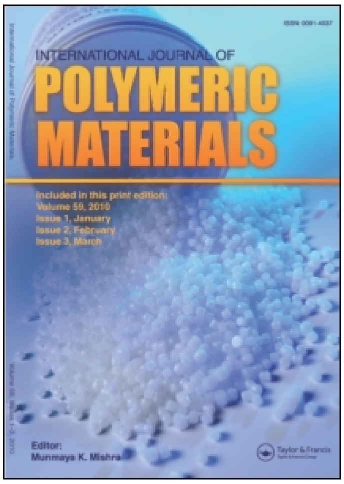


International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

Photoinitiated Cationic Polymerization of p-methylstyrene by Methoxy Trityl Salts

Ideisan I. Abu-Abdoun[a]
[a] Department of Chemistry, University of Sharjah, Sharjah, United Arab Emirates

To cite this Article Abu-Abdoun, Ideisan I.(2008) 'Photoinitiated Cationic Polymerization of p-methylstyrene by Methoxy Trityl Salts', International Journal of Polymeric Materials, 57: 6, 584 — 593

To link to this Article: DOI: 10.1080/00914030701818322

URL: http://dx.doi.org/10.1080/00914030701818322

International Journal of Polymeric Materials, 57:584–593, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 0091-4037 print/1563-535X online
DOI: 10.1080/00914030701818322

Photoinitiated Cationic Polymerization of p-methylstyrene by Methoxy Trityl Salts

Ideisan I. Abu-Abdoun
Department of Chemistry, University of Sharjah, Sharjah,
United Arab Emirates

Photoinitiated cationic polymerization of p-methylstyrene has been investigated in dichloromethane at 25°C, using stable, soluble, and nonhygroscopic di, tri and pentamethoxy trityl carbocationic salts, having non-nucleophilic anions such as SbF_6^-, AsF_6^-, PF_6^-. *The reactivity of these salts falls in the order: trimethoxy > dimethoxy > pentamethoxy. The effects of counter ion structure, salt concentration, photolysis time and photolysis wavelength on the polymerization rate are presented.*

Keywords: cationic photoinitiated polymerization, methoxy trityl salts, p-Methylstyrene

INTRODUCTION

Polymerization initiators that generate reactive species capable of initiating cationic polymerizations by photolysis are extremely important in photoresist and curing systems [1–3]. Crivello et al., [4] and Yagci et al. [5] reported pioneering research on different types of onium salt-based photoinitiators.

The use of triphenylmethyl salts as thermal initiators for polymerizations of highly reactive aromatic and vinyl ether monomers was reported. Extra care is needed in handling these salts [6,7]; however, replacement of hydrogen atoms in one or more of the phenyl rings of triphenylmethyl cation by electron-releasing conjugating substituents such as methoxy group, increases both the thermal stability, and the photochemical reactivity of the carbocation [8].

Received 30 October 2007; in final form 8 November 2007.

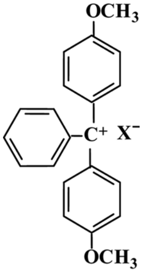
Address correspondence to Ideisan I. Abu-Abdoun, Department of Chemistry, University of Sharjah, Sharjah, P. O. Box 27272, U.A.E. E-mail: abuabdoun@sharjah.ac.ae.

Poly (p-methylstyrene) can be used interchangeably with polystyrene resins in many applications with some processing advantages and thermal stability [9].

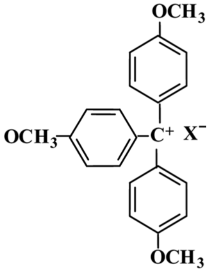
P-methylstyrene was homopolymerized [10,11] and copolymerized to obtain chloromethylated polystyrenes, which are key intermediates in the preparation of anion exchange resins [12], and act as supports for polymeric reagents and catalysts [13].

Recently p-trimethoxy trityl salt (2) has been reported to serve as photoinitiator for cationic polymerization of cyclohexene oxide, tetrahydrofuran and N-vinylcarbzole, due to its easy handling, chemical stability and low hygroscopic nature [14]. We would like to expand this work to vinyl aromatic monomers of the styrene family and investigate the effect of substituents on the activity of these trityl salts.

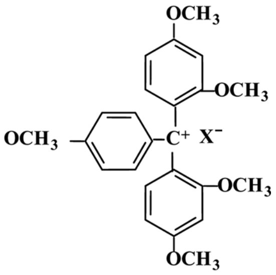
This article describes the application of methoxy substituted trityl salts 1–3 having non-nucleophilic anions, as cationic photoinitiators for p-methylstyrene polymerization in dichloromethane at room temperature.



Salt (1)



salt (2)



salt (3)

$X^- = SbF_6^-$, AsF_6^- , PF_6^- , BF_4^- , $SbCl_6^-$

EXPERIMENTAL

Chemicals

p-methylstyrene (Fluka) was freed from inhibitor by washing with 5% sodium hydroxide and then repeatedly with distilled water. After drying overnight over anhydrous sodium sulfate, it was distilled from calcium hydride under reduced pressure. Dichloromethane (Fluka) was dried over calcium hydride and distilled before use. Methoxytrityl chlorides and other chemicals (Aldrich Chemical Co.) were used without any further purification. Other chemicals were obtained from Aldrich Chemical Co. and used as received. The elemental analyses for these salts were within the expected ranges.

Spectroscopic Measurements

Ultraviolet spectra were obtained on a Cary-2300 spectrophotometer.

Polymerization

Selected amounts of the monomer and initiator in dichloromethane were placed in Pyrex glass vessels (15 mm diameter) sealed with a rubber septum after being flushed with dry nitrogen gas. Photopolymerization was carried out using a Rayonet merry-go-round photoreactor with selected UV lamps.

The polymer was precipitated from methanol, filtered, dried and weighed. The percent conversion to polymer was calculated on the basis of 100% theoretical yield being 897 g poly(p-methylstyrene) from one liter of the monomer at 25°C [10].

RESULTS AND DISCUSSION

Salts Synthesis

The reported trityl salts 1–3 were synthesized by reacting the corresponding methoxy trityl chloride with excess amount from the acid fluoride, $HSbF_6$, HBF_4, HPF_6, $KAsF_6$, or $SbCl_5$ (for the anion $SbCl_6^-$) in dried diethyl ether/dichloromethane mixture (50/50 ratio by volume). After stirring at room temperature for 30 min, the salt was recovered by pouring the reaction mixture into excess cold dry diethyl ether, followed by filtration and washing with diethyl ether, and finally drying under vacuum at room temperature. To purify the salt further, it was dissolved in a small volume of dichloromethane and reprecipitated in excess dry cold ether, filtered and dried under vacuum [14].

Table 1 illustrates the characterization of salts 1–3 having different anions. Typical UV/visible absorption spectra of salts 1–3 in dichloromethane are shown in Figure 1. These salts were recovered with 85% yield and were found to be pure, stable under laboratory conditions, soluble in dichloromethane and non-hygroscopic, and red-orange in color.

Figure 2 shows the UV absorption spectrum of p-methylstyrene in the range 220–320 nm. This spectrum shows a double maximum at 267 and 237 nm in dichloromethane.

The results of the photoinitiated polymerization of p-methyl styrene using salt (2) with different counter ions are shown in Figure 3. The monomer concentration was 2.53 M, the salt concentration was 3.30×10^{-4} M, and the photolysis was carried out using 350 nm light

TABLE 1 Characterization of Salts 1–3 in Dichloromethane

Salt #	X^-	M · Pt (°C)	λ_{max} (nm)	ε mol^{-1}cm^{-1}l
1	SbF_6^-	142–144	500	3.45×10^5
			418	5.36×10^5
2	SbF_6^-	161–163	485	1.90×10^5
			350	1.40×10^3
			300	8.12×10^2
3	BF_4^-	210–212	545	1.76×10^4
			480	1.79×10^4
			415	1.39×10^4
3	PF_6^-	174–176	545	1.75×10^4
			480	1.80×10^4
			415	1.30×10^4
3	SbF_6^-	215–217	545	1.76×10^4
			480	1.79×10^4
			415	1.40×10^4

source tubes. It is clear that the yields of polymer vary substantially with respect to the counter ion, and the reactivity of the salts based on the counter ion falls in the following order: $SbF_6^- > AsF_6^- > PF_6^-$. With salt (2), having $SbCl_6^-$, very little amount of polymer was obtained under the reported conditions as shown in Figure 3. No polymerization was observed when using the tritylchloride under these conditions.

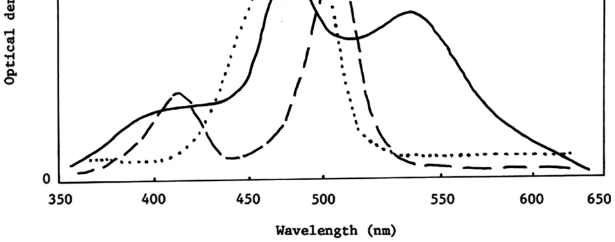


FIGURE 1 Ultraviolet absorption spectra of the salt 1–3. ____Salt (1); ....Salt (2); __ __ __Salt (3).

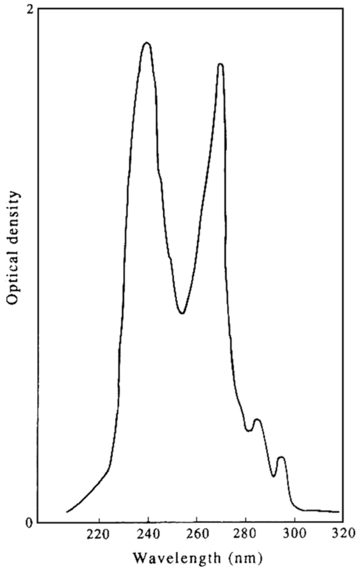


FIGURE 2 Ultraviolet absorption spectrum of p-methylstyrene monomer in dichloromethane.

It is worth mentioning here that regardless of the counter ion structure, no polymerization takes place when the reaction mixtures were left for three days in the dark under the same condition. This confirms

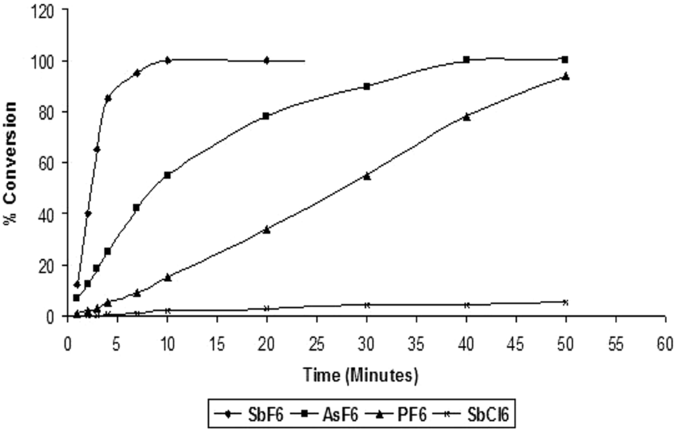


FIGURE 3 Photopolymerization of p-methyl styrene by salt (2) having different counter ions.

the photoinitiation activity of salt (2), and also the photostability upon storage, which is not possible in the case of unsubstituted trityl salts.

The counter ion effect depends on the geometry and the electronic configuration of the central atom of the counter ion, and its ability to acquire a negative charge. It also depends on the degree of separation and dissociation equilibria of the ion-pair and the monomer type [15]. Thus, non-nucleophilic counterions like SbF_6^- are highly reactive and give no fluoride ion (F^-) that may react with or interfere with the polymer-growing chains, while $SbCl_6^-$ anion showed a termination effect, possibly by back donating of the chloride ions. Accordingly, salts having SbF_6^- anion are good initiators for cationic polymerization of p-methylstyrene [12,16].

A comparison between the efficiency of the trityl salts 1–3 in the photopolymerization reaction of p-methylstyrene is shown in Figure 4. The monomer concentration was 2.53 M, and the salt concentration was 3.30×10^{-4} M. Now, the phenyl ring in trityl salt has the ability to delocalize the charge by resonance mechanism. This makes the methoxy group extremely efficient for the carbocation stabilization. Thus, a replacement of more hydrogen atoms in the phenyl groups by methoxy groups gives the indicated sequence of increasing carbocation stabilities. According to Figure 4, the reactivity of these salts falls in the following order, trimethoxy > dimethoxy > pentamethoxy.

This is due to the fact that trityl cation addition to olefinic monomers occurs at a para position on one of the phenyl rings (Scheme 1)

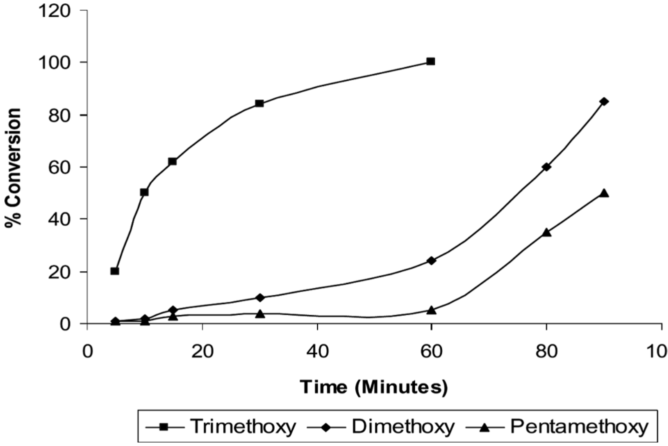
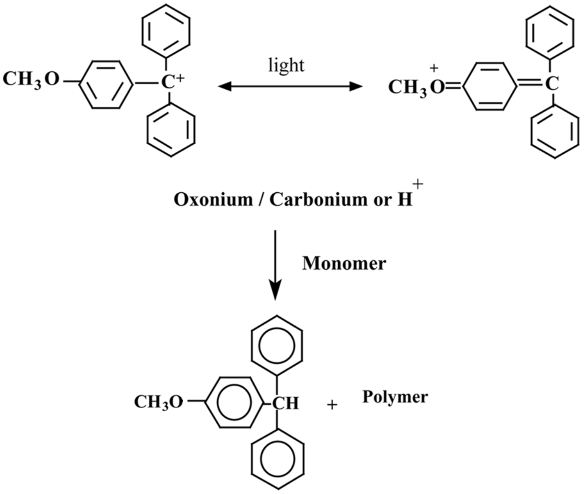


FIGURE 4 Photoinitiated polymerization by salts 1–3 [monomer] = 2.53 M, [salt] = 3.30×10^{-4} M, X = sbF_6^-.



SCHEME 1 Initiation step.

and not at the strictly crowded central carbocation as reported earlier in the literature [17,18].

According to Figure 4, the number and position of methoxy groups in benzene ring of salts 1–3 affect the rate of initiation step, propagation and termination; thus low salt concentration is used in this work to ensure complete dissociation of the cations from their respective counter ions.

Figure 5 shows the relationship between the percentage of conversion to polymer and the variation in salt (3) concentration in the range $(1.35\text{–}8.10) \times 10^{-4}$ M, at fixed reaction time of 95 min, with the monomer concentration of 6.66 M. Figure 5 shows that the rate of polymerization (R_p) is directly proportional to the initiator concentration. Accordingly, the equation for R_p in the polymerization of p-methylstyrene is formulated as follows:

$$\mathbf{R}_p = \mathbf{K}_p[\mathbf{M}][\mathbf{I}] \tag{1}$$

where: R_p = rate of polymerization.
K_p = rate constant of propagation.
$[M]$ = monomer concentration mol/L.
$[I]$ = initiator conconcentration mol/L.

This rate equation indicates that the initiation is proceeding by a cationic mechanism. The effect of air on the polymer conversion confirms that thought.

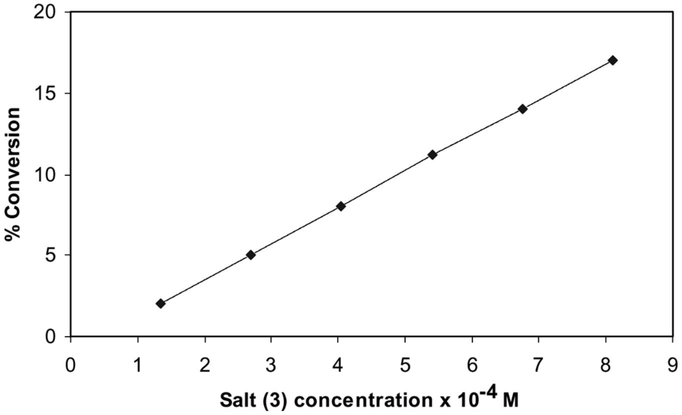


FIGURE 5 The relationship between percentage conversion to polymer and salt (3) concentration, at fixed time of 95 min, [monomer] = 6.66 M. X = SbF_6^-.

The effects of light wavelength and intensity on the polymerization of p-methylstyrene using salt (2) are shown in Figure 6, where polymerization was carried out at 300 nm in Pyrex tubes and at 300 nm and 350 nm in quartz tubes having the same diameters, in which the monomer concentration was 2.53 M and initiator concentration was 3.3×10^{-4} M. Figure 6 shows that polymerization in Pyrex tubes gives a higher yield of polymer when reaction mixture photolysis takes place by light having a wavelength 350 nm, while polymerization at 300 nm in Pyrex tubes is the lowest, under the same reaction

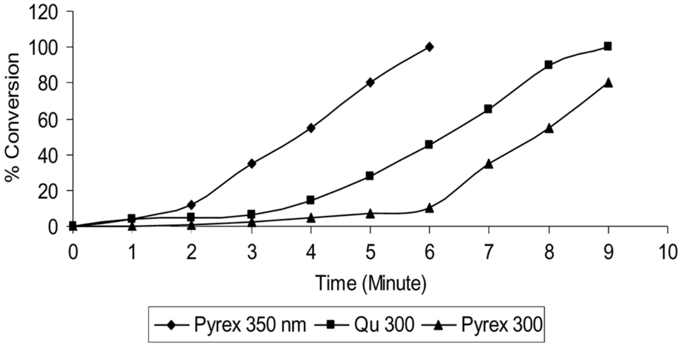
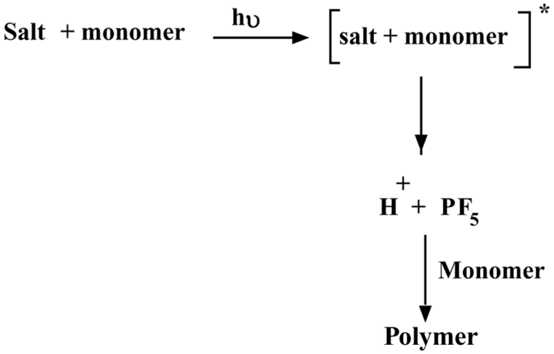


FIGURE 6 Effects of light intensity on the photopolymerization of p-methylstyrene by salt (2), X = SbF_6^-, 350 nm in Pyrex; 300 nm in Pyrex; 300 nm quartz.



SCHEME 2 Photo polymerization.

conditions. The rate of polymerization falls in the following sequences: 350 nm Pyrex $>$ 300 nm quartz $>$ 300 nm Pyrex.

These results suggest that interaction in the excited state between both the monomer and the salt is required for the initiation step, thus the concentration of initiating cations and the growing polymer chains may conveniently be adjusted by choosing appropriate light intensities or the wavelength of photolysis (Scheme 2).

Proposed Polymerization Mechanism

According to the reported results, initiation step can occur either by direct addition of the cation to the p-methylstyrene monomer or through a hydride ion abstraction from the monomer by the trityl cation leading to a monomer stabilized cation which is the real initiating species. However, the rate of hydride transfer to carbocation is affected by steric hindrance [19].

These results suggested that the excited state of the carbocation and the monomer undergoes the main reaction. Since no thermal polymerization was detected, the hydride transfer proceeds most probably via an activated complex. The direct addition of the trityl cation to the monomer was considered to be unlikely because of the steric effects. If this mechanism is ruled out then it is clear that the UV light causes the hydride transfer, and the hydride transfer is also accelerated by UV irradiation, as it is simplified by Scheme (2):

CONCLUSIONS

Three methoxy substituted trityl salts with non-nucleophilic counterions were synthesized, characterized and used as photo initiators for cationic polymerization of p-methylstyrene at 25°C. All these salts 1–3 are stable toward moisture and air. The activity of these photoinitiators was found in the order: trimethoxy > dimethoxy > pentamethoxy, under the same conditions.

REFERENCES

[1] Yagci, Y. and Endo, T., *Adv Polym Sci.* **59**, 127 (1997).
[2] Yagci, Y. and Reetz, I., *Prog Polym Sci.* **23**, 1485 (1998).
[3] Crivello, J. V., *Adv. Polym Sci.* **1**, 62 (1984).
[4] Crivello, J. V., *J. Polym Sci. Part A*: *Polym Chem.* **37**, 4241 (1999).
[5] Yagci, T. and Endo, T., *Adv. Polym Sci.* **16**, 78 (1996).
[6] Ledwith, A. and Sherrington, D. C., *Advan. Polym. Sci.* **19**, 1 (1975).
[7] Ledwith, A., *Pure and Appl. Chem.* **51**, 159 (1979).
[8] Diffenbach, R. A., Sano, K., and Taft, R. W., *J. Amer. Chem. Soc.* **88**, 4747 (1966).
[9] Kaeding, W. W. and Barile, G. C., (1986). In *Advances in Polymer Synthesis*. 223, B. M. Culbertson and J. E. McGrath, Eds., Plenum Press.
[10] Tanizaki, A., Sawamoto, M., and Higashimura, T., *J. Polym. Sci: Poly. Chem. Ed.* **25**, 87 (1986).
[11] Abu-Abdoun, I. and Aale-ali, *Europ. Polym. J.* **29**, 1439, 1445 (1993).
[12] Mohanraj, S. and Ford, W. T., *Macromolecules* **19**, 2470 (1986).
[13] Ford, W. T., Chandran, R., and Turk, H., *Pure & Appl. Chem.* **60**, 395 (1988).
[14] Abu-Abdoun, I. and Ledwith, A., *J. Polym. Res.* **14**, 99 (2007).
[15] Neckers, D. C. and Abu-Abdoun, I., *Macromolecules* **17**, 2468 (1984).
[16] Toncheva, V. D. and Velichkova, R. S., *Makromol. Chem.* **186**, 1739 (1985).
[17] Kampmeier, J. A., Geer, R. P., Meskin, A. J., and D'silva, R. M., *J. Amer. Chem. Soc.* **88**, 1257 (1966).
[18] Ledwith, A., *Advan. Chem. ser. (London)* **91**, 317 (1969).
[19] Panayotov, I. M., Manolova, N. E., and Velichkova, R. S., *Polym. Bull.* **4**, 653 (1981).