

Radical polymerization of styrene initiated by *p*-acetyl benzylidene triphenylarsonium ylide

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The kinetics of the polymerization of styrene in bulk and in dilute systems in the presence of *p*-acetyl benzylidene triphenylarsonium ylide (*p*-ABTAY) as radical initiator has been examined at $60 \pm 0.1^\circ\text{C}$ for 20 h under N_2 . The values of the initiator exponent and the monomer exponent showed that the system follows ideal radical kinetics with bimolecular termination. The overall activation energy and average value of k_p^2/k_t are 64.6 kJ mol^{-1} and $0.10 \times 10^{-2} \text{ l mol}^{-1} \text{ s}^{-1}$, respectively. The ylide dissociates to produce phenyl radical, which brings about polymerization.

(Keywords: *p*-acetyl benzylidene triphenylarsonium ylide; dilatometric technique; gas-liquid chromatography; mechanism; kinetics)

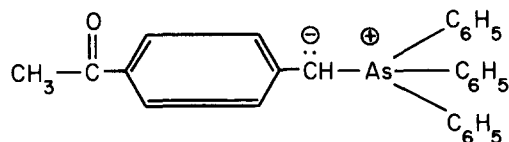
INTRODUCTION

Whereas some information has been published recently about the applications of nitrogen¹⁻³, phosphonium⁴ and sulphonium⁵ ylides in the field of polymer science, relatively little attention has been paid to arsonium ylides, which should have been paid due to their ease of preparation, more dipolar nature and reactivity than analogous phosphonium or sulphonium ylides. The difference in reactivity of arsonium and phosphonium ylides is commonly ascribed to less efficient $p\pi-d\pi$ overlap between the Csp^2 orbitals and the larger and more diffuse 4d orbitals of arsenic and to decreased electrostatic interaction across the ylide bond.

We, therefore, undertook the present investigation and for the first time application of *p*-acetyl benzylidene triphenylarsonium ylide (*p*-ABTAY) as a radical initiator for the polymerization of styrene is reported.

EXPERIMENTAL

Styrene and other solvents, purified by methods given by Overberger⁶ and Vogel⁷ respectively, were used in the polymerization. Triphenyl arsine (Fluka) was used as-received without further purification. The ylide (*p*-ABTAY), having the structure (1), was prepared by



the method given in the literature⁸. It was insoluble in non-polar solvents like benzene and carbon tetrachloride but partially soluble (>10%) in polar solvents like dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF).

A solution of *p*-ABTAY in styrene ($17.3 \times 10^{-2} \text{ mol}$) was subjected to polymerization in a polymerization tube

for 20 h at $60 \pm 0.1^\circ\text{C}$ under nitrogen atmosphere. The polymer was precipitated with acidified methanol and dried to constant weight. The rate of polymerization (R_p) was calculated from the slopes of the linear zone of per cent conversion vs. time plots (Figure 1).

The intrinsic viscosity $[\eta]$ ($100 \text{ cm}^3 \text{ g}^{-1}$) of the polymers was determined in benzene at $30 \pm 0.1^\circ\text{C}$ using an Ubbelohde viscometer. It was used to calculate the average degree of polymerization (\bar{P}_n) using the equation⁹:

$$\bar{P}_n = 1770[\eta]^{1.4} \quad (1)$$

The i.r. and n.m.r. spectra of polymer(s) were obtained on Perkin-Elmer 599 B and Varian 100 H A spectrometers, respectively.

RESULTS AND DISCUSSION

All experiments on the bulk polymerization were carried out with $17.3 \times 10^{-2} \text{ mol}$ of styrene monomer and varying the concentration of *p*-ABTAY. The results of styrene polymerization with an induction period of about 8 h are presented in Tables 1 and 2 and illustrated in Figures 1-5. The high induction period could be produced by *p*-ABTAY molecules being inhibitors as well as slowly dissociating to form initiating radicals.

Initiator exponent

Table 1 reveals that R_p increases with increasing [*p*-ABTAY]. The initiator exponent was calculated from the slope of the linear plot of $\log R_p$ versus $\log[\textit{p}\text{-ABTAY}]$ (Figure 2). These results show that the initiator exponent is 0.5, as expected for ideal radical polymerization.

The average degrees of polymerization (\bar{P}_n) of polystyrene samples formed at different [*p*-ABTAY] are shown in Table 1. These data show that \bar{P}_n decreased as [*p*-ABTAY] increased. The plot of $1/\bar{P}_n$ versus [*p*-ABTAY]^{0.5} passes through the origin (Figure 3), which suggests radical polymerization with bimolecular termination. The value of k_p^2/k_t determined from the slope

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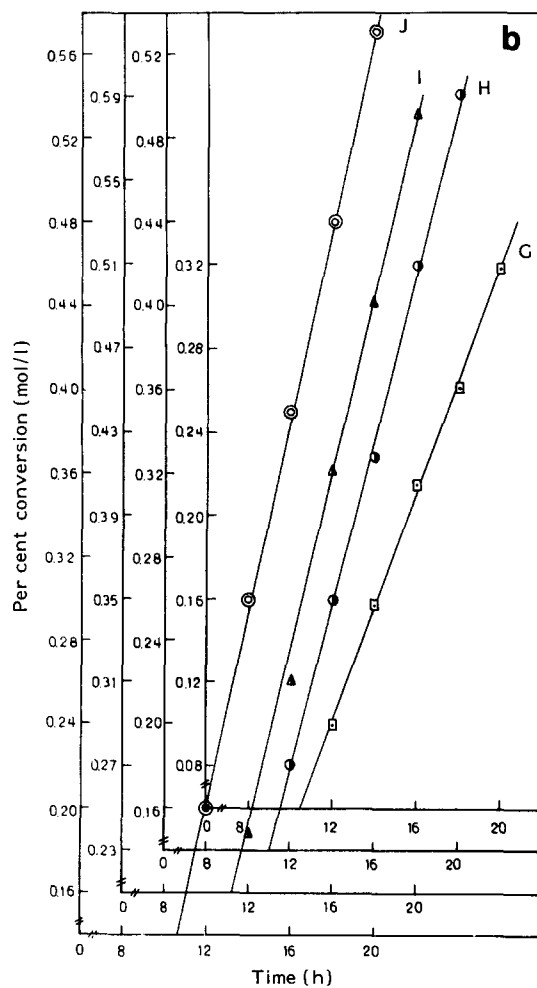
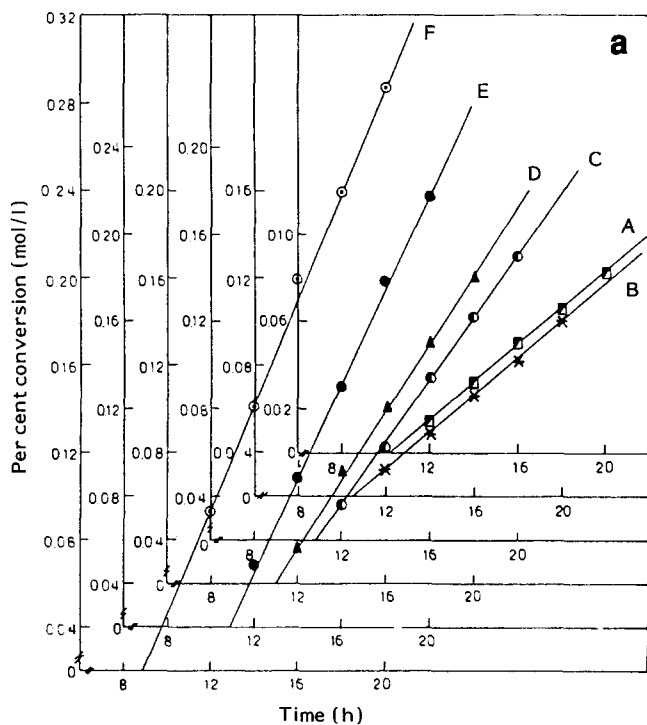


Figure 1 Conversion-time plots of radical polymerization of styrene using *p*-acetyl benzylidene triphenylarsonium ylide as radical initiator: (a) $[p\text{-ABTAY}] = 1.14 \times 10^{-4}$ (A), 3.42×10^{-4} (B), 6.84×10^{-4} (C), 9.13×10^{-4} (D), 11.40×10^{-4} (E), 13.60×10^{-4} mol $^{-1}$ (F), and (b) $[p\text{-ABTAY}] = 17.10 \times 10^{-4}$ (G), 22.20×10^{-4} (H), 34.20×10^{-4} (I), 45.60×10^{-4} mol $^{-1}$ (J). Styrene, 17.3×10^{-2} mol; time, 20 h; temperature, $60 \pm 0.1^\circ\text{C}$

Table 1 Effect of $[p\text{-ABTAY}]$ on the rate of polymerization of styrene^a initiated by *p*-acetyl benzylidene triphenylarsonium ylide at $60 \pm 0.1^\circ\text{C}$

$[p\text{-ABTAY}] \times 10^4$ (mol $^{-1}$)	Per cent conversion (mol $^{-1}$)	$R_p \times 10^6$ (mol $^{-1}$ s $^{-1}$)	\bar{P}_n
1.14	0.082	2.10	—
3.42	0.100	3.20	305
6.84	0.150	4.20	250
9.13	0.160	5.30	190
11.4	0.220	6.11	170
13.6	0.298	6.94	146
17.1	0.318	7.40	137
22.2	0.500	9.00	—
34.2	0.571	11.10	—
45.6	0.582	12.00	—

^a Styrene, 17.3×10^{-2} mol; time, 20 h

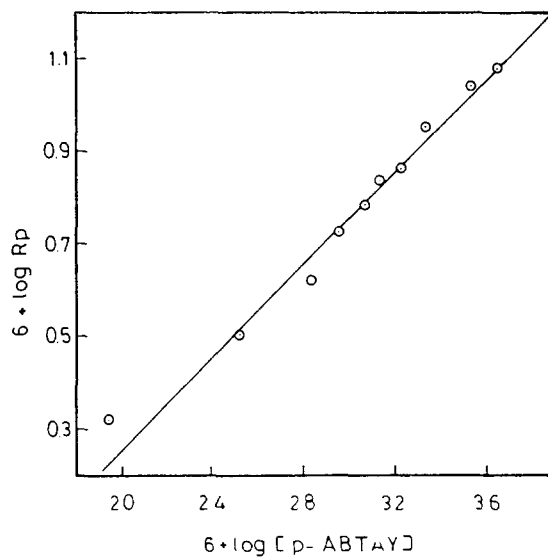


Figure 2 Plot of \log (rate of polymerization) vs. \log (*p*-ABTAY concentration). Styrene, 17.3×10^{-2} mol; time, 20 h; temperature, $60 \pm 0.1^\circ\text{C}$

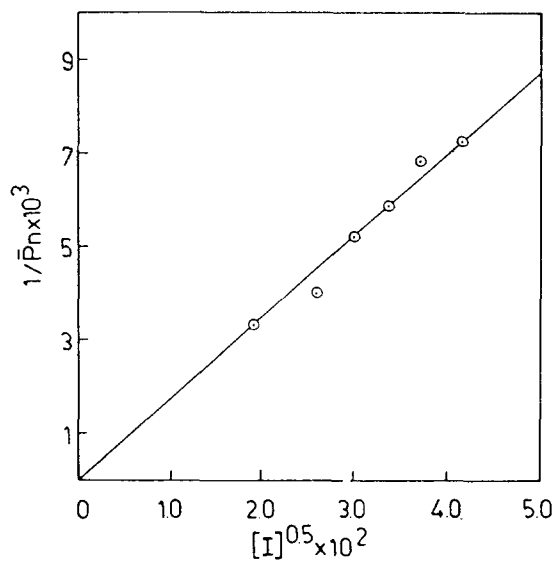


Figure 3 Plot of $1/\bar{P}_n$ vs. $[\text{initiator}]^{0.5}$ for the polymerization of styrene initiated by *p*-ABTAY at $60 \pm 0.1^\circ\text{C}$. Styrene, 17.3×10^{-2} mol; time, 20 h; temperature, $60 \pm 0.1^\circ\text{C}$

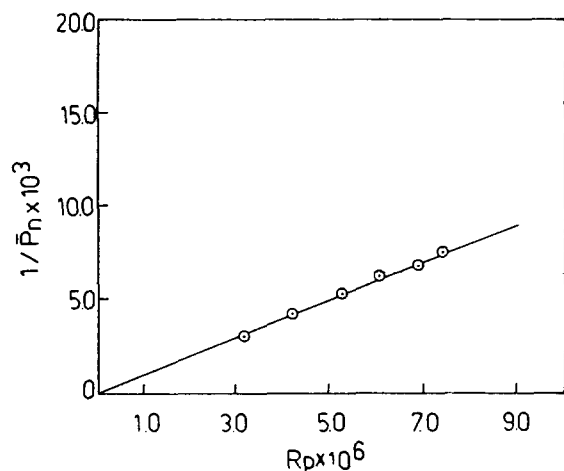


Figure 4 Plot of $1/\bar{P}_n$ vs. R_p for the polymerization of styrene initiated by *p*-ABTAY. Styrene, 17.3×10^{-2} mol; time, 20 h; temperature, $60 \pm 0.1^\circ\text{C}$

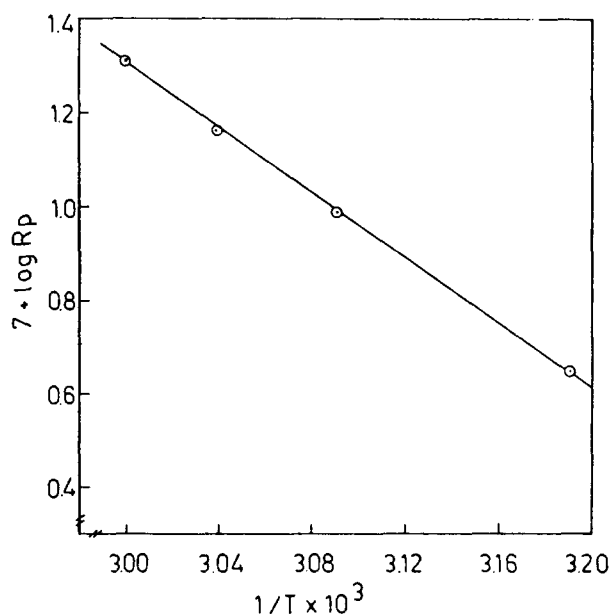


Figure 5 Plot of \log (rate of polymerization) vs. polymerization temperature (Arrhenius plot). [*p*-ABTAY], 1.14×10^{-4} mol $^{-1}$; styrene, 17.3×10^{-2} mol; time, 20 h

of a linear plot (Figure 4) of $1/\bar{P}_n$ versus R_p is $0.10 \times 10^{-2} \text{ mol}^{-1} \text{ s}^{-1}$.

Effect of temperature

The rate of polymerization increases with temperature, and the overall Arrhenius activation energy (ΔE) for the bulk polymerization, calculated from the corresponding slope of the Arrhenius plot of $\log R_p$ versus $1/T$ (Figure 5), is 64.8 kJ mol^{-1} .

Effect of additives

The effect of polar solvents, viz. dimethyl sulphoxide (DMSO), dimethyl formamide (DMF) and dioxane, and non-polar solvent, viz. benzene, has also been studied by diluting the monomer–initiator mixture. The results are compiled in Table 2. The results are unusual but interesting because often a higher per cent conversion gives low \bar{P}_n for radical polymerization. In the present work, a study of Table 2 shows that the \bar{P}_n of polymers obtained by bulk polymerization was higher than those obtained in the presence of polar solvents because of chain transfer. In case of dioxane and DMF the per cent conversion as well as \bar{P}_n are inverse functions of concentration of the solvents, presumably on account of the dependence of termination rate constant k_t on chain length. Similar results have been reported by Burezyk *et al.*¹⁰. However, in the case of DMSO, the per cent conversion and \bar{P}_n are direct functions of the concentration of DMSO, which could possibly be due to degradative addition of DMSO to the propagating polymer chain. Similar observations have also been made by Bamford *et al.*¹¹. The effect of hydroquinone (Table 2) confirms the radical mode of polymerization.

The analysis of i.r. and n.m.r. spectra of the polymers ruled out the possibility of ylide incorporation in the polymer chain, because (1) the i.r. spectrum shows no band at 1725 cm^{-1} due to the carbonyl group of ylide, and (2) no peak due to methyl protons (in the region of $9\text{--}10 \tau$) is present in the n.m.r. spectrum of the polymer.

MECHANISM

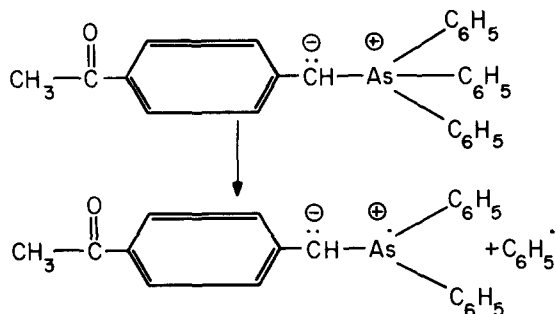
All results illustrated in Figures 1–5 and summarized in Tables 1 and 2 confirm that *p*-ABTAY initiates

Table 2 Effect of additives on the rate of polymerization of styrene^a initiated by *p*-acetyl benzylidene triphenylarsonium ylide at $60 \pm 0.1^\circ\text{C}$

Additive	[Additive] (mol $^{-1}$)	Per cent conversion (mol $^{-1}$)	$R_p \times 10^6$ (mol $^{-1} \text{ s}^{-1}$)	\bar{P}_n
DMSO	0	0.21	6.11	170
	0.79	0.66	13.8	—
	1.45	0.70	16.6	71.0
	2.49	0.75	20.8	80.5
	2.91	0.78	21.5	102.0
Dioxane	1.03	0.85	17.4	19.5
	1.89	0.50	11.5	10.1
	3.78	0.40	10.4	7.4
DMF	1.12	1.20	27.7	113.0
	2.05	0.71	17.3	70.4
	4.10	0.31	9.25	27.0
Benzene	1.04	0.16	3.24	—
	1.92	0.08	1.38	—
	3.84	0.07	1.11	—
Hydroquinone	2.27×10^{-3}	0.03	0.90	—
	4.54×10^{-3}		Inhibited	

^aStyrene, 17.3×10^{-2} mol; [*p*-ABTAY], 1.14×10^{-4} mol $^{-1}$; time, 20 h

radical polymerization of styrene. The *p*-ABTAY, like phosphonium ylide¹², sulphonium ylide¹³ and triphenyl sulphonium salts¹⁴, dissociates in the following manner to yield phenyl radical, which is responsible for initiating the polymerization:



This was confirmed by gas-liquid chromatography analysis on a CIC model 85-PRO Gas chromatograph using a flame ionization detector and 0.31 cm \times 2 m Carbowax 20 M column. Nitrogen was used as a carrier gas at a rate of 30 ml min⁻¹. The column and injector port temperatures were maintained at 220 and 260°C. The solution of *p*-ABTAY (9.13×10^{-4} mol l⁻¹) was prepared in dimethyl sulphoxide. The observed retention time of the compound formed was 0.97 min, which matches with the retention time of pure toluene, thus confirming the formation of toluene in the system. The formation of toluene confirms the existence of phenyl radical.

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