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A new iodine-free initiating system for the living polymerization of isobutyl vinyl ether

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Summary

A new iodine-free initiating system, MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5, was found to induce the living carbocationic polymerization (LC$^{\oplus}$Pzn) of isobutyl vinyl ether (IBuVE) at -20 °C in CH_2Cl_2. Using this system, poly(isobutyl vinyl ether) (PIBuVE) with the theoretical molecular weights (up to *ca.* 45,000) calculated from the initiator/monomer input and narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$<1.1) can be readily obtained. The polymerization is first order in the monomer. The coinitiating function of *n*-Bu_4NTiCl_5 may be due to a salt effect or to its Lewis acid character. An attempt for the synthesis of the polyisobutylene (PIB) - PIBuVE block copolymer has failed most likely because *n*-Bu_4NTiCl_5 is unable to activate the ~$C(CH_3)_2$-Cl bond of the PIB termini.

Introduction

Recently, Nuyken and Kröner (1) reported the LC$^{\oplus}$Pzn of IBuVE initiated by MeCH(O*i*-Bu)I in the presence of *n*-Bu_4NClO_4 and similar salts. Remarkably, this polymerization proceeds in the absence of Lewis acids which seems to suggest that it is due to a salt effect exerted by *n*-Bu_4NClO_4 on the relatively weak ~CH(O*i*-Bu)-I bond. The disadvantage of these systems, which is common to most vinyl ether polymerization systems reported to date (2), is the use of light and temperature sensitive iodine compounds. It would be more convenient to employ, as initiators, compounds containing the more stable ~C-Cl bond; however, this has been achieved only in a few instances. Thus, Higashimura *et al.* (3) reported the living polymerization of IBuVE with the MeCH(O*i*-Bu)Cl/$ZnCl_2$ combination; however, LC$^{\oplus}$Pzn was demonstrated only below a $\overline{DP}_n$ of ~100. The same team (4) obtained the desired ~C-Cl bond by the use of the Me_3SiCl/*p*-MeOPhCHO/$ZnCl_2$ combination; however, the polymerization was reported to be "long-living". Shappacher and Deffieux (5) demonstrated that the $CH_3CH(OCH_2CH_2Cl)Cl/ZnCl_2$ combination was able to induce the living polymerization of 2-chloroethyl vinyl ether, but the $\overline{M}_n$ of the polymers were under 11,000 g/mole.

Here we report that the salt *n*-Bu_4NTiCl_5 efficiently induces the LC$^{\oplus}$Pzn of IBuVE. This salt is similar to the salts used by Nuyken and Kröner (1) but differs from them in that it activates the terminal ~CH(O*i*-Bu)-Cl bond and produces high molecular weight polymers (up to *ca.* 45,000).

Experimental

Chemicals. IBuVE (Aldrich, 99%) was washed with aqueous KOH, dried over KOH pellets, distilled from CaH_2 (Aldrich, 95%), and stored over CaH_2 under nitrogen at -25 °C. Hexanes (Fisher, 99.9%) were refluxed with conc. H_2SO_4 for several days, washed with aqueous K_2CO_3 and water, and dried over $CaCl_2$. They were stored over CaH_2 under nitrogen and distilled before use. CH_2Cl_2 (Fisher, 99.9%) was stored over CaH_2 under nitrogen and distilled before use. *n*-Bu_4NCl (Aldrich, 98%) solution in CH_2Cl_2 was placed

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over CaH_2, stirred for several days, filtered, and dried in vacuo. $CDCl_3$ (Aldrich, 99.8 atom.% D) was dried by molecular sieves (Fisher, type 3A). $TiCl_4$ (Aldrich, 99.9%) and CH_3OH (Fisher, 99.9%) were used as received.

Syntheses. Tetra-*n*-butylammonium pentachlorotitanate, *n*-Bu_4NTiCl_5, was synthesized according to (6). Thus to a stirred solution of 4.2 g *n*-Bu_4NCl in 15 mL CH_2Cl_2, 1.6 mL $TiCl_4$ were added, at ambient temperature. After an hour, 150 mL hexanes were added, and the mixture was stored overnight. The precipitate was filtered and washed twice with an excess of hexanes, and the greenish-yellow solid was dried in vacuo. ^1H NMR ($CDCl_3$) δ 0.99 (t, 3H, CH_3); 1.44 (m, 2H, CH_2Me); 1.65 (m, 2H, CH_2Et); 3.21 (m, 2H, CH_2N). ^{13}C NMR ($CDCl_3$) δ 13.9 (CH_3); 20.0 (CH_2Me); 24.2 (CH_2Et); 59.3 (CH_2N). The product was used as a 0.2 *M* solution in CH_2Cl_2.

1-(1-Chloroethoxy)-2-methylpropane, MeCH(O*i*-Bu)Cl, was synthesized by the saturating IBuVE with dry HCl at 0 °C. The product was distilled in vacuo at 0.1 mm Hg. The first half of the product was collected at -78 °C and stored under nitrogen at -25 °C. ^1H NMR ($CDCl_3$) δ 0.90 (d, 6H, $C(CH_3)_2$); 1.76 (d, 3H, CH_3CCl); 1.87 (m, 1H, $CHMe_2$); 3.21, 3.65 (2dd, *J*=6.7 and 9.2 Hz, 2H, OCH_2); 5.68 (q, 1H, CHCl). ^{13}C NMR ($CDCl_3$) δ 18.9, 19.0 ($2CH_3$, *i*-Bu); 26.5 (CH_3); 27.8 ($CHMe_2$); 77.2 (OCH_2); 96.5 (CHCl). After half a year of the storage of this initiator, its ^1H NMR spectrum did not change.

Polymerization. Polymerizations were carried out in large test tubes (75 mL) in a glove-box under dry nitrogen at -20 °C. The monomer was the last component added to the charges. The total reaction volume was 10 mL. The charges were homogeneous light brown solutions. Reactions were terminated by prechilled CH_3OH containing ~2 %vol. of NH_4OH. The quenched solutions were washed three times with water, the water layer separated, and the solvents and unreacted monomer evaporated at ambient temperature. The products were vacuum dried. The polymers were colorless and showed no UV absorption at 254 nm (GPC detector).

Procedures. The MWDs of polymers were determined using the THF solutions by a Waters high pressure GPC instrument equipped with RI and UV detectors and five μ-Styragel columns. The calibration curve was obtained with the polystyrene standards. As in the case of chloroform solutions (7), the molecular weights determined in the THF solution showed satisfactory agreement with theoretical molecular weights calculated from the monomer - initiator ratio.

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 spectrometer at 200 and 50 MHz, respectively, at room temperature in 5-mm tubes in $CDCl_3$. Sample concentrations were ~10 mg/mL for proton and ~100 mg/mL for carbon spectroscopy. The internal standard was the solvent. The chemical shift of the residual protons of deuterochloroform was set at 7.24 ppm and the central peak of the triplet in the ^{13}C spectrum was set at 77.0 ppm. The standard DEPT and APT microprograms (Varian Company) were used for the assignment of the carbon spectra.

Results and discussion

Polymerization of IBuVE initiated by MeCH(Oi-Bu)Cl/n-Bu_4NTiCl_5.

Results are summarized in Tables 1 and 2. According to time - conversion experiments, the $\overline{M}_n$ of polymers increases linearly with the conversion (Fig.1), and the MWDs remain narrow in both CH_2Cl_2 and CH_2Cl_2/hexanes. The number of polymer chains remains constant in time and is within experimental error of the molar amount of the initiator used. These facts indicate the absence of the irreversible termination and the chain transfer , *i. e.*, the polymerization is living.

Table 2 shows the results of "All Monomer In" (AMI) and "Incremental Monomer Addition" (IMA) experiments and Figure 2 the corresponding plots constructed. As in the time - conversion experiments, the number of polymer chains is close to the molar amount of the initiator used, and the $\overline{M}_n$ is directly proportional to the polymer weight (Fig. 2). All polymers exhibit the unimodal, narrow MWDs.

According to the data shown in Figure 3, and similarly to data in (1), the polymerization is

Table 1. Polymerization of IBuVE initiated by MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5
[MeCH(O*i*-Bu)Cl]$_0$ = 8.2 m*M*; [*n*-Bu_4NTiCl_5] = 20 m*M*; [IBuVE]$_0$ = 1 *M*; -20 °C; *V*=10 mL.

time, min	yield, %	M_n g/mole	M_w/M_n	[N], m*M*	I_{eff}*, %
		methylene	**chloride**		
5	8.0	1,070	1.11	7.6	92
10	12	1,550	1.09	7.8	95
20	20	2,700	1.06	7.5	91
40	32	3,800	1.05	8.5	104
80	53	6,100	1.04	8.8	107
160	78	9,200	1.04	8.6	105
300	96	11,200	1.04	8.7	106
	methylene	**chloride**	**/ hexanes**	**(3 : 2**	**v/v)**
40	14	1,540	1.11	9.2	112
80	21	2,500	1.08	8.5	104
160	38	4,200	1.05	9.1	112
300	55	5,800	1.05	9.6	117
420	60	7,400	1.05	8.2	100

* Initiator efficiency = $10^4 W_p/M_n \cdot$[MeCH(O*i*-Bu)Cl]$_0$.

first order with respect to monomer in both solvent systems. Since the polymer chain concentration [N] is constant, $ln[1/(1-x)] = k'_{app} \cdot t$, where x is the portion of the monomer converted to the polymer and $k'_{app}=k_{app} \cdot [N]$. The apparent propagation rate constants are k'_{app}= (0.0102 ± 0.0007) min^{-1} for CH_2Cl_2 and k'_{app}= (0.0022 ± 0.0005) min^{-1} for the mixed solvent (errors estimated for the 95% confidence). The dilution of CH_2Cl_2 with hexanes strongly reduces the polymerization rate. Such a dramatic retardation of the rate by decreasing the overall polarity of the medium is common in the cationic polymerization (8,9).

In view of the nature of the initiating system used, it is safe to assume that the initiating (and subsequently propagating) species in our living system is the ~C-Cl bond. It is more difficult, however, to assess the function of the *n*-Bu_4NTiCl_5. It may operate as a weak Lewis acid (after all, the Ti atom still has empty *d*-orbitals) or as a strong dipole which induces a salt effect. Both effects may, of course, operate simultaneously, and it would be very difficult to separate them.

Table 2. "All Monomer In" (AMI) and "Incremental Monomer Addition" (IMA) experiments.
Solvent - CH_2Cl_2; -20 °C; *V*=10 mL.

[MeCH(O*i*-Bu)Cl]$_0$, m*M*	[*n*-Bu_4NTiCl_5], m*M*	[IBuVE]$_0$, *M*	time, h	yield, %	M_n, g/mole	M_w/M_n	[N], m*M*	I_{eff}, %
		A M I						
8.2	20	0.5	5	93	5,500	1.06	8.6	105
8.2	20	1	5	96	11,200	1.03	8.7	106
8.2	20	2	5	93	22,000	1.03	8.5	104
8.2	20	4	5	86	44,500	1.03	7.8	95
		I M A						
16.5	40	1	2	87	5,000	1.13	18	108
16.5	40	1+1	2+2	96	10,300	1.17	19	114
16.5	40	1+1+1	2+2+3	101	17,400	1.11	18	106

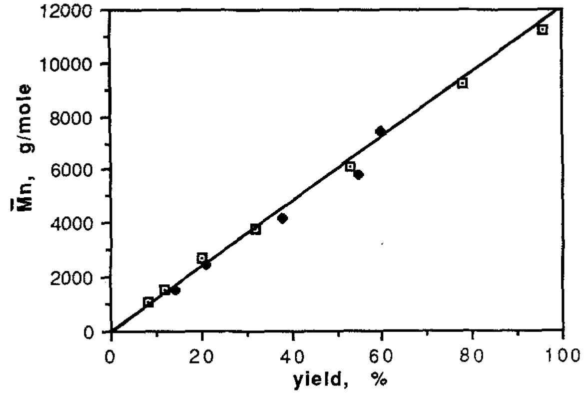

Figure 1. Molecular weight versus yield of polymer in IBuVE polymerization initiated by MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5.

◈ - in CH_2Cl_2

♦ - in CH_2Cl_2/hexanes 3:2 v/v

(see Table 1 for conditions)

The solid (theoretical) line was calculated from the monomer to initiator ratio.

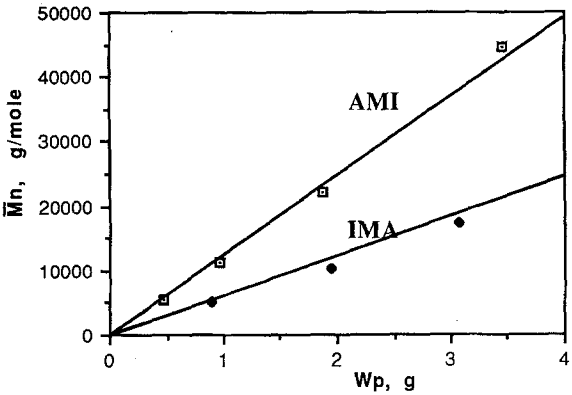

Figure 2. Polymer molecular weight versus yield in AMI and IMA experiments (the solid lines are theoretical).

(see Table 2 for conditions)

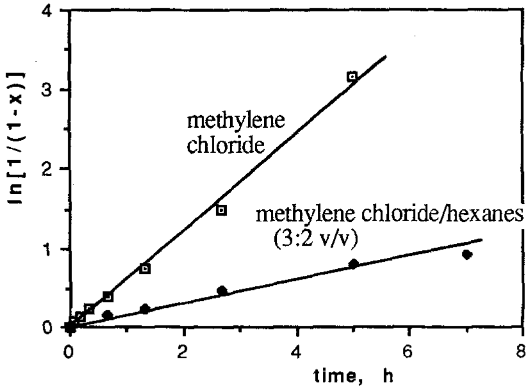

Fig. 3. First order plots of IBuVE polymerization initiated by MeCH(O*i*-Bu)Cl/*n*-Bu_4NTiCl_5. (see Table 1 for conditions)

A Failed Attempt for the Synthesis of an Olefin - Vinyl Ether Block Copolymer by the Use of n-Bu_4NTiCl_5.

In line with the above findings an attempt was made for the synthesis of poly(isobutylene-*b*-isobutyl vinyl ether).

It was amply documented (10) that the 2,4,4-trimethyl-2-chloropentane/$TiCl_4$/*n*-Bu_4NCl (where $TiCl_4$:*n*-Bu_4NCl=2:1) combination readily induces the LC⊕Pzn of isobutylene (IB). Formally, this system and that under investigation are quite similar since the initiators in both systems may be viewed to have arisen by combining the monomer (IB or IBuVE) and HCl. Thus, we hypothesized that under suitable conditions the crossover from living PIB⊕ to living PIB-PIBuVE⊕ could be achieved, and in this manner novel PIB-*b*-PIBuVE block copolymers could be synthesized in one pot by the sequential monomer addition.

The experiment was started by assembling a living PIB system under the conditions developed in (10) with $TiCl_4$:*n*-Bu_4NCl=2:1 at -80 °C. Upon ascertaining the completion of the living IB polymerization phase, predetermined amount of *n*-Bu_4NCl was added to reach stoichiometrically equivalent amounts of $TiCl_4$ and *n*-Bu_4NCl. To avoid the presence of excess $TiCl_4$ which is detrimental to vinyl ether polymerization (11), a slight molar excess (5-10 mole %) of *n*-Bu_4NCl was added. In this manner, "Kennedy's conditions" conducive for living olefin polymerization were converted to "Nuyken's conditions" that yield living vinyl ether polymerization. Subsequently, the temperature of the charge was raised to -20 °C and IBuVE was added. In repeated trials, the analytical data (NMR and GPC) did not show any evidence for the postulated crossover or for the IBuVE polymerization.

In the face of this observation, we conclude that *n*-Bu_4NTiCl_5 is unable to activate the ~$C(CH_3)_2$-Cl bond of the PIB termini. Evidently, the ~C-Cl bond is easier to activate in ~$CH_2CH(O$*i*-Bu)-Cl than in ~$CH_2C(CH_3)_2$-Cl.

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