

Cationic Polymerization of *p*-Methoxystyrene by the Triphenylmethyl Bromide/Iodine Initiating System: Formation of Long-Lived Polymers in Polar Solvent

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ABSTRACT: Triphenylmethyl bromide in conjunction with iodine ($\text{Ph}_3\text{CBr}/\text{I}_2$ initiator) induced cationic polymerization of *p*-methoxystyrene (pMOS) in 1,2-dichloroethane at -15°C to yield long-lived (living-like) polymers. The long lifetime of the polymers was indicated by a linear progressive increase of their number-average molecular weight (M_n) with pMOS conversion and the further increase of M_n on the addition of a fresh pMOS feed to a completely polymerized solution. UV/visible spectroscopic analysis showed that iodine promotes the dissociation of Ph_3CBr into the triphenylmethyl cation which in turn initiates the polymerization of pMOS. A mixture of triphenylmethyl thiocyanate (Ph_3CSCN) and iodine also acted as an initiator for pMOS polymerization; the overall polymerization rate decreased in the following order: $\text{Ph}_3\text{CBr}/\text{I}_2 > \text{Ph}_3\text{CSCN}/\text{I}_2 > \text{I}_2$.

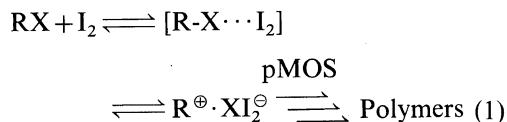
KEY WORDS Cationic Polymerization / Living Polymers / Long-Lived Polymers / Triphenylmethyl Bromide / Triphenylmethyl Thiocyanate / Iodine / *p*-Methoxystyrene / Triphenylmethyl Cation / Initiation /

The cationic polymerization of *p*-methoxystyrene (pMOS) initiated by iodine involves a long-lived propagating species that is favorably formed at low temperatures in non-polar media (*e.g.*, carbon tetrachloride).^{1,2} The reaction exhibits characteristics reminiscent of "living" polymerization; *i.e.*, a progressive increase in the number-average molecular weight (M_n) of the product polymers with increasing monomer conversion, its further raise on the addition of a fresh pMOS feed to a completely polymerized reaction mixture, and the formation of pMOS-isobutyl vinyl ether block copolymers.² These features indicate that chain transfer and termination reactions are considerably suppressed in the pMOS/iodine system,³ where the stable pMOS growing end is associated with the nucleophilic iodide

counteranion. We have theorized⁴ that the strong interaction of the counteranion with the propagating end is of key importance to suppress the side reactions deleterious to living polymerization. Such a strong cation-anion interaction in the growing species also occurs in the polymerization of vinyl ethers by a mixture of hydrogen iodide and iodine (HI/I_2 initiator) where perfectly living, monodisperse polymers are produced.^{5,6}

Among initiators for cationic vinyl polymerization, molecular iodine and HI/I_2 initiator are known to yield living/long-lived propagating species associated with a strongly interacting counteranion.⁴ It occurred to us that counteranions similar in nature to the iodide anion might form from a suitable carbocation source (RX) combined with

iodine, as illustrated in eq 1:



where R and X represent, respectively, the triphenylmethyl group and a leaving group (*e.g.*, halogen). If living/long-lived polymers are obtained with XI_2^\ominus as counteranion, the RX/I_2 initiator will be of importance not only as a new entry to the initiators for living polymerization of vinyl monomers but in generalizing our principle of living cationic polymerization based on the strong interaction between the growing carbocation and the counteranion.

In this study, we employed triphenylmethyl bromide (Ph_3CBr ; $\text{X}=\text{Br}$) and triphenylmethyl thiocyanate (Ph_3CSCN ; $\text{X}=\text{SCN}$) as RX in eq 1, and polymerized pMOS using these RX/I_2 initiating systems. Triphenylmethyl cation salts having a complex metal-halide counteranion (*e.g.*, SbF_6^\ominus) are well known and thoroughly studied as initiators for cationic polymerization of pMOS and vinyl ethers.⁷ Recently, two of us⁸ found that a series of triphenylmethyl halide/electron acceptor pairs (*e.g.*, Ph_3CBr /chloranil) can also polymerize pMOS in polar media. None of these triphenylmethyl cation-based initiators, however, successfully lead to living/long-lived poly(pMOS). We wish to report that the $\text{Ph}_3\text{CBr}/\text{I}_2$ initiating system effectively polymerizes pMOS in 1,2-dichloroethane (DCE) to give long-lived polymers. The polar solvent was required for the formation of long-lived poly(pMOS), rather than nonpolar media better suited for the iodine-initiated polymerization.^{1,2}

EXPERIMENTAL

Materials

Triphenylmethyl bromide was synthesized from triphenylmethanol and acetyl bromide (freshly distilled) in dry benzene by the stan-

dard method.⁹ The crude product was recrystallized from a benzene/hexane mixture (1:10 v/v). Triphenylmethyl thiocyanate was obtained by the reaction of triphenylmethyl chloride or bromide with potassium thiocyanate in carefully purified dry acetone.¹⁰ Recrystallization from acetone gave the pure thiocyanate as white needles. Iodine was sublimed over potassium iodide and stored under argon in the dark.

pMOS was prepared from *p*-methoxybenzaldehyde by the Grignard reaction with methylmagnesium bromide.¹¹ It was purified by vacuum distillation over calcium hydride and stored in a refrigerator. DCE as the polymerization solvent was purified by the usual method and distilled twice successively over phosphorus pentoxide and calcium hydride just before use.

Procedures

Polymerizations were carried out in DCE at -15°C under dry argon in a baked glass tube equipped with a three-way stopcock. The reaction was initiated by adding an initiator solution into a monomer solution and terminated with prechilled ammoniacal methanol. The initiator solution was prepared by dissolving iodine and triphenylmethyl bromide or thiocyanate in DCE at room temperature and then cooled to the polymerization temperature before mixed with the monomer. For some runs iodine alone was used as an initiator.

The conversion of pMOS was determined either by gravimetry of the isolated polymers (see below) or by ultraviolet (UV) spectroscopy monitoring a decrease in the pMOS absorption at 295 nm; the values by the two methods were in good agreement within 5%, indicating the absence of methanol-soluble oligomers in the product.

The produced poly(pMOS) was precipitated into methanol, filtered off, washed exhaustively with methanol, and dried in vacuo below 20°C . The molecular weight distribution (MWD) of the polymers was measured by size exclusion

chromatography (SEC) in tetrahydrofuran (1 ml min⁻¹) at 40°C on a Knauer FR-30 chromatograph equipped with 7 silica gel columns (Merck LiChrospher Si 4000, 1000, 500, 300, 100, and 60 (× 2); 4 mm i.d. × 250 mm each) and a UV detector operating at 254 nm. A 0.5 w/v% solution of the polymer sample was injected. The M_n and M_w/M_n ratio were calculated from SEC eluograms on the basis of a polystyrene calibration.

UV/visible spectra were recorded in DCE at 20°C on a SPECORD spectrophotometer (VEB Carl Zeiss, Jena), as previously described.¹²

RESULTS AND DISCUSSION

pMOS Polymerization by Triphenylmethyl Compound/Iodine Initiating Systems

pMOS was polymerized in DCE at -15°C by Ph₃CBr or Ph₃CSCN coupled with an equimolar amount of iodine. For comparison iodine alone was also used otherwise under the same conditions. Although neither Ph₃CBr nor Ph₃CSCN per se could induce *pMOS* polymerization, when coupled with iodine both triphenylmethyl compounds polymerized *pMOS* almost quantitatively. The overall polymerization rates by Ph₃CBr/I₂ and Ph₃CSCN/I₂ initiators clearly exceeded that by iodine alone; reaction time for 95% conversion: Ph₃CBr/I₂(10 min) > Ph₃CSCN/I₂(60 min) > I₂(180 min).

Another dependence on the initiators was found in the MWD of the produced polymers (Figure 1). Ph₃CBr/I₂ and Ph₃CSCN/I₂ initiators led to polymers with a unimodal MWD; iodine alone also gave a broad, unimodal MWD as already reported.^{1,2} Importantly, the MWD for Ph₃CBr/I₂ was considerably narrower than those for Ph₃CSCN/I₂ and iodine.

These dependences of the reaction rate and the MWD of polymers show that the triphenylmethyl salt-based initiators effect a *pMOS* polymerization clearly differing from

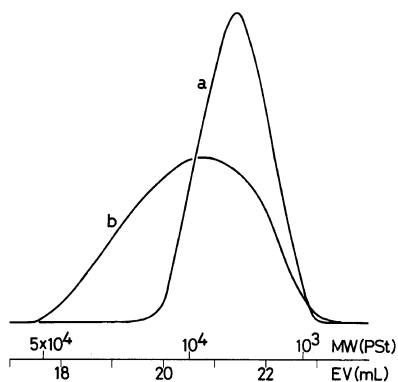


Figure 1. MWD of poly(*pMOS*) obtained in DCE at -15°C: [M]₀ = 0.40 M; conversion > 95%.
(a) [Ph₃CBr]₀ = [I₂]₀ = 5.0 mM;
(b) [Ph₃CSCN]₀ = [I₂]₀ = 5.0 mM.

that by iodine alone. Since the polymerizations by Ph₃CBr/I₂ and Ph₃CSCN/I₂ also considerably differ from each other, the counteranions (Br[⊖] and SCN[⊖]) of the triphenylmethyl salts should be involved in the initiation/propagation processes (see below).

Formation of Long-Lived Polymers by Ph₃CBr/I₂ Initiator

In view of the fairly narrow MWD ($M_w/M_n = 1.66$) of poly(*pMOS*) obtained by Ph₃CBr/I₂ initiator (Figure 1), living/long-lived polymers may form in the *pMOS* polymerization by this combined initiator. The most important diagnostic characteristic of living polymers is that they can resume propagation when an additional feed of monomer is supplied to a polymerization solution, leading to an increase in their M_n with increasing number of the monomer addition. We then examined the Ph₃CBr/I₂-initiated polymerization of *pMOS* more in detail from this viewpoint (so-called monomer-addition experiments⁴).

In DCE at -15°C *pMOS* was polymerized by Ph₃CBr/I₂ initiator, and a small amount of fresh *pMOS* (neat) was repeatedly added to the reaction mixture when the previously supplied monomer had completely depleted. Figure 2

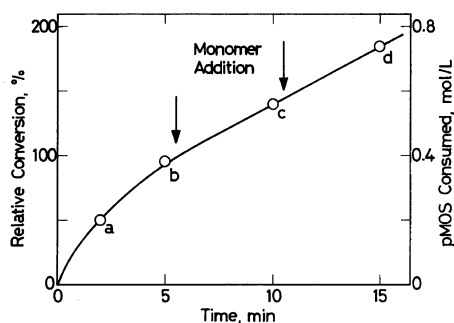


Figure 2. Time-conversion curve for a monomer-addition experiment in the pMOS polymerization by $\text{Ph}_3\text{CBr}/\text{I}_2$ initiator in DCE at -15°C : $[\text{M}]_0 = 0.40 \text{ M}$; $[\text{Ph}_3\text{CBr}]_0 = [\text{I}_2]_0 = 5.0 \text{ mM}$. At each monomer-addition step (indicated by the arrow), neat pMOS, one half the molar quantity of the initial charge, was added into the reaction mixture.

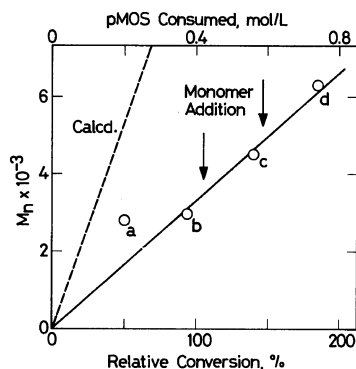


Figure 4. M_n -conversion profile for poly(pMOS) obtained in the monomer-addition experiment described in Figure 2. As to the sample codes and reaction conditions see the caption for Figure 2. The broken line indicates the calculated values based on the quantitative initiation of $\text{Ph}_3\text{CBr}/\text{I}_2$.

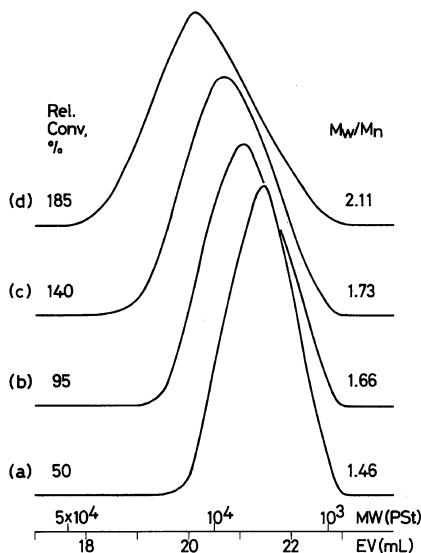


Figure 3. MWD of poly(pMOS) obtained in the monomer-addition experiment described in Figure 2. As to the sample codes and reaction conditions, see the caption for Figure 2.

shows the time-conversion curve for such a monomer-addition experiment. After each monomer addition, the added pMOS polymerized nearly quantitatively without an apparent change in polymerization rate, indicating the absence of termination.

Figure 3 illustrates the MWD of a series of polymer samples obtained in the monomer-

addition experiment. In the first-stage polymerization (Figure 3, a and b) the MWD clearly shifted toward high molecular weight with increasing conversion. A further increase in polymer molecular weight was observed in the second- and third-stage polymerizations (Figure 3, c and d, respectively), in which a new pMOS feed was added to the reaction mixture. The monomer addition also resulted in a considerable broadening of the MWD, although the peak molecular weight clearly increased at each stage.

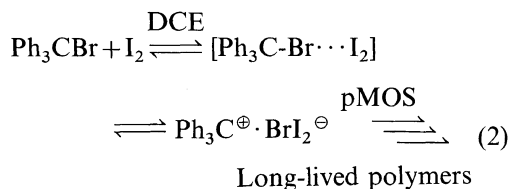
The increase in polymer molecular weight on the repeated monomer-addition is depicted more quantitatively in the M_n -conversion plots in Figure 4. The M_n was nearly proportional to pMOS conversion (or the total amount of pMOS consumed), and the linear rise of M_n continued after the monomer addition. All these facts show the formation of long-lived polymers in the polymerization initiated by $\text{Ph}_3\text{CBr}/\text{I}_2$ in DCE. Iodine alone, in contrast, does not yield such long-lived poly(pMOS) in polar media.^{1,2}

In spite of the linear increase in polymer molecular weight, however, the polymerization by $\text{Ph}_3\text{CBr}/\text{I}_2$ cannot be referred to as a "living" process, because of the consecutive

broadening of the MWD of polymers upon monomer addition (Figure 3, c and d). Thus, the propagating species does have a long lifetime, but may undergo chain transfer to some extent. Another indication of the occurrence of chain transfer is that the observed M_n 's (by SEC) are smaller than the calculated values (Figure 4, broken line) based on the quantitative initiation by Ph₃CBr/I₂.

Polymerization Mechanism: Dissociation of Triphenylmethyl Bromide Assisted by Iodine

The clear difference between the polymerizations by Ph₃CBr/I₂ initiator and by iodine alone, described above, shows a cooperative action of Ph₃CBr and iodine in the initiation/propagation processes. Eq 2 gives the most likely initiation mechanism in which Ph₃CBr



dissociates into the triphenylmethyl cation (Ph₃C[⊕]) with the aid of the electrophilic interaction of iodine on the bromine atom. To find evidence for this mechanism, we studied the interaction between Ph₃CBr and iodine, either in the presence or absence of pMOS monomer, by UV/visible spectroscopy in DCE at 20°C. Figure 5 presents typical spectra thus obtained.

Ph₃CBr alone shows very weak absorptions of the Ph₃C[⊕] cation at 413 and 440 nm (Figure 5a). The addition of a slightly excess of iodine to the Ph₃CBr solution led to a nearly 10-fold increase of the Ph₃C[⊕] cation (Figure 5c). In this spectrum the absorption of iodine (*ca.* 500 nm; *cf.* Figure 5b) is seen overlapping with the Ph₃C[⊕] band.

When the Ph₃CBr/I₂ mixture was added to an excess of pMOS, namely, under the conditions simulating the pMOS polymerization by Ph₃CBr/I₂ initiator, the double peak of

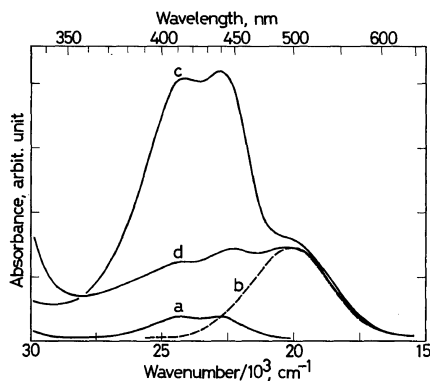


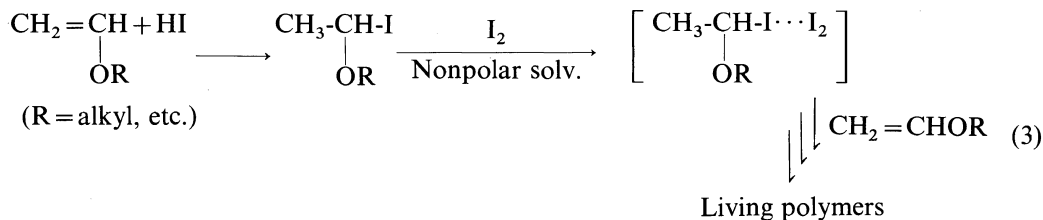
Figure 5. UV/visible spectra in DCE at +20°C (concentrations in mM): (a) Ph₃CBr (0.30); (b) I₂ (0.50); (c) Ph₃CBr (0.30) + I₂ (0.50); (d) Ph₃CBr (0.30) + I₂ (0.50) + pMOS (8.0). Spectra c and d were recorded immediately after mixing all ingredients.

Ph₃C[⊕] was still observable but its intensity decreased by factor of about 3 (Figure 5d). The iodine absorption was detected at *ca.* 500 nm even in the presence of pMOS, indicating that a part of the added halogen remains intact during the polymerization.

The enhanced formation of the Ph₃C[⊕] cation from Ph₃CBr in the presence of iodine (Figure 5b) shows that added iodine promotes the dissociation of the triphenylmethyl salt by its electrophilic interaction with the bromine atom; *i.e.*, iodine polarizes the carbon-bromine bond of Ph₃CBr. The resulting Ph₃C[⊕] cation in turn adds across the double bond of pMOS and thereby initiates cationic polymerization of this monomer. The considerable decrease of the Ph₃C[⊕] cation in the presence of pMOS (Figure 5d) supports its efficient addition (initiation) to the vinyl monomer. Thus, the proposed initiation mechanism (eq 2) was experimentally verified, although the rather intense tailings in the region from 340 to 390 nm, due to the absorptions of pMOS ($\lambda_{\text{max}} = 295$ nm) and Ph₃C[⊕], hampered us to detect the propagating pMOS cation that would exhibit a spectrum centered at 380 nm.¹³

The iodine-assisted polarization (dissociation) of a carbon-halogen bond, similar to that in the Ph₃CBr/I₂ system, has been

found in the living polymerization of vinyl ethers by HI/I₂ initiator (eq 3):^{5,6}



In this initiation process, the carbon-iodine covalent bond is polarized (electrophilically "activated"⁶) by iodine in *nonpolar* solvents.¹⁴ An important difference between Ph₃CBr/I₂ and HI/I₂ initiators, therefore, is that Ph₃CBr requires a *polar* solvent (DCE) for its dissociation assisted by iodine.

This study has shown that Ph₃CBr in conjunction with iodine is not only an effective initiator for the cationic polymerization of pMOS but produces long-lived polymers in DCE. The Ph₃CBr/I₂-initiated polymerization is unique in that long-lived polymers form, first, in a relatively polar solvent (DCE) and, second, with a mixed halide ion (BrI₂[⊖]) as the counteranion. It should be noted that in such polar media, iodine alone results in polymers with a broad MWD *via* transfer-dominant polymerization.^{1,2} The second point is of importance to expand the scope of initiators (counteranions) for living/long-lived vinyl polymers, which have thus far been confined to iodine and HI/I₂.

REFERENCES AND NOTES

1. T. Higashimura and O. Kishiro, *Polym. J.*, **9**, 87 (1977).
2. T. Higashimura, M. Mitsuhashi, and M. Sawamoto, *Macromolecules*, **12**, 178 (1979).
3. In a strict sense, this polymerization cannot be referred to as a "perfectly living" process where chain transfer and termination are absent, since the number of polymer chains produced per unit iodine increases with conversion and the product polymers are not monodisperse.^{1,2}
4. T. Higashimura and M. Sawamoto, *Adv. Polym. Sci.*, **62**, 49 (1984).
5. M. Miyamoto, M. Sawamoto, and T. Higashimura, *Macromolecules*, **17**, 265, 2228 (1984).
6. (a) T. Higashimura, M. Miyamoto, and M. Sawamoto, *Macromolecules*, **18**, 611 (1985). (b) M. Sawamoto, M. Miyamoto, and T. Higashimura, *Polym. Prepr., Jpn.*, **33**, 1399 (1984).
7. As reviews, see: (a) A Ledwith and D. C. Sherrington, *Adv. Polym. Sci.*, **19**, 1 (1975); (b) A. Gandini and H. Cheradame, *ibid.*, **34/35**, 1 (1980).
8. G. Heublein and S. Spange, *Acta Polym.*, **33**, 509 (1982).
9. W. E. Bachmann, *Org. Syn.*, **23**, 100 (1943); *Org. Synth. Coll. Vol.* **3**, 841 (1955).
10. A. Iliceto, A. Fava, and V. Mazzucato, *J. Org. Chem.*, **25**, 1445 (1960).
11. R. Cotrel, G. Sauvet, J. P. Vairon, and P. Sigwalt, *Macromolecules*, **9**, 931 (1976).
12. G. Heublein, S. Spange, and P. Hallpap, *Makromol. Chem.*, **180**, 1935 (1979).
13. M. Sawamoto and T. Higashimura, *Macromolecules*, **11**, 328 (1978).
14. We have recently found that the living polymerization of vinyl ethers by HI/I₂ initiator proceeds in not only nonpolar but polar media such as methylene chloride as well: T. Higashimura, T. Enoki, and M. Sawamoto, to be published.