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Cationic Polymerization of 3,4-Dimethoxystyrene by Trityl Hexachloroantimonate

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SUMMARY

Reactions between 3,4-dimethoxystyrene and trityl hexachloroantimonate in methylene dichloride were studied by liquid chromatography, i.r. and visible spectroscopy. Under certain conditions monomer consumption is quite low, permitting accurate analysis of the initiation kinetics. Polymerization is characterized by rapid rates of chain transfer through facile intramolecular cyclization and at least one major termination reaction. The appearance of a chromophore absorbing at 540 nm is probably the result of a termination reaction in which stable, substituted indanyl cations are formed.

INTRODUCTION

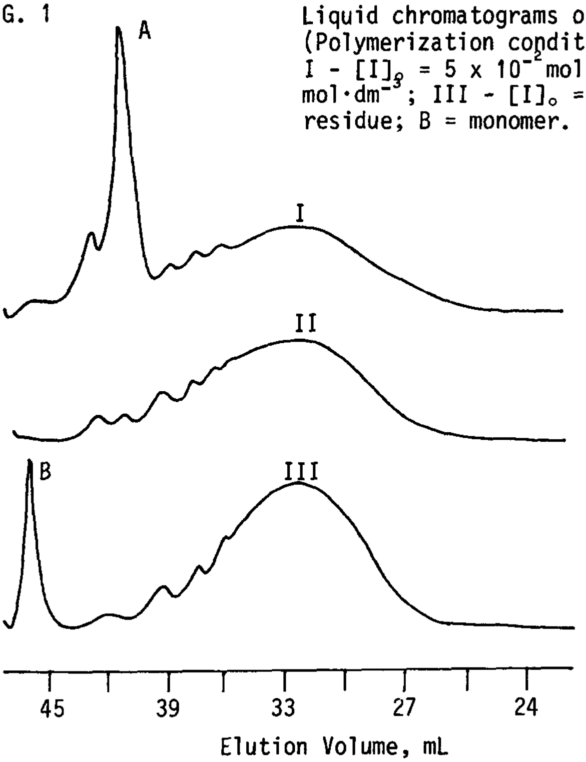
Recent studies on the interaction between trityl salts and various alkoxystyrenes have defined the fundamental characteristics of these systems. Comparison of the behaviour of anethole (ROONEY, 1978) with 1,2-dimethoxy-4-(1-propenyl)-benzene (DPB) (ROONEY, 1982) indicates that the presence of a second methoxy group on the ring in a position meta to the vinyl group does not appreciably alter the reactivity of the double bond. However, the reactivity of the ring towards electrophilic substitution is substantially increased, leading to a higher incidence of intramolecular cyclization. The cyclization acts as a chain transfer mechanism, reducing polymer molecular weights, and also appears to accelerate kinetic termination. In order to verify these conclusions, a comparison of the behaviour of p-methoxystyrene (COTREL et al, 1976) with 3,4-dimethoxystyrene (DMS) would be valuable. Apart from an early study (MAYEN and MARECHAL, 1972) little attention has been paid to the cationic polymerization of DMS and no work involving the use of stable carbocation salts with this monomer has been reported. The present work represents a study of the principal features of the polymerization of DMS initiated by trityl hexachloroantimonate (Ph_3CSbCl_6) in methylene dichloride at 25°C.

EXPERIMENTAL

DMS (Aldrich) was washed with aqueous NaOH, dried over $CaCl_2$ and distilled from calcium hydride under vacuum through a Vigreux column. The fraction boiling at 85°C under 0.4mm Hg pressure was collected and stored over molecular sieves.

The purification of other materials and experimental techniques have been described elsewhere (ROONEY, 1982).

FIG. 1



Liquid chromatograms of poly(DMS) in THF at 25°C (Polymerization conditions : $[M]_o = 0.15$ mol·dm^{-3}; I - $[I]_o = 5 \times 10^{-2}$ mol·dm^{-3}; II - $[I]_o = 5 \times 10^{-3}$ mol·dm^{-3}; III - $[I]_o = 5 \times 10^{-4}$ mol·dm^{-3}). A = trityl residue; B = monomer.

RESULTS

Polymerization of DMS initiated over a wide range of initiator concentrations, $[I]_o$, resulted in products of similar molecular weights (see Figure 1). A plot of the monomer and oligomer peak retention times against molecular weight (assuming each of the lower oligomers was represented by a peak in the chromatogram) yielded the calibration curve shown in Figure 2, from which estimates of polymer molecular weights could be drawn. Number-average molecular weights for all polymers were approximately 1000-1100 while weight-average molecular weights were about 1400-1500.

At low $[I]_o$ consumption of DMS was incomplete and at $[I]_o = 5 \times 10^{-5}$ mol·dm^{-3} monomer conversion was only 5-7%. In all cases after mixing initiator and monomer solutions a red colour appeared and increased in intensity as time passed. Repeated scanning of the visible spectrum revealed the development of a peak at 540 nm and the diminution of the peaks ascribed to the trityl cation. In reactions with low $[I]_o$, the decrease in optical density at 435 nm was found to be pseudo-first order (see Figure 3) and a plot of the initial rate of trityl cation consumption against DMS concentration (Figure 4) permitted an accurate estimate of the rate constant of initiation, $k_i = 0.4$ dm^{3}mol^{-1} sec^{-1} at 25°C.

Infrared spectroscopic analysis of DMS oligomers showed the disappearance of bands associated with the vinyl group at 3085, 1632, 993 and 906 cm^{-1} (See Figure 5). Aromatic bands were largely unchanged with the exception of the band at 860 cm^{-1}, which is ascribed to the presence of two adjacent C-H bonds on the phenyl ring. This band was found to decrease in relative intensity by about 15%.

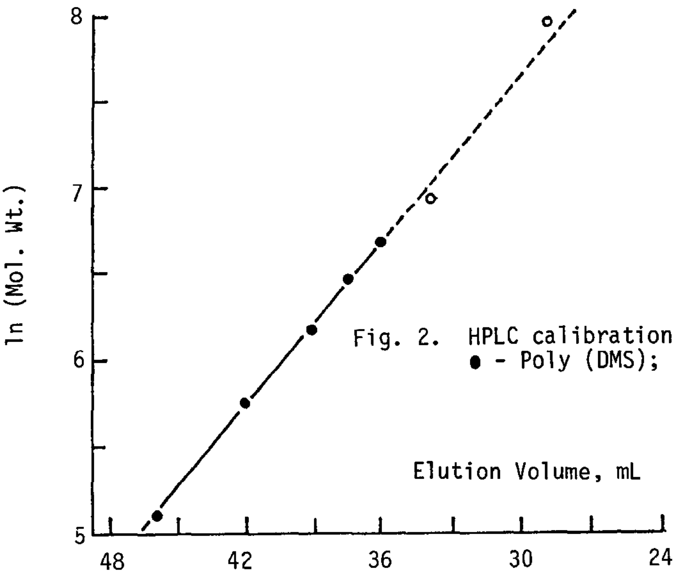


Fig. 2. HPLC calibration curve in THF at 25°C: ● - Poly (DMS); o - Polystyrene standards

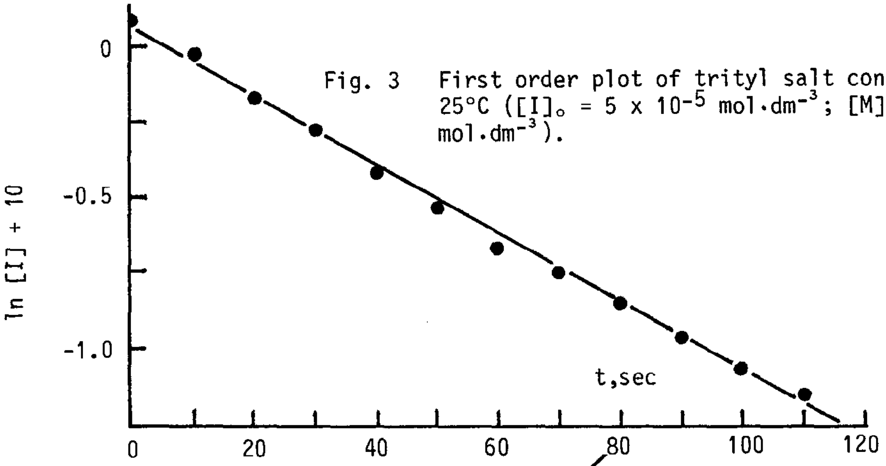


Fig. 3 First order plot of trityl salt concentration at 25°C ($[I]_o = 5 \times 10^{-5}$ mol·dm^{-3}; $[M]_o = 3 \times 10^{-2}$ mol·dm^{-3}).

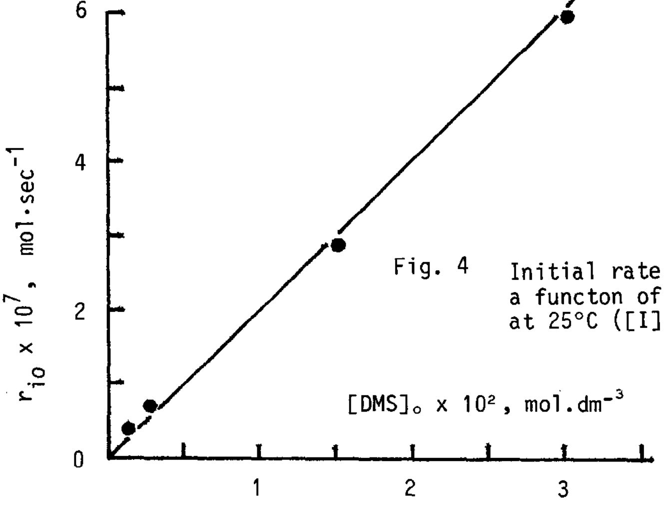


Fig. 4 Initial rate of trityl salt consumption as a functon of initial monomer concentration at 25°C ($[I]_o = 5 \times 10^{-5}$ mol·dm^{-3}).

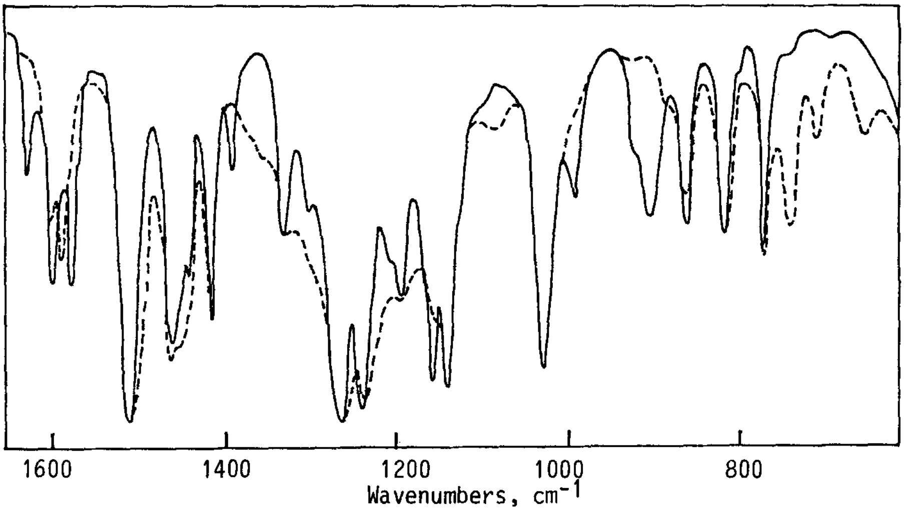


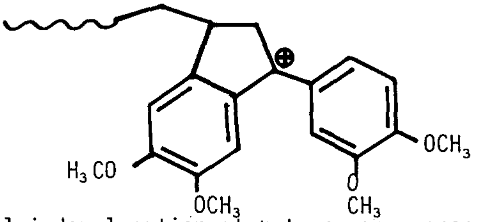
Fig. 5 Infrared spectra of 3,4 - dimethoxystyrene before (——) and after (---) complete polymerization at 25°C (Polymerization conditions: $[M]_o = 0.15\ mol{\cdot}dm^{-3}$; $[I]_o = 5 \times 10^{-3}\ mol{\cdot}dm^{-3}$).

DISCUSSION

Since trityl cations have been shown to add directly to the double bonds of β-methyl substituted alkoxystyrenes (ROONEY, 1982) it is reasonable to assume that the trityl cation adds directly to the less sterically hindered DMS. The measured rate constant of this reaction is only slightly lower than that reported for the trityl-p-methoxystyrene reaction, $0.9\ dm^{-3}mol{\cdot}^{-1}sec^{-1}$ (COTREL et al, 1976), and is more than two orders of magnitude greater than the values observed for trityl addition to anethole and DPB. This finding confirms the conclusion that the presence of the second methoxy substituent in the meta position does little to alter the reactivity of the styryl double bond towards electrophiles.

The fact that DMS polymer molecular weights are more than 10 times lower than those of p-methoxy styrene polymers produced under similar conditions indicates increased susceptibility to chain transfer reactions. The reduction in intensity of the infrared band at 860 cm^{-1} is consistent with the formation of cyclized structures in a manner analogous to that observed for DPB. Introduction of a meta-methoxy substituent onto the p-methoxystyrene ring appears to promote intramolecular ring alkylation and the chain transfer and kinetic termination entailed by this reaction.

Two further aspects of the cationic polymerization of DMS require analysis: the low monomer conversions at low values of $[I]_o$, and the appearance of the chromophore at 540 nm. The former phenomenon was noted in polymerizations of styrene by Ph_3CSbCl_6 (JOHNSON and PEARCE, 1976) and has been termed "false initiation" (GANDINI and CHERADAME, 1980). However, the presence of cyclized species in these systems suggests a strong analogy with the DPB-Ph_3CSbCl_6 reactions, in which case initiation is genuine but followed rapidly by termination. At higher $[I]_o$ the rate of propagation simply outstrips the rate of termination. The chromophore at 540 nm is reminiscent of that observed at 505 nm in cationic polymerizations of p-methoxystyrene and the similar bathochromic shift in this type of peak when DPB is substituted for anethole suggests that the second methoxy group plays the role of auxochrome. Given the relationship between the appearance of the chromophore and the onset of kinetic termination, a reasonable structure for the chromophore would be



This type of phenyl indanyl cation structure was proposed some years ago (BERTOLI and PLESCH, 1968) to account for visible absorbances and termination in polymerizations of styrene. The cation is generated through hydride abstraction by a propagating cation from cyclized end groups which have been shown to occur frequently in polymerizations of alkoxystyrenes. The location of the absorption maximum is almost identical to that of the structurally similar p-methoxybenzoyl [bis(p-methoxyphenyl)] methylium cation (TAKEUCHI et al, 1983).

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