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Living Carbocationic Polymerization
III. Demonstration of the Living Polymerization of Isobutylene

R. Faust and J.P. Kennedy

Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

Abstract

A new family of initiating systems has been discovered that efficiently induces the truly living polymerization of isobutylene (IB). The initiating systems are complexes of organic tertiary esters e.g., cumyl acetate, 2,4,4-trimethylpentane-2-acetate, with BCl_3. Living polymerizations proceed very rapidly in a variety of solvents, i.e., CH_3Cl, CH_2Cl_2, C_2H_5Cl, and mixtures of chlorinated solvents plus n-hexane, in the range from -10° to -50°C. The living nature of the polymerizations was demonstrated by linear $\overline{M}_n$ versus W_{PIB}(g of polymer formed) plots starting at the origin and horizontal N (number of PIB chains) versus W_{PIB} plots. The $\overline{DP}_n$ of the products obeys $[M_o]/[I_o]$ where $[M_o]$ and $[I_o]$ are initial monomer and initiator concentrations, respectively. Conversions and initiator efficiencies are ∿100%. In carefully controlled experiments narrow molecular weight distribution polyisobutylenes (PIB) have been obtained, i.e., $\overline{M}_w/\overline{M}_n = 1.17 - 1.3$. A mechanism is outlined that helps rationalize the findings. It is postulated that the living polymerization of IB initiated by organic tertiary ester·BCl_3 complexes most likely proceeds by a two-component group transfer polymerization process.

Introduction

While well-characterized complexes of esters of carboxylic acids and Lewis acids, i.e., BCl_3, are known since a long time (1), they have not been used as initiating systems for cationic polymerization. Indeed the presence of esters in carbocationic polymerizations is quite undesirable (2). The chemical behavior of ester·BCl_3 complexes has been studied by Gerrard and Wheelans (3).

Experimental

Materials. Cumyl acetate (CuOAc) was prepared from 2-phenyl-2-propanol and acetyl chloride in the presence of N,N-dimethyl aniline in anhydrous ether. 2,4,4-Trimethylpentane-2-acetate (TMPOAc) was synthesized from 2,4,4-trimethyl-2-pentanol and acetyl chloride. t-Butyl acetate (tBuOAc) was a commercial product (Aldrich). All the other materials were purified and characterized by accepted methods.

Procedures. Polymerizations were carried out in a stainless steel dry box under a dry nitrogen atmosphere using large test tubes or round bottom flasks. Molecular weights were determined by a Waters high pressure GPC instrument equipped with dual RI and UV detectors and five μ-Styragel columns, and a calibration curve made by well-fractionated PIB standards. ^{1}H NMR spectra were taken by a Varian T-60 Spectrometer.

Results and Discussion

Preliminary Experiments. Preliminary experiments have shown that various tertiary esters, i.e., tBuOAc, TMPOAc and CuOAc in conjunction with BCl_3 in polar diluents (i.e., CH_3Cl, CH_2Cl_2, C_2H_5Cl) readily initiate the polymerization of IB and yield high conversions over the range from -10 to -50°C. Initiation occurs only in tricomponent systems, i.e., organic acetate/BCl_3/IB, regardless of the introduction sequence of the chemicals. "Control" experiments i.e., experiments carried out by mixing IB with BCl_3 solutions in CH_3Cl yield insignificant conversions (<7%) and relatively higher molecular weights. Control experiments carried out by the use of CH_2Cl_2 yield high conversions; however, these results are in line with previous experience (4) which showed that initiation in the presence of BCl_3 in CH_2Cl_2 is due to traces of protic impurities (most likely moisture). Nonetheless even in these controls we obtained much higher molecular weights and the conversions were noticeably below 100%; in contrast, in the presence of acetates conversions were complete and the $\bar{M}_n$s were determined by the $[M]/[CH_3COOR^{\underline{t}}]$ ratio.

Table I shows the results of some representative experiments. Polymerizations were very fast, indeed they ensued instantaneously upon BCl_3 addition.

A closer examination of the molecular weight data indicates that the effect of moisture is most likely unimportant. The $\bar{M}_n$s obtained in CH_2Cl_2 and CH_3Cl are similar although the level of moisture is quite different (note the high conversions obtained in CH_2Cl_2 in contrast to the insignificant level of conversions found in CH_3Cl). The concentration of the $CH_3COOR^{\underline{t}}$ initiators and moisture in CH_2Cl_2 are probably of the same order of magnitude ($\sim 10^{-3}$M). This implies that the effect of the $H_2O \cdot BCl_3$ on the polymerization of IB induced by $CH_3COOR^{\underline{t}} \cdot BCl_3$ complexes is negligible.

Demonstration of Living Polymerization. Since the polymerizations were too fast for kinetic investigations, we were compelled to carry out experiments by a procedure we term the "incremental monomer addition" (IMA) technique. Thus 5-6 reactors were charged with CuOAc/IB or TMPOAc/IB in CH_2Cl_2 or CH_3Cl and at zero time was added to all the charges at -30°C. The systems were mixed and placed in a bath at -30°C. After 30 mins the polymerization was quenched in the first reactor (addition of a few ml prechilled methanol) whereas an additional quantity of IB was added to all the remaining reactors. After 30 mins the reaction in the second reactor was quenched and a further quantity of IB was added to the rest of the reactors. This procedure was continued until all the charges in the series have been quenched. The amounts of polymers formed (conversions) were determined by gravimetry, and $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ by GPC.

TABLE I

Demonstration of Initiating Activity of Various tert.-Acetate·BCl_3 Complexes under Various Conditions*

Conditions				Results				
CH_3COOR^t		Diluent	Temp	Conv.	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	I_{eff}
R^t	conc		°C	%	g/mole	g/mole	-	%
-	-	CH_3Cl	-50	6.6	116400	230000	2.0	-
t-Bu	$2.8x10^{-2}$	CH_3Cl	-50	100**	7370	15000	2.0	28
t-Bu	$5.6x10^{-2}$	CH_3Cl	-50	100	4240	7210	1.7	24
-	-	CH_3Cl	-30	60	36000	72000	2.0	-
t-Bu	$5.6x10^{-3}$	CH_3Cl	-30	13.5	31000	48200	1.5	32
t-Bu	$2.8x10^{-2}$	CH_3Cl	-30	100	4650	8930	1.9	44
t-Bu	$5.6x10^{-2}$	CH_3Cl	-30	100	2950	5590	1.9	35
-	-	CH_2Cl_2	-30	75	49800	103300	2.1	-
t-Bu	$5.6x10^{-3}$	CH_2Cl_2	-30	100	27500	66800	2.4	36
t-Bu	$2.8x10^{-2}$	CH_2Cl_2	-30	100	4230	10420	2.4	48
t-Bu	$5.6x10^{-2}$	CH_2Cl_2	-30	100	2470	5950	2.4	42
-	-	CH_2Cl_2	-10	68	28600	80000	2.8	-
t-Bu	$2.8x10^{-2}$	CH_2Cl_2	-10	100	4370	9200	2.1	47
t-Bu	$5.6x10^{-2}$	CH_2Cl_2	-10	100	2040	5090	2.5	51
-	-	CH_3Cl	-50	6.6	116400	23000	2.0	-
TMP	$5.6x10^{-3}$	CH_3Cl	-50	100	10500	21500	2.0	97
TMP	$2.8x10^{-2}$	CH_3Cl	-50	100	1800	6300	3.6	121
TMP	$5.6x10^{-2}$	CH_3Cl	-50	100	1400	3400	2.4	80
-	-	CH_3Cl	-30	6.0	36000	72000	2.0	-
TMP	$5.6x10^{-3}$	CH_3Cl	-30	100	10770	15150	1.5	94
TMP	$2.8x10^{-2}$	CH_3Cl	-30	100	2090	5320	2.5	103
TMP	$5.6x10^{-2}$	CH_3Cl	-30	100	1290	2800	2.2	88
-	-	CH_3Cl	-30	6.0	36000	72000	2.0	-
Cu	$5.6x10^{-3}$	CH_3Cl	-30	100***	8500	13600	1.6	115
Cu	$2.8x10^{-2}$	CH_3Cl	-30	100	2000	3400	1.7	104
Cu	$5.6x10^{-2}$	CH_3Cl	-30	100	1160	2820	2.4	96
-	-	C_2H_5Cl	-30	2.0	-	-	-	-
Cu	$5.6x10^{-3}$	C_2H_5Cl	-30	100***	9500	14100	1.5	107
Cu	$2.8x10^{-2}$	C_2H_5Cl	-30	100	2390	3980	1.7	90
Cu	$5.6x10^{-2}$	C_2H_5Cl	-30	100	1260	2050	1.6	91

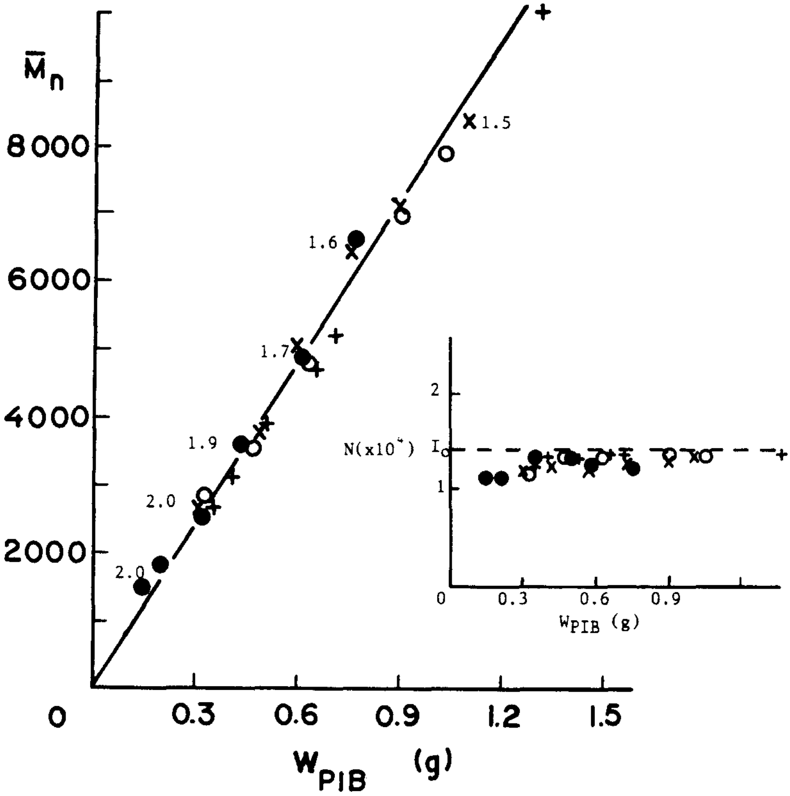
*$[BCl_3] = 2.6x10^{-1}$ mol/ℓ, [M] = 1.0 mol/ℓ, time = 30 min.

** Pzn. time was 1 hour

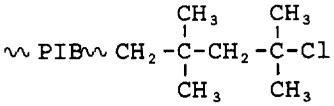
***Conv. was 100% after 1 min.

Figure 1 shows a representative $\overline{M}_n$ versus g polymer formed plot obtained in a series of experiments carried out with CuOAc at -30°C. The insert in Figure 1 shows the number of PIB chains N as a function of weight of polymer formed. The linear $\overline{M}_n$ and horizontal N versus g PIB plots suggest living polymerizations. The fact that the $\overline{M}_w/\overline{M}_n$ values decrease with increasing monomer addition suggests that the growing ability of the living species persists throughout the experiment.

Figure 1. $\overline{M}_n$ and N (the number of PIB chains, insert) Versus the Weight of PIB Formed W_{PIB} in the CuOAc/BCl_3/IB/CH_3Cl/-30°C System. $[I_o] = 5.6 \times 10^{-3}$M, $[BCl_3] = 2.8 \times 10^{-1}$M. Numbers Indicate $\overline{M}_w/\overline{M}_n$ Values



Termination Studies. If termination is desired (for example for terminal functionalization) it could be effected by increasing the temperature above the decomposition temperature of the propagating ester/BCl_3 complex or by the addition of nucleophiles, e.g., alcohols, amines ("killing"). We have examined the structure of the end groups of various PIBs after the active ester/BCl_3 complex was decomposed by heating to room temperature or by the addition of various amines, CH_3OH, etc. Surprisingly all the experiments irrespective of the particular killing method yielded t-chloro-end groups, i.e.,



$$\sim\sim PIB\sim\sim CH_2-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-Cl$$

The analysis of the end groups has been carried out by ^1H NMR spectroscopy by the use of well-established methods (5). The findings have been fully corroborated by the results of model experiments.

Conclusions: Mechanistic Speculations. Evidence has been presented that demonstrates for the first time the truly living polymerization of isobutylene. The PIBs so obtained do not contain terminal unsaturation which is evidence for the absence of chain transfer to monomer. PIB molecular weights are controlled by the relative ratio of monomer over initiator (i.e., $CH_3COOR^{\underline{t}}$) concentrations, i.e., $\overline{DP}_n = [M_o]/[I_o]$. The molecular weight distributions are somewhat broader, $\overline{M}_w/\overline{M}_n = 1.3 - 2.0$, most likely due to rapid propagation relative to initiation and various physical effects i.e., heterogeneity, insufficient stirring (heat effect) of rapid polymerizations. Experiments designed to give narrower MWDs have yielded $\overline{M}_w/\overline{M}_n = 1.17 - 1.3$.

Protic impurities (moisture) have little effect on these living polymerizations and the experiments can be carried out under conventional conditions by the use of conventionally dried solvents under a blanket of dry nitrogen.

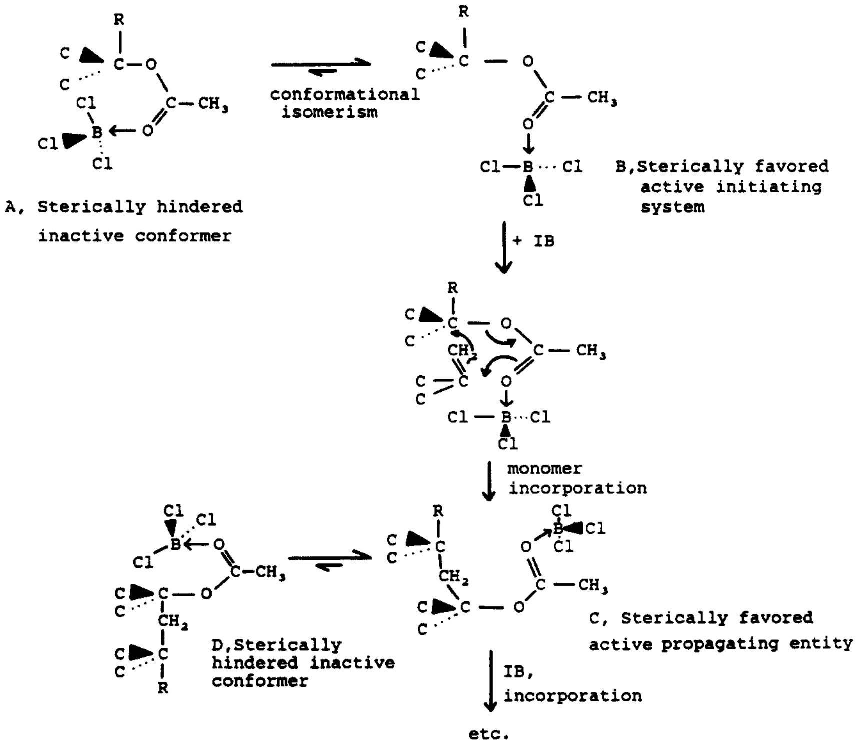
Scheme I may explain some of the features of living IB polymerizations by, for example, the TMPOAc/BCl_3 system ($R = CH_2-C(CH_3)_3$). The rate of complex formation between acetates and BCl_3 is very rapid. The site of complexation is the acyl oxygen (1). Conformer B is sterically more favored to incorporate incoming monomer. Significantly, monomer incorporation would yield a tertiary acetate·BCl_3 complex structurally identical to the initiating complex. In this sense this system is akin to a group transfer polymerization (6).

Scheme II helps visualize the mechanism of forced termination. Heating or nucleophilic attack on B may induce the proposed S_{N_i} rearrangement (molecular model study).

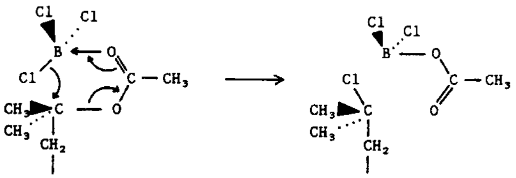
Terminal functionalization to the versatile tertiary chloro group is a valuable new route for the preparation of end-functional polymers.

Experimentation is in progress to extend the scope of this discovery over copolymerizations, telechelic derivatives, etc.

Scheme I. Initiation and Propagation in Living IB Polymerization



Scheme II. Forced Termination in Living IB Polymerization Initiated by the TMPOAc/BCl$_3$ System



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