Polymer Bulletin 19, 35–41 (1988)

Polymer Bulletin

Living carbocationic polymerization

XVIII. Living carbocationic polymerization of 2,4,6-trimethylstyrene

Rudolf Faust and Joseph P. Kennedy

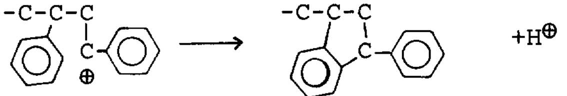
Institute of Polymer Science, University of Akron, Akron, OH 44325, USA

Summary

Rapid truly living carbocationic polymerization of 2,4,6-trimethylstyrene (TMeSt) has been achieved by the use of the cumyl acetate (CumOAc)/BCl_3 initiating system in CH_3Cl at -30°C. The $\overline{M}_n$ of the polymer is determined by the ratio [TMeSt]/[CumOAc]and $\overline{M}_w/\overline{M}_n$s are 1.1-1.2. Below about 2.5 x 10^{-3} mole/L CumOAc adventitious initiation most likely by "H_2O"·BCl_3 is nonnegligible. Forced termination with pyridine or by heating to ambient temperature yields benzylic chlorine end groups whereas with methanol both -Cl and -OCH_3 end groups are obtained in the ratio ∿60/40.

Introduction

The formation of indanyl terminal structures by intramolecular cyclization is an ever-present possibility during the cationic polymerization of styrene and its derivatives (1):



This undesirable side reaction readily proceeds in conventional (2,3) quasiliving (3) and inifer systems (4,5), and has also been evidenced to occur during the carbocationic polymerization of styrene initiated with highly ionizable ester·BCl_3 complexes (6). It occurred to us that indanyl skeleton formation could be avoided by the use of TMeSt. Experiments with TMeSt appeared also attractive because of the anticipated higher reactivity of this monomer relative to styrene and because the polymer PTMeSt has a much higher Tg (162°C (7)) than PSt (Tg = 100°C (7)).

The quasiliving polymerization of this monomer has been demonstrated to occur at -50°C in a rather nonpolar solvent mixture, however, chain transfer to monomer resulting in olefin end groups could not be avoided at higher temperatures or in polar solvents (8). This paper concerns the truly living carbocationic polymerization of TMeSt by living ester·BCl_3 initiating complexes and end group characterization of the polymers obtained upon forced termination.

Experimental

The synthesis of CumOAc has been described (9). 1(2,4,6-Trimethylphenyl)ethyl acetate (TMePhEtOAc) was synthesized from the corresponding olefin by quantitative hydrochlorination in CH_2Cl_2 at 0°C, followed by acetylation with silver acetate (10). TMeSt was distilled from CaH_2 at reduced pressure. The source and purification of CH_3Cl, and BCl_3 have been described (9).

Polymerization conditions have been described (9). A deep purple color appeared upon BCl_3 addition to TMeSt/CumOAc/CH_3Cl charges and the color persisted throughout the polymerization. Charges were quenched by prechilled MeOH or pyridine or were allowed to warm to room temperature by evaporating the CH_3Cl.

Instrumentation and procedures used for molecular weight determination have been described (9). A GPC calibration curve made with PSt standards has been used.

Results and Discussion

A. Living Polymer by the CumOAc/BCl_3 System

After some encouraging orienting investigations, a series of experiments have been carried out with the CumOAc/BCl_3 / TMeSt/CH_3Cl/-30°C system ([CumOAc] = 2.7×10^{-3} mole/L) by the use of the IMA technique (9). Figure 1 shows the results. The linear $\bar{M}_n$ versus W_{PTMeSt}(g of PTMeSt formed) plot passing through the origin, together with the horizontal N (moles of PTMeSt) versus W_{PTMeSt} plot originating at $N=I_O$ (initial moles of CumOAc initiator employed) indicate truly living polymerization within what is considered to be experimental error. The molecular weight distributions are reasonably close to a Poisson distribution ($\bar{M}_w/\bar{M}_n$ = 1.17-1.2) suggesting that the rate of initiation is faster than propagation, and the exchange between dormant (if any) and growing species is relatively fast.

B. Adventitious Initiation by "H_2O"/BCl_3

Figure 2 summarizes the results of three series of experiments carried out with [CumOAc] = 1.8×10^{-3} mole/L. While the polymerizations were undoubtedly living, a noticeable increase in the initiator efficiency (I_{eff}) occurs (see insert). Evidently the contribution of adventitious protogenic impurities ("H_2O") to initiation start to become noticeable at this low initiator concentration. The difference N-[I_O]the concentration of PTMeSt recovered minus that of CumOAc employed, consistently gave ∿6 x 10^{-4}, i.e., the concentration of "H_2O" in the system. Table I shows representative data. The presence of the "H_2O "/BCl_3 adventitious initiating system is also noticeable in the N versus W_{PTMeSt} plot shown in the inset of Figure 2. The corresponding linear $\bar{M}_n$ versus W_{PTMeSt} plot passing through the origin together with the low M_w/M_n data are consistent with a truly living system, however, the experimental N points are somewhat above I_O (horizontal line in the inset) indicating a nonnegligible contribution to initiation by "H_2O"/BCl_3.

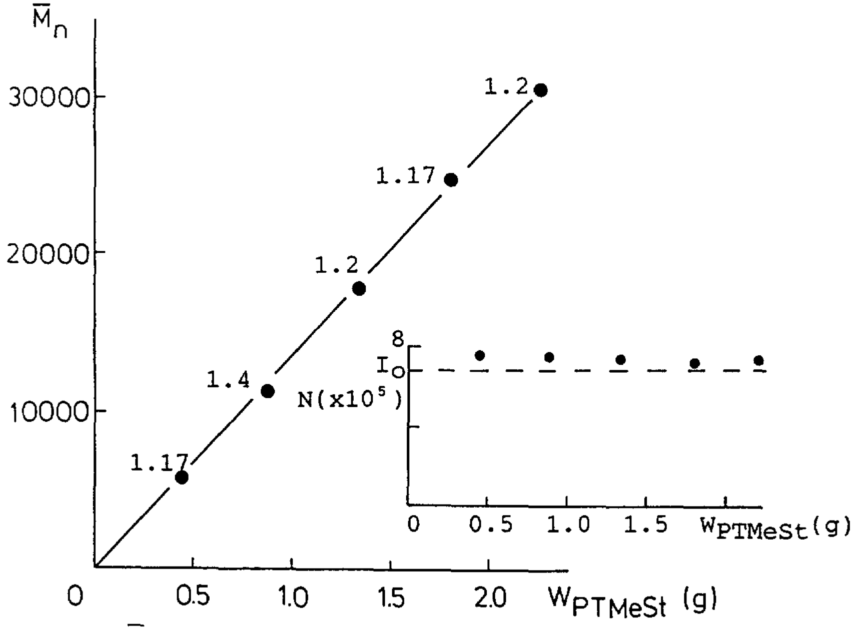


Figure 1. $\bar{M}_n$ (and N, the number of moles of PTMeSt, insert) versus the weight of PTMeSt formed (W_{PTMeSt}) in the CumOAc/BCl_3/TMeSt/CH_3Cl polymerization system using the IMA technique at -30°C. ([I_o] = 2.7 x 10^{-3}M, [BCl_3] = 5.1 x 10^{-2}M, vol. = 25 mL). Numbers indicate $\bar{M}_w/\bar{M}_n$ values

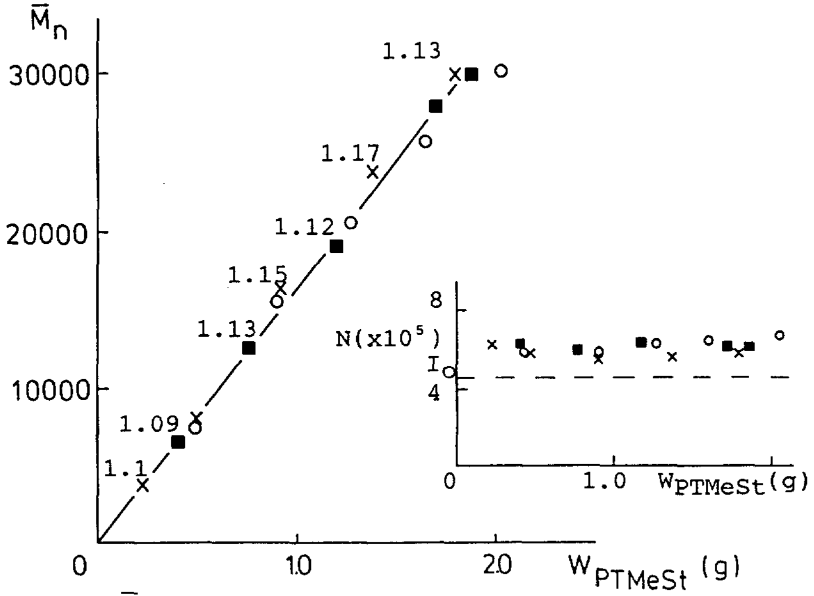


Figure 2. $\bar{M}_n$ (and N, the number of moles of PTMeSt, insert) versus the weight of PTMeSt formed (W_{PTMeSt}) in the CumOAc/BCl_3/TMeSt/CH_3Cl polymerization system at -30°C (O IMA, X AMI), and at -50°C (■ IMA). [I_o] = 1.8 x 10^{-3}M, [BCl_3] = 5.1 x 10^{-2}M, vol. = 25 mL

TABLE I

Polymerization of TMeSt with the CumOAc/BCl_3 Initiating System, in CH_3Cl at -30°C

CumOAc mole/L	Conversion %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	I_{eff} %	N -[I_o]
5.6×10^{-4}	85	27800	1.15	195	5.3×10^{-4}
	87	27400	1.15	195	5.6×10^{-4}
1.12×10^{-3}	∿100	19700	1.13	163	7.0×10^{-4}
	∿100	19700	1.1	153	6.2×10^{-4}
2.24×10^{-3}	∿100	11600	1.3	139	8.7×10^{-4}
	∿100	12700	1.5	120	4.8×10^{-4}
5.6×10^{-3}	∿100	5800	2.6	110	6.2×10^{-4}
	∿100	6200	2.3	99	-

[M] = 0.248 mole/L, [BCl_3] = 5.1 x 10^{-} mole/L, CH_3Cl solvent, -30°C

The presence and quantity of an adventitious initiating system is further corroborated by the $1/\overline{DP}_n$ versus $1/[M_o]$ plot shown in Figure 3. The slope of the $1/\overline{DP}_n$ versus $1/[M_o]$ plot should yield [I_o](9); the difference between the slopes of the experimental and theoretical plots is 5.8 x 10^{-4}, i.e., about the same value as that obtained by N -[I_o] (see above).

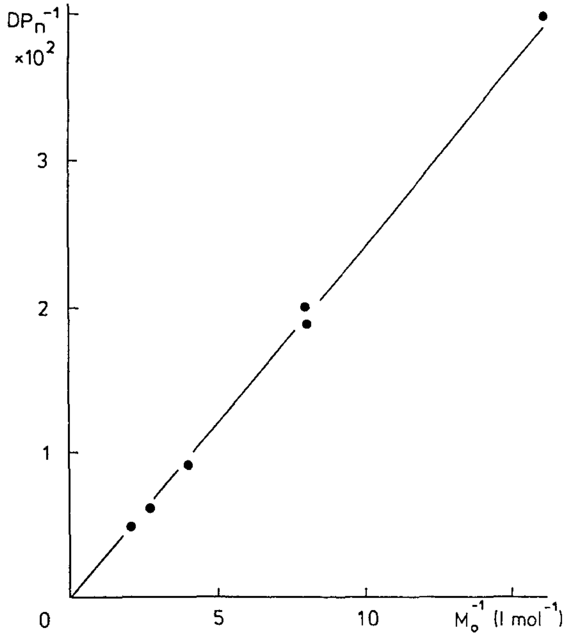


Figure 3. $1/\overline{DP}_n$ versus $1/[M_o]$plot for the CumOAc/BCl_3 /TMeSt/ CH_3Cl/-30°C system. [I_o] = 1.8 x 10^{-3}M, [BCl_3] = 5.1 x 10^{-2}M, vol. = 25 mL

These indirect evidences for initiation by "H_2O"/BCl_3 have been directly substantiated by "control" experiments, i.e., with experiments carried out by adding BCl_3 to TMeSt/CH_3Cl charges in the absence of CumOAc. Table II shows the results. Evidently N, the concentration of PTMeSt formed in the absence of CumOAc was also ∿5 x 10^{-4} mole/L, suggesting the same concentration for "H_2O"/BCl_3.

TABLE II

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

Polymerization time mins	Conversion %	$\overline{M}_n$ g/mole	$\overline{M}_w/\overline{M}_n$	[N] mole/L
15	13.8	13800	2.3	3.6×10^{-4}
30	59.8	37000	1.4	5.6×10^{-4}
75	91.9	93300	1.3	3.5×10^{-4}
* 30	32.7	22500	1.3	5.2×10^{-4}

CH_3Cl, -30°C (* -50°C), [TMeSt] = 0.248 mole/L, [BCl_3] = 5.1×10^{-2}

Importantly, these control experiments also suggest transferless polymerization in the presence of the "H_2O"/BCl_3 initiating system. According to the time/conversion data in Table II, although the overall polymerization rate is much lower than that observed with the CumOAc/BCl_3 system, chain transfer to monomer is negligible or absent, and the "H_2O"/BCl_3 system is most likely a living one. The reasonably narrow MWD data ($\overline{M}_w/\overline{M}_n$ = 1.3-2.3) are also in line with living polymerizations.

One question arises: How come the effect of "H_2O"/BCl_3 was found to be consistently negligible even at low CumOAc·BCl_3 concentrations in isobutylene polymerizations (9) but not in these TMeSt systems? While the answer to this question is far from obvious, it may be that in the TMeSt system initiation occurs by unionized "H_2O"·BCl_3 (i.e., in the absence of ionized $H^{\oplus}BCl_3OH^{\ominus}$), as demonstrated to proceed with αmethylstyrene by the use of proton traps (11), while in isobutylene polymerizations this is probably not the case.

In sum, living carbocationic polymerization of TMeSt can be readily achieved with the CumOAc/BCl_3 initiating system even in the presence of adventitious moisture, i.e., with "H_2O"/BCl_3, however, to swamp out the effect of this species the use of CumOAc concentrations in excess to that of protogenic impurities (∿5 x 10^{-4}) is preferable. In line with this analysis diluents such as CH_2Cl_2, that are usually contaminated with "H_2O" to the extent of ∿5 x 10^{-3}M even after aggressive chemical purification (distilling over Et_3Al or CaH_2), should be used with circumspect.

C. Forced Termination and End Group Characterization

^1H NMR spectroscopy of PTMeSts ($\overline{M}_n$ = 3-4000) obtained by the living CumOAc/BCl_3/TMeSt/CH_3Cl/-30°C system and quenched with pyridine or by raising the temperature to ambient (allowing the CH_3Cl to evaporate and the temperature to rise) gave

$-CH_3$-CHCl(TMePH)-Cl end group (δ = 5.5 q (CH-Cl)). Similar quenching experiments with CH_3OH yielded -Cl and $-OCH_3$ end groups, i.e., $-CH_2CH$(TMePH)-X where X = Cl and $-OCH_3$.

Since quantitation is rather cumbersome with polymer samples, additional model experiments have been carried out with the TMePhEtOAc·BCl_3 model complex. Figure 4 shows ^1H NMR spectra of the ester, and the products obtained upon pyridine and CH_3OH quenching. Quenching with pyridine (or decomposing by raising the temperature) yielded the chloro compound TMePhEtCl. Quenching with CH_3OH resulted in ∿60:40 mole % -Cl/$-OCH_3$ substitution.

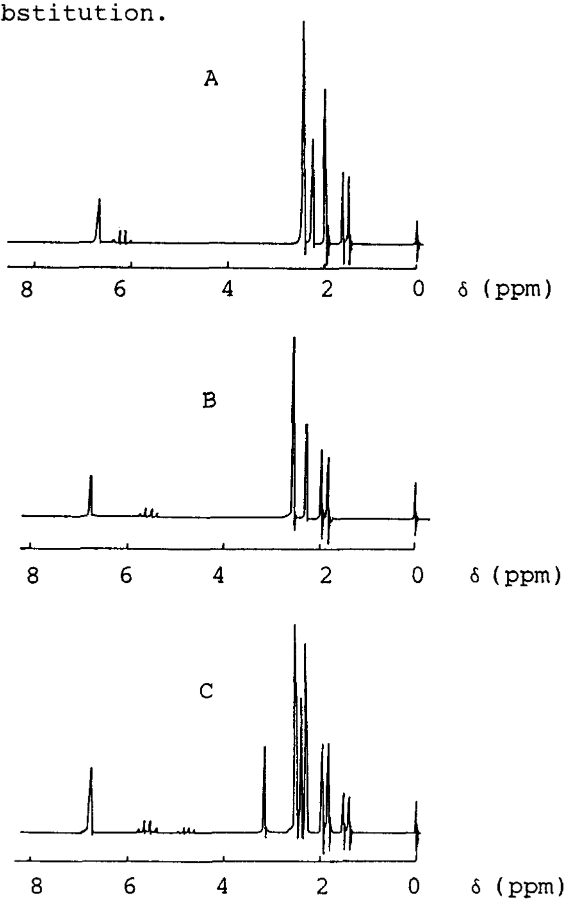


Figure 4. ^1H NMR spectra of the TMePhEtOAc (a), and the products obtained upon quenching the TMePhEtOAc·BCl_3 complex with pyridine (b) and methanol (c)

Additional model experiments have been carried out to ascertain that the $-OCH_3$ terminated product arose by direct termination and not by methanolysis from -Cl ended product. Thus CH_3OH was added to the TMePhEtOAc·BCl_3 complex in CH_3Cl at -30°C, and the solvent was rapidly evaporated (vacuum, ∿5 mins) at -40°C. The residue was heated to -10°C and the CH_3OH

was rapidly removed by vacuum. The solvolysis rate of TMePhEtCl is reportedly greatly influenced by temperature ($k_{S,25°C} = 3.65 \times 10^{-4}$ sec^{-1}, $k_{S,-10°C} = 3.1 \times 10^{-6}$ sec^{-1} (12)). According to ^{1}H NMR spectroscopy the methanol-treated model product gave ∿60:40 mole % of the expected TMPEtCl/TMePhEtOMe.

Acknowledgements

This material is based upon work supported by the NSF (Grant DMR-84-18617).

References

1. Carbocationic Polymerization, J. P. Kennedy and E. Maréchal, John Wiley Interscience, New York 1982
2. D. C. Pepper and P. J. Reilly, Proc. Roy. Soc. Ser. A291, 41 (1966)
3. R. Faust, A. Fehérvári, and J. P. Kennedy, J. Macromol. Sci. Chem. A18(9), 1229 (1982)
4. V. S. C. Chang, J. P. Kennedy and B. Iván, Polym. Bull. 3, 339 (1980)
5. V. S. C. Chang and J. P. Kennedy, Polym. Bull. 4, 513 (1981)
6. See paper XVI in this series, R. Faust and J. P. Kennedy, Polym. Bull., in this issue
7. Polymer Handbook, J. Brandrup, E. H. Immergut, John Wiley Interscience 1975
8. M. Győr, J. P. Kennedy, T. Kelen and F. Tüdős, J. Macromol. Sci. Chem. A21(10), 1295 (1984)
9. R. Faust and J. P. Kennedy, J. Polym. Sci., Polym. Chem. A25, 11847 (1987)
10. C. G. Swain, T. E. C. Knee and A. MacLachlan, J. Am. Chem. Soc. 82, 6101 (1960)
11. J. P. Kennedy and R. T. Chou, J. Macromol. Sci. Chem. A18(1) 47 (1982)
12. J. C. Charlton and E. D. Hughes, J. Chem. Soc. 56, 850

Accepted October 29, 1987 K