Polymer Bulletin 19, 29–34 (1988)

Polymer Bulletin

Living carbocationic polymerization

XVII. Living carbocationic polymerization of p-methylstyrene

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Summary

Rapid living carbocationic polymerization of p-methylstyrene pMeSt is readily induced by a variety of esters i.e., cumyl acetate (CumOAc), cumyl propionate (CumOPr), 1(2,4,6-trimethylphenyl)ethyl acetate (TMePhEtOAc) and 1(4-methylphenyl)ethyl acetate (pMePhEtOAc) in the presence of BCl_3 in CH_3Cl and C_2H_5Cl solvents at -30° and -50°C using both the IMA and AMI techniques. The $\overline{M}_n$ versus W_{PpMeSt} plots are horizontal, indicating truly living kinetics. The molecular weight distributions are rather broad ($\overline{M}_w/\overline{M}_n$ = 2-5) suggesting slow initiation and/or slow exchange between dormant and living species relative to propagation.

Introduction

In the course of our continuing studies on living carbocationic polymerizations it was of interest to examine the behavior of pMeSt. The p-methyl substituent was expected to render this monomer more reactive than styrene and to prevent possible branching by ring alkylation during polymerization. The Tg of PpMeSt is about 13°C higher than that of polystyrene (Tg PSt = 100°, PpMeSt = 113°) (1).

This paper describes the living carbocationic polymerization of pMeSt by various ester/BCl_3 initiating systems and the characterization of the end group of the PpMeSts obtained upon forced termination.

Experimental

The synthesis of CumOAc, CumOPr, and TMePhEtOAc have been described (2-5). pMePhEtOAc was synthesized from pMeSt by quantitative hydrochlorination in CH_2Cl_2 at 0°C, followed by acetylation with silver acetate (5). The pMeSt (Mobil Chemical Co.) was purified by washing first with 10% aqueous NaOH and subsequently with distilled water till neutral, then dried over $CaCl_2$, and distilled from CaH_2 under reduced pressure. The source and purification of CH_3Cl, C_2H_5Cl, and BCl_3 have been described (2).

Polymerization conditions and characterization methods have been described (2). The polymerization charges were homogeneous and became orange upon BCl_3 addition. The color persisted until the reactions were quenched by prechilled MeOH.

Model experiments of forced termination were carried out with CH_3Cl solutions of the pMePhEtOAc·BCl_3 complex prepared at -30°C by adding BCl_3 to the ester ([pMePhEtOAc] = [BCl_3] = 6.75 x 10^{-2} mole/L). In the chemical quenching study 1 mL of prechilled CH_3OH was added to 25 mL of the solution of the complex, the solvents evaporated, and the product analyzed by ^1H NMR spectroscopy. In the thermal decomposition study the temperature of the complex was rapidly raised from -30°C to ambient, thus the CH_3Cl solvent was rapidly evaporated, and the decomposition products were analyzed by ^1H NMR spectroscopy. Both methods indicated $CH_3CH(pMeC_6H_4)Cl$ as the exclusive product: (δ = 5.1 q (CH-Cl)). Instrumentation and procedures used for molecular weight determination have been described (2). A GPC calibration curve made with narrow MWD PSt standards have been used.

Results and Discussion

A. "Control" Experiments

The addition of BCl_3 to pMeSt/CH_3Cl or C_2H_5Cl charges, i.e., in the absence of purposely added initiators (esters), resulted in fast polymerizations yielding complete conversions in 5 minutes at -30°C. The molecular weights of the PpMeSts are high and decrease as a function of polymerization time which indicates chain transfer, e.g., from $\overline{M}_n$ = 123,500 with $\overline{M}_w/\overline{M}_n$ = 2.0 at ∿70% conv. after 1 min. to $\overline{M}_n$ = 82,500 with $\overline{M}_w/\overline{M}_n$ = 2.5 at ∿100% conv. after 5 mins. The presence of chain transfer is further indicated by the decreased $\overline{M}_n$ obtained upon the addition of an aliquot of fresh monomer to the completely converted charge, e.g., $\overline{M}_n$ = 70,000 with $\overline{M}_w/\overline{M}_n$ = 2.6 at 200% overall conversion. Continuing polymerizations also suggest slow or absent termination. The initiating system in these conventional polymerizations is most likely the "H_2O"·BCl_3 combination which arises from adventitious moisture, "H_2O", and which gives rise to rapid ionic polymerization involving the $BCl_3OH^{\ominus}$ counter anion.

B. Living Polymeriztion of pMeSt

Rapid polymerization of pMeSt has been initiated by a variety of esters, i.e., CumOAc, CumOPr, TMePhEtOAc and pMePhEtOAc in conjunction with BCl_3 in CH_3Cl and C_2H_5Cl solvents at -30° and -50°C by both the IMA (Incremental Monomer Addition) and AMI (All Monomer In) (2) techniques. Figure 1 shows the results and the legend specifies the concentrations used. According to the linear $\overline{M}_n$ versus W_{PpMeSt} plot passing through the origin and the horizontal N versus W_{PpMeSt} plot (insert)the polymerizations are living in nature. While the $\overline{M}_w/\overline{M}_n$ values are somewhat broad (Figure 1 shows a representative series obtained with the CumOAc/CH_3Cl/-30°C system), they definitively exhibit narrowing molecular weight distributions which also indicate living systems.

The number of P_{pMeSt} molecules formed N in this series of experiments is noticeably higher (∿20%) than the theoretical value (broken line in the inset). This discrepancy may be due to uncontrolled initiation by "H_2O"·BCl_3 (see above) or to chain transfer to monomer (by fast ionic path leading to indanyl head group formation) during the initial burst of polymerization. The latter possibility has already been discussed in connection with styrene polymerization with the same initiating systems (4). However, in contrast to the styrene systems, in the present case the experimental points obtained with pMePhEtOAc fall on the common line with the other initiators which indicates negligible (or the absence of) indanyl head group formation (5). Strongly reduced chain transfer is a desirable unexpected consequence of the p-methyl substituent (4).

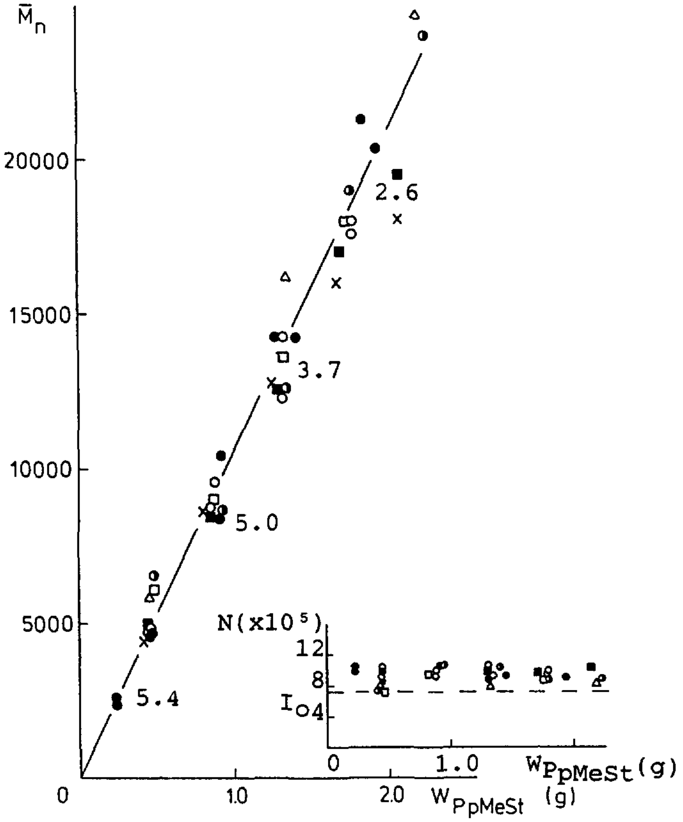
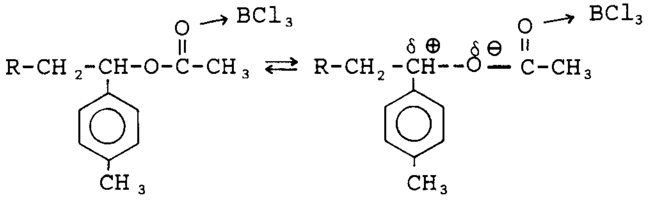


Figure 1. Plots of $\bar{M}_n$ and N (the number of moles of P_{pMeSt}) (insert), versus W_{PpMeSt} (the weight of PpMeSt) obtained in different systems ([I_o] = 2.7 x 10^{-3}M, [BCl_3] = 5.1 x 10^{-2}M, total volume 25 ml)
○ IMA CH_3Cl -30°C CumOAc; ● AMI CH_3Cl -30°C CumOAc; △ IMA CH_3Cl -50°C CumOAc; ■ IMA CH_3Cl -30°C CumOPr; □ IMA CH_3Cl -30°C TMePhEtOAc; X IMA EtCl -30°C CumOAc; ◐ IMA CH_3Cl -30°C pMePhEtOAc
(Numbers are $\bar{M}_w/\bar{M}_n$ values)

According to the results obtained in "control" experiments chain transfer to monomer proceeds with pMeSt (see above), however, is absent with styrene (4) or 2,4,6-trimethylstyrene (6) under quite similar conditions. The discrepancy noted between $[I_o]$ and N in the inset of Figure 1 could have been minimized by the use of higher $[I_o]$ because in the presence of higher ester concentrations uncontrolled initiation due to "H_2O" might have been swamped out.

According to the results of independent experiments, branch formation by ring alkylation is absent in pMeSt polymerization due to the p-methyl substituent. Thus polymerizations that have reached complete conversions in less than a minute have been quenched by CH_3OH after various lengths of times (from 1 minute to 30 minutes), and the $\overline{M}_n$s and $\overline{M}_w/\overline{M}_n$s remained essentially unchanged.

The data obtained with pMePhEtOAc are of special interest since this ester is viewed to be a model for the propagating living chain end. The rate of monomer addition to this model compound and that of monomer incorporation (insertion?) into the living acetate chain should be essentially identical; conceivably, these rates are controlled by the rate of the following "activation" (polarization?):



where R = H or polymer

Although the $\overline{M}_n$s of the polymers fall on the line starting at the origin which suggests a living polymerization, the MWDs are quite broad and their GPC traces exhibit long tails toward low molecular weights. Most likely the rate of ion-generation is slow relative to that of propagation. Similar slow reionization of the polymer chain end (i.e. slow exchange between living and dormant species) may be responsible for the broad MWDs and for the limited narrowing of MWDs with successive monomer additions in the case of other more reactive initiators (4).

Figure 2 provides additional insight into the kinetics. As discussed earlier (2), a linear $1/\overline{DP}_n$ versus $1/[M_o]$ plot that passes through the origin (i.e., the absence of intercept) indicates the absence of bimolecular chain transfer, and the slope of the plot yields $[I_o]$. Thus a series of experiments have been carried out at various pMeSt concentrations at the same CumOAc/BCl_3 concentration using the AMI technique. As shown by the results in Figure 2, bimolecular chain transfer is absent (absence of intercept), however, the slope yields a value that is about 20% larger than $[I_o]$ i.e., the CumOAc input. Possible reasons for this discrepancy have been discussed above.

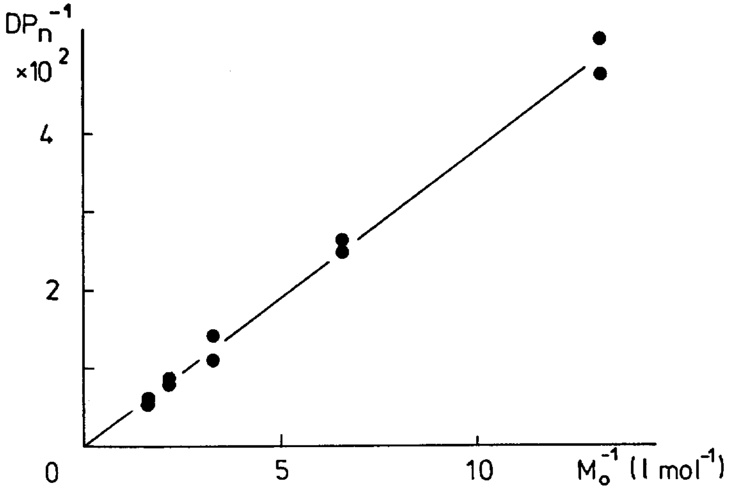
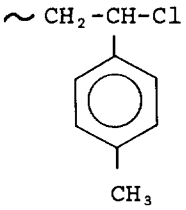


Figure 2. 1/$\overline{DP}_n$ versus 1/M_o plot for the CumOAc/BCl_3 /pMeSt/ CH_3Cl/-30°C system ([CumOAc] = 2.7 x 10^{-3}M, [BCl_3]= 5.1 x 10^{-2}M, total volume 25 ml, AMI method)

C. End Group Characterization

Direct end group characterization of the PpMeSts prepared in this study was difficult on account of the rather high molecular weights and consequent low molar end group concentrations. Thus quantitative albeit indirect end group information has been obtained by model studies in which forced termination (quenching) of polymerization was mimicked by the addition of methanol to the pMePhEtOAc·BCl_3 complex, or by rapidly heating (thermally decomposing) this complex to room temperature under simulated polymerization conditions (i.e., CH_3Cl solvent, -30°C. For details see Experimental). According to ^{1}H NMR spectroscopy decomposing the above complex by methanol or by heating to room temperature gave exclusively CH_3-CH(pC_6H_4CH)Cl. On the basis of these results and similar results obtained in various forced termination studies (2,4,6) we propose that quenching of living carbocationic polymerization of pMeSt will give rise to the secondary benzylic chlorine end group:



Acknowledgement

This material is based on research supported by the National Science Foundation under Grant DMR 84-18617. Support by the Mobil Chemical Co. (including a free sample of pMeSt) is gratefully acknowledged.

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