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Living carbocationic polymerization

XXVIII. Telechelic polyisobutylenes by bifunctional *tert*-dichloroacetate initiators*

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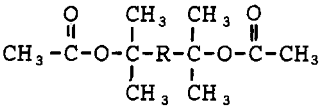
Abstract

The synthesis of α,ω-di-tert-chloropolyisobutylenes (^{t}Cl-PIB-Cl^{t}) with up to $\bar{M}_n$ ∿25,000 has been accomplished by the living polymerization of isobutylene (IB) using aliphatic di-tert-dichloroacetate initiators in conjunction with BCl_3 coinitiator in CH_3Cl and C_2H_5Cl solvents at -30°C. In comparison with the corresponding di-tert-diacetates, both rates and initiator efficiencies (I_{eff}) are greatly increased. Thus polymerizations are rapid and give 50-75 and 100% I_{eff}s with 2,5-dichloroacetoxy-2,5-dimethylhexane ($D(Cl_2AcO)DMeH_6$) and trans-2,5-dichloroacetoxy-2,5-dimethyl-3-hexene ($D(Cl_2AcO)DMeH_6^{=}$), respectively. With 2,5-dichloroacetoxy-2,5-dimethyl-3-hexyne ($D(Cl_2AcO)DMeH_6^{\equiv}$) the rates are relatively slower but the I_{eff}s are ∿100%. The number average end functionalities $\bar{F}_n$ were found to be 2.0 ± 0.1 by ^1H NMR spectroscopy.

Introduction

In an earlier publication (1) we have described the living polymerization of IB initiated with various tert-diacetates



$$CH_3-\overset{\overset{\large O}{\|}}{C}-O-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-R-\underset{\underset{\large CH_3}{|}}{\overset{\overset{\large CH_3}{|}}{C}}-O-\overset{\overset{\large O}{\|}}{C}-CH_3$$

where R = $-CH_2CH_2-$, $-C{\equiv}C-$, $-CH_2C(CH_3)_2CH_2-$, and $-C_6H_4-$. With R = $-CH_2CH_2-$ or $-C{\equiv}C-$ polymerizations in CH_3Cl were too slow due to low initiator activity. In the more polar CH_2Cl_2 diluent polymerizations were faster but I_{eff}s remained below 40% even at -20°C. Recently it has been reported that trans-2,5-diacetoxy-2,5-dimethyl-3-hexene, i.e., R = trans-CH=CH-, also gives rise to slow initiation (2). Dicumyl acetate, R = $-C_6H_4-$, gave extremely fast initiation due to fast ion generation, however, led to undesirable indanyl skeletons, which could be eliminated only by working at very low temperatures (< -70°C) and low solvent polarity (1).

Recently we have been investigating the living polymerization of IB initiated with 2,4,4-trimethylpentyl esters of different acids, $CH_3C(CH_3)_2CH_2C(CH_3)_2OCOR'$ in conjunction with BCl_3(3). It was concluded that due to induction the nature of the R' group affects the strength of the tert-C-OCOR' bond,

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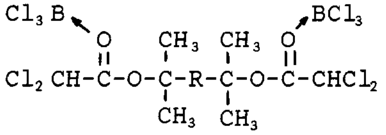
*For paper XXVII in this series see Polym. Bull. 21, 5 (1989)

**Visiting scientist; permanent address: Dept. Applied Chemistry, Kossuth Lajos University, H-4010 Debrecen, Hungary and thus influences the rate of propagation. Electron withdrawing or donating R' groups were found respectively to increase or decrease the rates.

We theorized, that similarly to propagation, initiation could also be accelerated by electron withdrawing R' groups, i.e., by substituting electron withdrawing groups i.e., R' = $-CH_2Cl$, $-CHCl_2$, for the parent R' = $-CH_3$ we would achieve fast initiation where there was none or only a very slow one. In line with this thought this paper concerns the polymerization of IB with di-tert-dichloroacetate/BCl_3 initiating systems:



$$Cl_2CH-\overset{\overset{Cl_3B\searrow}{O}}{\overset{\|}{C}}-O-\underset{CH_3}{\overset{CH_3}{C}}-R-\underset{CH_3}{\overset{CH_3}{C}}-O-\overset{\overset{\nearrow BCl_3}{O}}{\overset{\|}{C}}-CHCl_2$$

where R = $-CH_2CH_2-$, trans-$CH{=}CH-$, and $-C{\equiv}C-$ under a variety of conditions, and demonstrates that $^{\underline{t}}Cl-PIB-Cl^{\underline{t}}$ can be obtained in fast reactions with these systems.

Experimental

The source and purity of the materials used, i.e., IB, CH_3Cl, C_2H_5Cl and BCl_3, together with polymerization conditions, and characterization methods have been described (4).

$D(Cl_2AcO)DMeH_6$, $D(Cl_2AcO)DMeH_6^{=}$ and $D(Cl_2AcO)DMeH_6^{\equiv}$ were synthesized from the corresponding diols and dichloroacetylchloride (all chemicals from Aldrich Chemical Co.) using the procedure described in Ref. 1 but with dimethylaminopyridine as catalyst. After workup (1) these new di-tert-dichloroacetates were recrystallized from petroleum ether below 0°C, redissolved at room temperature in larger amounts of petroleum ether, repurified by column chromatography on neutral Al_2O_3 (activity III) with petroleum ether as solvent. The final product was prepared by crystallization from the eluent. $D(Cl_2AcO)DMeH_6$: Yield: 57%; mp = 64-65°C; ^1H NMR (1.50 ppm, s, 12H; 1.85 ppm, s, 4H; 5.60 ppm, s, 2H). $D(Cl_2AcO)DMeH_6^{=}$: Yield: 8.7%; mp = 66-67°C; ^1H NMR (1.57 ppm, s, 12H; 5.50 ppm, s, 2H; 5.73 ppm, s, 2H). $D(Cl_2AcO)MeH_6^{\equiv}$: Yield: 21%; mp = 64-65°C; ^1H NMR (1.70 ppm, s, 12H; 5.65 ppm, s, 2H).

The $D(Cl_2AcO)DMeH_6^{=}$ is unstable, after a few hrs at room temperature it decomposes to a deep purple liquid. Experiments with this initiator were carried out with freshly (same day) prepared and recrystallized material. The freshly recrystallized product was washed with petroleum ether, dried for $\sim$30 mins in vacuum, and chilled to -78°C for manipulations. The stability of $D(Cl_2AcO)DMeH_6$ and $D(Cl_2AcO)DMeH_6^{\equiv}$ are satisfactory, they can be stored in a refrigerator for a few weeks without significant decomposition. The Chemical Abstracts Formula Index (1927-1988) does not list these dichloroacetates.

Results and Discussion

Similarly to IB polymerizations initiated with the monofunctional tert-dichloroacetate $CH_3C(CH_3)_2CH_2C(CH_3)_2OCOCHCl_2$ in CH_3Cl (3), the corresponding di-tert-dichloroacetate $D(Cl_2AcO)DMeH_6$ also induced very fast polymerizations leading to complete conversions in less than one minute. After scouting experiments, we have carried out a series of incremental monomer addition (IMA) experiments using CH_3Cl and C_2H_5Cl diluents at -30°C. Figure 1 shows experimental conditions and the results treated as an $\bar{M}_n$ versus W_{PIB} (the weight of the PIB formed) plot and an N (the number of moles of PIB obtained) versus W_{PIB} plot (inset). The shape of the plots are characteristic of slow initiation (2). Initiator efficiencies start

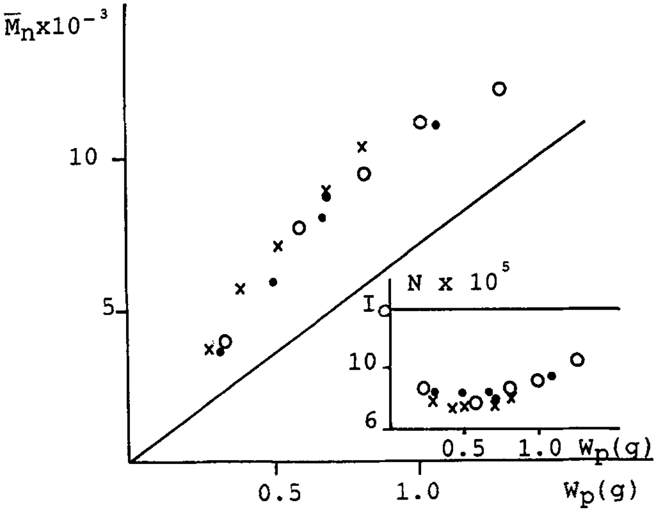


Figure 1. $\bar{M}_n$-W_{PIB}, and N-W_{PIB} plots for the polymerization of IB with the $D(Cl_2AcO)DMeH_6/BCl_3$ initiating system at -30°C (The solid lines are theoretical) (IMA, $[BCl_3] = 5.4 \cdot 10^{-2}$ mole/L, $[I] = 5.6 \cdot 10^{-3}$ mole/L, 5 x 0.5 mL IB, 25 mL, 30 min) CH_3Cl(●,o), C_2H_5Cl(x)

at ∿50% for the first experimental points and reach ∿75% after five monomer increments. As compared to the results obtained with a variety (i.e., with R = $-CH_2CH_2-$, $-CH_2C(CH_3)_2CH_2-$, $-C{\equiv}C-$), of tert-diacetates (1) polymerization rates and I_{eff}s obtained with this tert-dichloroacetate are vastly increased. While the 2,5-diacetoxy-2,5-dimethylhexane/BCl_3 system (i.e., R = $-CH_2CH_2-$) was inactive in C_2H_5Cl, under similar conditions the corresponding $D(Cl_2AcO)DMeH_6$ induced fast polymerizations and the rates were only slightly lower than in CH_3Cl. As shown in Figure 1, the $\bar{M}_n$ and W_p data obtained by the use of CH_3Cl and C_2H_5Cl diluents are indistinguishable. While C_2H_5Cl is a less favored diluent than CH_3Cl for living IB polymerization (3) it is a somewhat better solvent for PIB than CH_3Cl. Thus IMA series were carried out by the use of C_2H_5Cl diluent at lower initiator concentration to prepare higher molecular weight PIB. Figure 2 shows experimental conditions and results. The molecular weights obtained were indeed higher and the I_{eff}s increased from ∿50% to 75% at $\bar{M}_n$ ∿25,000. As judged by the shapes of the plots (2) the rate of initiation was relatively low.

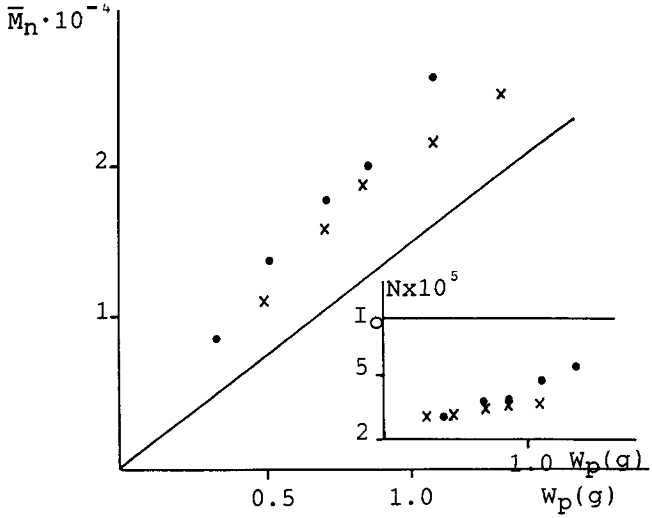


Figure 2. $\bar{M}_n$-W_{PIB}, and N-W_{PIB} plots for the polymerization of IB with the D(Cl_2AcO)DMeH_6/BCl_3 initiating system at -30°C. (IMA, [BCl_3] = 5.4 x 10^{-2} mole/L, [I] = 2.8·10^{-3} mole/L, 5 x 0.5 mL IB, C_2H_5Cl, 25 mL, 30 min) (Duplicate runs. The solid lines are theoretical)

In contrast to experiments with the tert-diacetates (2) and with D(Cl_2AcO)DMeH_6 described above, scouting experiments with the D(Cl_2AcO)DMe$H_6^{=}$ initiator, (i.e. with R = trans-CH=CH-) under otherwise identical conditions exhibited greatly enhanced initiating activity and readily yielded I_{eff}s ~100%. Enhanced initiator activity is most likely due to enhanced resonance stabilization of the initiating cationic species:

$Cl_2CHCOOC(CH_3)_2\text{-}CH{=}CH\text{-}\overset{\oplus}{C}(CH_3)_2 \cdots \overset{\ominus}{O}COCHCl_2 \cdot BCl_3$.

The molecular weight dispersities obtained with the tert-dichloroacetates are broader (see $\bar{M}_w/\bar{M}_n$ data in Figure 3) than those obtained with the corresponding tert-diacetates (2). The reason for this difference is unclear.

While the D(Cl_2AcO)DMeH_6 and D(Cl_2AcO)DMe$H_6^{=}$ initiators result in very fast polymerizations, D(Cl_2AcO)DMe$H_6^{\equiv}$ (i.e., R = -C≡C-) gave somewhat lower rates. A similar observation was reported with the corresponding tert-diacetates i.e., with R = -CH_2CH_2-, -CH=CH-, and -C≡C-, using both CH_3Cl and CH_2Cl_2 diluents at -30°C (1). The low polymerization rates enabled us to construct conversion-time and $\bar{M}_n$-conversion plots shown in Figure 4. The $\bar{M}_n$-conversion plot is linear starting at the origin and the experimental data are within what is considered to be experimental variation of the theoretical line, indicating living polymerization with I_{eff} ~100%. As shown by the data in Table I, the rates of polymerization (i.e., conversion data obtained at different [I]s) obtained with the

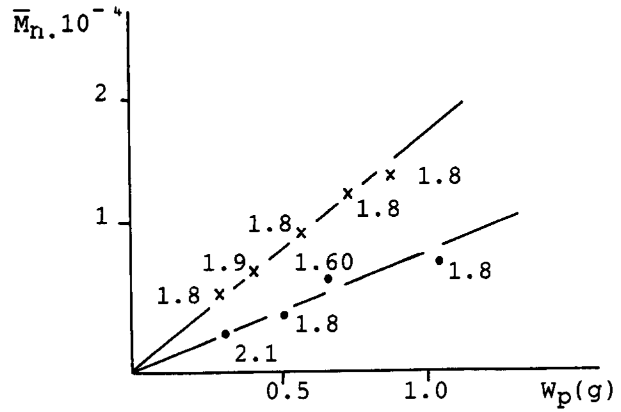


Figure 3. Living polymerization of IB by the $D(Cl_2AcO)DMeH_6^-/BCl_3$ system at -30°C in CH_3Cl(●) and C_2H_5Cl(x). (IMA, $[BCl_3] = 5.4 \cdot 10^{-2}$ mole/L, [I] in $C_2H_5Cl = 2.4 \cdot 10^{-3}$ mole/L, IB in $CH_3Cl = 5 \times 0.5$ mL, IB in $C_2H_5Cl = 5 \times 0.5$ mL, 25 mL, 30 min). Numbers are $\overline{M}_w/\overline{M}_n$ values. (The solid lines are theoretical)

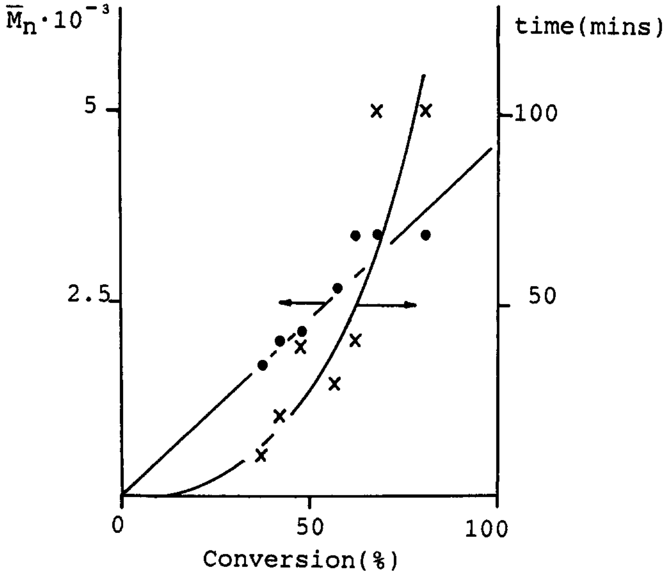


Figure 4. Conversion-time and conversion-$\overline{M}_n$ plots for the polymerization of IB, initiated by $D(Cl_2AcO)DMeH_6^=/BCl_3$ system in CH_3Cl at -30°C. ([IB] = 0.94 mole/L, $[BCl_3] = 5.4 \cdot 10^{-2}$ mole/L, $[I] = 4.9 \cdot 10^{-3}$ mole/L, 25 mL) (The solid line in the conversion-$\overline{M}_n$ plot is theoretical)

$D(Cl_2AcO)DMeH_6^{\equiv}/BCl_3$ system using CH_3Cl or C_2H_5Cl diluents are similar. These results are similar to those obtained with the $D(Cl_2AcO)DMeH_6$ and $D(Cl_2AcO)DMeH_6^{=}$ initiators. It is of interest that although all three initiators lead to living polymerizations only those with R = $-CH_2CH_2-$ and -CH=CH- gave relatively fast rates whereas that with R = $-C{\equiv}C-$ led to slower polymerization.

TABLE I

Comparison of Polymerization Results Using CH_3Cl and C_2H_5Cl Diluents

($D(Cl_2AcO)DMeH_6^{\equiv}$, $[BCl_3] = 5.4 \cdot 10^{-2}$ mole/L, [IB] = 0.94 mole/L, 25 mL, 30 min., -30°C)

	CH_3Cl		C_2H_5Cl	
I^* mole/ℓ	1.12×10^{-2}	2.8×10^{-2}	5.6×10^{-3}	1.4×10^{-2}
conversion, %	63.4	95.0	27.8	69.1
$\overline{M}_n$, g/mol	3300	2300	2800	2800
M_w/M_n	1.6	1.8	2.1	1.9
I_{eff}, %	90	81	93	93

$^*I = D(Cl_2AcO)DMeH_6^{\equiv}$

Quantitative End-Group Characterization

The ^1H NMR spectra of low molecular weight ($\overline{M}_n$ = $2\text{-}4 \times 10^3$) PIB samples have been investigated. Low $\overline{M}_n$ samples were chosen to facilitate spectroscopic characterization (4). All the products exhibited the characteristic resonances associated with the $-CH_2C(CH_3)_2Cl$ end group and there was no evidence for the presence of terminal unsaturation (i.e., evidence for chain transfer to monomer). The integrated ratio of terminal proton resonances $-CH_2C(C\underline{H}_3)Cl$ (δ = 1.6 ppm) plus $-C\underline{H}_2C(CH_3)_2Cl$ (δ = 1.90 ppm) relative to all other protons in $-C\underline{H}_2C(C\underline{H}_3)_2-$ units (i.e., δ_{CH_3} = 1.10 and δ_{CH_2} = 1.40 ppm) plus incorporated initiator fragments was used to calculate the number average end functionality $\overline{F}_n$. Table II shows a representative set of data. Evidently $\overline{F}_n$ = 2.0 ± 0.1 within experimental error in the $\overline{M}_n$ = $2\text{-}4 \times 10^3$ range.

TABLE II

$\overline{F}_n$'s of ^{t}Cl-PIBCl^t Prepared by di-tert-Dichloroacetate/BCl_3 Initiating Systems

R	$\overline{M}_n \cdot 10^3$	$\overline{M}_w/\overline{M}_n$	$\overline{F}_n$
$-CH_2CH_2-$	3.7	2.0	1.9 ± 0.15
-CH=CH-	2.3	2.1	2.0 ± 0.10 2.05 ± 0.09*
$-C{\equiv}C-$	2.0	1.8	1.9 ± 0.10

*Calculated from $-C\underline{H}_2C(C\underline{H}_3)_2Cl/-C\underline{H}=C\underline{H}-$ proton ratio

Acknowledgement

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