

Kinetic studies on the polymerization of acrylonitrile initiated by *p*-nitrophenacyl dimethyl sulfonium ylide

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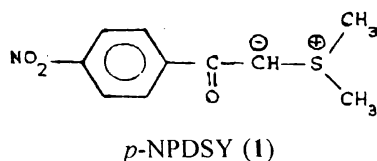
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Homopolymerization of acrylonitrile, initiated by *p*-nitrophenacyldimethyl sulfonium ylide has been studied at 40° under inert atmosphere using dilatometric technique. The radical polymerization of acrylonitrile follows non-ideal kinetics, since the monomer and initiator exponent values are found to be 1.1 and 0.39, respectively. The polymerization is retarded by hydroquinone. The overall activation energy is calculated to be 44 kJ mol⁻¹. Kinetic data indicate that the polymerization involves free radical mechanism.

Although polymerization of vinyl monomers through nitrogen^{1,2}, phosphonium³ and arsonium ylide⁴ are well known, only a few reactions of polymerization of vinyl monomers using sulfonium ylide have been reported. This is despite the fact that Doering *et al.*^{5,6} who made a comparative study on ylide stability as a function of the heteroatom, found that the phosphorus and sulfur ylides are the most stable ones. In view of this stability we have used sulfonium ylide as an initiator to polymerize acrylonitrile. In this paper we report the generation of *p*-nitrophenacyl dimethyl sulfonium ylide (*p*-NPDSY) and its use as initiator for polymerization of acrylonitrile.



Results and Discussion

The kinetic results for the polymerization of acrylonitrile (AN) initiated by *p*-nitrophenacyl dimethyl sulfonium ylide (*p*-NPDSY), are summarised in Tables 1–3 and (Figs. 1–5). The polymerization runs were associated with very short induction period of 1–2 min.

Effect of [ylide] : The effect of [ylide] on the rate of polymerization was investigated at 40 ± 0.1° by varying the concentration of ylide from 3.0 × 10⁻³ to 9.8 × 10⁻³ mol dm⁻³ (Table 1) shows that rate of polymerization (*R_p*) increases gradually with the increasing [ylide]. The initiator exponent value, calculated from the slope of log *R_p* vs log [ylide], is 0.39 (Fig. 1), which is appreciably less than 0.5 as expected for ideal radical polymerization. This non-ideality may be due to primary radical termination and

Table 1. Effect of *p*-NPDSY on polymerization of AN
Temp. = 40°, time = 90 min, [AN] = 4.8 mol⁻¹ dm⁻³

Sample no.	10 ³ [Ylide] mol dm ⁻³	% Conversion	10 ⁴ <i>R_p</i> mol dm ⁻³ s ⁻¹	[η]	<i>M_v</i>
1.	3.0	5.2	2.20	0.19	8806
2.	4.8	6.6	2.79	0.16	7003
3.	5.8	6.8	2.90	0.11	4949
4.	6.8	7.4	3.16	0.09	3251
5.	8.8	8.5	3.60	0.07	2325
6.	9.8	9.5	4.0	0.06	1893

degradative chain transfer process. Primary radical termination was analysed using eqn. (3) given by Deb and Meyerhoff⁷,

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_i k_p} \frac{R_p}{[M]^2}$$

where *f_k* is the total efficiency of initiator, *k_d* the dissociation constant of initiator, *k_t* the termination rate constant, *k_{prt}* the primary radical termination constant, *k_i* the initiation rate constant and *k_p* the propagation rate constant; I and M represent the initiator and the monomer, respectively. The plot of log *R_p*² / [I] [M]² vs *R_p* / [M]² (Fig. 2) gives a negative slope which is indicative of primary radical termination.

On the other hand, detection of degradative chain transfer was done by analysing the data by the equation given by Deb⁸ and modified by Ghosh and Mitra⁹,

$$\log \frac{R_p^2}{[I][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2 k_{tr} C_i [I]}{k_i k_j k_p [M]}$$

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Table 2. Effect of AN on the R_p using p -NPDSY as an initiator
Temp. = 40°, Time = 90 min. $[p\text{-NPDSY}] = 9.8 \times 10^{-3} \text{ mol dm}^{-3}$

Sample no.	[AN] mol dm ⁻³	$10^4 R_p$ mol dm ⁻³ s ⁻¹
1.	1.5	0.84
2.	3.3	2.11
3.	4.0	3.40
4.	4.8	4.0

Table 3. Effect of hydroquinone on the polymerization of AN initiated by p -NPDSY

$[Y_{\text{lide}}] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[AN] = 4.8 \text{ mol dm}^{-3}$, time = 40 min, temp. = 40°

Additive	Additive conc. mol dm ⁻³	% Conversion	$10^4 R_p$ mol dm ⁻³ s ⁻¹
No additive	0.0	5.2	2.2
Hydroquinone	3×10^{-2}	3.02	1.33
	4×10^{-2}	1.6	0.67

where C_i is the initiator transfer constant and k_{rti} the rate of degradative chain transfer to initiator. The plot of $\log R_p^2 / [I] [M]^2$ vs $[I] / [M]$ was linear (Fig. 3) with the negative slope suggesting measurable degradative transfer to acrylonitrile monomer.

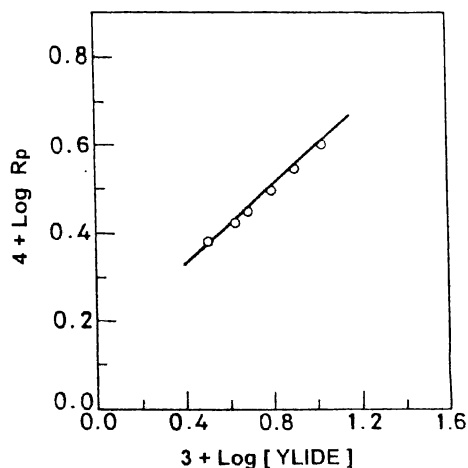


Fig. 1. Variation of $\log R_p$ as a function to ylide concentration in the polymerization of AN; $[AN] = 4.8 \text{ mol dm}^{-3}$, time = 90 min, temp. = 40°.

Effect of [monomer]: The effect of acrylonitrile was studied by varying the acrylonitrile from 1.5 to 4.8 mol dm⁻³. The rate of polymerization (R_p) gradually increased as the concentration of the monomer was increased at 40° (Table 2). The order of reaction with respect to acrylonitrile is unity (Fig. 4).

Effect of temperature: The polymerization was carried

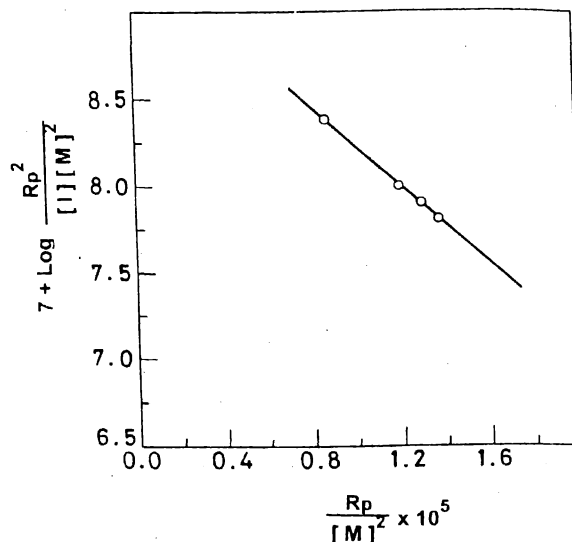


Fig. 2. Plot of $R_p^2 [I] [M]^2$ vs $R_p / [M]^2$ for the analysis of primary radical termination for polymerization of acrylonitrile in presence of p -NPDSY; $[AN] = 4.8 \text{ mol dm}^{-3}$, temp. = 40°.

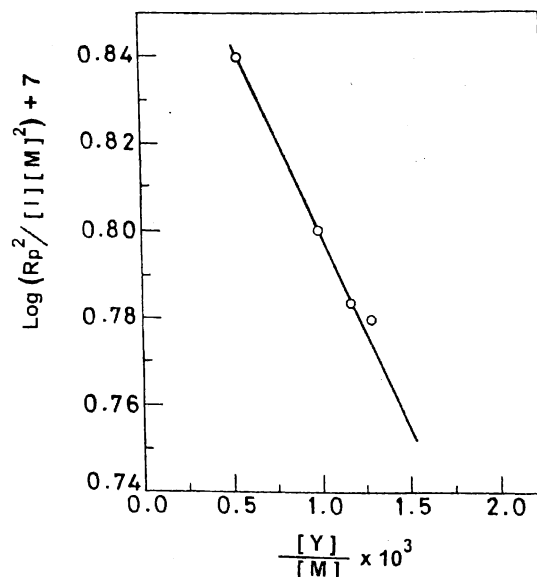


Fig. 3. Plot of $R_p^2 / [I] [M]^2$ vs $[I] / [M]$ for the analysis of degradative chain transfer with re-initiation for the polymerization of acrylonitrile initiated by p -NPDSY; AN = 4.8 mol dm⁻³, time = 90 min, temp. = 40°.

out at 30, 40, 50 and 60°. R_p is a direct function of temperature. The activation energy calculated from Arrhenius plot (Fig. 5) corresponds to 44 kJ mol⁻¹.

Effect of additive: Table 3 shows that the rate of polymerization is inhibited by hydroquinone, a radical quencher, thus confirming radical mode of polymerization.

Mechanism of initiation: From the above experimental data it is concluded that polymerization, initiated by p -

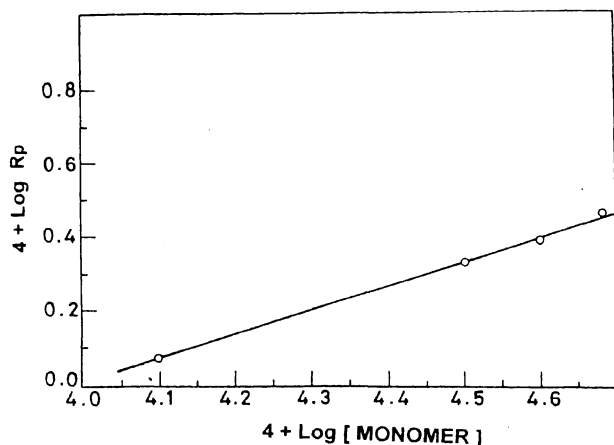
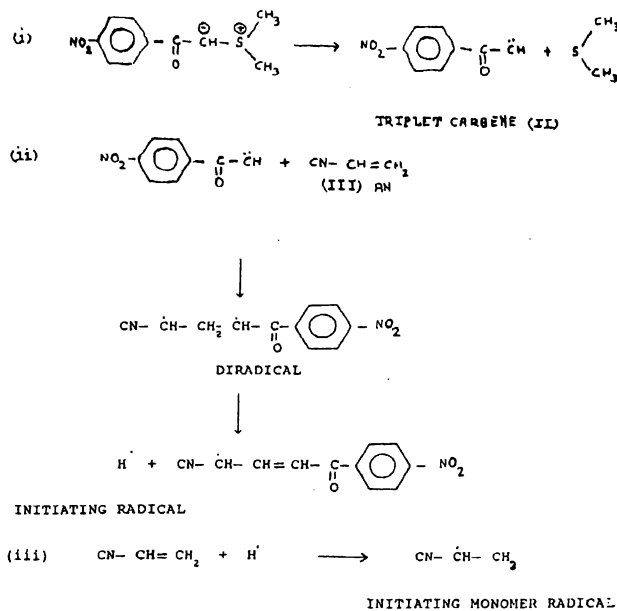


Fig. 4. Dependence of rate of polymerization of AN on concentration of AN; $[p\text{-NPDSY}] = 9.8 \times 10^{-3} \text{ mol dm}^{-3}$, time = 90 min, temp. = 40° .

NPDSY, follows nonideal kinetics. *p*-NPDSY possibly decomposes to a triplet carbene (II) which acts as a source of radical¹. The triplet carbene reacts with monomer to form a diradical which further decomposes to H^\cdot radical and a less reactive radical towards monomer. The reactivity is also decreased due to its resonance structure. Therefore, the polymerization takes place only in one direction only by H^\cdot radical¹⁰ (Scheme 1).



Scheme 1

Experimental

Acrylonitrile (AN) was purified¹¹. The ylide (1) was prepared according to the reported method¹² *in situ* by the

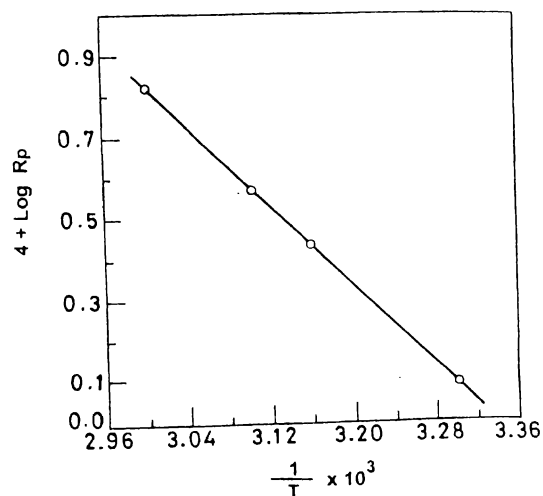


Fig. 5. Variation of rate of polymerization as a function of temperature; $[\text{ylide}] = 4.8 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{AN}] = 4.8 \text{ mol dm}^{-3}$, time = 90 min.

reaction of 10% NaOH with *p*-nitrophenacyl dimethyl sulfonium bromide, m.p. 110° (lit. $110\text{--}111^\circ$).

The polymerization reaction was carried out in a modified dilatometric apparatus (lower bulb capacity 5 ml, capillary diameter 0.2 mm, length of dilatometer 10 cm) for 90 min at 40° using chloroform as a solvent. The required concentration of monomer, ylide and solvent were injected into the dilatometer under inert atmosphere of nitrogen. The progress of the reaction was monitored as a function of fall of meniscus movement with the help of a cathetometer. Poly(AN) was precipitated with acidified methanol and dried to constant weight. The rate of polymerization (R_p) was calculated from the slope of conversion time plots¹³.

The intrinsic viscosity $[\eta]$ of poly(AN) was determined in dimethyl formamide at $30 \pm 0.1^\circ$ using an Ostwald viscometer. Viscosity average molecular weight (M_v) of poly(AN) was calculated from the equation¹⁴,

$$[\eta] = K[M_v]^\alpha$$

K and α having values of 20.9×10^{-5} and 0.746, respectively.

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