the amount of initiator but can be increased at will by the amount of protic compound added.

Registry No. 1 (X = OCH_2CH_3), 98539-97-0; 1 (X = $OCH_2C(CH_3)_3$), 113474-64-9; 1 (X = Cl), 71102-37-9; 1 (X = $O_2CCH_2CHClCH_3$), 113474-65-0; **2** (R = H), 25322-68-3; **2** (R = CH_3), 25322-69-4; **2** (R = CH_2CH_3) (homopolymer), 24969-07-1; **2** (R = CH_2CH_3) (SRU), 108421-58-5; **2** (R = CH_2OCH_3) (homopolymer), 28325-89-5; **2** (R = CH_2OCH_3) (SRU), 113474-57-0; **2** (R = CH_2Cl) (homopolymer), 24969-06-0; **2** (R = CH_2Cl) (SRU), 61710-61-0; **4** (R = CH_3) (homopolymer), 38566-36-8; **4** (R = CH_3) (SRU), 26099-72-9.

References and Notes

(1) (a) Szwarc, M. *Nature (London)* **1956**, *178*, 1169. (b) Dreyfuss, M. P.; Dreyfuss, P. *Polymer* **1965**, *6*, 93. (c) Boileau, S.; Champetier, G.; Sigwalt, P. *Makromol. Chem.* **1963**, *69*, 80. (d) Perry, S.; Hibbert, H. *J. Am. Chem. Soc.* **1940**, *62*, 2599. (e) Hamitou, A.; Ouhadi, T.; Jérôme, R.; Teyssié, P. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 865. (f) Lenz, R. W.; Dror, M.; Jorgensen, R. *Polym. Eng. Sci.* **1978**, *18*, 937. (g) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. U. *J. Am. Chem. Soc.* **1983**, *105*, 5706. (h) Sogah, D. Y.; Webster, O. W. *Macromolecules* **1986**, *19*, 1775. (i) Miyamoto, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1984**, *17*, 265. (j) Doi, Y.; Ueki, S.; Keii, T. *Macromolecules* **1979**, *12*, 814.

(2) (a) Szwarc, M. *Carbanion, Living Polymers, and Electron-Transfer Processes*; Interscience: New York, 1968. (b) Szwarc, M. *Adv. Polym. Sci.* **1983**, *49*, 1.

(3) For a preliminary paper, see: Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148.

(4) (a) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1162. (b) Aida, T.; Inoue, S. *Macromolecules* **1981**, *14*, 1166.

(5) (a) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1983**, *16*, 1792. (b) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1984**, *17*, 2217.

(6) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8.

(7) (a) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358. (b) Aida, T.; Sanuki, K.; Inoue, S. *Macromolecules* **1985**, *18*, 1049.

(8) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, A.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476.

(9) Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3564.

(10) Asano, S.; Inoue, S.; Aida, T. *Macromolecules* **1985**, *18*, 2057.

(11) (TPP)AlCl shows dark reddish purple in $CDCl_3$ but bluish purple in $CDCl_3$/dioxane.

(12) No change such as broadening was observed for the GPC curve of the prepolymer upon treatment of **3** or **5** with HCl.

(13) For $-(OCH_2CH_2)_x-$: δ 3.7 (CH_2). For $-(OCH(CH_3)CH_2)_x-$: δ 1.15 (CH_3), δ 3.6 (CH and CH_2). For $-(OCH(CH_2Cl)CH_2)_x-$: δ 3.7 (CH_2Cl), δ 3.6 (CH and CH_2) in $CDCl_3$ at room temperature.

(14) N_p/N_{Al} = (MW of **2**) ($[\mathbf{2}]_0/[\mathbf{1}]_0$) (conv/100)$\bar{M}_n^{-1}$.

(15) Yasuda, T.; Aida, T.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3938.

(16) Mayo, F. R. *J. Am. Chem. Soc.* **1943**, *65*, 2324.

Chain Transfer by 2-Iodopropane and Propionic Acid Chloride in the Polymerization of Tetrahydrofuran

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ABSTRACT: The polymerization of tetrahydrofuran was initiated by the addition of silver hexafluoroantimonate and an excess of 2-iodopropane or propionic acid chloride. Rapid chain transfer to the acid chloride was observed. Chain transfer to 2-iodopropane was slow and occurred with the incorporation of the 2-propyl group at the end of the chain. A mechanism is proposed which involves an iodonium ion intermediate.

Introduction

The ring-opening polymerization of cyclic ethers, initiated by the carbenium or oxocarbenium ion generated by the reaction of an alkyl or acyl halide with silver hexafluoroantimonate, has been extensively studied by this laboratory[1] and in others.[2] This system allows rapid and quantitative initiation with the proper choice of the alkyl or acyl halide. In previous experiments the ratio of halide to silver salt was intentionally kept below unity. Therefore the initiator concentration was determined by the halide concentration as the limiting reagent. This was preferred as the silver salt is much more difficult to purify than the halide. We now wish to report our results on the use of an excess of the halide on the polymerization of tetrahydrofuran.

Experimental Section

Silver hexafluoroantimonate was recrystallized in dry diethyl ether under high vacuum. The fine white needles which resulted were transferred under vacuum into a tared flask equipped with a Rotoflo stopcock and pumped on for 24 h. A few crystals were removed under dry nitrogen and the flask was weighed. The elemental analysis of the crystals was consistent with the formula $AgSbF_6 \cdot C_4H_{10}O$. A standard solution was prepared by distilling THF onto the silver salt and off of the salt twice under vacuum to remove the residual diethyl ether, followed by dilution to the mark with THF.

Polymerizations were carried out under vacuum as described elsewhere.[1] Tetrahydrofuran was distilled twice from sodium metal and stored under vacuum in the presence of sodium-potassium alloy. Propionic acid chloride and 2-iodopropane were distilled from calcium hydride and stored under vacuum in the dark.

Samples for NMR spectroscopy were prepared by the reaction of $AgSbF_6$ with 2-iodopropane in THF-d_8 at −78 °C under vacuum in a round-bottom flask. The polymerization mixture was decanted from the silver iodide into the NMR sample tube under vacuum and the tube sealed just prior to placing the tube in the probe.

Results and Discussion

Propionic Acid Chloride. The polymerization of THF was initiated in bulk by 0.141 M propionic acid chloride and 2.1×10^{-3} M $AgSbF_6$ and followed by dilatometry at 24.5 °C. Aliquots were removed at 90, 290, 570, and 7200 min and quenched with sodium phenoxide. The first-order plot for the consumption of the monomer was linear and went through the origin yielding a rate constant of 3.0×10^{-2} L mol^{-1} s^{-1}. This is identical with that determined by using the silver salt in excess of the halide. The GPC data on the aliquots from this run were in sharp contrast to those with the silver salt in excess, with the acid halide at 2.1×10^{-3} M. The initial aliquot had a broad molecular weight distribution with a low molecular weight tail (Figure

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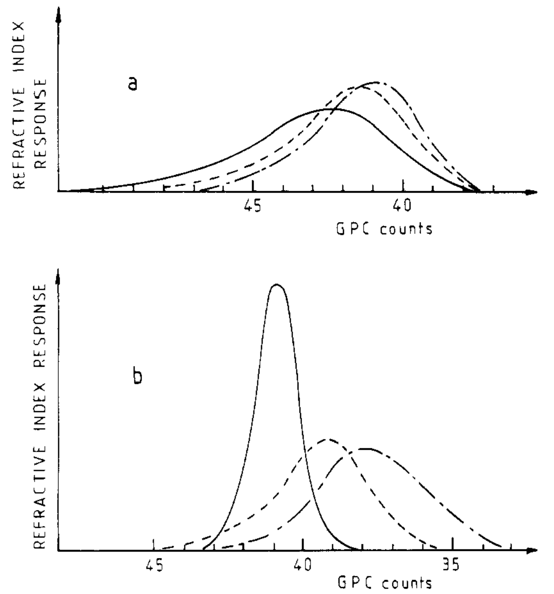
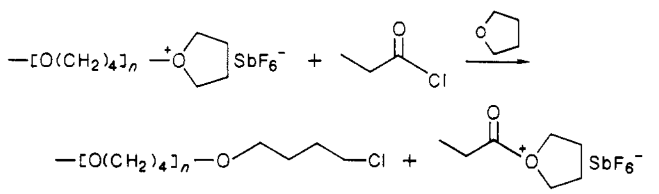


Figure 1. GPC curves of poly(tetrahydrofuran) prepared by using propionic acid chloride and $AgSbF_6$ as initiator. (a) [Propionic acid chloride]$_0$/[$AgSbF_6$] = 67.1; [$AgSbF_6$] = 2.1×10^{-3} M. Time: (—) 90 min; (---) 290 min; (– – –) 7200 min. (b) [2-Iodopropane]$_0$/[$AgSbF_6$] = 91.2; [$AgSbF_6$) = 1.9×10^{-3} M. Time: (—) 25 min; (---) 70 min; (– – –) 120 min.

Scheme I



1a). As the reaction progressed, the distribution became more narrow and the molecular weight increased. The molecular weight after 7200 min was approximately $^1/_{50}$ of that of the polymer prepared with an excess of silver salt.[3] This was consistent with transfer to the acyl chloride which was competitive with propagation as shown in Scheme I.[4]

2-Iodopropane. For various ratios of 2-iodopropane to $AgSbF_6$, with the halide in excess (10:1 to 170:1), the propagation rate constant at 24.5 °C was 3.0×10^{-2} L mol^{-1} s^{-1}, and the GPC data were consistent with those where the silver salt was in excess when the polymer was quenched within a few hours (Figure 1b). When the polymer was quenched after 24 h a slight decrease in molecular weight was observed. This could occur due to chain transfer to 2-iodopropane. To clarify this point the following experiment was carried out. A polymerization mixture with [$AgSbF_6$] = [2-iodopropane] = 1.9×10^{-3} M was divided into three portions under vacuum. The 2-iodopropane concentration of two of the aliquots was increased to 0.35 M. One of these aliquots and the aliquot with equimolar silver salt and iodide were terminated after 48 h with an excess of potassium methoxide in methanol. The other aliquot was terminated after 162 h. Its molecular weight (M_n = 160 000) was significantly lower than that observed for the aliquots terminated after 48 h, which had nearly identical molecular weights (M_n = 278 000 and 272 000 with excess halide).

In order to gain some insight into the transfer reaction, the following ^1H NMR experiment was carried out. By use of THF-d_8 mixed with sufficient THF-d_0 such that the 2-iodopropane methyl doublet did not saturate the signal, polymerization was carried out in the probe of a Brucker 200-MHz NMR spectrometer. During the first 2-h period the only change in the spectrum was due to the conversion of monomer to polymer. The sample was then stored in the dark at room temperature and spectra were taken after 3 and 12 months. As seen in Figure 2 the ratio of 2-iodopropane to 2-propyl ether end groups of the polymer decreased with time. No new signals appeared in these spectra.

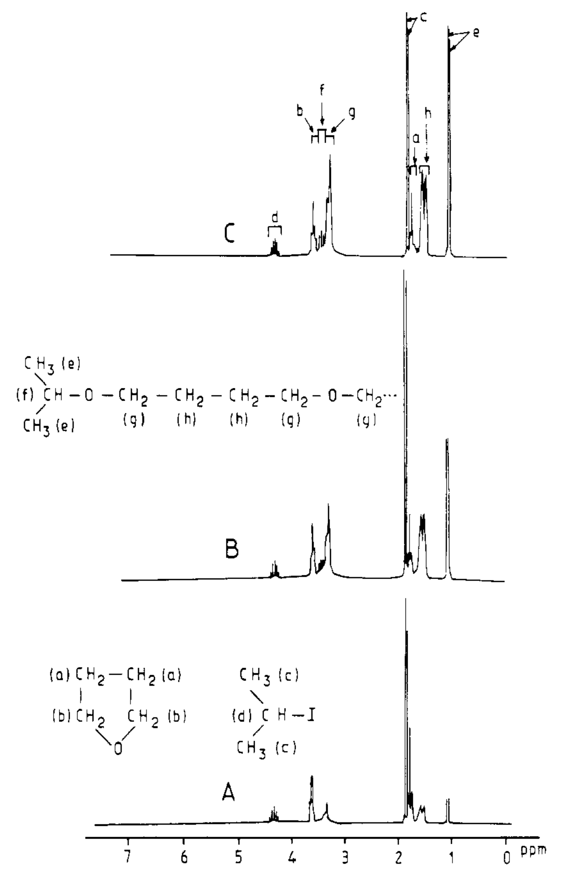
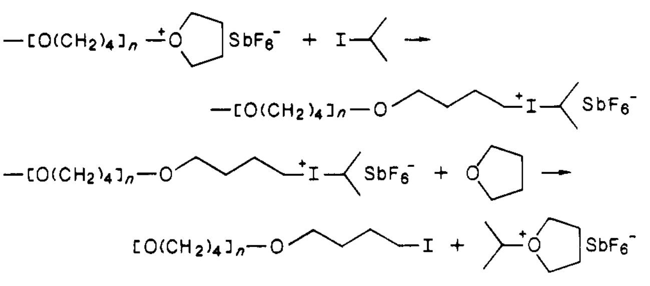
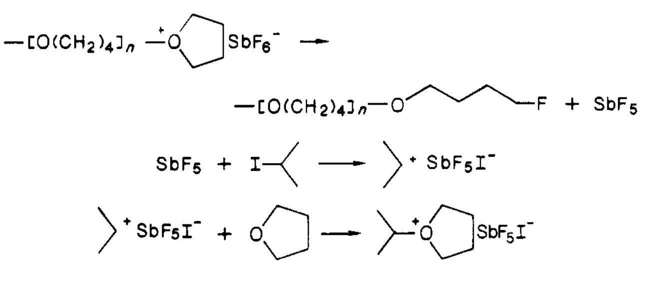


Figure 2. ^1H NMR spectra of poly(tetrahydrofuran) prepared with 2-iodopropane; [2-iodopropane]$_0$ = 0.1 M; [$AgSbF_6$] = 7×10^{-3} M. Reaction time: (A) 2 h; (B) 3 months; (C) 1 year.

Scheme II



Scheme III



The conversion of 2-iodopropane to 2-propyl ether end groups is evidence for the transfer reaction. We wish to postulate two possible mechanisms for the transfer. The first (Scheme II) occurs with nucleophilic attack on the oxonium ion by 2-iodopropane to form an iodonium ion.[5] Attack of the iodonium at the methine carbon by THF or polymer results in the formation of iodide-terminated chain and initiates a new chain. The other mechanism (Scheme III) involves the decomposition of the SbF_6 ion to form a fluoride-terminated chain and SbF_5. The Lewis acid reacts with 2-iodopropane to generate a carbenium ion which subsequently initiates a new chain.

The SbF_6 ion is one of the most stable counterions used in cationic polymerization. The rate of its decomposition is not known in this type of system. Likewise the relative stabilities of iodonium and oxonium ions are not clear.[6] Presently we favor the first of the two mechanisms for the following reasons. The ^{19}F NMR spectrum of the polymer after 3 months did not exhibit any signals for an alkyl fluoride end group. Additionally one may expect that Scheme II would be independent of the halide concentration, since the reaction of SbF_5 with alkyl halides is known to be fast[7] and the decomposition of the counterion would be rate-determining.[8] Although strict temperature control was not maintained for the NMR sample, we calculated from the NMR and GPC data the apparent rate constants for the two rate laws:[9]

$$-d[C_3H_7I]/dt = k_{app}[(C_4H_8O)_n{}^+SbF_6{}^-][C_3H_7I]$$

$$-d[C_3H_7I]/dt = k_{app}[(C_4H_8O)_n{}^+SbF_6{}^-]$$

The NMR data indicated a pseudo-first-order rate constant of 3×10^{-7} s^{-1}, while the GPC data indicated that the rate constant should be 2×10^{-6} s^{-1}, a discrepancy of 1 order of magnitude. Assuming a pseudo-second-order rate law, both the NMR and GPC data yield rate constants of 5×10^{-6} L mol^{-1} s^{-1}.

In conclusion, rapid chain transfer to propionic acid chloride and slow chain transfer to 2-iodopropane in the polymerization of THF have been demonstrated. Such reactions permit the preparation of polymers with the molecular weight determined by chain transfer allowing for the use of only small amounts of silver salt. Additionally, this may be useful in systems where chain transfer to polymer is slow, for the preparation of asymmetrically substituted telechelic polymers and block and graft copolymers.

Acknowledgment. M.A.B. acknowledges the support of the CRM and the CNRS.

Registry No. THF, 109-99-9; $AgSbF_6$, 26042-64-8; H_3CCH_2COCl, 79-03-8; $H_3C(CH_2)_2I$, 75-30-9.

References and Notes

(1) Reibel, L. C.; Durand, C. P.; Franta, E. *Can. J. Chem.* **1985**, *63*, 264. Lehmann, J.; Reibel, L.; Franta, E.; Penczek, S. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 139. Franta, E.; Afshar-Taromi, F.; Rempp, P. *Makromol. Chem.* **1976**, *177*, 2191. Afshar-Taromi, F.; Scheer, M.; Rempp, P.; Franta, E. *Makromol. Chem.* **1978**, *179*, 849.

(2) Dreyfuss, P.; Kennedy, J. P. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 135. Burgess, F. J.; Cunliffe, A. V.; Richards, D. H.; Scherrington, D. C. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 471.

(3) The molecular weight was determined by GPC with use of the universal calibration method. Grubisic, Z.; Rempp, P.; Benoit, H. *J. Polym. Sci., Part B* **1967**, *5*, 753.

(4) A similar mixture of THF and propionic acid chloride without the silver salt showed no change for the same ratio of THF to acid chloride as in this experiment and no additional chemical species after 350 h by gas chromatographic analysis.

(5) This mechanism would be equivalent to the formation of a carbenium ion by iodide exchange with an oxonium ion. The iodonium ion intermediate seems more reasonable as the equilibrium constant for the reaction $R'{-}I + R^+ \rightarrow R'{-}I{-}R^+$ is probably large; see Sen Sharma et al. and Olah (Sen Sharma, D. K.; Menza de Holer, S.; Kebarle, P. *J. Am. Chem. Soc.* **1985**, *107*, 3757. Olah, G. A. *Halonium Ions*; Wiley: New York, 1975).

(6) Although diaryliodonium salts do not initiate the polymerization of cyclic ethers in the dark (Crivello, J. V.; Lam, J. H. W. *Macromolecules* **1977**, *10*, 1307), dialkylhalonium ions have been used to prepare oxonium ions (Sen Sharma, D. K.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 19).

(7) Arnett, E. M.; Petro, S. C. *J. Am. Chem. Soc.* **1978**, *100*, 5402.

(8) One might expect to observe autocatalysis with this mechanism as the SbF_5I^- ion is less stable than the SbF_6^- ion. No evidence for autocatalysis was seen in the ^1H NMR spectra.

(9) These are pseudo-second-order and pseudo-first-order expressions, as the concentration of THF and ether oxygen are at their equilibrium value before any chain transfer is observed.

Polymer Monolayers Prepared by the Spontaneous Adsorption of Sulfur-Functionalized Polystyrene on Gold Surfaces[1]

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ABSTRACT: Polystyrene containing one terminal thiol group (PS-SH) and styrene–propylene sulfide block copolymers (PS–PPS) were allowed to adsorb on evaporated gold films supported on glass. The resulting supported films were characterized by X-ray photoelectron spectroscopy, external reflectance infrared spectroscopy, and scintillation counting of radioisotope-labeled polymers. The polymers adsorb rapidly and irreversibly, and the polymer monolayers can be washed with fresh solvent without desorption. The effects of molecular weight, concentration, and solvent power on adsorbance were determined for PS-SH. The effect of propylene sulfide block size for a series of PS–PPS copolymers on the number of adsorbed chains was determined.

Introduction

The modification of surfaces by adsorption of polymer molecules is important to a range of technologies (for example, corrosion,[3] lubrication,[4] colloid stabilization[5]) where interfacial effects are dominant. This field of research has received considerable attention recently from both theoretical[6-8] and experimental[9-11] groups.

This paper describes the preparation of thin films of polystyrene on evaporated gold surfaces by adsorption of modified polystyrenes from solution. Two types of modified polymer were studied: polystyrene containing one terminal thiol group (PS-SH) and styrene–propylene

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