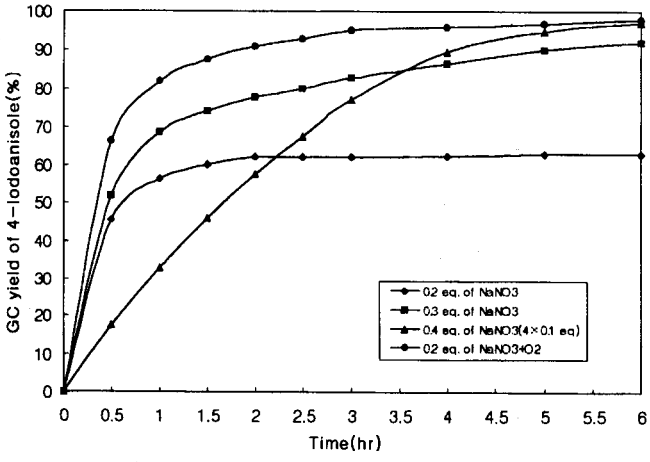

Figure 1. Effect of NO_3^- quantity on the iodination of anisole at 85 °C.

species at high temperature. In contrast, N-substituted carbazoles, strongly activated aromatic compounds, seem to undergo different reaction pathway since the iodination requires only 0.1 equivalent of nitrate in the absence of oxygen.

It is also interesting to note that the treatment of I_2/NO_3^- on phenylacetylene produces 1-iodo-2-nitro-1-phenylethene as a major product and no iodinated aromatic ring.[6] This result sheds an important clue for the understanding of iodination mechanism[7] and demonstrates the existence of INO_2 species[8] during a reaction with I_2/NO_3^-.

In summary, an easy and novel synthetic method using I_2/NO_3^- is developed for the effective iodination of aromatic ring with an electron-donating group. This method does not require any strong acid or oxygen. In addition, under an oxygen atmosphere only 0.2 equivalent of nitrate is enough for the successful iodination.

Acknowledgment. Dr. K.-W. Chi thanks Science and Technology Policy Institute and University of Ulsan for the financial support of this work. Dr. V. D. Filimonov also wishes to thank Russian Foundation for Fundamental Researchers for their generous support (96-03-033054).

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4. mp 174-175 °C (heptane/benzene); IR (KBr) 554 cm^{-1}; ^1H NMR (100 MHz, $CDCl_3$/TMS) δ 5.36 (s, 2H), 7.00-7.22 (m, 7H), 7.62 (d, 2H), 8.28 (s, 2H); C 44.82%, H 2.57%, N 2.75% for $C_{19}H_{13}NI_2$, found C 44.68%, H 2.63%, N 2.46%.
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$$2H^+ + NO_3^- \rightleftarrows NO_2^+ + H_2O$$
$$NO_2^+ + I_2 \rightleftarrows I^+ + INO_2$$
$$INO_2 \rightleftarrows I^+ + NO_2^-$$
$$NO_2^- + 2H^+ + 0.5I_2 \rightleftarrows I^+ + NO + H_2O$$
$$NO_3^- + 4H^+ + 1.5I_2 \rightleftarrows 3I^+ + NO + 2H_2O \text{ (net)}$$

However, it is not easy to rationalize every step of the tentative mechanism since I^+ has been known to exist as a kinetically independant species only in a strongly acidic condition.
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Polystyrene-Pendant Hydrazinium Salt as a Novel Grafting-Onto Cationic Initiator

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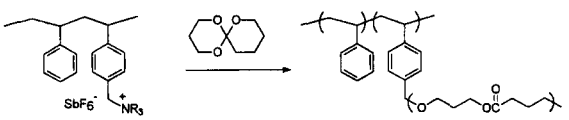
The interest in graft copolymers arises in part from the protection exerted by the grafts on the backbone. This specific feature has led to a number of applications such as emulsifiers, surface-modifying agents, coating materials, and compatibilizers in polymer blend.[1] Lots of grafting methods involving cationic polymerization might be summarized as

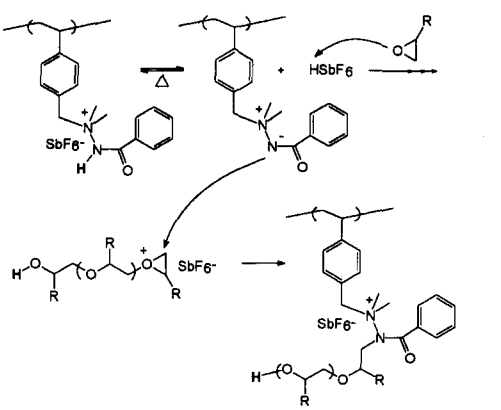
grafting from and grafting onto processes.[2] Cationic grafting from processes have been performed by Kennedy[3] and a similar method has recently been performed by Saekusa.[4] Cationic grafting onto processes was succeeded by Franta[5] and Goethals[6] has obtained similar results with poly(*t*-butylaziridine).

Meanwhile, several onium salts which induce cationic species by external stimulation such as photoirradiation or heating are of special interest since the initiation step of cationic polymerization could be controlled.[7~14] For example, N-benzyl group containing quaternary ammonium salts have been reported by Endo *et al.*[15~17] and Lee *et al.*[16,17] to serve as thermally latent cationic initiators in the bulk polymerization of cyclic ethers and a vinyl monomer. The idea was extended that benzyl cation is the real initiation species of N-benzyl group containing ammonium salts to a graft-polymer synthesis *via* the graft-from process (Eq. 1).[18]



(1)

Recently, we developed proton inducing thermally latent cationic initiators, hydrazinium salts, such as 1-benzyl-1,1-dimethyl-2-benzoylhydrazinium hexafluoroantimonate, **1**.[19,20] According to the proposed mechanism that proton and the liberated aminimide by heating of **1** were regarded as initiating and terminating species, respectively, graft-polymer should be obtained via graft onto process in the cationic polymerization of cyclic ether with polystyrene pendent hydrazinium salt (Eq. 2). The most significant feature of this system compared with that of Franta's[5] might be a one-component system.



(2)

This paper describes a new grafting method of glycidyl phenyl ether (GPE), a model compound of a flexible polymer, onto polystyrene, a model compound of a rigid polymer.

Polymeric pendant hydrazinium salts were obtained by the radical polymerization of styrene (St) and 1-(p-vinylbenzyl)-1,1-dimethyl-2-benzoylhydrazinium salt **2** with 3 mol % of AIBN in acetonitrile at 60 °C for 24 h (Eq. 3, Table 1). **2** is easily synthesized according to the similar method reported[16] using 4-vinylbenzyl chloride in place of benzyl bromide (Figure 1 and 2).

As shown in Table 1, yields were tended to decrease as

Table 1. Copolymerization of **2** and styrene in acetonitrile at 60 °C for 24 h with 3 mol % of AIBN

3	in feed		3				
	2 (mol %)	St (mol %)	Yield[a] (%)	n : m	$\overline{Mn}$[b]	$\overline{Mw}/\overline{Mn}$[b]	Tg[c] (°C)
3a	10	90	71.4	8.4:91.6	24000	1.66	111
3b	20	80	69.4	19.8:80.2	23000	1.95	133
3c	30	70	59.5	22.4:77.6	54000	1.34	138
3d	50	50	51.1	47.5:52.5	46000	1.25	152

[a] Determined by ^{1}H NMR peaks of benzyl and benzene ring proton. [b] Estimated by GPC of Methanol-insoluble polymers **3** using polystyrene standard. [c] Determined by DSC at a heating rate of 10 °C/min under nitrogen atmosphere.

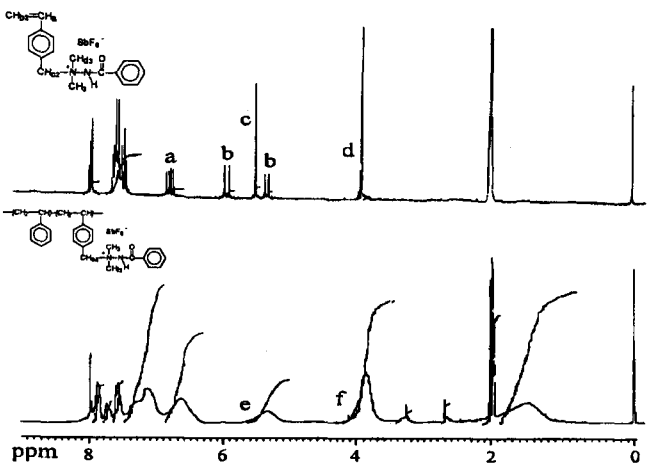


Figure 1. ^{1}H NMR spectrum of **2** and **3**.

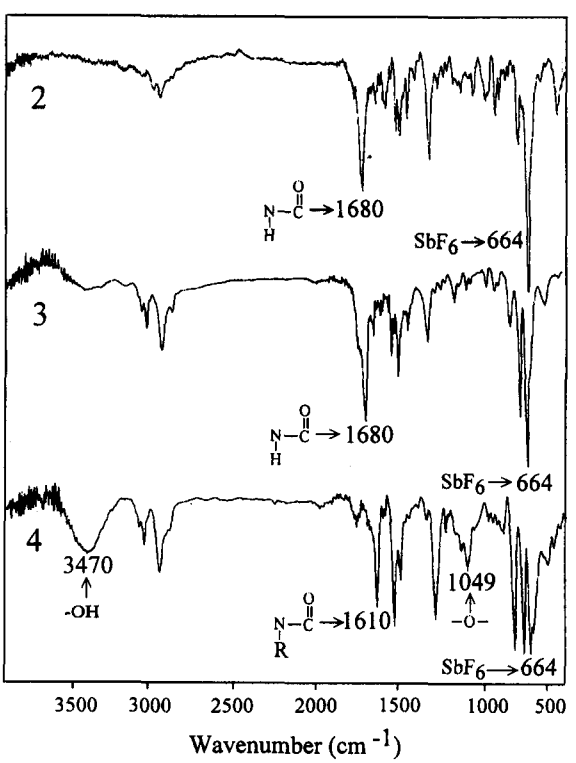
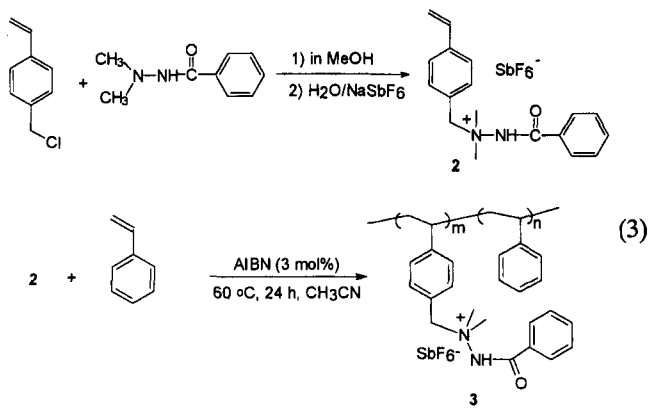


Figure 2. IR spectrum of **2**, **3** and **4**.

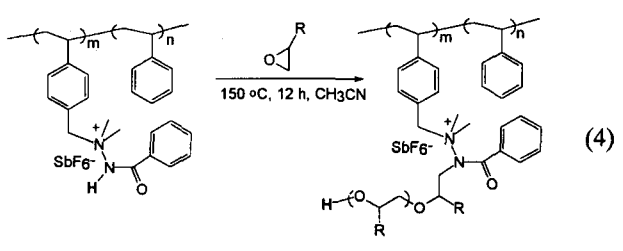


(3)

increasing the concentration of **2** in feed, however, the composition of **2** (m) in **3** was increased almost proportionally to the concentration of **2** in feed. This result suggests that hydrazinium salt structure does not affect to the reactivity of vinyl group. Mn and Mw/Mn were independent of the concentration of **2**. Relatively higher (> 23000) Mn indicate that **3** is formed not by cationic polymerization but by radical polymerization since lower Mn (< 10000) could be obtained in the cationic polymerization.[17]

The signal of benzyl proton which is appeared at about δ 5.5 ppm in ^{1}H NMR and the absorption bands of $\nu_{C=O}$ and ν_{Sb-F} which are appeared at 1680 and 664 cm^{-1} in IR, respectively in addition to many characteristic peaks of polystyrene clearly indicated that these are polymeric pendent hydrazinium salts (Figure 1 and 2). Increase of Tg as shown in Table 1 as increasing the composition of **2** in **3** support **3** are copolymers of **2** and styrene, polymeric pendent hydrazinium salts.

All of the **3** were insoluble in common organic solvents used generally in cationic polymerization such as benzene, methylene dichloride, ethylene dichloride, etc., but soluble in polar solvents such as acetonitrile, dimethylformamide (DMF), etc. Therefore, the graft polymerization by **3** was carried out in acetonitrile, although acetonitrile is not a normal solvent for cationic polymerization. The graft polymerization of GPE (0.302 g) with **3c** (0.204 g, 16.70 mol % for GPE) in acetonitrile (1 mL) was attempted at 150 °C for 12 h in an ampule tube. The reaction mixture was poured into methylene dichloride for the removal of homopolyGPE to give 0.250 g of grafted polymer **4** [grafted yield; (weight **4** − weight **3**)× 100/weight **3**=22%].



(4)

3 **4**

Though we did not have an analysis of **4** by ^{1}H NMR due to its insolubility in common NMR solvents, the three strong absorption bands in IR at 3500, 1050, and 660 cm^{-1} attributable to OH, R'-O-R', Sb-F, respectively in addition

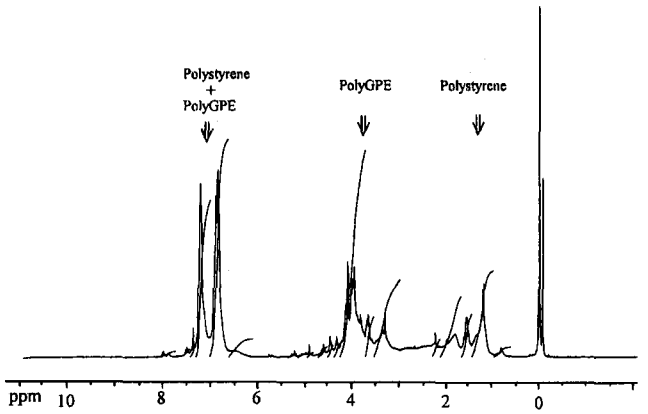


Figure 3. ^{1}H NMR spectrum of hydrolyzed product of **4**.

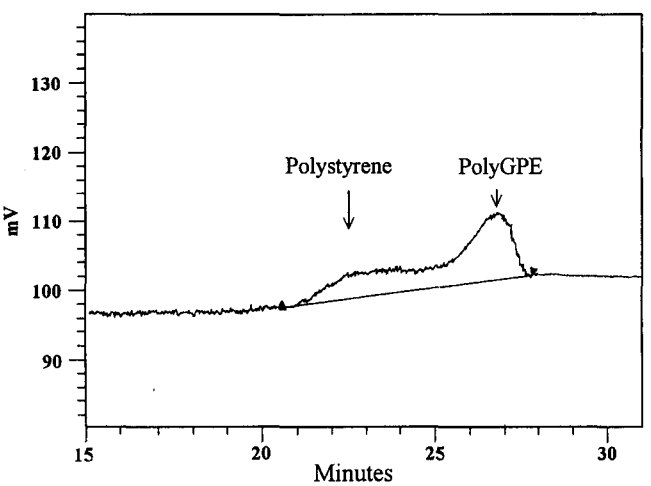


Figure 4. GPC trace of hydrolyzed product of **4**.

to many characteristic peaks of polystyrene clearly indicate that these are polystyrene-graft-polyGPE (Figure 2). The shift of $\nu_{C=O}$ from 1680 (-CON-H, **3**) to 1610 (-CON-CHR, **4**) cm^{-1} supports that **4** is polystyrene-graft-polyGPE. The mixed signals of polystyrene and homopolyGPE in ^{1}H NMR and GPC chart of the acid-catalyzed hydrolyzed product of **4** (Figure 3 and 4)[17,21] clearly indicate that **4** is polystyrene-graft-polyGPE. The grafted yield was estimated as about 20% calculated from the obtained weight of homopolyGPE of the hydrolyzed product of **4**.

In conclusion, we have found out a new grafting method of polyether to polystyrene via graft onto process in situ using a polymeric pendant hydrazinium salt, a proton inducing-thermally latent cationic initiator.

Acknowledgment. Support of this work by the Ministry of Science and Technology is gratefully acknowledged.

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21. 10 mL of 1 N HCl was added to **4** and refluxed for 15 h in order to hydrolyze the most weak C-N(N^+Me_2)(C=O) bond of **4**. The hydrolyzed polymer was collected with 20 mL of methylene dichloride for 3 times.

The New Procedure for the Preparation of α-Trifluoromethylated Arylacetamides

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Trifluoromethylated organic molecules have recently been received much attention because of their unique properties in the areas of materials, pharmaceuticals and agrochemicals.[1,2] α-Trifluoromethylated arylacetamides, in particular, are very important synthetic intermediates for the preparation of biologically active compounds. For examples, hydrolysis of α-trifluoromethylated arylacetamides provides α-trifluoromethylated arylacetic acids which are potential antiinflammatory agents such as trifluoro-analog of ibuprofen and naproxen.[3] 3,3-Difluoro-2-arylallylamines,[4] potential monoamine oxidase inhibitors, can also be prepared from the reduction followed by HF-elimination reaction of α-trifluoromethylated arylacetamides.

Although numerous methods for the synthesis of trifluoromethylated compounds have been developed in last two decades,[5,6] there are only limited reports on the synthesis of α-trifluoromethylated arylacetamides. These reports involve the reaction of the electrochemically generated trifluoromethyl radical with acrylamide[7] and chlorination of α-trifluoromethylated acids, followed by reaction of amines.[8] In recent years, it has been also reported that hydrogenation of α-hydroxy-α-(trifluoromethyl)arylacetamide which can be prepared *via* α,α,α-trifluoroacetophenone cyanohydrin provided α-trifluoromethylated arylacetamides.[9] However, these methods have disadvantages such as low yields, multistep procedure and lack of generality. As an alternative approach to overcome these synthetic drawbacks, we decided to use β,β-difluoro-α-trifluoromethylstyrenes **1**[10] as a trifluoromethylated building block. In this communication, we wish to describe about the addition-elimination of β,β-difluoro-α-trifluoromethylstyrene derivatives with sodium alkylamides, followed by hydrolysis as one pot procedure for the preparation of α-trifluoromethylated arylacetamides.

When β,β-difluoro-α-trifluoromethylstyrene **1a** was reacted with 1 equiv. of sodium *n*-butylamide in acetonitrile at room temperature, only monosubstituted product **2a** was obtained in 67% yield. We anticipated that deprotonation of **2a** by excess sodium *n*-butylamide afforded imine anion (or metalloenamine) which undergoes β-defluorination to give ketenimine. The formed ketenimine is further reacted with sodium *n*-butylamide, followed by hydrolysis, to yield α-trifluoromethylated arylacetamide **3a**. However, the treatment of **1a** with 3 equiv. of sodium *n*-butylamide in acetonitrile under the same reaction condition did not provide **3a**, while a messy reaction mixture was formed. An alternative approach to give α-trifluoromethylated arylacetamide **3a** is the hydrolysis of monosubstituted product **2a**. Therefore, the reaction of **1a** with 1 equiv. of sodium *n*-butylamide in acetonitrile followed by treatment of 10% H_2SO_4 afforded **3a** in 85% yield. The use of HCl or $MgSO_4$ instead of H_2SO_4 provided the similar result, but the basic condition needed a prolonged reaction time. The reactions of **1a** with isopropylamine, *t*-butylamine and benzyl amine anions, followed by hydrolysis also provided **3b**, **3c** and **3d** in 86%,