 6f/[(f + 1)(f + 2)]$$

where f represents the number of arms.

The viscosity ratio of star and linear polymers (g') can be calculated by comparing the molecular weights (M) and viscosities ($[\eta]$) of linear and star polymers as follows.

$$g' = [\eta]_{\text{star}}/[\eta]_{\text{linear}} = K_{\text{star}}M^a_{\text{star}}/K_{\text{linear}}M^a_{\text{linear}}$$

where K and a represent Mark–Houwink constants.

In this work, we obtained g' from the ratio of the viscosities of star and linear poly(ϵ-CL)s determined by SEC equipped with viscometer and light scattering detectors. Linear poly(ϵ-CL)s with the M_n's (M_w/M_n's) of 1600 (1.30), 5300 (1.14), 12 700 (1.25), and 24 500 (1.15) were prepared by the polymerization with the 1-butanol/HCl·Et_2O initiator system according to the previously reported method.[10] It is possible to estimate the degree of branching by comparing the ratio between $g^{1/2}$ and g'. Table 2 also summarizes the $g^{1/2}/g'$ of three- and four-armed star-shaped pol(ϵ-CL)s. The good agree-

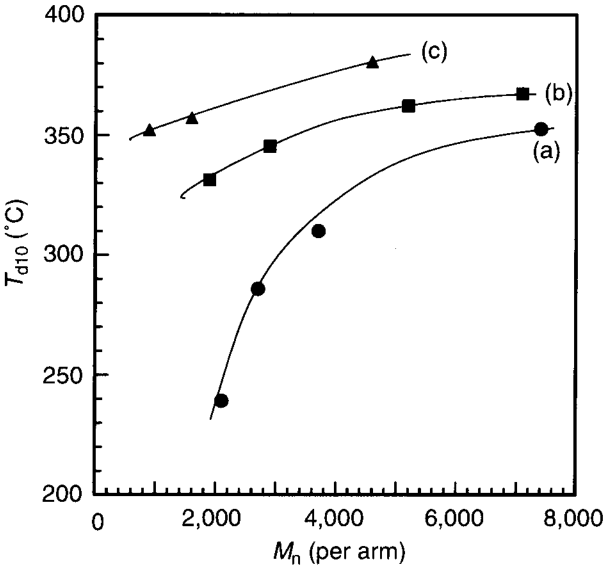

Figure 2. Dependence of T_{d10} of poly(ϵ-CL) on the M_n: (a) linear poly(ϵ-CL), (b) three-armed star-shaped poly(ϵ-CL), and (c) four-armed star-shaped poly(ϵ-CL).

ment between $g^{1/2}$ and g' suggested that the star polymers contained small arm defects.

Figure 1 shows the DSC traces of three- and four-armed star-shaped poly(ϵ-CL)s along with linear poly(ϵ-CL), which were synthesized by polymerization of ϵ-CL with trimethylolpropane, pentaerythritol, and 1-butanol as the initiator. Comparing the T_m's among the polymers with similar molecular weights, the order of T_m's was as follows: linear polymer > three-armed polymer > four-armed polymer (Figure 1A). On the other hand, the polymers with similar arm length showed T_m's similar to each other, irrespective of the arm numbers (Figure 1B). It is concluded that the arm length affects the T_m rather than total molecular weight. This results reasonably explain the difference of polymer forms according to the molecular weights and arm numbers as described above.

Figure 2 depicts the relationships between the M_n per arm and T_{d10} of linear and three- and four-armed star polymers. The T_{d10} increased according to the M_n per arm. Comparing the T_{d10}'s for the polymers with similar molecular weights, the order was as follows: four-armed polymer > three-armed polymer > linear polymer. The increase of thermal stability may be explained by the mobility of the arms.

In summary, we disclosed the synthesis of three- and four-armed star-shaped poly(ϵ-CL)s with controlled molecular weights and branched structures by ring-opening polymerization of ϵ-CL with trimethylolpropane and pentaerythritol as the initiators, using fumaric acid as the activator. The star polymers showed T_m in accordance of the arm length and the T_{d10} higher than linear polymers. The star-shaped poly(ϵ-CL)s synthesized by the metal-free polymerization system are expected as biocompatibe/biodegradable polyesters for biomedical and pharmacological materials.

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