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Tri-Armed Star Polymers by Living Cationic Polymerization. 1. Trifunctional Initiators for Living Polymerization of Isobutyl Vinyl Ether

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ABSTRACT: Tri-armed star polymers of isobutyl vinyl ether (IBVE) were synthesized by living cationic polymerization with a mixture of $EtAlCl_2$ and a trifunctional initiator $[CH_3C(C_6H_4OCH_2CH_2OCH(CH_3)OCOCF_3)_3$ (1) or $C_6H_3(COOCH_2CH_2OCH(CH_3)OCOCF_3)_3$ (2)] at 0 °C in the presence of 1,4-dioxane (an added base for carbocation stabilization). The tris(trifluoroacetate)-type initiators, 1 and 2, were obtained from the corresponding trifunctional vinyl ethers. The number-average molecular weights ($\bar{M}_n$) of the polymers thus prepared increased in direct proportion to monomer conversion and were close to the calculated values, assuming that each molecule of 1 or 2 produces one living chain; the molecular weight distribution (MWD) was very narrow ($\bar{M}_w/\bar{M}_n < 1.1$) throughout the polymerizations. The generation of three living ends per molecule of 1 or 2 was confirmed by comparing the polymerization with that by its monofunctional analogue $[C_6H_5OCH_2CH_2OCH(CH_3)OCOCF_3$ (3) or $C_6H_5COOCH_2CH_2OCH(CH_3)OCOCF_3$ (4), respectively], as well as by end-capping analysis with sodiomalonic ester. When the ester-type core of the poly(IBVE) obtained by 2 was hydrolyzed under alkaline conditions, the $\bar{M}_n$ was reduced to one-third with the narrow MWD unchanged, thus indicating that the polymer possesses exactly three arm chains with a uniform and controlled length.

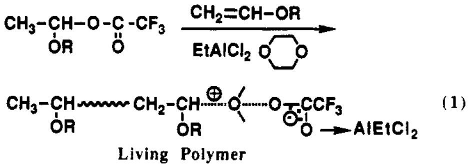
Introduction

Tri-armed star polymers are among advanced polymer materials that may find uses, for example, as cross-linking agents, ionomers, surface active agents, compatibilizers, and prepolymers for elastomer. For their usefulness and versatility, they should satisfy at least two criteria: (i) perfect end functionality (exactly three living ends per polymer molecule) and (ii) controlled molecular weight and narrow molecular weight distribution (MWD) of each arm chain. These criteria may be achieved most readily by living polymerization with a trifunctional initiator.

We have recently found living cationic polymerizations of vinyl ethers and styrene derivatives.[2] However, most of them are based on monofunctional initiators. Some trifunctional initiators have been developed by Kennedy et al., who obtained three-armed star polyisobutylenes via the inifer method[3] and living cationic polymerization.[4–8] However, these methods have been limited to nonpolar hydrocarbon monomers (isobutylene, etc.), and tri-armed polymers with functional pendant groups have not been obtained yet. In addition, all but one[9] study have given no direct proof for the attachment of exactly three arms to a single core entity, as well as for their uniformity in length.

A series of these studies are concerned with the synthesis of tri-armed star polymers with controlled molecular weight, low polydispersity, and controlled arm lengths, via living cationic polymerization of vinyl ethers and related monomers initiated by new trifunctional initiators. Another important objective is the synthesis of tri-armed star polymers with functional pendant groups, particularly from vinyl ethers, to which a variety of polar functions can readily be introduced without adversely affecting their living cationic polymerization.[10,11]

As reported previously,[12] living cationic polymerization of vinyl ethers may be initiated with a carboxylate adduct in conjunction with ethylaluminum dichloride ($EtAlCl_2$) and an excess amount of weak Lewis base (eq 1). The adduct is obtained from a vinyl ether and CF_3COOH, and its trifluoroacetate group initiates cationic polymerization of vinyl ethers with $EtAlCl_2$, in the presence of such a weak Lewis base as 1,4-dioxane, and generates living polymer, where the growing carbocation is stabilized by the added base.



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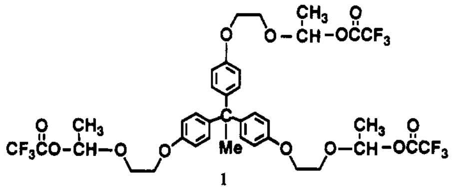
Based on this methodology, this first study of our series employs trifunctional compounds 1 and 2, which were prepared from CF_3COOH and trifunctional vinyl ethers (6 and 8, respectively), as trifunctional initiators for living cationic polymerization of isobutyl vinyl ether (IBVE) (see below). For comparison, monofunctional counterparts, 3 and 4, were also employed for 1 and 2, respectively. The primary object of the present study was to verify the feasibility of this method for the synthesis of tri-armed star polymers with well-defined structures and uniform chain length.



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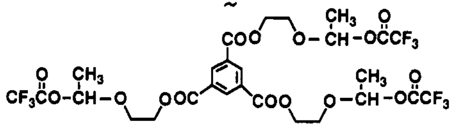

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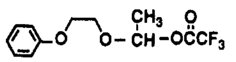

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Results and Discussion

1. Synthesis of Trifunctional Initiators. Initiators 1 and 2 are both trifunctional trifluoroacetates, but they

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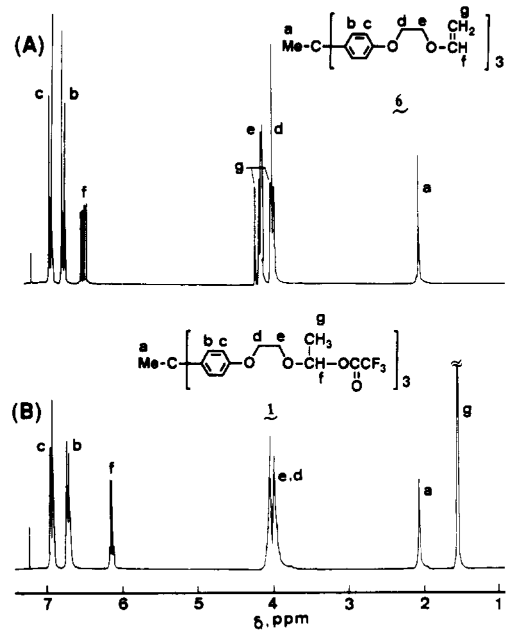


Figure 1. ^{1}H NMR spectra (270 MHz, $CDCl_3$) of (A) trivinyl ether 6 and (B) its trifluoroacetate form 1.

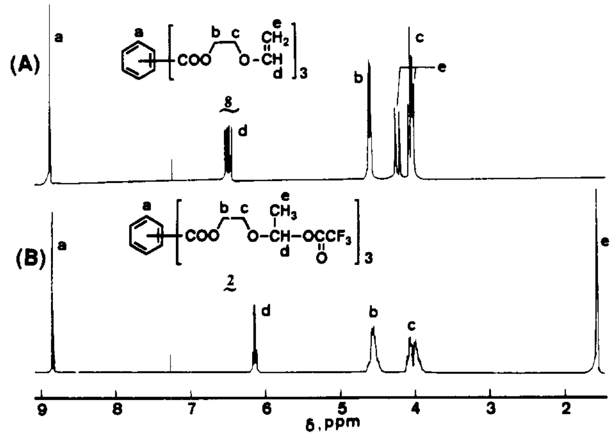
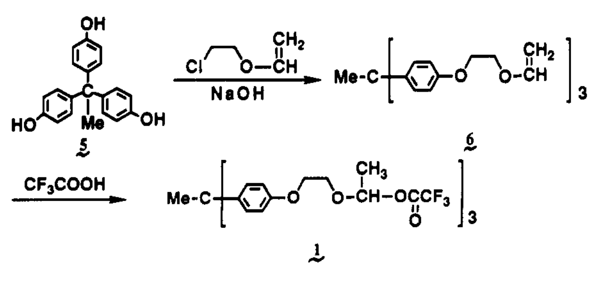


Figure 2. ^{1}H NMR spectra (270 MHz, $CDCl_3$) of (A) trivinyl ether 8 and (B) its trifluoroacetate form 2.

differ in the core structure; namely, in 1, three ester functions are connected to the aromatic core via chemically stable ether bonds, whereas in 2 the connections are via hydrolyzable ester linkage.

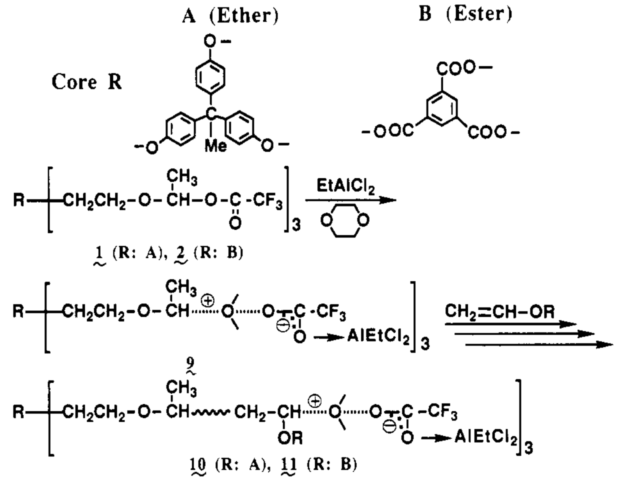
These initiators (1 and 2) were synthesized by the routes shown in eqs 2 and 3, respectively. For example, trifunctional vinyl ether 6 was prepared by the reaction of 2-chloroethyl vinyl ether with the sodium salt of 1,1,1-tris(hydroxyphenyl)ethane (5) (eq 2). Subsequent treatment of 6 with 3 equiv of CF_3COOH in CCl_4 at room temperature under dry nitrogen led to triester 1 (see Experimental Section). The ^{1}H NMR spectra of 6 and 1 are shown in Figure 1, along with peak assignments.



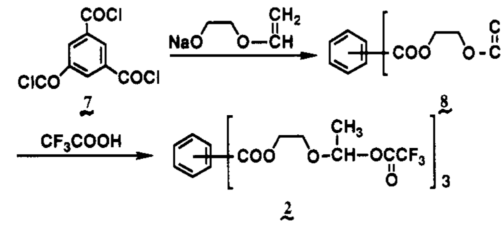
(2)

The addition of CF_3COOH into a solution of 6 in CCl_4 caused the disappearance of the vinyl protons (Figure 1A, peaks f and g) and in turn the appearance of a quartet and a doublet (Figure 1B, peaks f and g, respectively). The quartet is assignable to the $CHOCOCF_3$ group; the doublet is due to the methyl protons adjacent to the ester group. Signals of other products were absent. These NMR spectral data thus show the quantitative formation of trifunctional initiator 1.

Scheme I



Similarly, as illustrated in eq 3, the ester-core type trifunctional initiator 2 was obtained by the addition of CF_3COOH to the corresponding trifunctional vinyl ether (8), which was prepared by the reaction of trimesic chloride (7) with the sodium salt of 2-hydroxyethyl vinyl ether (see Experimental Section). The ^{1}H NMR spectra of 8 and 2 are shown in Figure 2, which also shows the quantitative formation of 2.



(3)

The solutions of the initiators 1 and 2 were directly employed without isolation for subsequent living polymerization.

2. Living Cationic Polymerization. Tri-armed star polymers were prepared via the general route illustrated in Scheme I, where the ether and ester cores of 1 and 2 are designated A and B, respectively. Thus, IBVE was polymerized in n-hexane at 0 °C by 1 or 2, coupled with $EtAlCl_2$ in the presence of 1,4-dioxane (10 vol % to the solvent). The polymerizations by 1 and 2 were first compared with those by the corresponding monofunctional analogues 3 and 4, respectively.

2.1. Polymerization Rate. Figure 3 shows the time-conversion curves obtained with the two pairs of trifunctional and monofunctional initiators (Figure 3A for 1 and 3; Figure 3B for 2 and 4). When each of 1–4 alone was added to a monomer solution in the presence of 1,4-dioxane, virtually no polymer was formed in several hours, but the addition of $EtAlCl_2$ to this quiescent mixture effected a rapid polymerization that proceeded quantitatively without an induction phase. When the initial concentrations of the trifluoroacetate functions (potential growing sites) were kept the same for the tri- and monofunctional initiators (10 mM; i.e., $[1]_0 = 3.5$ mM and $[3]_0 = 10$ mM; $[EtAlCl_2]_0 = 10$ mM), the polymerization

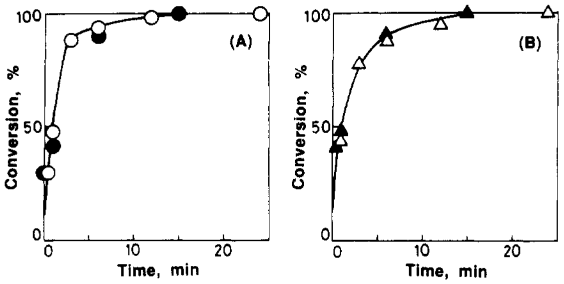


Figure 3. Time–conversion curves for the polymerization of IBVE with (A) 1 and 3 or (B) 2 and 4 coupled with $EtAlCl_2$ in *n*-hexane at 0 °C ($[M]_0$ = 0.76 M, $[EtAlCl_2]_0$ = 10 mM, [1,4-dioxane] = 1.2 M). Initiator: (○) 1, 3.5 mM; (●) 3, 10 mM; (△) 2, 3.5 mM; (▲) 4, 10 mM.

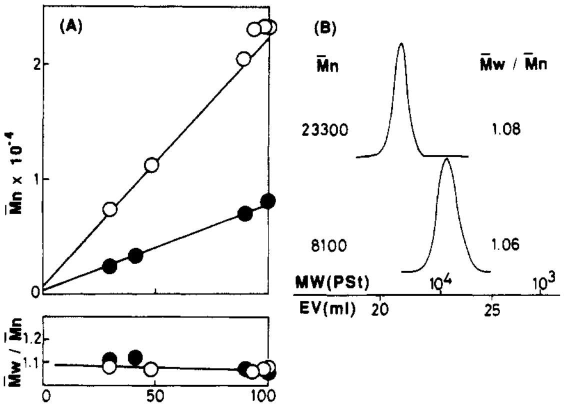


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(IBVE) obtained with (A) 1/$EtAlCl_2$ (○) and (B) 3/$EtAlCl_2$ (●) in *n*-hexane at 0 °C (the same experiments as for Figure 3A). The intercepts in the $\bar{M}_n$–conversion plots show the molecular weights of the initiators (1 and 3).

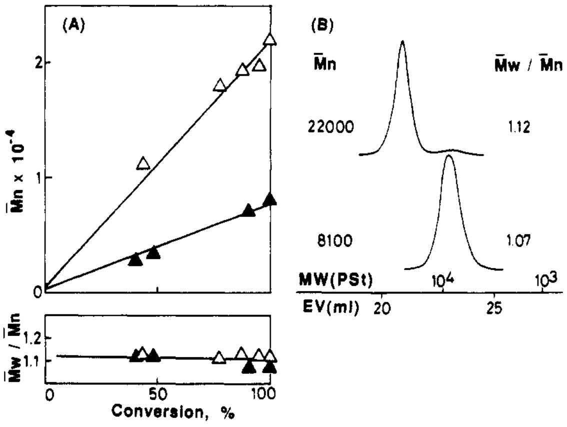
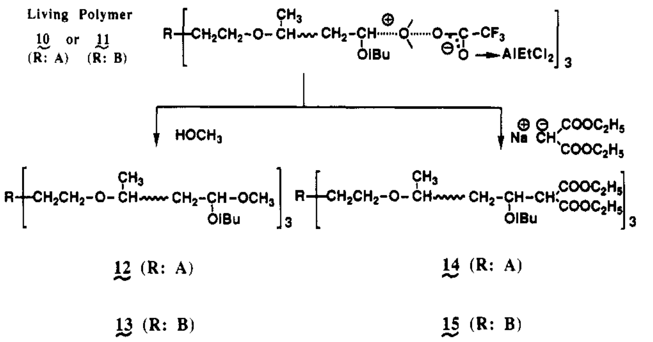


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of poly(IBVE) obtained with (A) 2/$EtAlCl_2$ (△) and (B) 4/$EtAlCl_2$ (▲) in *n*-hexane at 0 °C (the same experiments as for Figure 3B). The intercepts in the $\bar{M}_n$–conversion plots show the molecular weights of the initiators (2 and 4).

rates with both initiating systems were in good agreement with each other (Figure 3A). Essentially the same results were obtained for the 2/$EtAlCl_2$ (3.5/10 mM) and 4/$EtAlCl_2$ (10/10 mM) initiating systems (Figure 3B). Therefore, each trifluoroacetate group of 1 and 2 can independently initiate IBVE polymerization in the presence of $EtAlCl_2$, and 1 or 2 gives the growing site at a concentration 3 times that from its monofunctional counterpart (3 or 4, respectively).

2.2. Polymer Molecular Weight and MWD. Figures 4 and 5 illustrate the number-average molecular weight ($\bar{M}_n$), polydispersity ratio ($\bar{M}_w/\bar{M}_n$), and MWD of the polymers obtained in the experiments shown in Figure 3.

Scheme II[a]



[a] See Scheme I for the core structures A and B.

Regardless of the core structure (ether vs ester) and functionality (tri- vs monofunctional), all four initiating systems led to living polymers, as shown by the linear increases in $\bar{M}_n$ against conversion (Figures 4A and 5A) as well as very narrow MWDs ($\bar{M}_w/\bar{M}_n$ < 1.1; Figures 4B and 5B) (for the small peaks seen in the low molecular weight region, see ref 13). However, the $\bar{M}_n$ values for the trifunctional initiators 1 and 2, though based on a polystyrene calibration, were nearly 3 times those for the monofunctional counterparts 3 and 4, respectively. These facts show that trifunctional initiators 1 and 2 generate three living sites per molecule as in 10 and 11 (Scheme I), respectively. In addition to these MWD and relative $\bar{M}_n$ analyses by size exclusion chromatography, the living nature of the polymerization with 1 or 2 was confirmed by determination of absolute $\bar{M}_n$ and end functionality by ^1H NMR spectroscopy (see below).

The living polymers (10 and 11, Scheme I) were able to initiate polymerization again, when additional feeds of IBVE were added to reaction mixtures in which the first IBVE doses had completely been polymerized. During such "monomer addition" experiments in *n*-hexane at 0 °C, the $\bar{M}_n$ values increased in direct proportion to conversion and reached as high as 150 000 after the third monomer addition.

2.3. End-Capping Analysis. To confirm the quantitative formation of tri-armed polymers, the living polymers (10 and 11) obtained with trifunctional initiators 1 and 2 were terminated with methanol or a solution of sodiomalonic ester (Scheme II), which are known to react, quantitatively and cleanly, with the living end to give methoxy- (12 and 13) and malonate-capped poly(IBVE) (14 and 15).[14] The quenching reactions with both quenchers proceeded rapidly and quantitatively.

Figure 6 illustrates the ^1H NMR spectra of the products obtained from living polymer 10 with 1/$EtAlCl_2$ in *n*-hexane at 0 °C. The sample quenched with methanol (Figure 6A) shows all key absorptions of the poly(IBVE) main chain (g–k), the ether-type core A arising from initiator 1 (a–f), and the terminal acetal groups (m and n), all of which confirm the structure expected for polymer 12. Similarly, Figure 6B for the malonate-capped sample is fully consistent with structure 14, as evidenced by signals for the main chain (g–k), the ether core A (a–f), and the terminal malonate group (m and n).

The number-average end functionality ($\bar{F}_n$) of the terminal acetal for 12 and the malonate groups for 14 was determined from the ratios of the integrated ^1H NMR peak areas: m/a, m/b, m/c, and m/f (m for the acetal end or for the malonate end; a–c and f are the peaks arising from core A; see Figure 6). As shown in Table I, all $\bar{F}_n$ values, determined from various key peaks independent of each other, are close to three, indicating the existence

Table I
Synthesis of End Functional Tri-Armed Star Poly(IBVE)[a]

	structure					$\bar{F}_n$[e]			
compd	core	terminal	$\overline{DP}_n$[b] (calcd)	$\bar{M}_w/\bar{M}_n$[c]	$\overline{DP}_n$[d] (obsd)	m/a	m/b	m/c	m/f
12	A	OCH_3	64.5	1.08	62.1	3.03	2.90	2.92	2.90
14	A	$CH(COOEt)_2$	87.3	1.08	84.9	3.09	3.04	2.98	
13	B	OCH_3	94.9	1.13	92.7		3.03	2.98	2.97
15	B	$CH(COOEt)_2$	39.1	1.12	38.1		3.01	2.96	

[a] Polymerizations were carried out in n-hexane at 0 °C. Initiator: 1 for 12 and 14; 2 for 13 and 15; $[\text{initiator}]_0/[EtAlCl_2]_0 = 3.5/10$ mM. [b] $\overline{DP}_n$ (calcd) = ($[IBVE]_0/[2]_0$) × conversion. [c] Measured by SEC. [d] Determined by ^1H NMR (270 MHz, $CDCl_3$), from the peak ratio k/m (see Figures 6 and 7). [e] Number-average end functionality, determined from the ^1H NMR intensity ratios of the indicated peaks; see Figures 6 and 7 for spectra.

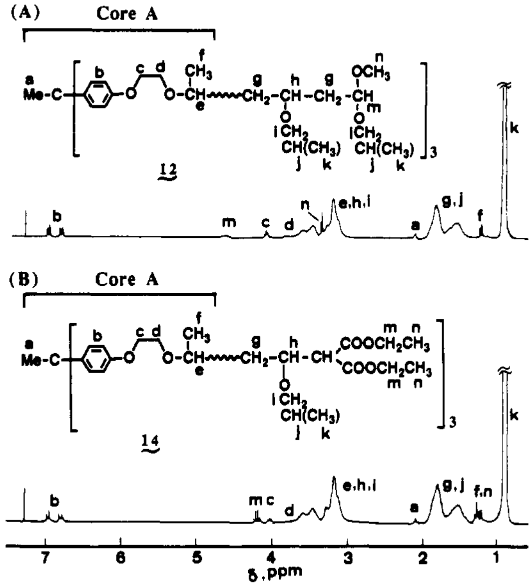


Figure 6. ^1H NMR spectra (270 MHz, $CDCl_3$) of tri-armed star poly(IBVE): (A) 12, methoxy-capped; (B) 14, malonate-capped.

of three terminals per polymer molecules in both 12 and 14 or three living ends per molecule for 10.

Moreover, separate experiments showed the terminal malonic ester of polymer 14 to be quantitatively and cleanly converted into the corresponding carboxyl group [$\sim CH_2CH(OiBu)CH_2COOH$] by the alkaline hydrolysis followed by thermal decarboxylation to give a tris(carboxy-capped) tri-armed star poly(IBVE).[14a]

Very similar results were obtained for the samples that were prepared by quenching the living polymer 11 (with the ester-type core B; Scheme II). The ^1H NMR spectra (Figure 7A,B) of the products again verified the methoxy- (13) and the malonate-capped (15) terminals as well as the overall tri-armed structure. All $\bar{F}_n$ values are also close to three for both methoxy and malonate terminals (Table I), which shows the trifunctional living ends to be present in each molecule of 11.

2.4. Ester-Core Hydrolysis: Uniformity of Three Arm Chains. Besides the existence of three living ends per molecule, the uniformity in length of the three arm chains is another important structural factor that should be verified for well-defined tri-armed polymers. To this end, the ester linkages of polymer 13 (capped with methanol), which connect the three arm chains to the aromatic core, were hydrolyzed under mild alkaline conditions, and then it would give three linear arm chains (Scheme III), from the analysis of which one would see whether or not the starting polymer 11 indeed carries three arms having uniform chain lengths. Figure 7C shows the ^1H NMR spectrum of the hydrolysis product (from the sample of 13 given in Figure 7A). Comparison between the spectra of parts A and C of Figure 7 shows the complete

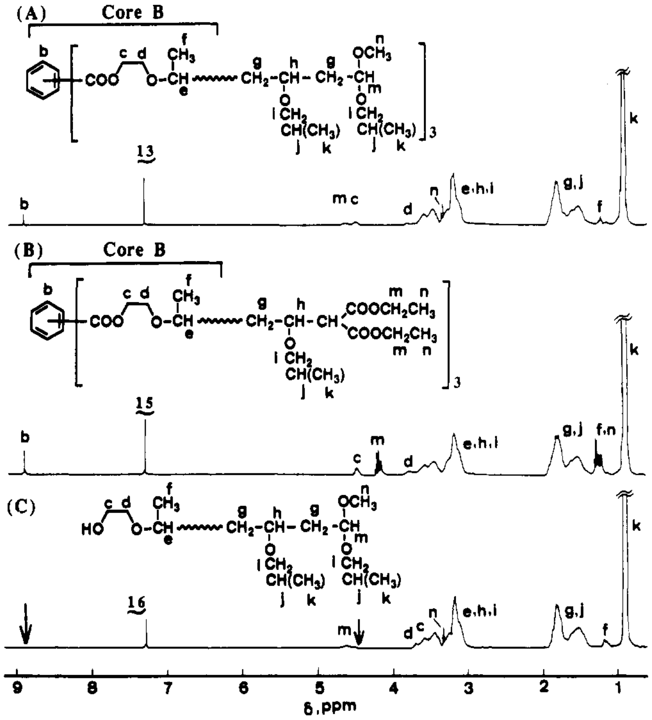
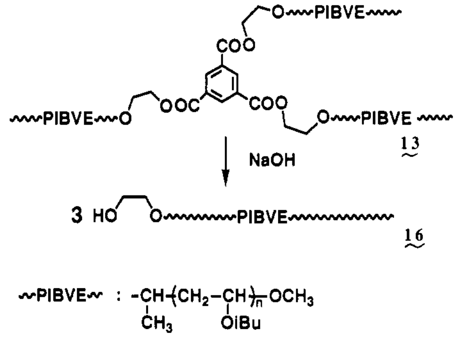


Figure 7. ^1H NMR spectra (270 MHz, $CDCl_3$) of tri-armed star poly(IBVE): (A) 13, methoxy-capped; (B) 15, malonate-capped; (C) 16, the hydrolysis product from 13 (sample A).

Scheme III



conversion of the tri-armed star polymer 13 into a linear arm polymer (16) that carries a hydroxyl terminal derived from the ester core. For instance, signals b and c in Figure 7A, due to the core B, are absent in Figure 7C.

The $\overline{DP}_n$ of this sample was determined from the pendant methyl/terminal methine (k/m) ratio, which was nearly one-third of the overall $\overline{DP}_n$ of the precursor (13); the relevant data are shown in Table II for two series of polymer samples.

Equally important, as shown in Figure 8, the MWD of these polymers (13 and 16) remained very narrow even after the core hydrolysis.[13] The peak positions, moreover,

Table II
Synthesis and Core Hydrolysis of Tri-Armed Star Poly(IBVE) 13

tri-armed star poly(IBVE) 13[a]				hydrolysis product 16[b]		
conv, %	$\overline{DP}_n$[c] (calcd)	$\bar{M}_w/\bar{M}_n$[d]	$\overline{DP}_n$[e] (obsd)	$\overline{DP}_n$ (calcd)	$\bar{M}_w/\bar{M}_n$[d]	$\overline{DP}_n$[e] (obsd)
44	94.9	1.13	92.7	31.6	1.14	30.0
100	217	1.12	209	72.4	1.10	71.0

[a] Polymerizations were carried out in *n*-hexane at 0 °C with 2/EtAlCl$_2$. [IBVE]$_0$ = 0.76 M; [2]$_0$ = 3.5 mM; [EtAlCl$_2$]$_0$/[2]$_0$ = 3; [1,4-dioxane] = 1.2 M; quenched with methanol. [b] With sodium hydroxide in ethanol at room temperature for 2 days; see Experimental Section for details. [c] $\overline{DP}_n$ (calcd) = ([IBVE]$_0$/[2]$_0$) × conversion. [d] From SEC, calibrated with standard polystyrene samples. [e] Determined by ^{1}H NMR (270 MHz, CDCl$_3$), from the peak ratio k/m (see Figure 7A,C).

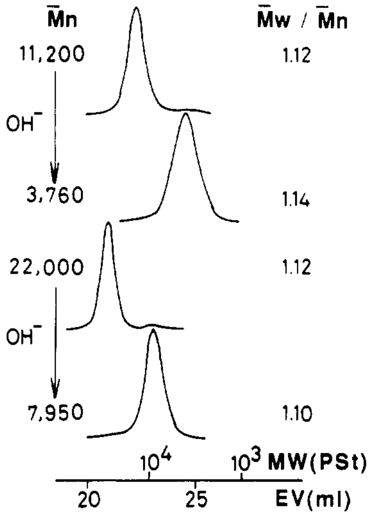


Figure 8. MWD of tri-armed star poly(IBVE) 13 and its hydrolysis product 16.

clearly shifted, in accordance with the expected molecular weight reduction; see also the relative $\bar{M}_n$ values that are reduced to one-third upon hydrolysis, through size exclusion chromatography and a polystyrene calibration.

Table II and Figures 6 and 7, therefore, give direct experimental evidence for the well-controlled tri-armed structure of polymer 11 (or 13), perhaps for the first time for such polymers; namely, 11 possesses exactly three arm chains with a uniform and controlled length ($\overline{DP}_n$) as well as with a very narrow, nearly monodisperse MWD. Such direct evidence could not be obtained for another polymer 10, whose ether-type core is chemically stable, but the same conclusion is most likely the case for 10 also, because initiator 1 (for 10) is less sterically crowded than 2 (for 11); thus, from the former an independent and undisturbed living propagation of the three active sites may be easier than from the latter.

Experimental Section

Synthesis of Tris(trifluoroacetate) Initiator 1 (Eq 2). In a 300-mL, three-necked, round-bottom flask fitted with a mechanical stirrer, a reflux condenser, and a dropping funnel were charged 1,1,1-tris(4-hydroxyphenyl)ethane (5) (Tokyo Kasei, purity 99%) (10.0 g, 32.6 mmol), powdered NaOH (23.5 g, 0.587 mol), and dimethyl sulfoxide (75 mL). After 30 min of stirring at room temperature, the reaction mixture was warmed to 70–75 °C in an oil bath, and stirring was continued for an additional 2.5 h. 2-Chloroethyl vinyl ether (59.7 mL, 0.587 mol) was then added slowly via the addition funnel at such a rate as to maintain the temperature below 80 °C. When the addition was complete in 1.5 h, the reaction mixture was kept at 75–80 °C with stirring for an additional 5 h, cooled to room temperature, and poured into 500 mL of water. The aqueous phase was extracted with three 50-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each), dried with sodium sulfate overnight, and evaporated under reduced pressure. The crude product (a yellowish powder) was recrystallized from a toluene/*n*-hexane mixture (1/1 v/v) to give 1,1,1-tris[4-((vinyloxy)ethoxy)phenyl]ethane (6) as a white powder: yield, 62% from 5; purity > 98% by ^{1}H NMR (Figure 1A); ^{13}C NMR (CDCl$_3$) δ 156.5 (aromatic carbon adjacent to the oxygen), 151.6 (=CH), 142.0 (aromatic carbon adjacent to the quaternary carbon), 129.5 and 113.7 (unsubstituted aromatic carbons), 86.9 (=CH$_2$), 66.3 (CH$_2$CH$_2$), 50.5 (quaternary carbon), 30.6 (CH$_3$).

Trivinyl ether 6 (1.72 g, 3.33 mmol) was dissolved in 15 mL of CCl$_4$ at room temperature under dry nitrogen in a baked round-bottom flask equipped with a three-way stopcock, and to this solution was added CF$_3$COOH (1.14 g, 0.770 mL, 10 mmol) with stirring via a syringe at such a rate as to keep the temperature below 40 °C. The reaction was completed (by ^{1}H NMR) within 15 min after the end of the acid addition. Quantitative formation of 1 was verified in situ by ^{1}H NMR (Figure 1B; see text). The solution was then sealed in brown ampules under dry nitrogen and stored in a freezer until employed.

Synthesis of Tris(trifluoroacetate) Initiator 2 (Eq 3). In a 200-mL three-necked, round-bottom flask fitted with a stirrer, a reflux condenser, and a dropping funnel were charged 2-hydroxyethyl vinyl ether (Nisso Maruzen Chemical, purity >99%, H$_2$O <1%) (9.96 g, 0.113 mol), sodium hydride (2.71 g, 0.113 mol), and toluene (50 mL); the sodium hydride (supplied commercially as an oil dispersion) was made free from mineral oil by washing with toluene just before use. The mixture was stirred at room temperature for 1 h, and trimesic chloride 7 (Aldrich, purity 98%) (10.0 g, 33.7 mmol, dissolved in 20 mL of DMF) was added dropwise through the dropping funnel. After the addition has been completed, tetra-*n*-butylammonium iodide (0.5 g) was added. The mixture was then warmed to 80 °C in 30 min in an oil bath, stirred at this temperature for 4 h, cooled to room temperature, and poured into 200 mL of water. The aqueous phase was extracted with three 50-mL portions of diethyl ether, and the ether extracts were combined with the organic layer. The combined organic phase was washed twice with water (100 mL each), dried with sodium sulfate overnight, and evaporated under reduced pressure. The crude product (a yellowish powder) was recrystallized twice from a toluene/*n*-hexane mixture (1/1 v/v) to give tris[2-(vinyloxy)ethyl] 1,3,5-benzenetricarboxylate (8) as a white powder: yield, 74% from 7; purity >98% by ^{1}H NMR (Figure 2A); ^{13}C NMR (CDCl$_3$) δ 164.7 (C=O), 151.4 (=CH), 134.9 and 131.0 (aromatic carbons), 87.2 (=CH$_2$), 65.5 and 63.8 (CH$_2$CH$_2$).

In a manner similar to those for 1, tris(trifluoroacetate) initiator 2 was prepared from trivinyl ether 8 and CF$_3$COOH (see above; see also Figure 2B).

Monofunctional Initiators 3 and 4. In a manner similar to those for 1 and 2, initiators 3 and 4 were prepared from 2-(phenoxy)ethyl and 2-(benzoyloxy)ethyl vinyl ethers, respectively, both of which were obtained by the reported methods.[15,16] ^{1}H NMR (CDCl$_3$): 3, δ 7.10 and 6.70 (5 H, aromatic carbon), 6.00 (q, 1 H, CH), 3.90 (m, 4 H, CH$_2$CH$_2$), 1.40 (d, 3 H, CH$_3$); 4, δ 8.05, 7.55 and 7.40 (5 H, aromatic proton), 6.10 (q, H, CH), 4.45 and 4.00 (m, 4 H, CH$_2$CH$_2$), 1.55 (d, 3 H, CH$_3$).

Other Materials. Commercial IBVE was washed with an aqueous alkali solution and then with water, dried (KOH pellets), and distilled twice over calcium hydride before use. Commercial EtAlCl$_2$ (Kanto Chemicals, 1.0 M *n*-hexane solution) and CF$_3$COOH (Nakarai Chemicals, purity >99%, supplied in sealed ampules) were used under dry nitrogen without further purification. *n*-Hexane (polymerization solvent), 1,4-dioxane (added base), and *n*-heptane (internal standard for gas chromatography) were purified by the usual methods[16] and distilled twice over calcium hydride just before use. Sodiomalonic ester was prepared as reported.[14a]

Procedures. IBVE was polymerized with the 1 (or 2)/EtAlCl$_2$ initiating system at 0 °C in the presence of 1,4-dioxane (10 vol %) under dry nitrogen in baked glass tubes, each equipped with a three-way stopcock. The reactions were initiated by adding, sequentially, prechilled solutions of initiator 1 (or 2) and EtAlCl$_2$

(in toluene and *n*-hexane, respectively; 0.50 mL each) to a monomer solution (in *n*-hexane; 4.0 mL). After a predetermined period, the polymerization was terminated with prechilled methanol containing ammonia or with the solution of sodiomalonic ester (2.5 mL). The quenched reaction mixtures were washed sequentially with 10 vol % aqueous hydrochloric acid and then with water to remove the aluminum-containing residues, evaporated to dryness under reduced pressure, and vacuum-dried overnight to give the product polymers.

IBVE conversion was measured by gravimetry of the product polymers or for some runs by gas chromatography with *n*-heptane as an internal standard (2.5 or 5.0 vol %).

Hydrolysis of 13. A sample of tri-armed star poly(IBVE) **13** (0.1 g) was dissolved in ethanol (10 mL), and 5 N NaOH (50 equiv to the COOEt units in the polymer) was added. The mixture was magnetically stirred for 3 h, water (10 mL) was added, and stirring was continued for an additional 2 days. The product, **16**, was extracted with diethyl ether, washed with water, and then isolated by evaporation followed by vacuum-drying.

Polymer Characterization. The MWD of the products was determined by size exclusion chromatography in chloroform at room temperature on a Jasco Trirotar chromatograph equipped with three polystyrene gel columns (Shodex K-802, K-803, and K-804; 8.0 mm i.d. × 300 mm each) and refractive index/ultraviolet dual detectors. The number-average molecular weight ($\bar{M}_n$) and polydispersity ratio ($\bar{M}_w/\bar{M}_n$) were calculated from size exclusion eluograms on the basis of a polystyrene calibration. ^{1}H and ^{13}C NMR spectra (270 and 67.5 MHz, respectively) were recorded at 22 °C on a JEOL GSX-270 spectrometer in $CDCl_3$.

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References and Notes

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(13) The small peaks seen in the low molecular weight region in Figures 5B and 8 for the tri-armed polymers are probably due to monofunctional (living) polymers that might have been initiated by a protonic source (most likely a trace of free CF_3COOH coming from the preparation of 1 or 2). The reasons are as follows: (a) the absence of UV absorption; thus, this fraction is not derived from an incomplete initiation from the trifunctional initiator; (b) its formation from the beginning of the polymerization; thus, it is not due to chain transfer or termination; (c) the molecular weight ($\bar{M}_n$), which is one-third that of the trifunctional polymer and directly proportional to conversion.

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