



Trimethylsilyl aryloxides as reagents in polymer reactions

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ABSTRACT : Trimethylsilyl aryloxides of composition, Me_3SiOAr , (where $\text{OAr} = -\text{OC}_6\text{H}_4-\text{CH}_3-\text{o}$, $-\text{OC}_6\text{H}_4-\text{CH}_3-\text{p}$, $\text{OC}_6\text{H}_4-\text{Cl}-\text{o}$, $-\text{OC}_6\text{H}_4-\text{Cl}-\text{p}$) have been successfully prepared from the reacting Me_3SiCl with respective substituted phenols in the presence of triethyl amine. Reactions of these trimethylsilyl aryloxides with poly(methyl methacrylate) PMMA yields copolymers viz. poly[MMA-(*o*-methylphenyl MA)], poly[MMA-(*p*-methylphenyl MA)], poly[MMA-(*o*-chlorophenyl MA)] and poly[MMA-(*p*-chlorophenyl MA)]. The synthesized products have been characterized by ^1NMR and FTIR spectral studies. Flame retardant properties of copolymers has been done with thermal (TG-DTA) analysis and it has been observed that electron withdrawing substituents in general and when present at *para*- position in the aromatic ring, in particular, continue to show fire retardancy to a greater extent, whereas no such fire retardancy has been observed with the electron releasing substituents.

INTRODUCTION

Polymers undergo the same reactions as their low molecular weight homologs, e.g. acetylation of hydroxyl groups of cellulose is basically the same reaction as the acetylation of ethanol and chlorination of polyethylene follows the same mechanism as chlorination of *n*-hexane. It is usually assumed that reactivity of a functional group in a polymer and a small organic molecule are the same. Thus, new polymers may be synthesized by modification of the existing polymers using a variety of reactants [1-4]. Polymer reactions are possible with those functional groups, which are present only in amorphous regions of the polymer network, whereas the functional groups present in the crystalline portions of the polymer are generally inaccessible to chemical reagents [5]. The product of such a reaction is heterogeneous and is well suited for an application requiring the modification of the surface properties of a polymer without affecting its bulk properties. Surface modification of polymers also results into flame retardancy. This has been achieved by examining the effects of many different additives on the thermal degradation of poly(methyl methacrylate) such as red phosphorus [6, 7], Wilkinson's catalyst, $\text{RhCl}(\text{PPh}_3)_3$ [8, 9], nafions [10], copolymers of 2-sulphonyl methacrylate and methyl methacrylate [11], a variety of transition metal halides (MnCl_2 , CrCl_3 , FeCl_2 , NiCl_2 , CuCl_2 and CuCl) [12-14], various phenyltin chlorides [15] and tetraphenyl- and tetrachloro- tin [16]. Phosphorus functionalization is considered to be one of the efficient means of conferring flame retardancy on polymeric systems by modifying the mode of decomposition of the basic polymer during ignition [17].

Survey of literature, thus reveals that although much work has been done on the use of variety of inorganic material in modifying the polymer surfaces, yet no work has been reported regarding the use of organo silicon aryloxides as reagents in polymeric reactions. In view of this, some of the trimethylsilyl aryloxides synthesized in the present project has been used as reagents in polymer reactions.

EXPERIMENTAL

All the chemicals used in the present studies were of analytical grade. FTIR spectra were scanned in the range $4000-200\text{ cm}^{-1}$ on Nicolet 5700 FTIR spectrophotometer in KBr pellets. $^1\text{H N.M.R.}$ spectra of trimethylsilyl aryloxides were recorded on Jeol JNM PMX 60SI NMR spectrometer in CDCl_3 using TMS as an internal standard.

Thermograms (TGA & DTA) of PMMA and the copolymers were recorded on a double pan Shimadzu DT-40 Thermal Analyzer (simultaneous DT/TGA module) using Pt crucible and Pt/Pt-Rh (10%) thermocouple at a heating rate of $10^\circ\text{C min}^{-1}$ in static air. 5-10 mg of the samples were taken in Pt crucible on one pan and $\pm\text{-Al}_2\text{O}_3$ was used as a standard reference material on the other pan in the decomposition chamber.

Synthesis of Trimethylsilyl Aryloxides, $\text{Me}_3\text{Si}(\text{OAr})$

[where $\text{OAr} = -\text{OC}_6\text{H}_4-\text{CH}_3-\text{o}$, $-\text{OC}_6\text{H}_4-\text{CH}_3-\text{p}$, $\text{OC}_6\text{H}_4-\text{Cl}-\text{o}$, $-\text{OC}_6\text{H}_4-\text{Cl}-\text{p}$]

In a typical procedure, trimethylsilyl aryloxides were prepared by adding trimethylsilyl chloride dissolved in carbon tetrachloride dropwise with constant stirring to the ice-cooled solution of the respective substituted phenol and triethylamine taken in the same solvent in equimolar ratios. White precipitates of triethylamine hydrochloride settle down from the solution. To ensure the completion of the reaction, the mixture solution was brought to room temperature while stirring and was refluxed over water bath for half an hour. Triethylamine hydrochloride was filtered out under vacuum and trimethylsilyl aryloxides of the respective phenols were recovered from the filtrate by vacuum distillation in quantitative yields (85-90 %).

Purity of the synthesized products was checked by comparing their $^1\text{H NMR}$ spectra with those of pure substituted phenols (Table 1).

Table 1 : ¹H NMR Data of Trimethylsilyl Aryloxides.

Compound		Chemical Shift' (ppm)		Multiplicity	Assignment
Substituted Phenol	Trimethylsilyl Aryloxide	Substituted Phenol	Trimethylsilyl Aryloxide		
HOC ₆ H ₄ -CH ₃ - <i>o</i>	Me ₃ SiOC ₆ H ₄ -CH ₃ - <i>o</i>	6.38-7.0	6.4-7.12	Multiplet (4H)	Aromatic protons
		4.51	—	Singlet (1H)	-OH proton
		2.28	2.3	Singlet (3H)	<i>o</i> -CH ₃ protons
		—	0.20	Singlet (9H)	-SiMe ₃ protons
HOC ₆ H ₄ -CH ₃ - <i>m</i>	Me ₃ SiOC ₆ H ₄ -CH ₃ - <i>m</i>	6.48-7.12	6.5-7.0	Multiplet (4H)	Aromatic protons
		4.18	—	Singlet (1H)	-OH proton
		2.17	2.15	Singlet (3H)	<i>m</i> -CH ₃ protons
		—	0.26	Singlet (9H)	-SiMe ₃ protons
HOC ₆ H ₄ -CH ₃ - <i>p</i>	Me ₃ SiOC ₆ H ₄ -CH ₃ - <i>p</i>	6.50-6.62	6.50-6.63	Double doublet (4H)	Aromatic protons
		4.65	—	Singlet (1H)	-OH proton
		2.21	2.22	Singlet (3H)	<i>p</i> -CH ₃ protons
		—	0.17	Singlet (9H)	-SiMe ₃ protons
HOC ₆ H ₄ -Cl- <i>o</i>	Me ₃ SiOC ₆ H ₄ -Cl- <i>o</i>	6.8-7.38	6.8-7.4	Multiplet (4H)	Aromatic protons
		6.25	—	Singlet (1H)	-OH proton
		—	0.29	Singlet (9H)	-SiMe ₃ protons
HOC ₆ H ₄ -Cl- <i>p</i>	Me ₃ SiOC ₆ H ₄ -Cl- <i>p</i>	6.71-7.10	6.70-7.10	Double doublet (4H)	Aromatic protons
		6.33	—	Singlet (1H)	-OH proton
		—	0.20	Singlet (9H)	-SiMe ₃ protons

Synthesis of Poly(methyl methacrylate), PMMA

Poly(methyl methacrylate), PMMA, was synthesized by a well-known chemical method. Methyl methacrylate (10 ml) was taken in a 50 ml round bottom flask containing 10 ml distilled water, 3-4 ml conc. nitric acid and the polymerization was carried out in presence of ceric ammonium nitrate (CAN) at 70°C for 2-3 hours. The polymer (PMMA) was then extracted from the resulting solution by adding distilled water and was dried in the oven at approximately 40°C.

Reactions of Trimethylsilyl Aryloxides (Me₃SiOAr) with PMMA

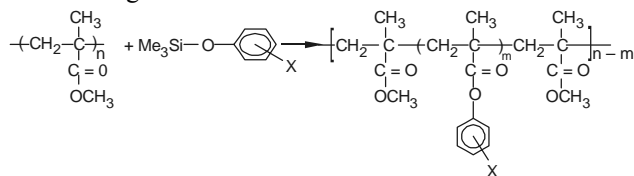
(Where OAr = -OC₆H₄-Cl-*o*, -OC₆H₄-Cl-*p*, -OC₆H₄-CH₃-*o*, -OC₆H₄-CH₃-*p*)

These reactions were carried out by refluxing the respective trimethylsilyl aryloxides (1 ml) and PMMA (1.074 gm) using ethanol as the solvent for 5-6 hours. The reaction solution was then concentrated by distilling off the solvent and the resulting copolymers were separated out by the

addition of petroleum ether, washed with water and finally dried in the oven at approximately 40°C.

RESULTS AND DISCUSSION

Four trimethylsilyl aryloxide derivatives prepared from *ortho*- and *para*-substituted methyl- and chloro- phenols were made to react separately with PMMA under reflux for 5-6 hrs. in ethanol, resulting into the formation of polymeric material (copolymer) and can be rationalized as shown in the following reaction:



(where X = -Cl or -CH₃)

These polymeric materials (copolymers) were then analyzed by scanning their FTIR spectra and have been characterized by flammability test and thermal analysis (TG/DTA).

FTIR Spectra

The important IR bands observed for these four copolymers and pure PMMA have been presented in Table 2. It follows from there that in addition to the usual IR absorption bands present in case of pure PMMA, new bands in the region 1558-1460 cm^{-1} assignable to aromatic $\nu_{(c=c)}$ stretching frequencies have also been observed. The presence of bands in the region 1390-1380 cm^{-1} and 752-640 cm^{-1} in case of copolymers with *ortho*- and *para*-methylphenols and *ortho*- and *para*-chlorophenols assignable to $\nu_{(\text{Cring-CH}_3)}$ and $\nu_{(\text{Cring-Cl})}$ modes respectively suggests the incorporation of aryloxy moiety into the PMMA chain, thus confirming the formation of new copolymers.

Further, the qualitative determination of pure PMMA and its copolymers made from *ortho*- and *para*-methylphenols and chlorophenols towards flammability (fire retardancy) was carried out by burning the samples on candle flame. It was observed that PMMA and its copolymers prepared from *ortho*- and *para*-methylphenols burns immediately leaving no residue. Copolymer made from *ortho*-chlorophenol, *i.e.*, poly[MMA-(*o*-chlorophenyl methacrylate)], burns at a comparatively slow rate leaving only a small amount of residue. Whereas, copolymer made from *para*-chlorophenol, *i.e.*, poly[MMA-(*p*-chlorophenyl methacrylate)], however, burns only in the presence of flame. The flame on the copolymer gets extinguished as soon as it is moved away from the candle flame, thus showing a tendency towards fire retardant.

Table 2 : Principal IR Spectral Bands (cm^{-1}) of Pure PMMA and its Copolymers.

Compound	Bands (cm^{-1})
Poly(methyl methacrylate) (PMMA)	2361, 1701, 1651, 1456, 1384, 1277, 1157, 965, 519, 419.
Poly[MMA-(<i>o</i> -chlorophenyl methacrylate)]	3000, 2955, 2616, 2361, 2339, 1971, 1732, 1558, 1484, 1453, 1156, 1062, 966, 839, 752, 979, 648, 518, 420.
Poly[MMA-(<i>p</i> -chlorophenyl methacrylate)]	3000, 2953, 2598, 2361, 2338, 1734, 1558, 1493, 1453, 1270, 1156, 966, 831, 752, 671, 643, 506.
Poly[MMA-(<i>o</i> -methylphenyl methacrylate)]	2954, 2603, 2361, 2338, 1967, 1734, 1558, 1455, 1386, 1269, 1155, 966, 843, 672, 522, 420.
Poly[MMA-(<i>p</i> -methylphenyl methacrylate)]	2920, 2852, 2361, 2341, 1738, 1654, 1561, 1545, 1512, 1460, 1386, 1097, 796, 671, 465.

Thermal Analysis

Thermal analysis is the measurement of changes in physical properties of a substance as a function of temperature when the substance is subjected to a controlled temperature programme. It is also considered as an extremely active field with applications in numerous directions and has registered a remarkable development as a useful technique [18] by which chemical and structural changes in the sample can be directly observed. The effect of ageing on the thermal stability of the SiO_2 based inorganic-organic hybrid materials obtained from tetraethoxy silane, triethoxy methylsilane, triethoxy vinylsilane, tetramethoxy silane, trimethoxy methylsilane and trimethoxy vinylsilane has been studied and it has been found that the structure of the gels and consequently, their thermal stability is strongly influenced by the type of alkoxides used as precursors in the sol-gel preparation [19]. In view of the above background, the thermal behaviour of pure poly(methyl methacrylate) and its copolymers, *i.e.*, poly[MMA-(aryl methacrylate)] (where aryl represents, *o*-methylphenyl, *p*-

methylphenyl, *o*-chlorophenyl or *p*-chlorophenyl) have been studied by using TG and DT analytical techniques. These investigations are expected to provide not only an insight into the thermal stability of the copolymers and the nature of thermal decomposition but also on the final residue left.

Thermogravimetric (TG) and differential thermal analysis (DTA) curves of PMMA and its copolymers synthesized in the present work are shown in Figs. 1 to 5 and their thermal decomposition data is presented in Table 3.

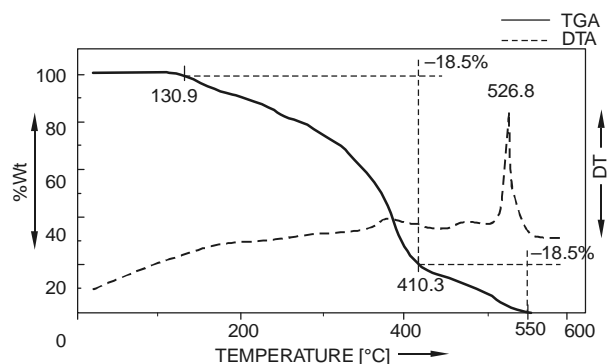


Fig.1. TGA/DTA curves of Poly[methyl methacrylate].

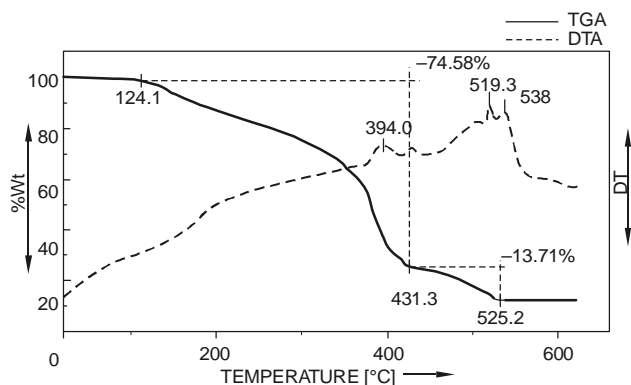


Fig.2. TGA/DTA curves of Poly[MMA-(*o*-chlorophenyl methacrylate)].

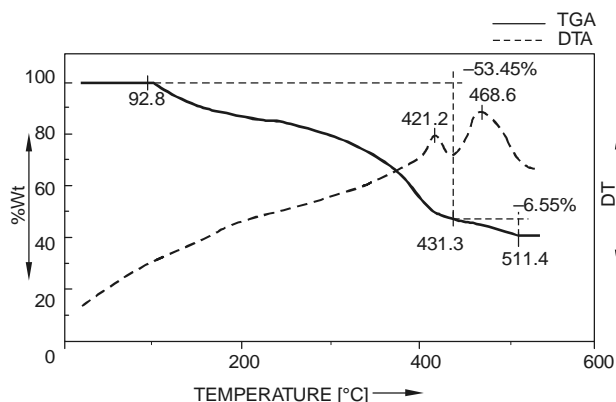


Fig.4. TGA/DTA curves of Poly[MMA-(*o*-methylphenyl methacrylate)].

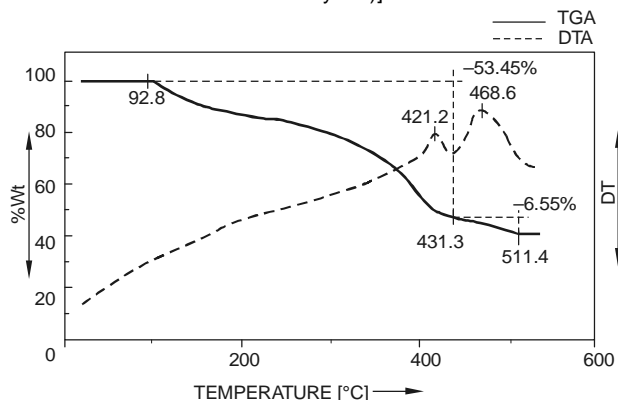


Fig.3. TGA/DTA curves of Poly[MMA-(*p*-chlorophenyl methacrylate)].

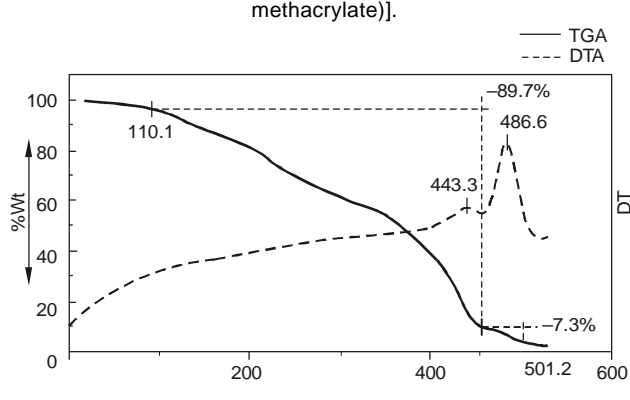


Fig.5. TGA/DTA curves of Poly[MMA-(*p*-methylphenyl methacrylate)].

Table 3 : Thermal Behaviour of PMMA and its Copolymers prepared from Trimethylsilyl Aryloxides.

Sample	Initial Decomp. Temp IDT (°C)	Final Decomp. Temp. FDT (°C)	DTA Peak Temp. (°C) (* Exothermic)	Total % Wt. Loss	% Residue Left	Remarks
Poly(methyl methacrylate) (PMMA)	130.9	550.0	526.8(-)*	100	nil	-
Poly[MMA-(<i>o</i> -chlorophenyl methacrylate)]	124.1	525.2	394.0(-)* 519.3(-)* 538.0(-)*	88.29	11.71	Fairy fire retardant
Poly[MMA-(<i>p</i> -chlorophenyl methacrylate)]	92.8	511.4	421.2(-)* 468.6(-)*	60	40	Good fire retardant
Poly[MMA-(<i>o</i> -methylphenyl methacrylate)]	136.9	543.3	536.9(-)*	100	nil	-
Poly[MMA-(<i>p</i> -methylphenyl methacrylate)]	110.1	501.2	433.3(-)* 486.6(-)*	97	3	-

A careful examination of the figures shows the resemblance of TG curves of copolymers to that of pure PMMA, with only the difference in their initial decomposition temperatures (IDT). This observation suggests the similarity in the basic structure of the polymeric chains of the copolymers with that of PMMA and different initial decomposition temperatures explains the substitution of $-\text{OCH}_3$ group of PMMA by aryloxide (OAr) ligands having different substituents in the aromatic rings. This fact is

further substantiated by the presence of $\tilde{\nu}_{(\text{CP}\% \text{C})}$ bands in IR spectra of the copolymers as has already been explained. The decreasing order of thermal stability of copolymers can be shown as :

poly[MMA-(*o*-methylphenyl MA)] > poly[MMA-(*p*-methylphenyl MA)] > poly[MMA-(*o*-chlorophenyl MA)] > poly[MMA-(*p*-chlorophenyl MA)] (where MMA= methyl methacrylate and MA= methacrylate)

From above, it is clear that copolymers with different substituents at *ortho*-position in the aromatic ring show higher thermal stability in comparison to their analogues with substituents at *para*-positions. Further, the higher thermal stability of copolymers made from *ortho*- and *para*-methylphenols than those made from *ortho*- and *para*-chlorophenols may be attributed to the role played by the electronic effects of the substituents present at *ortho*- and *para*- positions in the aromatic ring.

The amount of residue left after decomposition is higher (*i.e.* 40.96 %) in case of poly[MMA-(*p*-chlorophenyl MA)] as compared to poly[MMA-(*o*-chlorophenyl MA)] in which case the residue left is 11.71 % only, thus suggesting higher tendency towards flame retardancy in the former case than the latter one. This observation is further supported by the positive flammability test on poly[MMA-(*p*-chlorophenyl MA)] as mentioned earlier. It has been known that incorporation of halogen or nitrogen or phosphorus on polymer improves their flame retardancy. The present observations lead us to believe that the spatial position of chlorine at *para*-position of phenyl ring takes part in some reaction forming intermediate, which is stable to thermal degradation as reflected in the higher amount of residue left. No residue is left in case of copolymers with *ortho*- and *para*- methylphenols.

CONCLUSION

In the present work, it can be concluded from the above discussion that, new copolymers can be synthesized by use of trimethylsilyl aryloxides as reagents in polymer analogous reactions. The evidence of polymer analogous reactions has decisively been provided by the analysis of FTIR spectra and thermal analysis of resultant copolymers. In copolymers, a role is definitely being played by substituents at different positions in the aromatic ring, *e.g.*, in the present case, it has been observed that electron withdrawing substituents in general and when present at *para*- position, in particular, continue to show fire retardancy to a greater extent, whereas no such fire retardancy has been observed with the electron releasing substituents.

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