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# Carbocationic polymerization of electron-rich olefins by a carbon Bronsted acid

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## Abstract

Polymerization of electron-rich vinyl monomers, p-methoxystyrene (p-MeOSt), N-vinylcarbazole (NVCz), and isobutyl vinyl ether (IBVE), were carried out with a carbon Bronsted acid, bis(trifluoromethanesulfonyl) methane (BTM) at -78° to 0° in several solvents. High molecular weight polymers were obtained from p-MeOSt and NVCz, but without molecular weight control. The molecular weight of polymers obtained from IBVE was low, and the presence of a vinyl group and low molecular weight of the polymer indicate that chain transfer reaction occurred in the polymerization.

## Introduction

Carbocationic polymerization of electron-rich vinyl monomers is traditionally initiated by either protonic Bronsted acids or by Lewis acids. The Bronsted acids reported to date have been those where the proton is attached to halogen, such as hydrogen fluoride, or to oxygen carrying electron attracting groups, such as trifluoromethane sulfonic acid. As yet no CH Bronsted acid has been reported as a cationic initiator.

The work of Siedle and his colleagues at 3M opened an opportunity to explore this possibility (1,2). They synthesized the extremely acidic bis(trifluoromethanesulfonyl)methane (BTM):

$$(CF_3SO_2)_2CH_2$$

Its high acidity enables it to catalyze various reactions, including epoxide polymerization (3). We now show that BTM is an effective initiator for the carbocationic polymerization of several electron-rich vinyl monomers.

## Results and Discussion

p-Methoxystyrene (p-MeOSt) Polymerization of p-MeOSt was carried out in various solvents. Some of the results are summarized in Table 1.

Polymerization in dichloromethane was rather slow. In nitromethane, p-MeOSt polymerized easily to yield methanol-insoluble polymer. Because of low solubility of poly-p-MeOSt in nitromethane, the reaction in nitromethane proceeded heterogeneously except in the initial stage. The molecular weight of the polymer is high.

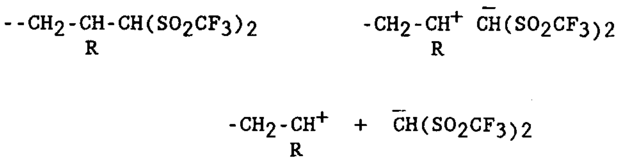
Table 1. **Polymerization of p-MeOSt with BTM**[a]

| Expt. No. | [M] mol/l | Initiator mol% | Solvent | Temp. °C | Time hr | Yield[b] % | Mn[b,c] x10$^{-3}$ | MWD[b,c] |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 3 | $CH_2Cl_2$ | 0 | 20 | trace | | |
| 6 | 1 | 3 | $CH_2Cl_2$ | -45 | 45 | trace | | |
| 7 | 1 | 3 | $CH_2Cl_2$ | -78 | 45 | trace | | |
| 9 | 1 | 3 | $CH_3NO_2$ | 0 | 24 | 71 | 23 | 1.7 |
| 11 | 1 | 5 | $CH_3NO_2/CH_2Cl_2$ 3/1 | 0 | 24 | 82 | 52 | 5.7 |
| 12 | 1 | 5 | $CH_3NO_2/CH_2Cl_2$ 1/1 | 0 | 24 | 100 | 70 | 4.3 |
| 18 | 1 | 1 | $C_2H_5NO_2$ | 0 | 48 | 87 | 12 | 13.9 |
| 17 | 1 | 2 | $C_2H_5NO_2$ | 0 | 24 | 95 | 13 | 13.1 |
| 16 | 1 | 5 | $C_2H_5NO_2$ | 0 | 15 | 74 | 6.9 | 14.3 |
| 15 | 1 | 10 | $C_2H_5NO_2$ | 0 | 7 | 89 | 9.0 | 14.3 |
| 28 | 1 | 1 | $CH_3NO_2/CH_2Cl_2$ 1/20 | 0 | 67 | trace | | |
| 27 | 1 | 2 | $CH_3NO_2/CH_2Cl_2$ 1/20 | 0 | 63 | trace | | |
| 26 | 1 | 5 | $CH_3NO_2/CH_2Cl_2$ 1/20 | 0 | 24 | trace | | |

[a] Monomer, 3mmol.
[b] Methanol insoluble polymer.
[c] By SEC.

When a small amount of nitromethane was added to dichloromethane, the polymerization was not significantly accelerated, but in nitromethane/dichloromethane (2/1 v/v) the polymerization in was as fast as in nitromethane. Since the polymer is soluble in this mixed solvent, this reaction was homogeneous. Again, the molecular weight of the polymer obtained in nitromethane/dichloromethane (2/1) was very high. This indicates that the propagation is much faster than the initiation.

Polymers obtained in nitroethane solution have low molecular weights and large molecular weight distribution (MWD). The large MWD suggests the presence of plural active sites (eq. 1).



$$\text{--CH}_2\text{-}\underset{\text{R}}{\text{CH}}\text{-CH(SO}_2\text{CF}_3)_2 \qquad \text{-CH}_2\text{-}\underset{\text{R}}{\text{CH}^+}\ \overline{\text{C}}\text{H(SO}_2\text{CF}_3)_2$$

$$\text{-CH}_2\text{-}\underset{\text{R}}{\text{CH}^+} + \overline{\text{C}}\text{H(SO}_2\text{CF}_3)_2 \qquad (1)$$

The molecular weight distributions of the polymers prepared in homogeneous nitroalkane solutions were much broader than the ones obtained from heterogeneous polymerization in nitromethane.

N-Vinylcarbazole (NVCz). As shown in Table 2, polymerization of NVCz was very fast and high molecular weight polymers were obtained. Because of the low solubility of the resulting polymer, most of the reactions proceeded in the heterogeneous state. Polymers obtained in dichloromethane at -45°C are insoluble in most organic solvents at room temperature. The low solubility of the polymer indicates that the molecular weight and (or) the stereoregularity of the polymers are very high.

Table 2. Polymerization of NVCz with BTM[a]

| Expt. No.. | [M] mol/l | Initiator mol% | Solvent | Temp. °C | Time hr | Yield[b] % | $\eta_{inh}$[b,c] |
|---|---|---|---|---|---|---|---|
| 24 | 1 | 1 | $CH_2Cl_2$ | 0 | 25 min. | 23 | 1.94 |
| 23 | 1 | 2 | $CH_2Cl_2$ | 0 | 15 min. | 91 | 1.76 |
| 25 | 1 | 5 | $CH_2Cl_2$ | 0 | 5 min. | 99 | 1.38 |
| 33 | 1 | 0.5 | $CH_2Cl_2$ | -45 | 5 hr | 96 | —[e] |
| 32 | 1 | 1 | $CH_2Cl_2$ | -45 | 5 hr | 98 | —[e] |
| 42 | 0.3 | 1 | toluene | -45 | 50 hr | 37 | 0.75 |
| 41 | 0.3 | 2 | toluene | -45 | 25 hr | 41 | 0.80 |
| 40 | 0.3 | 5 | toluene | -45 | 20 hr | 59 | 0.51 |

[a] Monomer, 3 mmol.
[b] Methanol insoluble polymer
[c] Chloroform; concentration - 0.5g/dl.
[e] Insoluble in chloroform.

Polymers obtained in dichloromethane at 0°C and in toluene at -45°C are soluble in chloroform, dichloromethane, benzene, and toluene at room temperature, but are insoluble in toluene and swell in dichloromethane at lower temperature. Because of the low solubility and high molecular weight of the polymers, it was not practical to determine the molecular weight by SEC and VPO. The inherent viscosity of the polymers was measured in chloroform at 30°C. The viscosities are high, as expected. Especially, the viscosities of the polymers obtained in dichloromethane at -45°C are larger than 1.0.

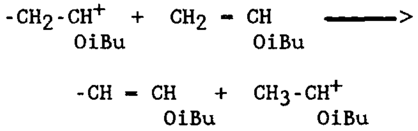
Again, high molecular weights of the polymers indicate that the propagation is much faster than the initiation.

Table 3. Polymerization of IBVE with BTM[a]

| Expt. No. | [M] mol/l | Initiator mol% | Solvent | Temp. °C | Time hr | Yield % | Mn[b] x10$^{-3}$ | MWD[b] |
|---|---|---|---|---|---|---|---|---|
| 35 | 1 | 1 | $CH_2Cl_2$ | 0 | 24 | 55 | 7.4 | 3.1 |
| 34 | 1 | 2 | $CH_2Cl_2$ | 0 | 24 | 59 | 2.9 | 4.3 |
| 39 | 1 | 1 | $CH_3NO_2/CH_2Cl_2$ 2/1 | 0 | 24 | 90 | 2.9 | 2.5 |
| 38 | 1 | 2 | $CH_3NO_2/CH_2Cl_2$ 2/1 | 0 | 24 | 77 | 1.3 | 1.8 |
| 37 | 1 | 5 | $CH_3NO_2/CH_2Cl_2$ 2/1 | 0 | 24 | 61 | 1.7 | 1.5 |
| 43 | 1 | 5 | toluene | 0 | 24 | 55 | | |
| 44 | 1 | 5 | toluene | -45 | 24 | 7 | | |
| 45 | 1 | 5 | toluene | -78 | 24 | 9 | | |

[a] Monomer, 3 mmol.
[b] By SEC.

Isobutyl Vinyl Ether (IBVE). Polymerization of IBVE was different from p-MeOSt and NVCz. The molecular weight of the polymers is very low. Vinyl groups and terminal methyl groups were detected in $^1$H-NMR spectra of the polymers. The presence of vinyl groups and the low molecular weight of the polymers indicate that chain transfer reaction (eq. 2) occurred in the polymerization.



$$-\mathrm{CH_2}-\underset{\mathrm{OiBu}}{\mathrm{CH^+}} + \mathrm{CH_2}=\underset{\mathrm{OiBu}}{\mathrm{CH}} \longrightarrow -\mathrm{CH}=\underset{\mathrm{OiBu}}{\mathrm{CH}} + \mathrm{CH_3}-\underset{\mathrm{OiBu}}{\mathrm{CH^+}} \qquad (2)$$

## Experimental

Materials. Commercial p-methoxystyrene, N-vinylcarbazole, and isobutyl vinyl ether were used. p-Methoxystyrene was distilled over calcium hydride before use. N-Vinylcarbazole was recrystallized from n-hexane and dried in vacuum. iso-Butyl vinyl ether was washed with aqueous sodium hydroxide solution and then with water and was distilled twice over sodium.

General Methods. $^1$H-NMR spectra were recorded on a Bruker WM-250 spectrometer. Deuterochloroform and tetramethylsilane were used as the solvent and internal reference. Molecular weights of polymers were measured on Dupont Zorbax PSM-60S, Dupont Zorbax 300S and IBM GPC/SEC Pore Type A columns calibrated with polystyrene standards with chloroform as eluent and a Spectra Physics detector at 254 nm or a RI detector. Inherent viscosities were determined on Ubelohde viscosimeter at 30°C. Chloroform was used as the solvent.

Polymerization. Polymerization was carried out under argon atmosphere in a Y-tube. The reaction was terminated by the addition of methanol. The reaction mixture was dissolved in dichloromethane and then poured into a large amount of methanol to precipitate the polymer. In the case of isobutyl vinyl ether, the reaction mixture was dissolved in dichloromethane, washed three times with water, dried over magnesium sulfate, and the solvent and unreacted monomer thoroughly evaporated. The residue was washed three times with methanol and dried in vacuum.

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