

## Non-Ideal Kinetics for Radical Polymerisation of N-Vinylpyrrolidone

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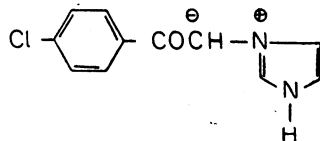
The radical polymerisation of N-vinylpyrrolidone (N-VP), initiated by  $\alpha$ - $\alpha'$  azobisisobutyronitrile (AIBN) in the presence of imidazolium-p-chloro-phenacylide (ICPY) in dimethylformamide at 60°C follows non-ideal kinetics. The kinetic equation for the present system is  $R_p \propto [AIBN]^{1.50} [ICPY]^{1.50} (N-VP)^{2.0}$ . The degradative chain transfer and primary radical termination reasonably explains the kinetic non-ideality.

### INTRODUCTION

Although the chemical literature<sup>1-4</sup> on polymer-ylide chemistry is growing rapidly we have thought to investigate further the application of ICPY for radical polymerisation of N-vinylpyrrolidone for which reliable data are still scarce. This communication focuses the application of ICPY as degradative chain transfer agent for radical polymerisation of N-vinylpyrrolidone.

### EXPERIMENTAL

N-Vinylpyrrolidone (Fluka) was used as such.  $\alpha$ - $\alpha'$  Azobisisobutyronitrile was recrystallized twice from ethanol (m.pt. 102°C). Imidazolium-p-chlorophenacylide was prepared by the method of Boekelheide and Fedoruk<sup>5</sup> and has the following structure (1)



(1)

imidazolium -p- chlorophenacylide

The homopolymerisation runs for different [ICPY] were made for 50 minutes at 60°C under N<sub>2</sub>, AIBN being used as an initiator and DMF as solvent in a modified dilatometric apparatus.<sup>6</sup> The progress of reaction was monitored as meniscus movement (per unit volume per unit time) with the help of cathetometer. The polymer, precipitated with carbon tetrachloride (CCl<sub>4</sub>), was dried to constant weight.

The rate of polymerisation ( $R_p$ ) was calculated from slopes of linear zone of conversion-time plots (Figure 1).

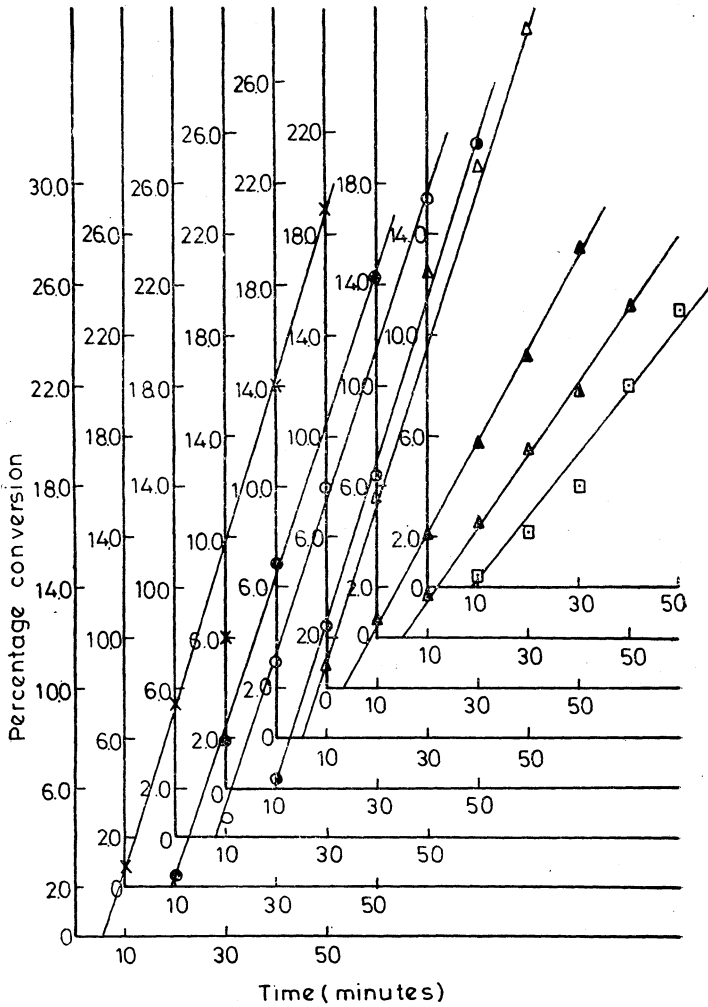


Fig. 1. Time-conversion plot for the polymerisation of N-VP

- $\times$  = 0.00 mol/l  
 $\bullet$  =  $0.16 \times 10^{-3}$  mol l $^{-1}$   
 $\odot$  =  $0.82 \times 10^{-3}$  mol l $^{-1}$   
 $\ominus$  =  $1.64 \times 10^{-3}$  mol l $^{-1}$   
 $\triangle$  =  $2.46 \times 10^{-3}$  mol l $^{-1}$   
 $\blacktriangle$  =  $3.29 \times 10^{-3}$  mol l $^{-1}$   
 $\blacktriangle$  =  $4.11 \times 10^{-3}$  mol l $^{-1}$   
 $\square$  =  $4.93 \times 10^{-1}$  mol l $^{-1}$
- [N-VP] = 2.72 mol l $^{-1}$   
 [AIBN] =  $2.77 \times 10^{-2}$  mol l $^{-1}$   
 Time = 50 min.  
 Temp. = 60°C

The intrinsic viscosities  $[\eta]$  of the polymers, in distilled water, were measured at 30°C using an Ubbelohde viscometer. Results were expressed in dl/g. The  $[\eta]$  of the polymers were used to calculate the average molecular weight using the following equation

$$[\eta] = K \bar{M}_v^\alpha$$

The value<sup>7</sup> of  $K$  and  $\alpha$  were  $14 \times 10^{-5}$  and 0.70 respectively.

## RESULTS AND DISCUSSION

Table 1 summarizes the polymerisation conditions and results. Figure 1 shows that polymerisation is preceded by a short induction period (6–8 min.). A study of Table 1 reveals that  $R_p$  increases with increasing [ICPY] upto  $2.46 \times 10^{-3}$  mol  $l^{-1}$  and then decreases with increasing [ICPY] upto  $4.93 \times 10^{-3}$  mol  $l^{-1}$ . The decrease in rate is due to lowering of initiator efficiency as a consequence of primary radical leading to mutual annihilation to a certain extent as reported for other systems<sup>8</sup>.

The order of reaction in ICPY (upto  $2.46 \times 10^{-3}$  mol  $l^{-1}$ ) calculated from the linear part of slope of  $\log R_p$  vs.  $\log$  [ICPY], is 1.5. The  $\bar{M}_n$  of polymers decreases with increasing [ICPY]. The  $k_p^2/k_t$  value, determined from the slope of the linear plot of  $1/\bar{M}_n$  vs.  $R_p/[M]^2$ , is  $0.50 \times 10^{-2}$   $l \text{ mol}^{-1} \text{ s}^{-1}$ .

TABLE 1  
EFFECT OF [ICPY] IN DMF ON THE POLYMERISATION OF N-VP AT 60°C

[ICPY] $\times 10^3$ (mol $l^{-1}$ )	Percentage conversion	$R_p \times 10^4$ (mol $l^{-1} \text{ s}^{-1}$ )	$\bar{M}_n$
0.00	28.95	6.04	17,320
0.16	24.46	5.44	10,230
0.49	24.90	5.52	4,420
0.82	25.43	5.64	2,130
1.64	25.60	5.74	1,027
2.46	27.19	5.84	946
3.29	17.40	3.32	—
4.11	13.02	2.72	—
4.93	11.00	2.26	—

[N-VP] = 2.72 mol  $l^{-1}$  [AIBN] =  $2.77 \times 10^{-2}$  mol  $l^{-1}$   
Time = 50 min.

Table 2, illustrates the effect of [AIBN] on the  $R_p$  in the presence of ICPY. The initiator exponent, calculated from the slope of the linear plot of  $\log R_p$  vs.  $\log$  [AIBN], is 1.50. This value is higher than the square root relationship for radical polymerisation.

TABLE 2  
EFFECT OF [AIBN] IN DMF ON THE  
POLYMERISATION OF N-VP AT 60°C

[AIBN] × 10 <sup>2</sup> (mol l <sup>-1</sup> )	Percentage conversion	R <sub>p</sub> × 10 <sup>4</sup> (mol l <sup>-1</sup> s <sup>-1</sup> )
1.10	4.81	1.00
1.66	12.22	2.26
2.21	18.00	4.00
2.27	25.43	5.64

[N-VP] = 2.72 mol l<sup>-1</sup> [ICPY] = 0.82 × 10<sup>-3</sup> mol l<sup>-1</sup>  
Time = 50 min.

The data showing influence of [N-VP] on R<sub>p</sub> are listed in Table 3. The R<sub>p</sub> is direct function of [monomer] and the monomer exponent, calculated from the slope of the linear plot of log R<sub>p</sub> vs. log [N-VP] is 2.0.

TABLE 3  
EFFECT OF [N-VP] IN DMF ON THE  
POLYMERISATION OF N-VP AT 60°C

[N-VP] (mol l <sup>-1</sup> )	Percentage conversion	R <sub>p</sub> × 10 <sup>-4</sup> (mol l <sup>-1</sup> s <sup>-1</sup> )
0.68	4.54	0.25
1.36	10.34	1.13
2.04	17.15	2.72
2.72	25.43	5.64

[ICPY] = 0.82 × 10<sup>-3</sup> mol l<sup>-1</sup>. [AIBN] = 2.77 × 10<sup>-2</sup> mol l<sup>-1</sup>  
Time = 50 min.

The higher initiator and monomer exponent values and presence of an intercept on the plot of 1/M<sub>v</sub> vs. [I]<sup>0.5</sup> suggests that the system follows non-ideal kinetics. The kinetic non-ideality can be explained by analysing the role of ICPY as primary radical terminator and degradative chain transfer agent for the present system. To analyse the effect of primary radical termination, a suitably modified expression, given by Deb and Meyerhoff<sup>9</sup> in the following form, is used:

$$\log \frac{R_p^2}{[Y][M]^2} = \log \frac{2f_k k_a k_p^2}{k_t} - 0.8684 \frac{k_{prt}}{k_y k_p} \cdot \frac{R_p}{[M]^2}$$

Here Y and M represent ylide and monomer, respectively. A plot of the left hand side of the above equation vs. R<sub>p</sub>/[M]<sup>2</sup> (Figure 2(a)) gave a

negative slope, indicating significantly primary radical termination due to ylide for the present system.

The following equation, derived by Deb<sup>10</sup> and further simplified by Ghosh and Mitra<sup>11</sup>, was used to examine the role of ylide as degradative chain transfer agent

$$\ln \frac{R_p^2}{[Y][M]^2} = \ln \frac{2f_k k_d k_p^2}{k_t} - 2 \frac{k_p^2}{k_t} \cdot \frac{k_{rt} Y}{k_y Y} \cdot C_1 \left[ \frac{Y}{M} \right]$$

or

$$\log \frac{R_p^2}{[Y][M]^2} = \log \frac{2f_k k_d k_p^2}{k_t} - 0.434 \frac{k_p^2}{k_t} \cdot \frac{k_{rt} Y}{k_y Y} \cdot C_1 \left[ \frac{Y}{M} \right]$$

when  $C_1$  is the ylide transfer constant. The plot of the left hand side of the above equation vs.  $[Y]/[M]$  (Figure 2(b)) also gave a negative slope suggesting measurable degradative chain transfer reaction due to ylide. The mechanism of present system is analogous to our early reports<sup>2</sup> for radical polymerisation of methylacrylate using ICPY as a degradative chain transfer agent.

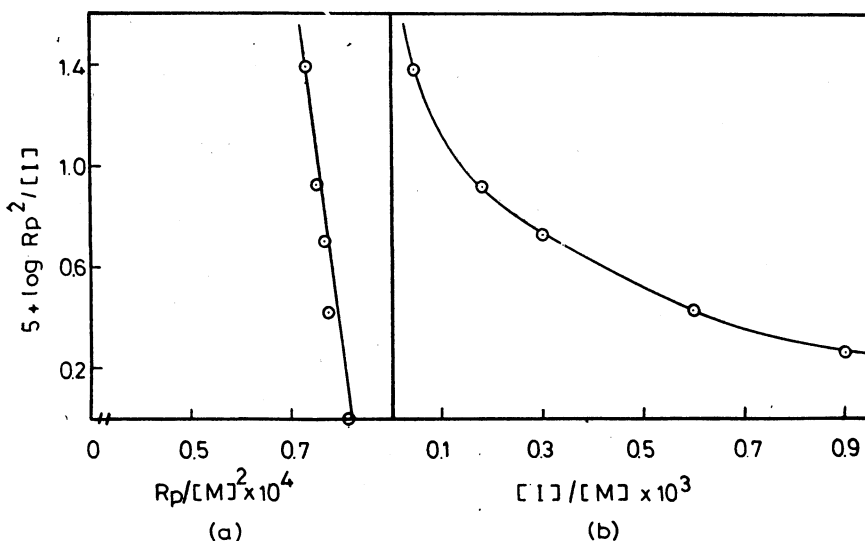


Fig. 2. (a) Plot between  $\log R_p^2/[Y][M]^2$  vs.  $R_p/[M]^2$ .  
 (b) Plot between  $\log R_p^2/[Y][M]^2$  vs.  $[Y]/[M]$ ; for the polymerisation of N-VP.  
 $[N-VP] = 2.72 \text{ mol l}^{-1}$ , Time = 50 min., Temp. = 60°C

Thus, it may be concluded that radical polymerisation of N-VP, in presence of ICPY, follows non-ideal kinetics due to degradative chain transfer as well as primary radical termination.

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