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Kinetics of Polymerization of Acrylamide initiated by P-Nitrophenyl Carbethoxy Azomethylene Triphenyl Phospherane

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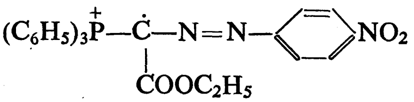
Initiation of the polymerization of acrylamide (AM) by p-Nitrophenyl carbethoxy azomethylene triphenyl phospherane (p-NPCATP) in tetrahydrofuran-acetic-acid solution (1 : 9) has been studied kinetically at 65°C using dilatometric technique. Initiator and the monomer exponent values were 0.6 and 0.9 respectively. Energy of activation was 38.32 KJ mol^{-1} and the value at k_p^2/k_t was found to be 1.9×10^{-1} L mol^{-1} S^{-1}. Polymerization was inhibited in the presence of hydroquinone. The results are explained in terms of radical mode of polymerization with bimolecular mode of termination.

INTRODUCTION

Triphenyl phosphonium ethoxy carbonyl methylide[1] has been used as an initiator for the photopolymerizations of methyl methacrylate and styrene since 1983. There have been investigations of thermal polymerizations of vinyl monomers using picolinium ylides as initiators[2-5]. The present paper describes studies of the thermal polymerization of acrylamide using p-nitrophenyl carbethoxy azomethylenetriphenyl phosphorane(I) as initiater.



$$(C_6H_5)_3\overset{+}{P}-\underset{\displaystyle COOC_2H_5}{\underset{|}{\dot{C}}}-N=N-C_6H_4-NO_2$$

(I)

EXPERIMENTAL

p-NPCATP was synthesised by reacting p-nitrophenyl hydrazidoyl bromide and triphenyl phosphine in the presence of triethyl amine in dry benzene[6]. Acrylamide (SISCO) was recrystallised twice from methanol and then dried in vacuum over silica gel, m. pt. 84.5° C. Standard solutions of initiator and monomer were prepared using tetrahydrofuran in 5N acetic acid (1 : 9 by volume). Appropriate quantities were then mixed and syringed in to assembled dilatometer clamped vertically in a thermostatic bath controlled to ± 0.1°C.

Progress of the reaction was monitored with the help of cathetometer as volume contraction in cms. (meniscus movement) and was converted into percentage (%) conversion by means of master graph. The master graph was prepared when known amounts of dilatometric contents at different volume contractions were precipitated with alcohol and the polymer samples thus obtained were dried to a constant weight. The % conversion was calculated by weight of polymers using equation (1):

$$\text{Percentage (\%) Conversion} = \frac{\text{Wt. of polymer}}{\text{Wt. of monomer}} \times 100 \qquad (1)$$

Thus % conversions at volume contractions 0.5, 1.0, 1.2, 1.7, 2.2, 2.5 and 2.7 cm were obtained and graph was plotted. Using this master graph any volume contraction data can be converted into % conversion.

Rate of Polymerization

Rates of polymerization were evaluated from the slope of time-conversion plots.

Intrinsic Viscosities and Degree of Polymerization

Intrinsic viscosities $[\eta]$ of the fractionated polyacrylamide (PAM) samples were determined in water at 29°C using an Upbelohde viscometer and the molecular weights were calculated from equation[7] (2):

$$[\eta] = 6.31 \times 10^{-5}\, \overline{M}_v^{0.80} \qquad (2)$$

Degree of Polymerization ($\overline{P}_n$) was calculated using equation[8] (3):

$$\log \overline{P}_n = 3.3987 + 1.25 \log [\eta] \qquad (3)$$

Structure of polyacrylamide was confirmed using elemental analysis, IR and NMR spectra. IR spectrum of the polymer shows the presence of NH and CO bond stretching at 3300 cm^{-1} and 1630 cm^{-1} respectively whereas vinyl group stretching at 1645 cm^{-1} was absent. Methylene protons appeared in NMR spectrum as a broad doublet at 2.25 δ and methine proton at 4.0 δ as a complex triplet. Amide nitrogen protons appeared at 6.5 δ.

RESULTS AND DISCUSSION

Rates of polymerization were evaluated using increasing concentrations from 1.8×10^{-4} to 19.0×10^{-4} mol L^{-1} of p-NPCATP (Table 1) and the plot of log R_p against log [p-NPCATP] is linear with a slope of 0.6. The effect of change in monomer concentrations from 0.90 to 3.63 mol L^{-1} at a fixed initiator concentration (9.9×10^{-4} mol L^{-1}) also studied. The slope of the straight line is equal to 0.9 indicating that the rate is proportional to $[AM]^{0.9}$. Thus the overall rate of polymerization of AM

TABLE 1

EFFECT OF p-NPCATP ON POLYMERIZATION OF AM*

[P-NPCATP] $\times 10^4$ mol L^{-1}	% Conversion						$R_p \times 10^2$ mol L^{-1} S^{-1}	$[\eta]$ al/g	$\overline{P}_n$	$\overline{M}_v$
	Time (min)									
	5	10	15	20	25	30				
1.8	4.0	11.0	18.0	17.0	36.0	44.0	2.6	0.36	698.2	49600
2.7	5.0	13.0	23.0	32.0	41.0	48.0	3.2	0.35	674.1	48000
5.8	7.0	17.0	27.0	37.0	44.0	50.0	3.3	0.15	233.7	16600
8.9	9.0	21.0	28.5	37.5	46.0	55.0	3.5	0.14	214.4	15000
19.3	11.0	24.0	35.0	43.0	50.0	62.0	3.6	0.14	195.4	14000

* AM = 1.81 mol L^{-1}; Temperature-65°C; Solvent: THF in Ac. Acid (1 : 9 by vol).

in the presence of p-NPCATP is given by the equation (4):

$$R_p = k\,[\mathrm{AM}]^{0.9}\,[\text{p-NPCATP}]^{0.6} \tag{4}$$

Average degree of polymerization decreases on increasing the concentration of the ylide. Plot of reciprocal degree of polymerization ($1/\overline{P}_n$) against $[\text{p-NPCATP}]^{1/2}$ is linear and passing through the origin suggesting bimolecular mode of termination in the present system. The value of k_p^2/k_t, determined from the slope of linear plot of $1/\overline{P}_n$ vs R_p, is 1.9×10^{-1} L mol^1 S^{-1}.

R_p is also a direct function of temperature. The value of soverall activation energy in the presence of 9.9×10^{-4} mol L^{-1} of p-NPCATP has been calculated from the Arrhenius plot is 38.32 kJ mol^{-1}.

Addition of hydroquinone to the present system of polymerization had profound inhibitory effect on the rate of polymerization suggesting that initiation step involved radical species formed during thermal decomposition of the ylide[9].

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