Grafting of a Bicyclo Ortho Ester onto Polystyrenes Having Quaternary Ammonium Salt Moieties

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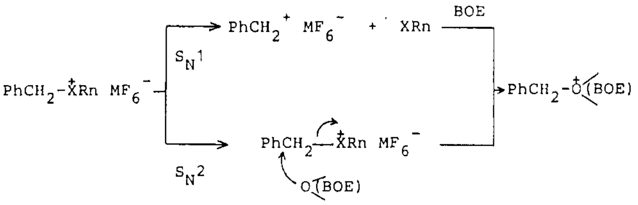
ABSTRACT: Two vinyl monomers having ammonium salt structures, *N*-(*p*-vinylbenzyl)-*N*-methylpyrrolidinium hexafluoroantimonate (**2**) and *N*-(*p*-vinylbenzyl)-*p*-cyanopyridinium hexafluoroantimonate (**3**), were synthesized. The polymers obtained by homopolymerization of **2** and **3** initiated the cationic polymerization of a bicyclo ortho ester with heating to around 120 °C to yield the grafted polymers. The copolymer of **3** with styrene (**6**) catalyzed similarly the polymerization to form the corresponding grafted polymer. The activity of the copolymer **6** as the cationic initiator in the polymerization of the bicyclo ortho ester was higher than that of the homopolymer of **3** but lower than that of the monomeric one, *N*-benzyl-*p*-cyanopyridinium hexafluoroantimonate (**1**), at the latter half of the polymerization. A new styrene monomer containing bicyclo ortho ester moiety **9**, 1-ethyl-4-[((*p*-vinylbenzyl)oxy)methyl]-2,6,7-trioxabicyclo[2.2.2]octane, was also prepared by the reaction of 1-ethyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane with *p*-(chloromethyl)styrene. The copolymerization of **2** with **9** proceeded to give only vinyl copolymer, which was self-cured by heating at 120 °C with 3–5% expansion in volume.

Introduction

In ionic polymerizations and cross-linking reactions, catalysts that function as initiators solely by heating or photoirradiation are useful as latent catalysts. We have already presented our works on exploration of such catalyst, in which benzyl dialkylsulfonium salts have been shown to be highly effective thermally latent catalysts in the cationic polymerizations of cyclic ethers and their derivatives, i.e., spiro ortho carbonates,[1] bicyclo ortho ester,[2] and epoxy resins.[3] Recently, we have extended our study on the thermally latent catalysts to quaternary ammonium salts, i.e., benzyl trialkylammonium and benzyl pyridinium salts. Surprisingly, they have been also available as thermal initiators for the cationic polymerization of a bicyclo ortho ester (BOE).[4] This is very attractive since these quaternary ammonium salts are easy to synthesize and to handle, and further it is feasible to design a variety of ammonium salts.

On the other hand, in view of the initiation step of the polymerization, these onium salts are believed to generate benzyl cation via an S_N1 process or be attacked by monomer via an S_N2 process.



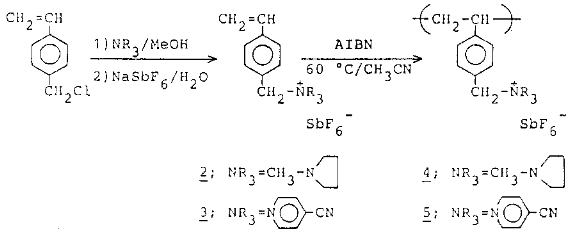
If this is true, graft copolymerization is possible when the polymer-supported onium salts are employed. In fact, the polymerization of BOE with a polymer containing benzyl-type sulfonium salt moieties was carried out, and the corresponding graft copolymer was prepared in high yield.[5]

Herein, this paper describes the grafting of 1-phenyl-4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE) onto polymers bearing quaternary ammonium salt structures.

Results and Discussion

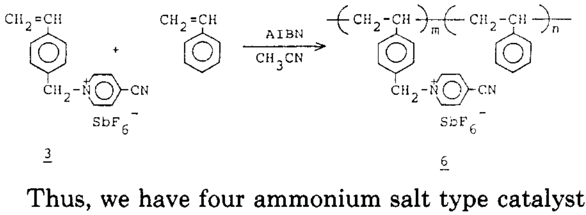
Synthesis and Polymerization of *p*-Vinylbenzylammonium Salts. *N*-Methyl-*N*-(*p*-vinylbenzyl)pyrrolidinium hexafluoroantimonate (**2**) and *N*-(*p*-vinylbenzyl)-*p*-cyanopyridinium hexafluoroantimonate (**3**) were selected as readily polymerizable monomers with quaternary ammonium salt structures. Hexafluoroantimonate anion, SbF_6^-, was selected as a suitable counteranion in light of the reported data indicating that SbF_6^- is the best one of all nonnucleophilic anions examined in the cationic polymerization of cyclic ethers and their derivatives with sulfonium salts.[1,2,6]

The monomer **2** was synthesized by the quaternization of *N*-methylpyrrolidine with (*p*-chloromethyl)styrene in methanol at room temperature for 3 days followed by anion exchange with $NaSbF_6$ in water in 75% yield (eq 1). Meanwhile, the pyridinium salt **3** was obtained only in very low yield by the same way, doubtless because nucleophilicity of cyanopyridine is relatively lower than that of *N*-methylpyrrolidine since generally such anion exchange is a fast and high yield process (more than 80%).[4] Therefore, the quaternization reaction was conducted at higher temperature (in refluxing methanol), and **3** was formed in 38% yield.



(1)

Polymerizations of **2** and **3** were performed at 60 °C in acetonitrile using azobisisobutyronitrile (AIBN) to obtain corresponding polymers **4** and **5**, respectively. In addition to these homopolymers, copolymer **6** of **3** with styrene was also prepared to compare its catalytic activity with those of the other pyridinium salts (eq 2, *m*:*n* = 42:58).



(2)

Thus, we have four ammonium salt type catalysts involving *N*-benzyl-*p*-cyanopyridinium salt, **1**, a simple monomeric ammonium salt.

Graft Copolymerization of BOE onto Polystyrene Backbone. All these polymer-supported ammonium salts were insoluble in common organic solvents used generally in cationic polymerization such as benzene, methylene dichloride, ethylene dichloride, etc., but soluble in polar

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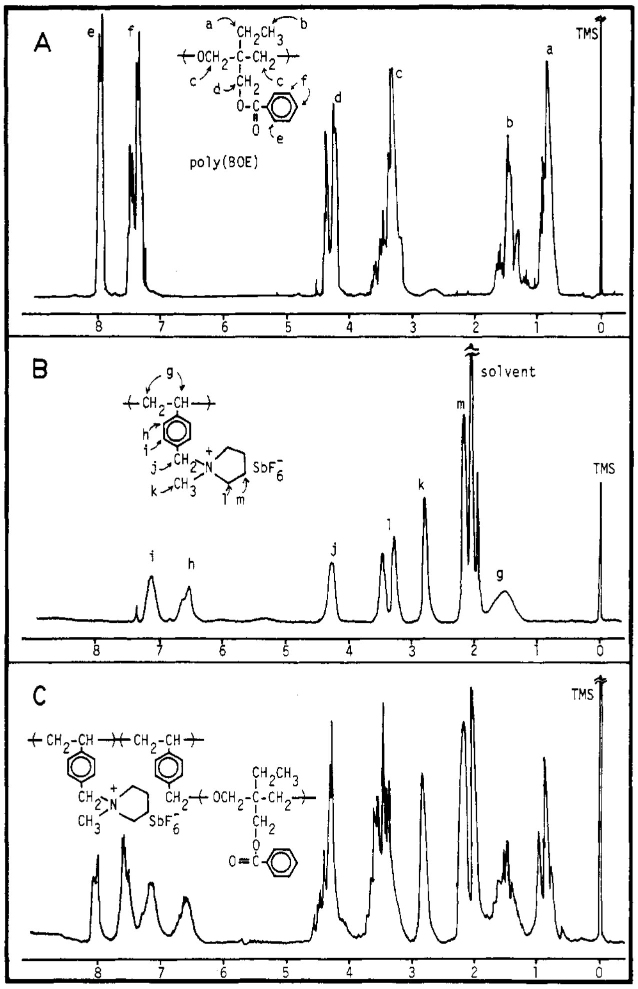
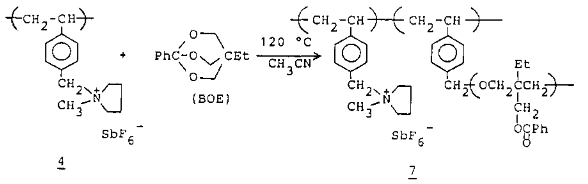


Figure 1. FT ^{1}H NMR spectra (270 MHz) of polymers: A, poly(BOE) (60 °C, $CDCl_3$); B, homopolymer **4** (70 °C, CD_3CN); C, graft copolymer **8** (70 °C, CD_3CN).

solvents such as acetonitrile, dimethylformamide (DMF), etc. Therefore, the graft copolymerization by polymer-supported ammonium salts (**4**, **5**, and **6**) were carried out in acetonitrile, although acetonitrile is not a normal solvent for cationic polymerization. The graft polymerization of BOE with polymer **4** (10 mol % for BOE) was attempted at 120 °C for 72 h in acetonitrile. The reaction mixture was poured into methanol to give grafted polymer **7** (degree of grafting, 31%). The IR spectrum of the obtained polymer showed three strong absorption bands at 1720, 1110, and 660 cm^{-1} attributable to C=O, C-O-C, and Sb-F, respectively. the ^{1}H NMR spectrum of the obtained polymer (Figure 1C) in deuterioacetonitrile strongly supported the graft polymer structure **9**, which consisted of all components of both ^{1}H NMR spectra of the parent polymer **4** (Figure 1B) and homopoly(BOE) (Figure 1A). The ^{13}C NMR spectrum of **7** was also consistent with its structure, showing that the signal at 166.3 ppm corresponding to the ester carbonyl carbon probably was due to the ring-opening transfer polymerization of BOE. These spectral data suggested formation of the grafted copolymer **7**, which still retained part of the ammonium salt moiety (eq 3).



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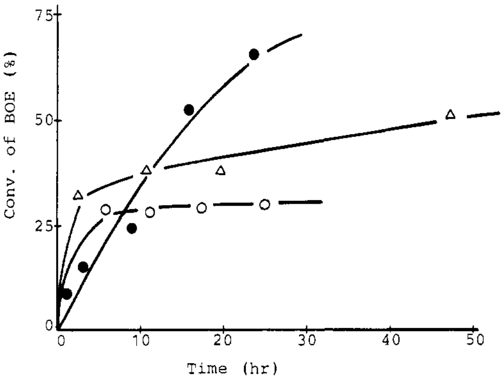


Figure 2. Time-conversion curves of the polymerizations of BOE with a few pyridinium salts at 120 °C in acetonitrile. Initiator (a pyridinium salt): 2 mol % for BOE. [BOE] = 2.5 M. (●) **1**; (○) **5**; (△) **6**.

The graft copolymerization of BOE with **5** was similarly carried out at 120 °C for 24 h. The polymer obtained was insoluble in common organic solvents, including acetonitrile. However, the IR spectrum of the polymer clearly indicated the grafting of BOE onto the polystyrene backbone of **5** (see Experimental Section). In this case the degree of grafting was 22%.

Time conversions of the polymerizations of BOE with **1**, **5**, and **6** were examined by ^{1}H NMR, and the results are shown in Figure 2. In the polymerizations with **5** and **6**, initial rapid stages (faster than that of **1**) were followed by subsequent slow stages. As a result, the conversion of BOE did not reach 50%, and the catalyst activity follows the order **1** > **6** > **5**. From these results, it is conceivable that the polymer-supported ammonium salts (**5** and **6**) might maintain higher catalytic activity, perhaps due to electrostatic repulsion between adjacent salts to facilitate the elimination of amine, but termination reactions would be rapid because propagating reactions by attack of BOE monomer may be suppressed owing to steric hindrance of the polymer backbone.

Thus, it was found that the polymer-supported ammonium salts can be grafted with BOE only by heating around 120 °C although their catalytic activity is rather low. The results mentioned above suggest that, in this case, the grafting is believed to be initiated apparently by polymer-linked benzylic cation liberated from the ammonium salt moiety supported in the side chain.

In order to more convincingly determine the occurrence of the graft copolymerization, we studied the polymerization of BOE using a cross-linked polymer containing ammonium salt moieties. The cross-linked polymer, **8**, was prepared by the copolymerization of styryl-type pyridinium salt **3**, styrene, and divinylbenzene (mole ratio 50:50:4) in the presence of AIBN (3 mol %) at 60 °C for 24 h.

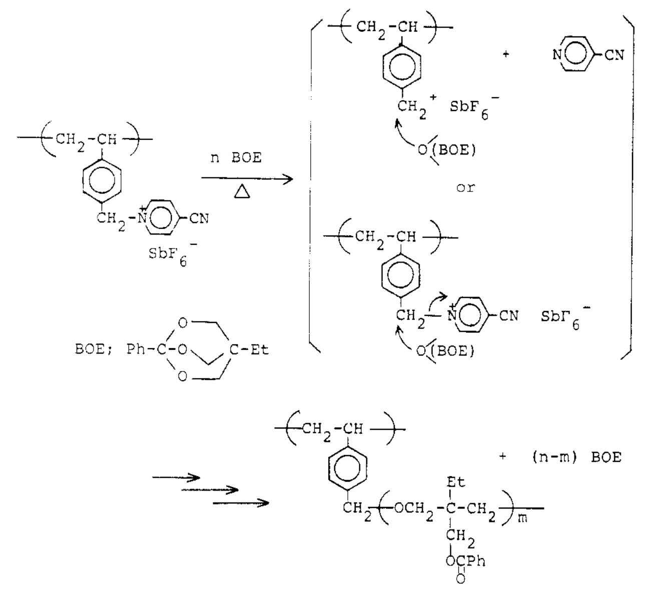
The graft copolymerization of BOE using **8** (9.3 mol % vs BOE) was carried out at 120 °C for 4 days in acetonitrile. The cross-linked polymer obtained was separated from the polymerization system and washed with acetonitrile and ether. The IR spectrum of the polymer showed the stretching vibration (1720 cm^{-1}) based on C=O, which is attributed to the ester group of poly(BOE). In addition, increase of the isolated yield of the cross-linked polymer (degree of grafting, 33%) supported the occurrence of the grafting of BOE. Surprisingly, from the soluble part after removal of the cross-linked polymer, only unreacted monomer BOE (76%) was recovered without any homopoly(BOE) (grafting efficiency, ca. 100%). This fact seems to suggest that little transfer reaction to monomer occurs

Table I
Copolymerization of 2 with 9[a]

run	feed ratio, mol %		solvent[b]	yield, %	copolymer composition[c]		density,[d] g/cm^3
	2	9			*m*	*n*	
1	0	100	DMF	76[e]			1.17
2	5	95	DMF	84[e]	4.7	95.3	1.39
3	20	80	DMF	75[e]	26	74	1.27
4	40	60	CH_3CN	55	46	54	1.35
5	50	50	CH_3CN	63	53	47	1.40

[a] AIBN 3 mol %, 60 °C, 24 h. [b] 50 wt % vs sum of the monomers. [c] Estimated by elemental analysis. [d] Measured by using density gradient tubes. [e] Gel polymer was formed in CH_3CN.

Scheme I



during the graft polymerization.

The results obtained with the cross-linked polymer seem to indicate that (i) the ammonium salt moiety does not act as a proton donor and (ii) the graft polymerization of BOE involves no transfer reaction, since no homopoly(BOE) was detected in the soluble fraction in the graft polymerization. The grafting mechanism, therefore, involves initial thermal cleavage of the C–N bond of the ammonium (or pyridinium) salt via an S_N1 process followed by trapping of benzylic cation with BOE or initial nucleophilic attack of BOE at the benzylic position to cause C–N bond cleavage (Scheme I). The successful attachment of BOE leading to the graft copolymer is thereby achieved. It is interesting that no homopoly(BOE) was formed during the graft copolymerization, although the reason is uncertain at the present time.

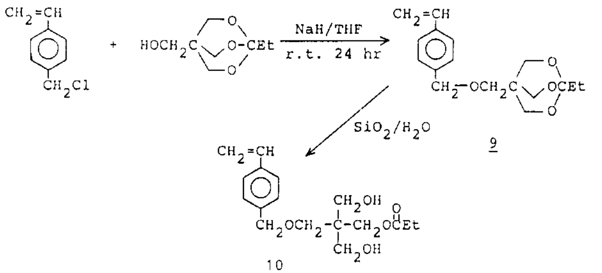
Thermal Self-Cross-Linking Reaction. As mentioned above, the polymer-supported ammonium salts were found to behave as the polymeric thermal latent catalysts initiating the polymerization of BOE leading to the grafted polymers. If this grafting reaction is extended to the reaction of polymers having both quaternary ammonium salt and BOE structure in the same molecule, we can get cross-linked polymer only by heating via graft-type polymerization of polymer-supported BOE onto polymer backbone, which is initiated by the ammonium moiety. This is the so-called self-cross-linking reaction. From another point of view, such bifunctional polymer can be regarded as a new material showing no shrinkage in volume on thermal self-cross-linking since BOE is known to be one of the monomers that undergoes no shrinkage on polymerization, as we have previously performed in another system.[7]

Table II
Thermal Cross-Linking Reaction[a]

run	*m*	*n*	yield, %	density, g/cm^3 [b]		volume change,[c] %
				before CL[e]	after CL	
1[d]	0	100	84	1.17	1.13	+3.5
2	4.7	95.3	95	1.39	1.34	+3.9
3	26	74	92	1.27	1.21	+5.0

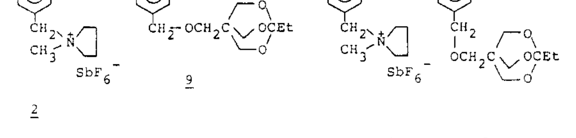
[a] 120 °C, 24 h in acetonitrile. Soluble polymers were removed by washing with acetonitrile with a Soxhlet extractor. [b] Measured by density gradient tube. [c] Volume change was calculated from density change: +, expansion. volume change (%) = [(density before heating − density after heating)/density before heating] × 100. [d] Added catalyst: *N*-(phenylmethyl)-*N*-methylpyrrolidinium hexafluoroantimonate (3 mol %). [e] CL = cross-linking.

Subsequently, a new styryl-type monomer, **9** (1-ethyl-4-[((*p*-vinylbenzyl)oxy)methyl]-2,6,7-trioxabicyclo[2.2.2]octane), possessing BOE structure was synthesized by the reaction of (*p*-chloromethyl)styrene with 1-ethyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane[8] derived from condensation of triethyl orthopropionate and pentaerythritol (eq 4). The crude product was purified by passing through a silica gel column pretreated with triethylamine to give colorless crystals of **9** in 62% yield. However, without such pretreatment, the hydration product **10** was formed. The structures of **9** and **10** were identified by spectra data.



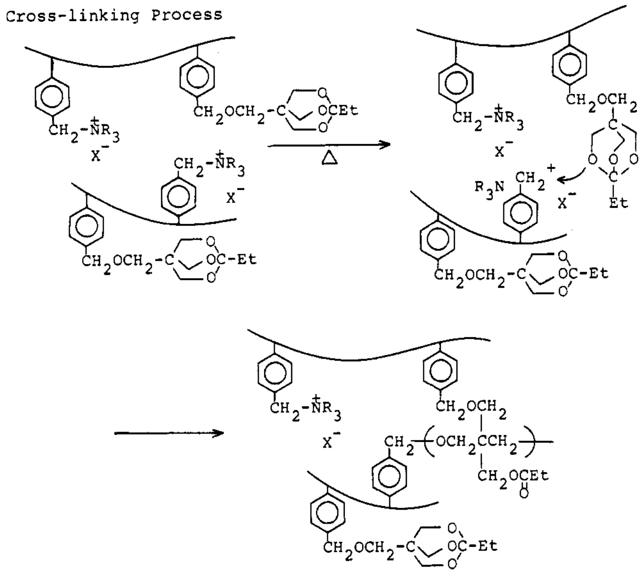
(4)

Copolymerization of **9** with the styryl-type ammonium salt **2** was carried out in various feed ratios in polar solvents such as DMF and acetonitrile to give corresponding copolymers in good yields (eq 5, Table I). The copolymerization, however, had a tendency to be accompanied by the formation of gel polymer in acetonitrile (runs 1–3). Copolymer compositions were determined by elemental analyses. A good correlation between density and content of **2** in the copolymers was observed (Table II). In other words, the density of the copolymers mainly de-



(5)

Scheme II



pends on the amount of the counteranion, SbF_6^-.

These copolymers were heated at 120 °C for 24 h in acetonitrile, which resulted in gelation. The results are shown in Table II (runs 2 and 3). The homopolymer of **9** was heated similarly in the presence of *N*-benzyl-*N*-methylpyrrolidinium hexafluoroantimonate (3 mol % for BOE unit) to give cross-linked polymer in 84% yield (run 1, Table II). IR spectra of all the polymers showed the stretching vibration of C=O at 1720 and of C–O at 1200 cm^{-1} attributable to the ester group formed by ring-opening polymerization of BOE. The mechanism of the self-cross-linking is presumed to be similar to that of the grafting reaction described above, as shown in Scheme II.

As for the change of the density of the polymers before and after the cross-linking, 3–5% of expansion in volume was observed in each case, which is associated undoubtedly with the cationic ring-opening polymerization of pendant BOE with the pyrrolidinium salt, which coexists in the polymer side chains. In the cases in which the content of **2** was over 40 mol % (Table I, runs 4 and 5), it was very difficult to estimate the actual degree of expansion, because the amount of the counteranion influenced the densities of the polymers too strongly.

In summary, new polymer-supported quaternary ammonium salts were prepared and shown to be new potent grafting agents onto the polystyrene backbone as well as fairly good thermally latent cationic catalysts. Further, the polymers containing both bicyclo ortho ester and quaternary ammonium salt moieties were synthesized and gave new materials which underwent small expansions in volume upon thermal self-cross-linking reaction.

Experimental Section

Instrumentation. ^1H and ^{13}C NMR spectra were recorded with JEOL NMR spectrometers, PMX-60, FX-100, and GX-270. Infrared spectra (FT mode) were obtained with a JASCO FT/IR-3 spectrometer. Densities of polymers were measured by density gradient tubes. Measurement of inherent viscosity $[\eta]$ was performed at 30 °C in acetonitrile by using the Ubbelohde apparatus. Melting points were measured with a Yamato scientific melting point apparatus and are uncorrected. Elemental analyses were done by the elemental analysis center of this institute.

1-Phenyl-4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE) was prepared in 86% yield according to the method previously reported.[2]

***N*-Benzyl-*p*-cyanopyridinium Hexafluoroantimonate (1).** A mixture of benzyl chloride (8.2 g, 50 mmol) and *p*-cyanopyridine (5.2 g, 50 mmol) in methanol (80 mL) was stirred at 40 °C for 6.5 h. Methanol was evaporated, and the residue was extracted with ether–water. To the aqueous layer, $NaSbF_6$ (13 g, 50 mmol) was added, and resulting white precipitates were recrystallized from ethanol: yellow needles, yield 20%; mp 156–157 °C; IR (KBr) 1640, 1455, 760, 720, 700, 660 cm^{-1}; ^1H NMR (δ/CD_3CN) 8.90 (d, 2 H, $^+NC_5H_4$-*p*-CN), 8.55–8.15 (br, 2 H, $^+NC_5H_4$-*p*-CN), 7.45 (s, 5 H, Ph), 5.80 (s, 2 H, CH_2) ppm.

Anal. Calcd for $C_{13}H_{11}N_2$: C, 36.23; H, 2.57; N, 6.50. Found: C, 35.95; H, 2.50; N, 6.55.

***N*-Methyl-*N*-(*p*-vinylbenzyl)pyrrolidinium Hexafluoroantimonate (2).** (*p*-Chloromethyl)styrene (2.3 g, 15 mmol) and *N*-methylpyrrolidine (1.04 mL, 10 mmol) were dissolved in 20 mL of methanol. The solution was stirred at room temperature for 3 days. Thereafter, methanol and unreacted *N*-methylpyrrolidine were evaporated, and the residue was extracted with ether–water. $NaSbF_6$ (2.6 g, 10 mmol) was added into the aqueous layer, and resulting precipitates collected were recrystallized from methanol–ether: white crystals, yield 75% mp 82–83.5 °C; IR (KBr) 1640, 1615, 1440, 1420, 1400, 995, 920, 860, 835, 660 cm^{-1}; ^1H NMR (δ/CD_3CN) 7.5 (s, 4 H, Ph), 6.85 (dd, 1 H, $H_2C{=}CH$), 5.90 (dd, 1 H, $H(H)C{=}CH$), 5.40 (dd, 1 H, $H(H)C{=}CH$), 4.40 (s, 2 H, CH_2), 3.85–3.10 (br, 4 H, $2{\times}CH_2$), 2.90 (s, 3 H, CH_3), 2.50–1.95 (br, 4 H, $2{\times}CH_2$) ppm; ^{13}C NMR (δ/CD_3CN) 139.6, 132.7, 127.6, 126.8 (Ph), 135.7 ($CH_2{=}CH$), 115.8 ($CH_2{=}CH$), 66.1 (CH_2), 63.3 ($^+NC_4H_8$), 47.7 (CH_3), 20.9 ($^+NC_4H_8$) ppm.

Anal. Calcd for $C_{14}H_{20}N$: C, 38.39; H, 4.61; N, 3.20. Found: C, 38.80; H, 4.71; N, 3.22.

***N*-(*p*-Vinylbenzyl)-*p*-cyanopyridinium Hexafluoroantimonate (3).** A mixture of (*p*-chloromethyl)styrene (6.1 g, 40 mmol) and *p*-cyanopyridine (2.08 g, 20 mmol) in methanol (40 mL) was refluxed for 6 h. The reaction mixture was worked up by the same method described for **2**. The crude product was recrystallized from ethanol to give pure **3**: yellow needles, yield 38%, mp 138.0–139.5 °C; IR (KBr) 2230, 1640, 1610, 1460, 990, 920, 770, 730, 660 cm^{-1}; ^1H NMR (δ/CD_3CN) 8.98 (d, 2 H, $^+NC_5H_4$-*p*-CN), 8.25 (d, 2 H, $^+NC_5H_4$-*p*-CN), 7.48 (s, 4 H, Ph), 7.62 (dd, 1 H, $H_2C{=}CH$), 5.77 (d, 1 H, $H(H)C{=}CH$), 5.70 (s, 2 H, CH_2), 5.25 (d, 1 H, $H(H)C{=}CH$) ppm.

Anal. Calcd for $C_{15}H_{13}N_2$: C, 39.42; H, 2.87; N, 6.13. Found: C, 39.43; H, 2.84; N, 6.13.

1-Ethyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane.[8] A mixture of 49.5 g (0.28 mol) of triethyl orthopropionate, 38.2 g (0.28 mol) of pentaerythritol, and 0.15 g of *p*-toluenesulfonic acid in 250 mL of DMF was placed in a flask. After the mixture was heated at 120 °C for 3 h, the solution was cooled in ice bath, and 0.25 mL of triethylamine was added. DMF was removed under reduced pressure, and the residue was purified by vacuum distillation: yield 78%, bp 113–115 °C/0.06 mmHg [lit.[8] bp 120–125 °C/0.12 mmHg]; IR (neat) 3500, 1270, 1100, 1040, 1000 cm^{-1}; ^1H NMR (δ/CCl_4) 3.85 (s, 6 H, $3{\times}CH_2$), 3.33 (d, 2 H, CH_2OH), 2.50 (t, 1 H, OH), 1.60 (q, 2 H, CH_2), 0.85 (t, 3 H, CH_3) ppm.

1-Ethyl-4-[((*p*-vinylbenzyl)oxy)methyl]-2,6,7-trioxabicyclo[2.2.2]octane (9). Commercial sodium hydride (0.3 g, 13 mmol) was washed with *n*-hexane several times and dried by removal of *n*-hexane. To a suspension of the sodium hydride in tetrahydrofuran (THF, 10 mL) was added slowly 1.3 M of a THF solution (5 mL) of 1-ethyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane at room temperature. After the mixture was stirred for 3 h, (*p*-chloromethyl)styrene (1.0 g, 6.6 mmol) was added dropwise, and the resulting mixture was stirred for an addition 24 h. The mixture was concentrated under vacuum and extracted with ether–water. The residue after evaporation of ether was purified by passing through a silica gel column pretreated with triethylamine (silica gel, Wako Gel C-200; solvent, *n*-hexane followed by chloroform): yield 62%; mp 52.2–54.5 °C; IR (KBr) 1630, 1100, 1060, 990, 915, 830, 760 cm^{-1}; ^1H NMR ($\delta/CDCl_3$) 7.30 (d, 4 H, Ph), 6.71 (dd, 1 H, $H_2C{=}C(H)$), 5.74 (dd, 1 H, $H(H)C{=}CH$), 5.25 (dd, 1 H, $H(H)C{=}CH$), 4.41 (s, 2 H, CH_2), 4.00 (s, 6 H, $3{\times}CH_2$), 3.17 (s, 2 H, CH_2), 1.71 (q, 2 H, CH_2), 0.95 (t, 3 H, CH_3) ppm; ^{13}C NMR ($\delta/CDCl_3$) 137.2, 137.1, 127.6, 126.3 (Ph), 136.3 ($CH_2{=}CH$), 114.0 ($CH_2{=}CH$), 109.8 (O–C), 73.2 (OCH_2), 69.4 ($3{\times}CH_2O$), 68.2 (OCH_2), 35.0 (C≡), 29.8 (CH_2), 7.5 (CH_3) ppm.

Anal. Calcd for $C_{17}H_{22}$: C, 70.32; H, 7.64. Found: C, 69.93; H, 7.39.

3-[(*p*-Vinylbenzyl)oxy]-2,2-bis(hydroxymethyl)propyl Propionate (10). The residual crude oil obtained in the preparation of **9** was passed through a silica gel column (silica gel, Wako gel C-200; solvent, *n*-hexane and thereafter ethyl acetate): yield 20%; IR (neat) 3450, 1740–1720, 1635, 1200, 910, 830, 810 cm^{-1}; ^{1}H NMR (δ/CDCl$_3$) 7.25 (d, 4 H, Ph), 6.68 (dd, 1 H, $H_2C{=}CH$), 5.71 (dd, 1 H, H(H)C=CH), 5.22 (dd, 1 H, H(H)C=CH), 4.45 (s, 2 H, $-CH_2OC{=}O$), 4.15 (s, 2 H, CH$_2$), 3.60 (br, 4H, 2×CH_2OH), 3.42 (s, 2 H, $OCH_2C{\equiv}$), 3.05 (br, 2 H, 2×OH), 2.25 (q, 2 H, CH$_2$), 1.10 (t, 3 H, CH$_3$) ppm.

Polymerization of 2 and 3. Monomer **2** (0.88 g, 2 mmol) or **3** (0.95 g, 2 mmol), AIBN (0.01 g, 3 mol %), and 1.5 mL of acetonitrile were put into a small ampule tube. The ampule was cooled, degassed, and sealed off. After the ampule was heated at 60 °C for 24 h, the reaction mixture was poured into a large amount of methanol and the corresponding polymer precipitated. The polymer was collected by filtration and washed with methanol. **4**: white powder, yield 79%; [η] 3.24 dL/g (acetonitrile); IR(KBr) 1620, 1480, 1460, 860, 830, 660 cm^{-1}; ^{1}H NMR (δ/CD$_3$CN) 7.50–6.25 (br, 4 H, Ph), 4.65–3.95 (br, 2 H, CH$_2$), 3.85–3.00 (br, 4 H, 2×CH$_2$), 3.00–2.50 (br, 3 H, CH$_3$), 2.50–1.20 (br, 7 H, 2×CH$_2$, $CH_2CH{=}$) ppm.

Anal. Calcd for $C_{14}H_{20}N$: C, 38.39; H, 4.61; N, 3.20. Found: C, 38.25; H, 4.66; N, 3.41.

5: yellow powder, yield 64%; [η] 0.60 dL/g (acetonitrile); IR (KBr) 1640, 1610, 1460, 840, 660 cm^{-1}; ^{1}H NMR (δ/CD$_3$CN) 8.90–8.55 (br, 2 H, $^+NC_5H_4$-*p*-CN), 8.45–8.10 (br, 2 H, $^+NC_5H_4$-*p*-CN), 7.40–6.25 (br, 4 H, Ph), 5.90–5.30 (br, 2 H, CH$_2$), 2.30–0.70 (br, 3 H, $CH_2CH{=}$) ppm.

Anal. Calcd for $C_{15}H_{13}N_2$: C, 39.42; H, 2.87; N, 6.13. Found: C, 39.05; H, 2.75; N, 6.14.

Copolymer 6. A mixture of **3** (1.0 g, 2.2 mmol), styrene (0.23 g, 2.2 mmol), and AIBN (0.03 g) in acetonitrile (1 mL) was heated at 80 °C for 24 h. The solution was poured into a large amount of methanol, and the precipitates formed were collected: yellow powder, yield 84%; [η] 0.12 dL/g (acetonitrile); IR (KBr) 1640, 1610, 1450, 830, 760, 700, 660 cm^{-1}.

Anal. Found: C, 48.06; H, 3.62; N, 5.27.

Polymerization of BOE with 1, 5, and 6. BOE and one of the initiators (2 mol % for monomer) were placed in an ampule. The ampule was degassed, sealed, and heated for 25 or 48 h at 120 °C. During the polymerization, conversion of BOE was measured at intervals by ^{1}H NMR (integral ratio of 2 H for $O({=}O)C{-}C_6H_5$ of the polymer to 6 H for 3×CH$_2$ of BOE).

Grafting of BOE with 4 and 5. BOE (1.1 g, 5 mmol) was polymerized with **4** (0.22 g, 10 mol% for BOE) in acetonitrile (1.6 mL) at 120 °C for 72 h. The reaction mixture was poured into methanol (100 mL) to obtain the grafted polymer: white powder, yield 0.32 g (degree of grafting, 33%); IR (KBr) 1720, 1115, 710, 660 cm^{-1}; ^{1}H NMR (δ/CD$_3$CN) 8.15–7.85 (br, $O({=}O)C{-}C_6H_5$), 7.65–7.40 (br, $O({=}O)C{-}C_6H_5$), 7.32–6.20 (br, Ph), 4.55–3.90 (br, CH$_2$OCO), 3.80–3.05 (br, 2×CH$_2$O), 3.00–2.50 (br, CH$_3$), 2.50–1.80 (br, 2CH$_2$), 1.80–1.10 (br, CH$_2$), 1.10–0.60 (br, CH$_3$) ppm; ^{13}C NMR (δ/CD$_3$CN) 166.3 (C=O) ppm.

BOE was polymerized with **5** in a similar way to give the grafted polymer, which was insoluble in common organic solvents (degree of grafting, 22%): IR (KBr) 2200, 1710, 1660, 1640, 660 cm^{-1}.

Anal. Found: C, 53.00; H, 4.95; N, 4.84.

Cross-Linked Polymer-Supported Cationic Initiator 8. A mixture of **3** (1.0 g, 2.2 mmol), styrene (0.23 g, 2.2 mmol), and divinylbenzene (4 mol % for monomers) in 1.0 mL of acetonitrile was heated in an ampule tube at 60 °C for 24 h. The obtained gel was washed with acetonitrile and ether by using a Soxhlet extractor: yield 71%; IR (KBr) 1640, 1610, 1450, 760, 700, 660 cm^{-1}.

Anal. Found: 50.95; H, 3.95; N, 4.66.

Grafting of BOE onto Cross-Linked Polymer. A mixture of 0.14 g (10 mol % for BOE) of the cross-linked polymer **8** and BOE (0.55 g) in acetonitrile (2.5 mL) was heated at 120 °C for 4 days. The insoluble polymer was collected, washed with acetonitrile and ether, and dried in vacuo: yield 0.21 g. The evaporation of the soluble fraction gave no homopolymer of BOE (grafting efficiency, 100%; degree of grafting, 33%): IR (KBr) 3500, 1710, 1640, 1610, 1600, 1450, 1110, 760, 700, 660 cm^{-1}.

Anal. Found: C, 58.99; H, 5.10; N, 3.53.

Copolymerization of 2 with 9. Typical Procedure (Table I, Run 5). Two vinyl monomers, **2** (0.88 g, 2 mmol) and **9** (0.58 g, 2 mmol), AIBN (0.02 g, 3 mol % for monomers), and acetonitrile (2.0 mL) were put into an ampule tube. The ampule was degassed and sealed off. After the reaction mixture was heated at 60 °C for 24 h, the solution was poured into a large amount of methanol to yield the corresponding copolymer. The copolymer obtained was collected by filtration, washed with methanol, and dried in vacuo: yield 63%; IR (KBr) 1620, 1485, 1475, 1280, 1105, 1060, 940, 830, 760, 660 cm^{-1}; ^{1}H NMR (δ/CD$_3$CN) 7.40–6.15 (br, 8 H, aromatic protons), 4.60–4.08 (br, 4 H, CH_2N^+, CH$_2$O), 3.92 (s, 6 H, 3×CH$_2$), 3.70–2.93 (br, 6 H, $^+NC_4H_8$, $OCH_2C{\equiv}$), 2.93–2.55 (br, 3 H, CH$_3$), 2.40–1.22 (br, 9 H, $^+NC_4H_8$, $CH_2CH{=}$, CH$_2$), H, $^+NC_4H_8$), $CH_2CH{=}CH_2$), 1.22–0.65 (br, 3 H, CH$_3$) ppm.

Anal. Found: C, 50.66; H, 5.96; N, 2.05.

Thermal Self-Cross-Linking Reaction. Typical Procedure (Table II, Run 2). A solution of copolymer of **2** with **9** (copolymer composition was **2**:**9** = 5:95, 0.11 g) in ca. 0.5 mL of acetonitrile was heated at 120 °C for 24 h in a sealed tube. Thereafter the obtained gel polymer was washed with acetonitrile and ether by using a Soxhlet extractor and dried in vacuo: yield 95%; IR (KBr) 3500, 1730, 1610, 1480, 1460, 1280, 1200, 1090, 1120, 830, 660 cm^{-1}.

Anal. Found: C, 76.14; H, 7.34; N, 0.22.

Registry No. **1**, 116146-28-2; **2**, 118950-29-1; (**2**)(**9**) (copolymer), 118950-39-3; **3**, 118950-30-4; (**3**)(BOE)(styrene) (graft copolymer), 118950-35-9; (**3**)(BOE) (graft copolymer), 118950-37-1; (**3**)(styrene)(divinylbenzene) (copolymer), 118978-07-7; (**3**)(styrene)-(divinylbenzene)(BOE) (graft copolymer), 118978-08-8; **4**, 118950-32-6; **5**, 118950-33-7; **6**, 118950-34-8; **7**, 118950-36-0; **9**, 118950-40-6; **10**, 118950-31-5; BOE (homopolymer), 80057-28-9; benzyl chloride, 100-44-7; *p*-cyanopyridine, 100-48-1; *p*-(chloromethyl)styrene, 1592-20-7; *N*-methylpyrrolidine, 120-94-5; triethyl orthopropionate, 115-80-0; pentaerythritol, 115-77-5; 1-ethyl-4-(hydroxymethyl)-2,6,7-trioxabicyclo[2.2.2]octane, 74358-92-2.

References and Notes

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