Living carbocationic polymerization
XVI. Living carbocationic polymerization of styrene

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Summary

Living carbocationic polymerization of styrene (St) has been achieved by the use of the 1(p-methylphenyl)ethyl acetate (pMePhEtOAc)·BCl_3 complex in CH_3Cl solvent at -30°C using both the IMA and AMI techniques. The living nature of the polymerizations has been demonstrated by linear $\overline{M}_n$ versus W_{PSt} (weight of polystyrene) plots passing through the origin and horizontal N (moles of PSt) versus W_{PSt} plots starting at N = I_o (the number of moles of initiator used). The molecular weight distribution MWD of the PSts is broad ($\overline{M}_w/\overline{M}_n$ = ∿5-6) due to slow initiation and/or slow exchange between dormant and active species relative to propagation. The structure of the ester initiator strongly affects the rate and outcome of living polymerization, e.g., cumyl acetate (CumOAc), cumyl propionate (CumOPr), and 2,4,6-trimethylphenylethyl acetate (TMePhEtOAc), do not lead to truly living St polymerizations. The findings with the latter esters is explained in terms of a two path process comprising a slow living polymerization and a faster conventional cationic chain reaction. With phenylethyl acetate (PhEtOAc) living polymerization is achieved, however, initiation (cation generation) is slow. Forced termination by pyridine or methanol, or heating to ambient temperature leads to -$CH_2CH(C_6H_5)Cl$ end groups.

Introduction

Recently we have discovered that certain organic esters or ethers in the presence of Friedel-Crafts acids give rise to truly living polymerization of isobutylene (1,2). This paper concerns the first phase of our investigations on styrene and its derivatives, specifically the demonstration of living carbocationic polymerization of styrene by various ester·BCl_3 complexes.

Experimental

The synthesis of CumOAc and CumOPr have been described (2,3). pMePhEtOAc and TMePhEtOAc were synthesized from the corresponding olefins by quantitative hydrochlorination in CH_2Cl_2 at 0°C, followed by acetylation with silver acetate (4). PhEtOAc (Pfaltz and Bauer) was used after distillation. St was washed first with 10% aqueous NaOH then with distilled water till neutral, dried over $CaCl_2$, and distilled from CaH_2

at reduced pressure. The source and purification of CH_3Cl and BCl_3 have been described (1,2).

Polymerizations were carried out in large test tubes by introducing BCl_3 into ester/St/CH_3Cl charges of 25 ml total volume. Polymerization conditions and characterization methods have been described (1,2). The charges were colorless and homogeneous (PSt is soluble in CH_3Cl). Reactions were quenched by prechilled MeOH, or were terminated by decomposing the initiating ester·BCl_3 complex by allowing the charges rapidly ($\sim$5 min) to warm to room temperature. Thus the CH_3Cl was rapidly evaporated.

Instrumentation and procedures used for molecular weight determination have been described (1,2). A GPC calibration curve made with narrow MWD PSt standards has been used.

Results and Discussion

A. "Control" Experiments

The addition of BCl_3 to St/CH_3Cl charges (i.e., in the absence of purposely added initiators) yielded 50-80% conversions in the -30° to -50°C range. Table I shows the results of these "control" experiments. The number of PSt molecules formed N is about equal to the number of moles of adventitious "H_2O" in the system (10^{-3} to 10^{-4} mole/L) which suggests that "H_2O"·BCl_3 is the true initiating system in these runs and that chain transfer is insignificant or absent. Incomplete conversions and the fact that conversions increase with decreasing temperatures suggest a termination-dominated system (5).

TABLE I

Polymerization of Styrene in the Absence of Added
Initiator (Controls)

Temperature °C	Time mins	Conversion %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	[N] mole/L
-30	1	8.4	67,000	2.0	4.4×10^{-5}
-30	5	42.9	60,700	2.1	2.6×10^{-4}
-30	15	59.0	53,800	2.2	4.0×10^{-4}
-30	30	58.2	60,000	2.1	3.5×10^{-4}
-50	30	81.1	79,100	1.9	3.7×10^{-4}
-50	90	85.3	78,100	1.9	4.0×10^{-4}

CH_3Cl, [M] = 0.35 mole/L, [BCl_3] = 5.1×10^{-2} mole/L, total volume 25 mL

B. Truly Living Polymerization of St by the pMePhEtOAc·BCl_3 System

As a consequence of detailed orienting experiments (see Section C) truly living polymerization of St has been obtained by the use of the pMePhEtOAc·BCl_3 complex in CH_3Cl solvent at -30°C with both the IMA or AMI (1,2) techniques. Figure 1 shows the evidence, the linear $\overline{M}_n$ versus W_{PSt} line passing through the origin together with the horizontal N versus W_{PSt} plot with N = I_O. The MWDs are broad ($\overline{M}_w/\overline{M}_n$ = 5-6) due to slow initiation (ion generation) and/or slow exchange between

growing and dormant species <u>re</u>lative to propagation. Further, as shown in Figure 2, the $1/\overline{DP}_n$ versus $1/[M_o]$ plot, whose slope gives $[I_o]$ (2), indeed gave~2.7 x 10^{-3} mole/L, the concentration of pMePhEtOAc employed.
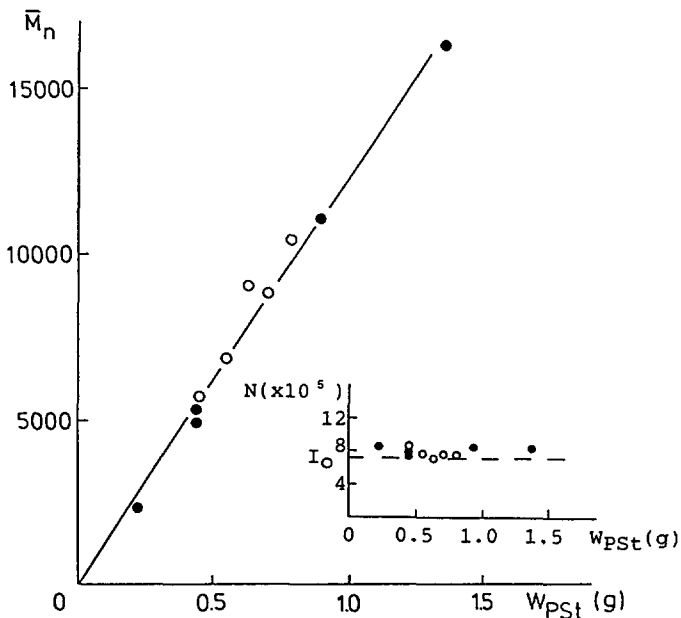

Figure 1. $\overline{M}_n$ and N, the number of moles of PSt chains (insert), versus the weight of PSt formed (W_{PSt}) in the pMePhEtoAc/BCl_3/St/CH_3Cl system using the IMA (O), and AMI (●) technique at -30°C. $[I_o]$ = 2.7 x 10^{-3} M, $[BCl_3]$ = 5.1 x 10^{-2} M

C. Experiments with BCl_3 Complexes of CumOAc, CumOPr, and TMePhEtOAc

While the pMePhEtOAC·BCl_3 complex gave truly living St polymerization, albeit with broad MWD, similar experiments with BCl_3 complexes of CumOAc, CumOPr and TMePhEtOAc did not yield truly living systems. As displayed in Figure 3, these systems are characterized by linear $\overline{M}_n$ versus W_{PSt} plots passing through the origin, however, the level of the horizontal N versus W_{PSt} plots are higher than $[I_o]$. Also the $1/\overline{DP}_n$ versus $1/[M_o]$ plot for the CumOAc run (Figure 2) gave a much larger value (6 x 10^{-3} mole/L) for $[I_o]$ than that employed. The fact that this plot is rectilinear and passes through the origin indicates the absence of chain transfer. It seems as though these polymerizations started with a burst of chain transfer after which the systems became living.

Independent experiments have shown that intermolecular ring alkylation (branch formation), which would reduce the overall number of PSt molecules formed, (i.e., would reduce the level of the horizontal N versus W_{PSt} line) was absent. Thus rapid polymerizations that have reached complete conversions in less than a minute have been quenched after various
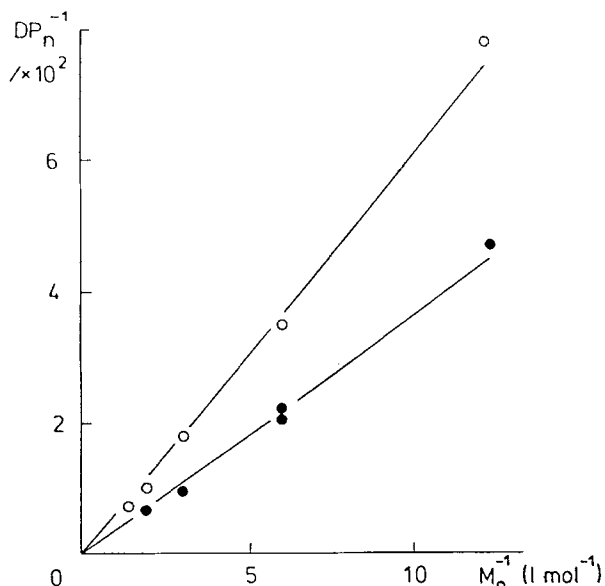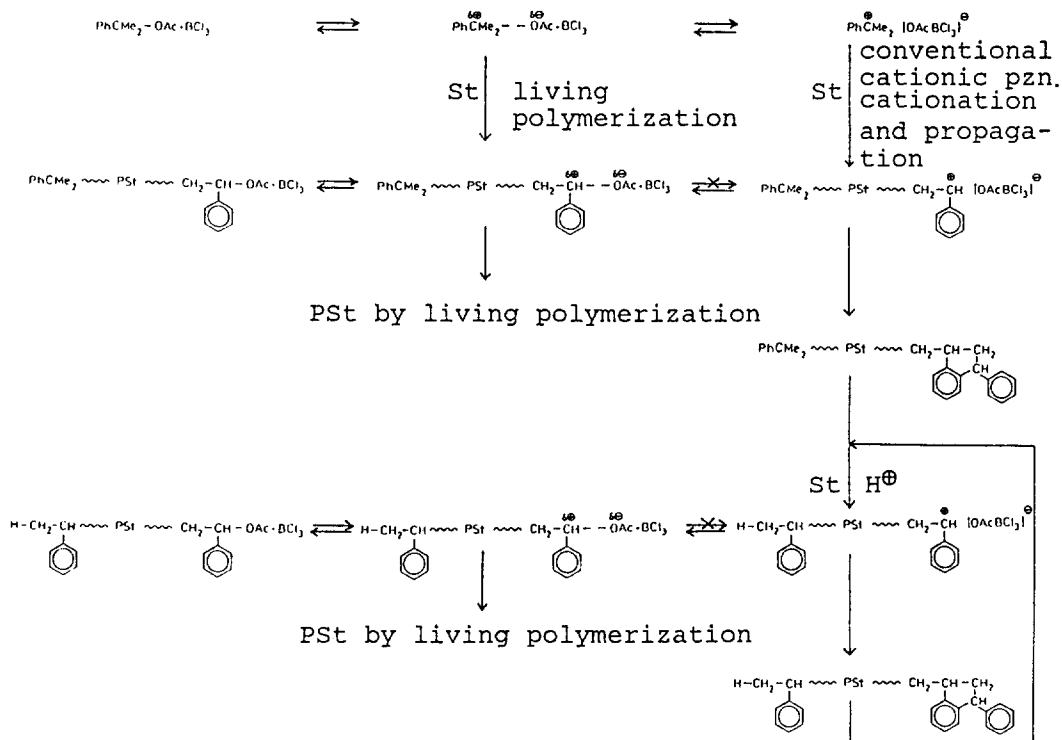
Figure 2. $1/\overline{DP}_n$ versus $1/[M_O]$ plot for the $St/BCl_3/CH_3Cl/$
$-30°C$ system using CumOAc(O) and pMePhEtOAc (●)
initiators.   [CumOAc]= [pMePhEtOAc] = 2.7×10^{-3} M,
$[BCl_3] = 5.1 \times 10^{-2}$ M

lengths of times (from 1 min up to 30 mins), however, the $\overline{M}_n$s
and $\overline{M}_w/\overline{M}_n$s remained essentially the same.   Also, the $\overline{M}_n$s of
PSts obtained in polymerizations carried out with various mon-
omer concentrations fell on the same line shown in Figure 3,
suggesting the absence of branch formation.

     The results with CumOAc, CumOPr and TMePhEtOAc may be
explained by assuming that these polymerizations proceed along
two paths: A slower living path initiated by covalent pol-
arized ester·BCl_3 complexes [C($\delta\oplus$)--($\delta\ominus$)O], and a rapid con-
ventional cationic path initiated by dissociated ion pairs
(i.e., Ph$\overset{\oplus}{C}$Me$_2$[OAcBCl$_3$]$^\ominus$, Ph$\overset{\oplus}{C}$Me$_2$[OPrBCl$_3$]$^\ominus$, or 2,4,6TMePhCMe$^\oplus$-
[OAcBCl$_3$]$^\ominus$).   The latter progresses either until ion pair
collapse leads to covalent polarized esters and thence to liv-
ing polymerizations, or until indanyl end group formation by
proton elimination occurs and the proton sustains conventional
styrene polymerization until the ionized species collapses to
the covalent polarized ester.   The Scheme helps to visualize
these systems (shown for CumOAc·BCl_3).   The CumOAc·BCl_3 com-
plex rapidly ionizes (via the polarized covalent intermediate
which induces the living path) to the tertiary benzylic
Ph$\overset{\oplus}{C}$Me$_2$ [OAcBCl$_3$]$^\ominus$ ion pair which in turn rapidly initiates the
conventional cationic path.   In contrast, the secondary benz-
ylic $\sim$CH$_2$CH(Ph)OAc·BCl_3 complex (second row) yields the cor-
responding polarized covalent intermediate which, however, is
reluctant to ionize (note the $\rightleftharpoons$).   In line with this propo-
sition the solvolysis rate of PhC(Me)$_2$Cl is by some three-four
orders higher than that of PhCH(Me)Cl (6,7).

PhCMe$_2$-OAc·BCl$_3$ ⇌ PhCMe$_2^{\oplus}$- -$^{\ominus}$OAc·BCl$_3$ ⇌ PhCMe$_2^{\oplus}$ [OAcBCl$_3$]$^{\ominus}$

St | living polymerization

St | conventional cationic pzn. cationation and propagation

PhCMe$_2$ ∿ PSt ∿ CH$_2$-CH-OAc·BCl$_3$ ⇌ PhCMe$_2$ ∿ PSt ∿ CH$_2$-CH$^{\oplus}$- -$^{\ominus}$OAc·BCl$_3$ ⇌✗⇌ PhCMe$_2$ ∿ PSt ∿ CH$_2$-CH$^{\oplus}$ [OAcBCl$_3$]$^{\ominus}$

PSt by living polymerization

PhCMe$_2$ ∿ PSt ∿ CH$_2$-CH-CH$_2$ (CH)

St | H$^{\oplus}$

H-CH$_2$-CH ∿ PSt ∿ CH$_2$-CH-OAc·BCl$_3$ ⇌ H-CH$_2$-CH ∿ PSt ∿ CH$_2$-CH$^{\oplus}$- -$^{\ominus}$OAc·BCl$_3$ ⇌✗⇌ H-CH$_2$-CH ∿ PSt ∿ CH$_2$-CH$^{\oplus}$ [OAcBCl$_3$]$^{\ominus}$

PSt by living polymerization

H-CH$_2$-CH ∿ PSt ∿ CH$_2$-CH-CH$_2$ (CH)

In regard to the conventional path, indanyl end group formation has been corroborated by model experiments and spectroscopic investigations. Thus St was oligomerized ($\overline{M}_n \approx$ 300) by CumOAc·BCl$_3$ using St/CumOAc = 2/1; proton NMR of the product clearly indicated indanyl end groups; i.e., resonances at δ = 4.3 t (Ph$_2$CH) and δ = 3.3 m (PhCH) (8) .

Representative $\overline{M}_w/\overline{M}_n$ values are shown in Figure 3. The somewhat broad MWDs obtained in these experiments are due to relatively slow ion generation, slow equilibration between the different growing centers, and presence of chain transfer to monomer. The progressive narrowing of MWDs with extended polymerizations as usually observed in similar systems (1,2), cannot occur on account of the slow exchange between dormant and growing species relative to propagation. Slow exchange is also reflected by the low rate of ion generation (low activity) of PhEtOAc·BCl$_3$ (see below).

The series of polymerizations carried out with PhEtOAc· BCl$_3$, i.e., the ester complex that most closely mimics the living chain end, gave much higher than theoretical $\overline{M}_n$s (i.e., the $\overline{M}_n$s expected to arise from [St]/[PhEtOAc] at 100% initiation efficiency, drawnout line in Figure 3). Evidently initiation is quite slow with this complex. The rate remained low even after premixing PhEtOAc with BCl$_3$ and aging for ∿10 mins, prior to adding the complex to the monomer charge, i.e., the rate of PhEtOAc·BCl$_3$ complex formation is not polymerization rate determining. Thus the reactivity of this complex is insufficient to result in rapid and complete initiation.
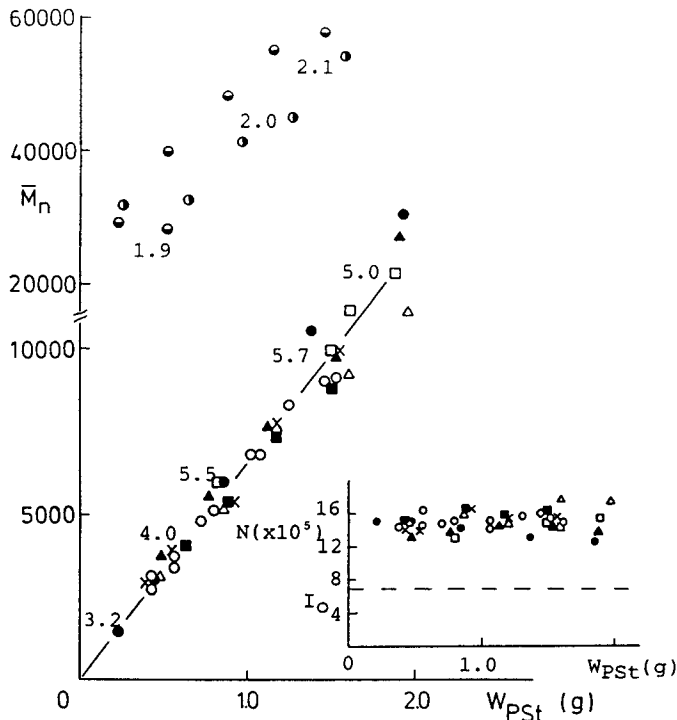
Figure 3.   The $\overline{M}_n$ and N, the number of moles of PSt chains (insert), versus the weight of PSt formed (W_{PSt}) plots in different systems.   O IMA CH_3Cl -30°C CumOAc,X IMA EtCl -30°C CumOAc. $\triangle$ IMA CH_3Cl -50°C CumOAc,□ IMA CH_3Cl -30°C CumOPr,● AMI CH_3Cl -30°C CumOAc ▲ IMA CH_3Cl -30°C TMePhEtOAc, ⊖ IMA CH_3Cl -30°C PhEtOAc (premixed), ◑ IMA CH_3Cl -30°C PhEtOAc, $[I_O] = 2.7 \times 10^{-3}M$, $[BCl_3] = 5.1 \times 10^{-2}M$

W_{PSt} versus time profiles obtained in IMA experiments with CumOAc and PhEtOAc shown in Figure 4 substantiate the dual path nature of these systems. Thus, with CumOAc·BCl_3 100% conversion was obtained within ∿0.5 min, in the first re-actor, however, when additional aliquots of St were added in the IMA series, the rates became lower and the conversions dropped below 100%, (below the "theoretical" dotted line in Figure 4). In line with the Scheme, the first monomer aliquot rapidly yields 100% PSt mostly by the conventional path. Sub-sequent aliquots polymerize slower by the living path induced by the -$CH_2\overset{\delta\oplus}{CH}$(Ph)-- $\overset{\delta\ominus}{O}AcBCl_3$ complex that has formed by a step that is tantamount to termination of the conventional path (note the $\overset{\delta\oplus}{\rightleftharpoons}$). That the slower polymerization is indeed due to -CH_2CH(Ph)-- $\overset{\delta\ominus}{O}Ac·BCl_3$ complexes is shown by the results of the series of experiment with PhEtOAc·BCl_3 (open circles in Figure 4) that mimicks the growing PSt end. The close proxim-ity of the weights of PSts obtained with CumOAc and PhEtOAc in
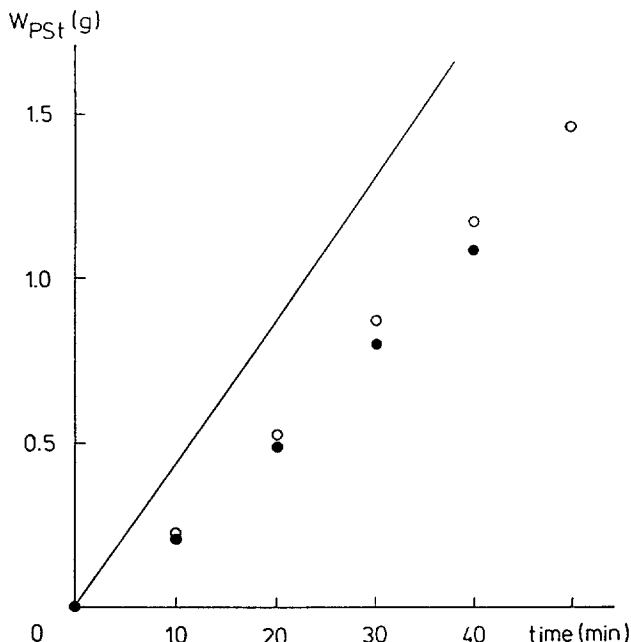
Figure 4. W_{PSt} versus time plot for the $St/BCl_3/CH_3Cl/-30°C$ polymerization system using the IMA technique with CumOAc($\bullet$) and PhEtOAc(O) initiators. [CumOAc] = [PhEtOAc] = 2.7×10^{-3}M, [BCl_3] = 5.1×10^{-2}M (With CumOAc the origin was shifted and the plot starts with the second monomer increment)

these runs suggests that the rates of these polymerizations must have been virtually identical, i.e., the concentration and reactivities of the growing chain ends arising from these esters must also be identical.

D. Forced Termination and End Group Structure

^{1}H NMR spectroscopy of the PSt ($\overline{M}_n$ = 2250) obtained by the living pMePhEtOAc/BCl_3/$St/CH_3Cl/-30°C$ system and quenched with methanol, indicated the presence of $-CH_2CH(C_6H_5)Cl$ end groups (δ = 5.1 q (CH-Cl)). Results of these experiments have been corroborated and quantitatively evaluated by model studies using PhEtOAc. Thus PhEtOAc was mixed with BCl_3 in CH_3Cl at $-30°C$, and the PhEtOAc·BCl_3 complex formed was quenched either with CH_3OH, or was decomposed by raising the temperature of the charge to ambient (and thus evaporating the CH_3Cl). According to ^{1}H NMR spectroscopy both methods quantitatively yielded PhEtCl.

Acknowledgement

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