

Photo-copolymerization Kinetics of Acrylonitrile with Styrene in the Presence of Imidazolium-p-Chlorophenacylide

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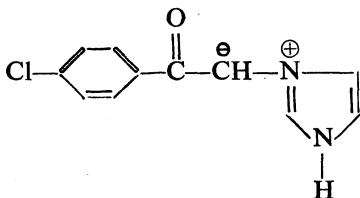
The copolymerization of acrylonitrile (AN) with styrene (Sty) initiated by *azobisisobutyronitrile* (AIBN) in the presence of imidazolium-p-chlorophenacylide (ICPY) as a photoretarder at 30°C has been investigated. The rate of polymerization (R_p) is a direct function of [AN] and [AIBN] but is an inverse function of [ICPY] and [Styrene]. The initiator exponent value is 0.63 instead of 0.5. The monomer(s) exponent value is unity. The ylide (ICPY) is not incorporated in the copolymer, which has been evidenced by NMR-spectroscopy. Kinetic data and UV studies indicate that the ICPY does not affect the rate of termination (R_t) as well as rate of propagation (R_p).

INTRODUCTION

The ylides are 1 : 2 dipolar compounds, which have received much attention and a lot of interest in synthetic organic chemistry. The applications of ylide in the field of polymer chemistry has recent origin due to pioneering work of Kondo¹⁻³, who reported the synthesis as well as polymerization of sulfonium/phosphonium ylides. We have also reported dipolar compounds as initiator/accelerator/retarder in the homo⁴⁻⁸ and copolymerization⁹⁻¹¹ of vinyl monomers. The present work is followed up, which is an extension, and reveals that it could be used as a radical retarder/inhibitor.

EXPERIMENTAL

Reagent grade monomers and solvents were purified according to the method given by Overberger¹². Imidazole (Koch-Light) and bromine (E. Merck, AR grade) were used without further purification. ICPY(I), having the following structure, was prepared by the method of Boekelheide and Fedoruk¹³.



(I)

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The polymerization was carried out in glass ampoules (quartz, 8 ml capacity). The ampoule filled with the required amount of monomers, AIBN, and ICPY in dioxan, was flushed with nitrogen, and kept under visible light of 440 nm wavelength using a high-pressure mercury vapour lamp. The copolymer content, precipitated with acidified methanol and dried to a constant weight, was then refluxed with acetonitrile in order to remove homopolymers. The weight of polymers was used to calculate the percentage conversion (PC) and the rate of polymerization (R_p) was calculated from the slope of linear plot between percentage conversion and time (Fig. 1).

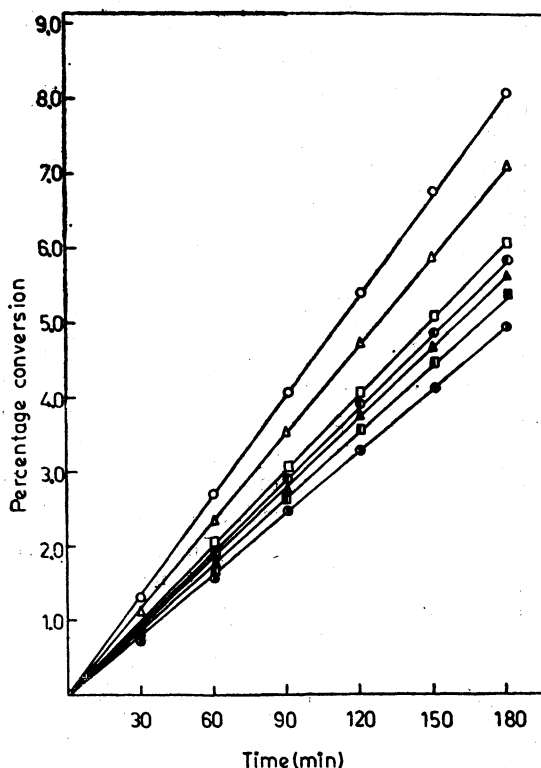


Fig. 1. Graph between polymerization time and percentage conversion. $[\text{ICPY}] \times 10^3$; ● 0.57; ■ 1.42; ▲ 2.83; ◆ 4.25; □ 5.67; △ 7.09; ○ 8.50, $[\text{AIBN}] = 3.81 \times 10^{-3} \text{ mol l}^{-1}$, Polymerization temperature = 30°C. Time = 180 min

The intrinsic viscosity (η_{int}) of the copolymers was measured in butanone at 30°C using an Ubbelohde viscometer. Results were expressed in decilitre per gram.

The NMR and UV-spectra were recorded with a Perkin Elmer Spectrometer at room temperature using CDCl_3 as solvent and tetramethyl silane (TMS) as an internal reference.

RESULTS AND DISCUSSION

The effect of [ICPY] on R_p has been studied by varying the concentration from 1.42×10^{-3} to 8.50×10^{-3} mol l⁻¹ keeping [AIBN] (0.38 mol l⁻¹) constant and results are shown in Table 1 and Fig. 2. The R_p increases with increasing [ICPY]. The order of reaction with respect to [ICPY], calculated from the slope of plot of log R_p against log [ICPY], is -0.17 .

$$R_p \propto \frac{1}{[\text{ICPY}]^{0.17}} \quad (1)$$

TABLE 1

EFFECT OF IMIDAZOLIUM-p-CHLOROPHENACYLIDE ON RADICAL COPOLYMERIZATION OF ACRYLONITRILE WITH STYRENE IN THE PRESENCE OF AIBN

[AN] = 1.77 mol l⁻¹; [Sty] = 1.63 mol l⁻¹; [AIBN] = 0.38 mol l⁻¹;
Polymerization time 180 min.

[ICPY] × 10 ³ (mol l ⁻¹)	Wt. of copolymer (gms)	Conversion %	(η_{int})	$R_p \times 10^4$ (mol l ⁻¹ sec ⁻¹)
0.00	1.26	15.75	0.65	0.17
0.57	0.85	8.13	0.37	7.41
1.42	0.57	7.13		6.58
2.83	0.49	6.13		5.73
4.25	0.47	5.88		5.45
5.67	0.45	5.63		5.17
7.09	0.43	5.38		4.93
8.50	0.40	5.00		4

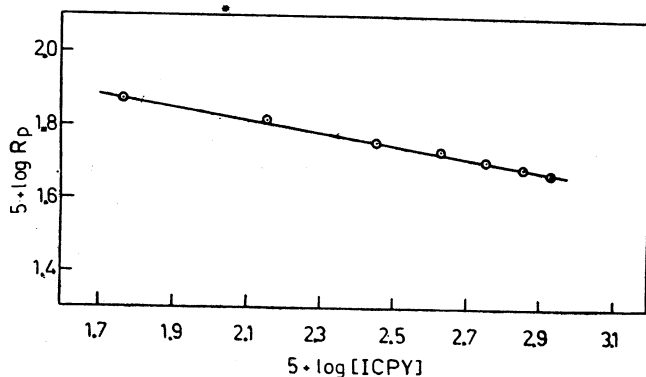


Fig. 2. Graph between log reciprocal rate of polymerization and log concentration of ICPY in the presence of AIBN, [AIBN] = 3.81×10^{-3} mol l⁻¹. [AN] = 1.77 mol l⁻¹, [Sty] = 1.63 mol l⁻¹. Polymerisation temperature = 30°C, Time = 180 min.

The effect of [AIBN] on the R_p has been studied by varying the concentration from 0.15 to 0.46 mol l⁻¹ keeping [ICPY] (0.57×10^{-3} mol l⁻¹) constant. The exponent value, calculated from the slope (Fig. 3) of linear plot of log R_p and log [AIBN], is 0.63.

$$R_p \propto [\text{AIBN}]^{0.63} \quad (2)$$

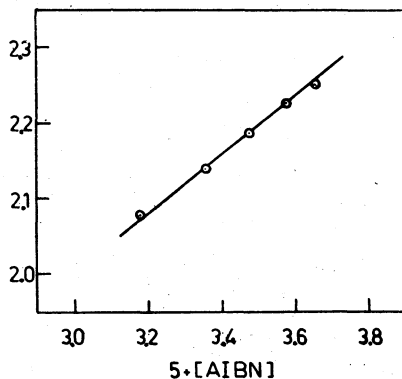


Fig. 3. Graph between log rate of polymerization and log concentration of AIBN in the presence of ICPY. [AN] = 1.77 mol l⁻¹, [Sty] = 1.63 mol l⁻¹, [ICPY] = 0.57×10^{-3} mol l⁻¹. Polymerization temperature = 30°C. Time = 180 min.

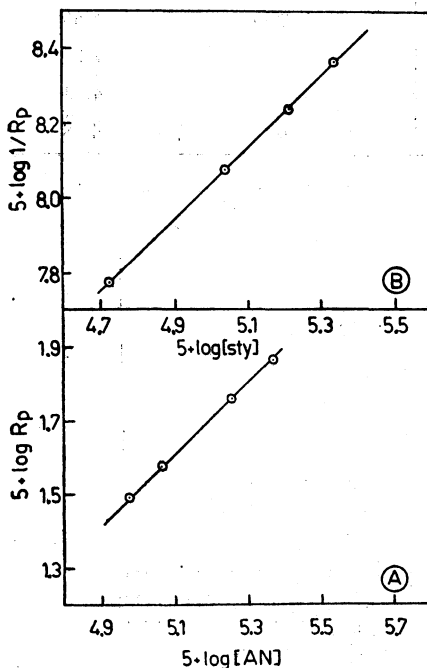


Fig. 4. (A) Graph between log rate of polymerization and log concentration of AN. [ICPY] = 2.57×10^{-3} mol l⁻¹, [AIBN] = 3.81×10^{-3} mol l⁻¹, [Sty] = 1.63 mol l⁻¹. Polymerization temperature = 30°C. Time = 180 min. (B) Graph between log reciprocal rate of polymerization and log concentration of styrene. [ICPY] = 0.54×10^{-3} mol l⁻¹, [AIBN] = 3.81×10^{-3} mol l⁻¹, [AN] = 1.77 mol l⁻¹. Polymerization temperature = 30°C. Time = 180 min.

The effect of AN on the R_p has been studied by varying $[AN]$ from 0.56 to 2.25 mol l⁻¹, whereas $[Sty]$, $[AIBN]$ and $[ICPY]$ are kept constant. It is noticed that the R_p is directly proportional to $[AN]$. A plot between $\log R_p$ and $\log [AN]$ gives a straight line (Fig. 4A), the slope of which gives the following relationship:

$$R_p \propto [AN]^{1.0} \quad (3)$$

The effect of $[Sty]$ on R_p is studied by varying its concentration from 0.54 to 2.17 mol l⁻¹, whereas the $[AN]$, $[AIBN]$, and $[ICPY]$ are kept constant. It is observed that Sty has an inverse effect on R_p . A plot between $\log 1/R_p$ and $\log [Sty]$ gives straight line (Fig. 4B), the slope of which gives the following relationship:

$$1/R_p \propto [Sty]^{1.0} \quad (4)$$

The NMR spectrum of the copolymer (Fig. 5) showed phenyl protons at 2.8–3.6 τ and the aliphatic protons at 8.8 τ . The ratio of the peak areas

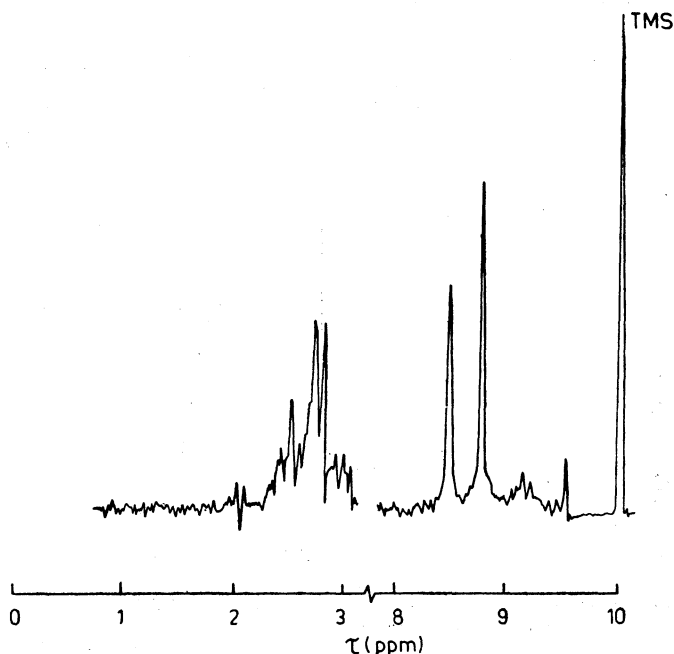


Fig. 5. N.m.r. spectrum of AN-Sty copolymer. $[ICPY] = 0.57 \times 10^{-3}$ mol l⁻¹. $[AIBN] = 3.81 \times 10^{-3}$ mol l⁻¹. $[AN] = 1.77$ mol l⁻¹. $[Sty] = 1.63$ mol l⁻¹. Polymerization temperature = 30°C. Time = 180 min.

for the phenyl and aliphatic protons is 5 : 6, which confirms the alternative nature of the copolymer. The absence of peak at 1.9 τ (multiplet, 8H, aromatic) suggests that ICPY is not incorporated in the copolymer.

The retarding effect of ICPY may be due to any one of the following reasons:

- (i) Decrease of the rate of initiation (R_i),
- (ii) Decrease of the rate of propagation (R_p'),
- (iii) Increase of the rate of termination (R_t).

The effect of ICPY on R_i has been studied by plotting a graph between $\log(R_p/R_p^0)$ vs. $\log(\eta_{int}/\eta_{int}^0)$ (whereas R_p and η_{int} are the rate of polymerization and intrinsic viscosity of the polymer, respectively, in the presence of ICPY; R_p^0 and η_{int}^0 , the corresponding values in the absence of ICPY). The linearity of graph confirms that R_i is unaffected. Intrinsic viscosity is independent, which further suggests that R_i is unaffected.

The effect of ICPY on the R_p' has been examined by studying the possibility of formation of complex between ICPY and monomer using UV spectra at 320 nm. A comparison of UV spectra (Fig. 6A and B), suggests that the tendency of complex formation is nil; hence it may be assumed that R_p' is unaffected.

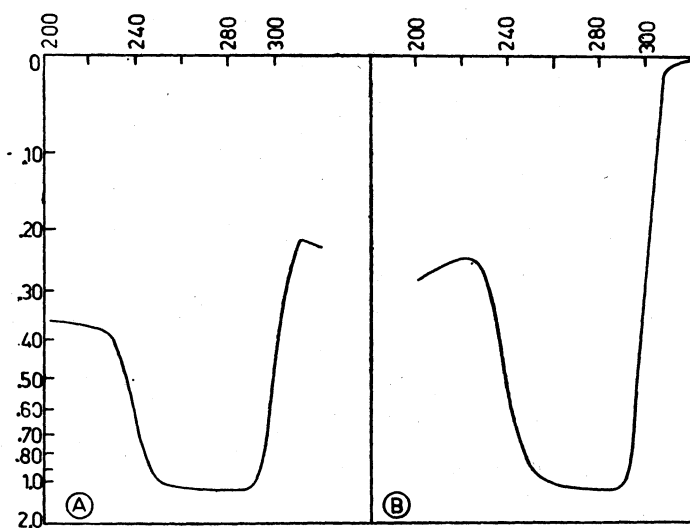


Fig. 6. UV spectrum of AN-Sty copolymer. $[ICPY] = 10.57 \times 10^{-3}$ mol l $^{-1}$. $[AIBN] = 3.81 \times 10^{-3}$ mol l $^{-1}$. $[AN] = 1.77$ mol l $^{-1}$. $[Sty] = 1.63$ mol l $^{-1}$. Polymerization temperature = 30°C. Time = 180 min.

Hence, it may be concluded that the ylide decreases the rate of initiation (R_i) whence retardation is noted.

ACKNOWLEDGEMENT

Authors are thankful to Prof. A. K. Vasishtha, Director, H.B.T.I., Kanpur for providing necessary facilities.

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[Received: 15 March 1988; Accepted: 10 October 1988]