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# A New Grafting Method by Use of Polymeric Sulfonium Salt. Grafting of Bicyclo Ortho Ester onto Polystyrene

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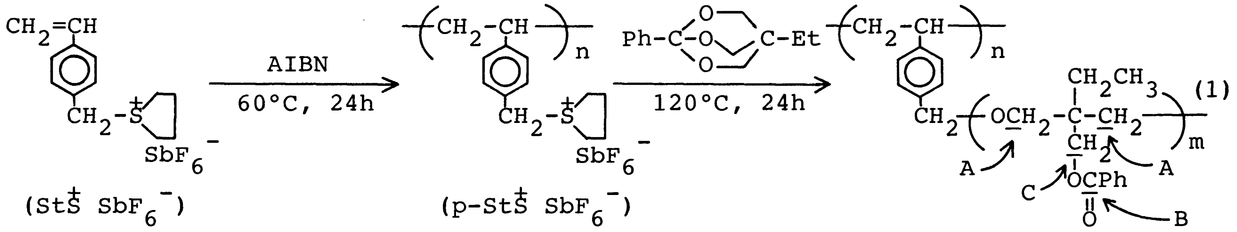
Polymer containing sulfonium salt structure, which was obtained by the polymerization of p-vinylbenzyl tetramethylenesulfonium hexafluoroantimonate, was found to behave as a polymeric thermal latent catalyst for the polymerization of bicyclo ortho ester and lead to the grafted polymer.

We have reported that benzyl tetramethylenesulfonium salt ($B_z\overset{+}{S}\ SbF_6^-$) is a useful thermal latent catalyst in the polymerization of bicyclo ortho ester1) and spiro ortho carbonate.2) Specially, it is expected that the graft polymerization of bicyclo ortho ester (BOE) may be possible by using the polymer containing the sulfonium salt moiety.

We would like to report the synthesis of p-vinylbenzyl tetramethylenesulfonium hexafluoroantimonate ($St\overset{+}{S}\ SbF_6^-$), and the new grafting reaction of BOE onto polystyrene back bone by initiating from the polymeric sulfonium salt obtained from the monomer.

1-Phenyl-4-ethyl-2,6,7-trioxabicyclo[2.2.2]octane (BOE) can be polymerized with $B_z\overset{+}{S}\ SbF_6^-$ to polyether containing ester group in the side chain through isomeric polymerization at an elevated temperature1,3) without shrinkage during polymerization. The radical polymerization of a new monomer ($St\overset{+}{S}\ SbF_6^-$)4) was carried out using AIBN to obtain the corresponding polymer5) without side reaction.

The polymerization of BOE with polymeric sulfonium salt was carried out to obtain the grafted polymer at an elevated temperature (120 °C) (Eq. 1). The polymer, obtained by precipitating the solution into methanol, was a slightly yellow product and insoluble in ordinary organic solvents. IR spectra show a C=O stretching vibration (1720 $cm^{-1}$) attributable to ester group in the side chain of the grafted polymer. $^{13}C$ NMR spectra of the grafted polymer swollen with $CD_3CN$ recorded on a JEOL-GX-500 spectrometer show the signals of two methylene carbon (A) at 65.2-62.7, of ester carbon (B), and methylene carbon (C) in the side chain at 166.3-165.9 and 73.5-70.5 ppm, respectively. These spectral data support the grafting of BOE onto polystyrene.



grafted polymer

It is extremely interesting that the polymer containing sulfonium salt structure $(p\text{-}St\overset{+}{S}\ SbF_6^-)$ behaves as a thermal grafting agent for the cationic polymerization of BOE to lead to the grafted polymer without any side reaction.

## References

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2) T. Endo and H. Arita, Makromol. Chem., Rapid Commun., 6, 137 (1985).

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4) $St\overset{+}{S}\ SbF_6^-$ was prepared from p-chloromethylstyrene (15.2 g, 0.1 mol) and tetrahydrothiophene (3 ml, 0.034 mol) by stirring in methanol at r. t. for 3 days. After methanol was removed, the solution was extracted with ether-water. To the aqueous layer, $NaSbF_6$ (8.8g 0.034 mol) was added to obtain the product. Yield 47%. mp 51.5-52.5 °C, IR(KBr); 1640, 1600, 1520, 1430, 1305, 1255, 990, 915, 840, 760, 730, 660 $cm^{-1}$, $^1H$ NMR($\delta/CD_3COCD_3$); 7.65 (s, Ph), 6.85 (dd, $\begin{smallmatrix}H\\H\end{smallmatrix}\!>C=C<\begin{smallmatrix}\underline{H}\\ \end{smallmatrix}$), 5.90 (dd, $\begin{smallmatrix}H\\H\end{smallmatrix}\!>C=C<\begin{smallmatrix}H\\ \end{smallmatrix}$), 5.40 (dd, $\begin{smallmatrix}\underline{H}\\H\end{smallmatrix}\!>C=C<\begin{smallmatrix}H\\ \end{smallmatrix}$), 4.75 (s, $-C\underline{H}_2-\overset{+}{S}<$), 3.90-3.40 (broad, $-\overset{+}{S}<\begin{smallmatrix}C\underline{H}_2-CH_2\\C\underline{H}_2-CH_2\end{smallmatrix}$), 2.52-2.25 (broad, $-\overset{+}{S}<\begin{smallmatrix}CH_2-C\underline{H}_2\\CH_2-C\underline{H}_2\end{smallmatrix}$) ppm.

5) $St\overset{+}{S}\ SbF_6^-$ (0.58 g, 2.3 mmol) was polymerized with AIBN (0.008 g, 4 mol% for monomer) in acetonitirile at 60 °C for 24 h to obtain the polymer. Yield 0.46 g (79%). IR(KBr); 1600, 1510, 1420, 1305, 1260, 830, 660 $cm^{-1}$, $^1H$ NMR($\delta/CD_3COCD_3$); 7.52-6.05 (broad, Ph), 4.80-4.04 (broad, $C\underline{H}_2\overset{+}{S}<$), 3.97-3.36 (broad, $-\overset{+}{S}<\begin{smallmatrix}C\underline{H}_2-CH_2\\C\underline{H}_2-CH_2\end{smallmatrix}$), 2.52-2.04 (broad, $-\overset{+}{S}<\begin{smallmatrix}CH_2-C\underline{H}_2\\CH_2-C\underline{H}_2\end{smallmatrix}$), 1.89-0.80 (broad, $C\underline{H}_2$, $C\underline{H}$) ppm.

6) BOE (2.2 g, 0.01 mol) was polymerized with $p\text{-}St\overset{+}{S}\ SbF_6^-$ (0.88 g, 20 mol% for monomer) in acetonitirile at 120 °C for 24 h. The mixture was poured into methanol to precipitate the polymer. Yield 1.28 g (20% for monomer). IR(KBr); 3500, 1720, 1600, 1320-1240, 1140-1020, 780, 710, 660 $cm^{-1}$, $^{13}C$ NMR($\delta/CD_3CN$); 166.3-165.9 ($O\underline{C}=O$), 146.4-144.2 ($-\underline{C}H_2\overset{+}{S}<$), 133.6-124.7 (Ph), 73.5-70.5 ($\underline{C}H_2OC=O$), 65.2-62.7 ($O\underline{C}H_2$), 45.6 ($-\overset{+}{S}<\begin{smallmatrix}\underline{C}H_2-CH_2\\\underline{C}H_2-CH_2\end{smallmatrix}$), 42.6 ($OCH_2\underline{C}CH_2$), 40.5 ($-\overset{+}{S}<\begin{smallmatrix}CH_2-\underline{C}H_2\\CH_2-\underline{C}H_2\end{smallmatrix}$, $-\underline{C}H-$), 28.3 ($-\underline{C}H_2-$), 23.6-22.3 ($\underline{C}H_2$), 7.13 ($\underline{C}H_3$) ppm.

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