

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Studies on the Kinetics of Polymerization of Styrene Initiated by Arsenic Trichloride

A. K. Srivastava<sup>a</sup>; A. K. Shukla<sup>a</sup>

<sup>a</sup> Department of Chemistry, Harcourt Butler Technological Institute, Kanpur, India

**To cite this Article** Srivastava, A. K. and Shukla, A. K.(1984) 'Studies on the Kinetics of Polymerization of Styrene Initiated by Arsenic Trichloride', *Journal of Macromolecular Science, Part A*, 21: 6, 867 – 874

**To link to this Article:** DOI: 10.1080/00222338408077249

**URL:** <http://dx.doi.org/10.1080/00222338408077249>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Studies on the Kinetics of Polymerization of Styrene Initiated by Arsenic Trichloride

A. K. SRIVASTAVA\* and A. K. SHUKLA

Department of Chemistry  
Harcourt Butler Technological Institute  
Kanpur 208002, India

### ABSTRACT

The cationic polymerization of styrene initiated by arsenic trichloride ( $\text{AsCl}_3$ ) in the presence of traces of acetic acid (co-catalyst) at  $-8$ ,  $-4$ , and  $0^\circ\text{C}$  for 100 min using the dilatometric technique in an inert atmosphere yielded low molecular weight polymer. The rate of polymerization ( $R_p$ ) is a direct function of the concentration of  $\text{AsCl}_3$ , monomer, and polar solvent, but inversely proportional to the polymerization temperature and nonpolar solvent. Hydroquinone has no effect on  $R_p$ . Various kinetic parameters have been evaluated and a kinetic scheme is proposed.

### INTRODUCTION

A number of cationic initiators, such as  $\text{Cl}_3\text{CCOOH}$  [1],  $\text{HClO}_4$  [2], and  $\text{SnCl}_4$  [3], have been used for the polymerization of styrene. How-

---

\*To whom correspondence should be addressed.

ever, the polymerization of styrene initiated by  $\text{AsCl}_3$  has not been reported in detail.

### EXPERIMENTAL

Purified styrene (SRL make), solvents, and nonsolvents were used.  $\text{AsCl}_3$  (Fuming, Riedal, Germany) was used as received without further purification. Polymerization was carried out in a modified dilatometric apparatus [4, 5] (consisting of a 1.5-cm long bulb of 3 mL monomer capacity attached to a 6-cm long capillary of 2.0 mm diameter) at  $-8$ ,  $-4$ , and  $0^\circ\text{C}$  ( $\pm 0.05^\circ\text{C}$ ) for 100 min in an inert atmosphere.

A master graph (Fig. 1) was used to convert volume contraction data into percentage conversion which was used to calculate the rate of polymerization ( $R_p$ ) using Eq. (3).

If  $W$  grams of polymer was obtained from 1 mL of polymerized monomer in time  $t$  (in minutes), then

$$\text{Percentage conversion (c)} = \frac{W \times 100}{0.9090} \quad (1)$$

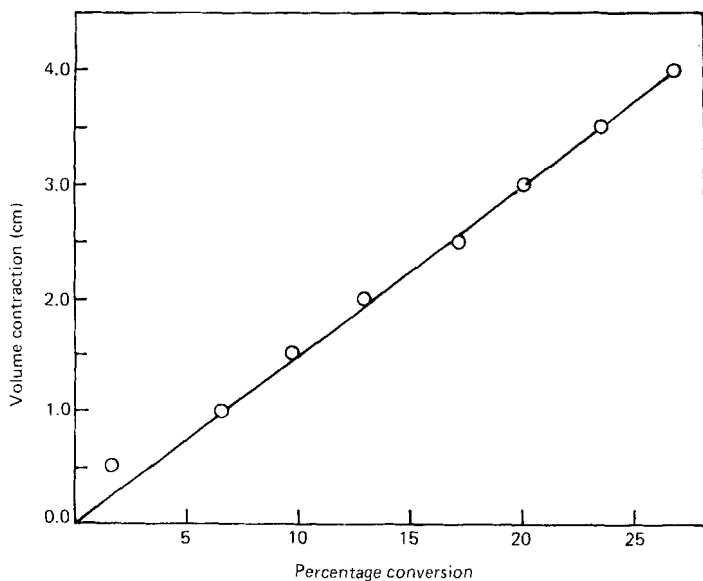


FIG. 1. Master graph showing the relationship between volume contraction and percentage conversion of styrene. Capillary diameter: 2.0 mm.

and

$$R_p = \frac{W \times 1000}{104.41 \times 60 \times t} \quad (2)$$

where 104.41 and 0.9090 are the molecular weight and the density of the styrene, respectively.

Now, using the value of  $W$  from Eq. (1) in Eq. (2):

$$R_p = \frac{1.4507 \times 10^{-3} \times c}{t} \quad (3)$$

The intrinsic viscosity ( $\eta_{int}$ ) of the polymer, determined in benzene with a Ubbelohde viscometer, was used to calculate the average degree of polymerization ( $\bar{P}_n$ ) as follows [6]:

$$\bar{P}_n = 1.712(\eta_{int})^{1.37} \quad (4)$$

## RESULTS AND DISCUSSION

The polymerization of styrene initiated by  $AsCl_3$  (concentration: 0.5–4.0 mol/L) in the presence of traces of acetic acid (cocatalyst) proceeds without an induction period. The results are reported in Table 1.  $R_p$  is a direct function of the concentration of  $AsCl_3$ , and the exponent value of the initiator, determined from the slope of  $\log R_p$  vs the log concentration of  $AsCl_3$  (Fig. 2), is found to be  $2.9 \pm 0.10$ . It is observed that no polymerization occurs in the absence of the cocatalyst. Therefore, it can be assumed that the cocatalyst is responsible for the formation of active centers as shown later by Eqs. (a) and (b) in our kinetic scheme. The propagation step is as usual, but termination is spontaneous as shown by the low molecular weight polymer obtained.

The effect of styrene concentration on  $R_p$  and  $\bar{P}_n$  was studied by varying the styrene concentration from  $2.61 \times 10^{-2}$  to  $5.22 \times 10^{-2}$  mol/L, as shown in Table 2.  $R_p$  and  $\bar{P}_n$  are directly influenced by the styrene concentration, and the following quantitative relationship was obtained from the slope of the linear plot between  $\log R_p$  and the log concentration of styrene (Fig. 3):

$$R_p \propto [\text{styrene}]^{2.0} \quad (5)$$

TABLE 1. Effect of  $\text{AsCl}_3$  on the Polymerization of Styrene<sup>a</sup>

Concentration of $\text{AsCl}_3$ (mol/L)	$R_p \times 10^4$ mol/L·s		
	-8°C	-4°C	0°C
0.50	2.278	2.035	1.723
1.00	2.637	2.278	1.940
1.50	2.751	2.449	2.129
2.00	2.901	2.581	2.247
2.50	3.084	2.675	2.328
3.00	3.084	2.751	2.449
3.50	3.184	2.675	2.581
4.00	3.202	2.901	2.581

<sup>a</sup>Styrene concentration =  $2.61 \times 10^{-2}$  mol/L, time = 100 min.

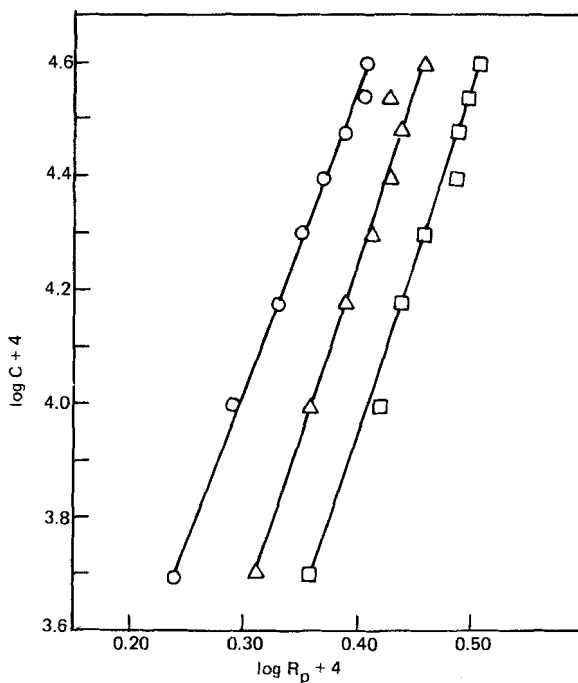


FIG. 2. Log rate of polymerization vs log concentration of  $\text{AsCl}_3$ . Styrene concentration:  $2.61 \times 10^{-2}$  mol/L. Time: 100 min. Temperature: (○) 0°C, (△) -4°C, (□) -8°C.

TABLE 2. Effect of Styrene Concentration on the Polymerization of Styrene<sup>a</sup>

Concentration of styrene (mol/L)	$R_p \times 10^4$ mol/L·s	$\bar{P}_n$
$2.61 \times 10^{-2}$	1.723	22.22
$3.48 \times 10^{-2}$	1.7988	20.00
$4.35 \times 10^{-2}$	1.988	18.18
$5.22 \times 10^{-2}$	2.114	17.24

<sup>a</sup>AsCl<sub>3</sub> concentration = 0.5 mol/L, time = 100 min, 0°C.

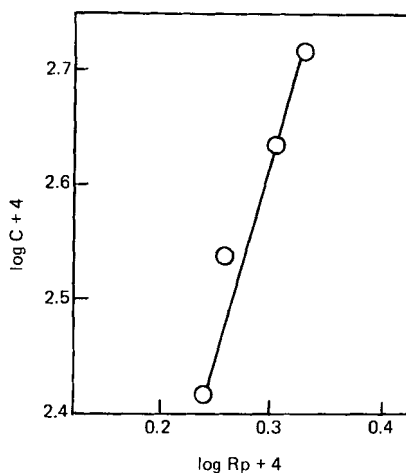


FIG. 3. Log concentration of styrene vs log rate of polymerization. AsCl<sub>3</sub> concentration: 0.5 mol/L. Temperature: 0°C. Time: 100 min.

$R_p$  is inversely related to the polymerization temperature. An Arrhenius plot (Fig. 4) leads to a value of 1.2 kcal/mol for the activation energy of the overall polymerization reaction.  $R_p$  is favored by the polar solvent (CH<sub>3</sub>CN) but decreases with a nonpolar solvent (CCl<sub>4</sub>) as shown in Table 3. Hydroquinone, however, has no effect on  $R_p$ . We could not study the effects of bases as methylamine, pyridine, and aniline on  $R_p$  due to the reaction of these bases with AsCl<sub>3</sub>.

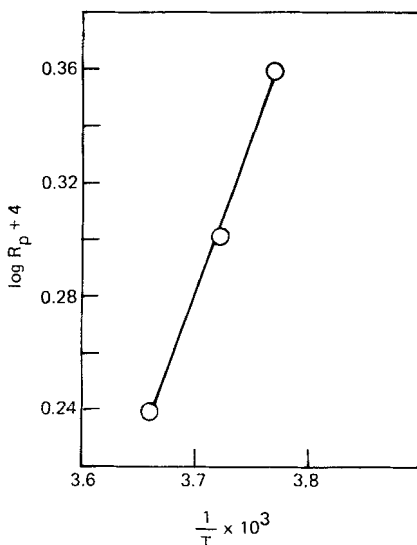


FIG. 4. Log rate of polymerization vs (polymerization temperature)<sup>-1</sup>. AsCl<sub>3</sub> concentration: 0.5 mol/L. Styrene concentration: 2.61 × 10<sup>-2</sup> mol/L. Time: 100 min.

TABLE 3. Effect of Additives on R<sub>p</sub> of Styrene Initiated by AsCl<sub>3</sub><sup>a</sup>

Concentration of CH <sub>3</sub> CN/CCl <sub>4</sub> (mol/L)	R <sub>p</sub> × 10 <sup>4</sup> mol/L·s	
	CH <sub>3</sub> CN	CCl <sub>4</sub>
0.0	1.723	1.723
1.0	1.789	1.617
2.0	1.846	1.489
3.0	1.940	1.362

<sup>a</sup>Styrene concentration = 2.61 × 10<sup>-2</sup> mol/L, AsCl<sub>3</sub> concentration = 0.5 mol/L, time = 100 min. 0°C.

On the basis of above evidence, it is concluded that  $\text{AsCl}_3$  acts as a cationic initiator, and the following kinetic scheme is proposed.

The formation of active center ( $\text{A}^*$ ) and the initiation step are



where I, C, and M represent the initiator, the cocatalyst, and the monomer, respectively.

Propagation step:



Termination step:



The rates of initiation ( $R_i$ ), propagation ( $R_p$ ), and termination ( $R_t$ ) are given by

$$R_i = K_c K_i [\text{C}] [\text{I}]^3 [\text{M}] \quad (\text{e})$$

$$R_p = K_p [\text{M}_n^*] [\text{M}] \quad (\text{f})$$

$$R_t = K_t [\text{M}_n^*] \quad (\text{g})$$

Assuming steady-state:

$$[\text{M}_n^*] = \frac{K_c K_i [\text{C}] [\text{I}]^3 [\text{M}]}{K_t} \quad (\text{h})$$

By keeping the value of  $\text{M}_n^*$  in Eq. (f), the rate of polymerization is given by

$$R_p = \frac{K_c K_i K_p [\text{C}] [\text{I}]^3 [\text{M}]^2}{K_t} \quad (\text{i})$$



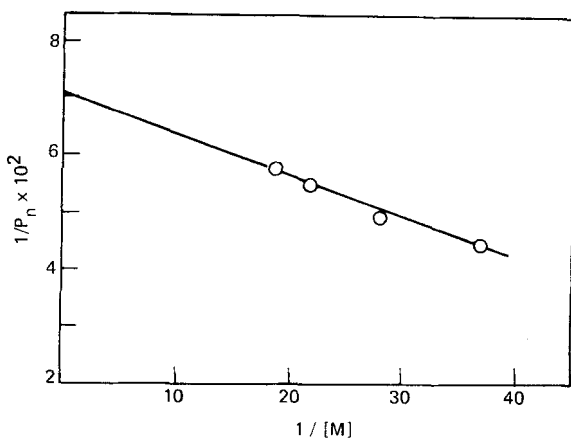


FIG. 5. Reciprocal of average degree of polymerization vs styrene concentration.  $\text{AsCl}_3$  concentration: 0.5 mol/L. Temperature:  $0^\circ\text{C}$ . Time: 100 min.

and the average degree of polymerization is given by

$$\bar{P}_n = \frac{R_p}{R_t} = \frac{K_p[M]}{K_t} \quad (j)$$

A plot of  $1/\bar{P}_n$  and  $1/[M]$  (Fig. 5) yields a straight line, the slope of which gives a value [7] of  $K_t/K_p = 6.6 \times 10^{-4}$ .

#### REFERENCES

- [1] C.P. Brown and A. R. Mathieson, *J. Chem. Soc.*, p. 3613 (1957).
- [2] D. C. Pepper and P. J. Reilly, *J. Polym. Sci.*, **58**, 639 (1962).
- [3] S. Okomura and T. Higoshimura, *Ibid.*, **21**, 289 (1956).
- [4] A. K. Srivastava and G. N. Mathur, *Polymer*, **22**, 391 (1981).
- [5] A. K. Srivastava and G. N. Mathur, *Indian J. Chem.*, **A-19(11)**, 1118 (1980).
- [6] I. Kar, B. M. Mandal, and R. S. Palit, *Makromol. Chem.*, **127**, 195 (1969).
- [7] G. Odian, *Principles of Polymerization*, McGraw-Hill, New York, 1970, p. 315.

Accepted by editor December 3, 1983

Received for publication January 6, 1984