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Polymerization of Styrene in the Presence of a 1,3-Dipolar Compound

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Polymerization of Styrene in the Presence of a 1,3-Dipolar Compound

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ABSTRACT

Free-radical polymerization of styrene initiated by α,α'-azobisisobutyronitrile (AIBN) has been studied in the presence of a 1,3-dipolar compound (methylnitrile ylide, MNY) by a dilatometric technique. The MNY retards the reaction by decreasing the rate of propagation and increasing the energy of activation. Polar solvents have very little influence on the rate of polymerization, but nonpolar solvents favor retardation. MNY has no influence on the average degree of polymerization, and the system attains a steady state.

INTRODUCTION

The nitrile ylides are highly reactive species and, therefore, not easily isolated. However, Bittner and his collaborators [1] synthesized the following nitrile ylide which shows some stability, remaining unchanged for several days at normal temperature.

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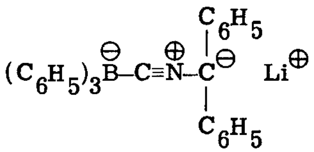
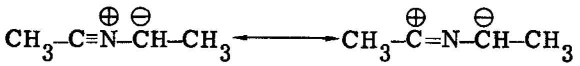


$$(C_6H_5)_3\overset{\ominus}{B}-C\equiv\overset{\oplus}{N}-\underset{C_6H_5}{\overset{C_6H_5}{C}}{}^{\ominus}\ \ Li^{\oplus}$$

There have been hardly any applications of 1,3-dipoles in the field of polymerization. Therefore, we have undertaken the present study of polymerization reactions in the presence of a 1,3-dipolar compound, methylnitrile ylide (MNY), which has following structure:



$$CH_3-C\equiv\overset{\oplus}{N}-\overset{\ominus}{C}H-CH_3 \longleftrightarrow CH_3-\overset{\oplus}{C}=N-\overset{\ominus}{C}H-CH_3$$

EXPERIMENTAL

MNY was synthesized by the reaction of triethyl amine with imidoyl chloride [2]. The polymerization was carried out in a modified dilatometric apparatus [3, 4] (of 3.00 mL capacity and with a capillary 2.00 mm in diameter). The dilatometer was filled with monomer containing the required amount of α,α'-azobisisobutyronitrile (AIBN) and a solution of MNY in acetonitrile. The progress of the reaction was monitored by the volume contraction with the help of a cathetometer and was converted into percentage conversion by use of a master graph [5].

The rate of polymerization (R_p) was calculated by the following equation [5]:

$$R_p = \frac{1.4507 \times 10^{-3} \times C}{t} \tag{1}$$

where R_p = rate of polymerization, mol/(L·s)

C = percentage conversion of styrene

t = polymerization time, min

1.4507×10^{-3} = (density of styrene, 0.9090) × (1000 mL/L)/ [(MW of styrene, 104.41) × (60 s/min) × (100%)]

The intrinsic viscosity $[\eta]$ of the polymers, determined in benzene at 30°C in an Ubbelohde viscometer, was converted to the average degree of polymerization ($\overline{P}_n$) by the following equation [6]:

$$\overline{P}_n = 1700[\eta]^{1.4} \tag{2}$$

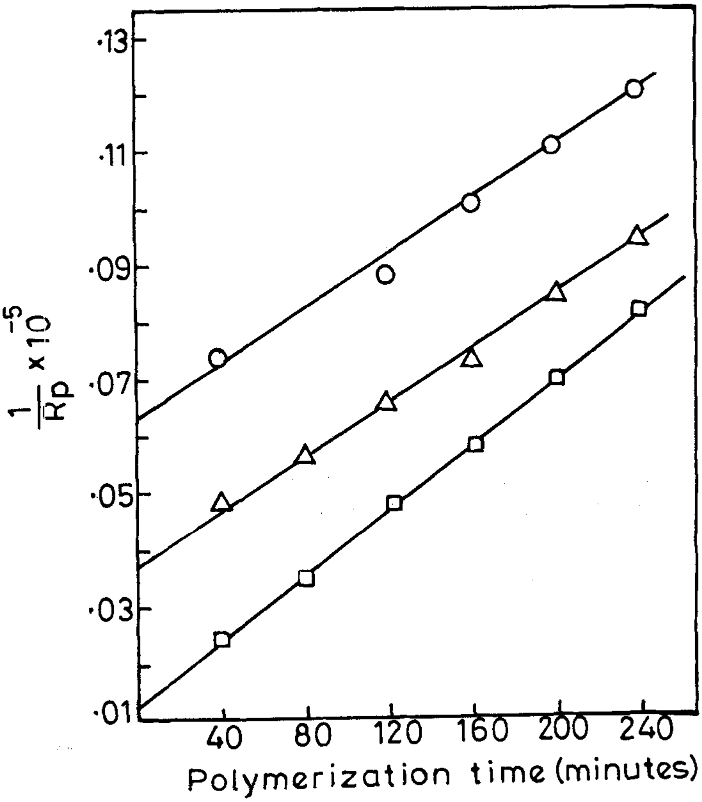


FIG. 1. Relation between inverse polymerization rate and polymerization time. [MNY]: 2.90 × 10^{-7} mol/L (○), 1.45 × 10^{-7} mol/L (△), 0.29 × 10^{-7} mol/L (□). [STY] = 1.75 mol/L, [AIBN] = 6.10 × 10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization time = 240 min, polymerization temperature = 65°C.

The rate of initiation (R_i) was calculated by plotting a graph of the inverse of the rate of polymerization versus the time according to the following formula [7] (Fig. 1):

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{R_i}{[\text{MNY}]} \tag{3}$$

RESULTS AND DISCUSSION

The effect of MNY on the kinetics of free-radical polymerization of styrene initiated by AIBN was studied by varying the concentration of MNY from 0.29×10^{-7} to 2.90×10^{-7} mol/L and keeping the concentrations of styrene (STY) (1.75 mol/L) and AIBN (6.10×10^{-2} mol/L) constant. The results are presented in Tables 1-3 and Figs. 1-6.

In the absence of MNY, R_p was found to be 14.1×10^{-5} mol/(L·s). However, when MNY was added and its concentration changed from 0.29×10^{-7} to 2.90×10^{-7} mol/L, R_p decreased from 12.3×10^{-5} to 8.3×10^{-5} mol/(L·s) as shown in Table 1. This clearly indicates that MNY retards the reaction.

The value of R_p increases with polymerization temperature, and the energy of activation, determined from the Arrhenius plot (Fig. 2), was found to be 8.29 and 10.6 kcal/mol in the absence and in the presence of MNY (1.45×10^{-7} mol/L), respectively. The energy of activation further increased to 13.8 kcal/mol when the concentration of MNY was raised to 2.90×10^{-7} mol/L.

The order of reaction, calculated from the slope of linear plot of log $1/R_p$ versus log [MNY], was found to be 0.36 ± 0.06 (Fig. 3).

It was found that R_p is a direct function of monomer concentration, with an order of reaction, calculated from the slope of linear plot of log R_p versus log [STY], of 1.11 (Fig. 4).

The effects of various solvents on R_p are reported in Table 3. Such nonpolar solvents as carbon tetrachloride and cyclohexane accelerate retardation, while such polar solvents as dimethylsulfoxide and tetrahydrofuran have a negligible effect on R_p.

The number-average degree of polymerization, $\overline{P}_n$, is unaffected by polymerization time and concentration of MNY, but conversion increases with polymerization time. This suggests that the system has attained the steady state. A plot of $1/\overline{P}_n$ versus the square root of MNY concentration is linear (Fig. 5), which suggests bimolecular termination for this system.

The retarding effect of MNY may be due to the following: (i) decrease of the initiation rate (R_i), (ii) decrease of the propagation rate (R_p), (iii) increase of the termination rate (R_t).

The MNY affects neither R_i nor R_t, as shown in Table 1, and the nonlinearity of a plot of R_p/R_{po} versus $\sqrt{[\eta]/[\eta]_0}$ (where R_p and R_{po} are the rate of polymerization in presence and absence of MNY, respectively, and $[\eta]$ and $[\eta]_0$ are the corresponding intrinsic viscosities, respectively). This also supports the conclusion that the system has attained the steady state.

TABLE 1. Polymerization of Styrene in the Presence of MNY Initiated by AIBN[a]

No.	[MNY] × 10^7, mol/L	Conversion, %	$R_p \times 10^5$, mol/(L·s)	$\overline{P}_n$	$R_i \times 10^{11}$, mol/(L·s)	Energy of activation, kcal/mol
1	0.00	23.3	14.1			8.3
2	0.29	20.4	12.3	125	1.60	
3	0.58	18.2	11.0			
4	0.87	18.8	11.4	124		
5	1.16	18.4	11.1			
6	1.45	17.7	10.7	123	1.61	10.6
7	1.74	16.6	10.0			
8	2.03	15.7	9.5	122		
9	2.32	15.2	9.2			
10	2.61	14.4	8.7	121		
11	2.90	13.7	8.3		1.78	13.8

[a] [STY] = 1.75 mol/L, [AIBN] = 6.10×10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization temperature = 65°C, polymerization time = 240 min.

TABLE 2. Effect of Monomer Concentration on the Polymerization of Styrene in the Presence of MNY Initiated by AIBN[a]

No.	[STY], mol/L	Conversion, %	$R_p \times 10^5$, mol/(L·s)
1	1.75	17.7	10.7
2	2.18	23.0	13.9
3	2.62	26.0	15.7
4	3.06	33.0	19.9

[a] [MNY] = 1.45×10^{-7} mol/L, [AIBN] = 6.10×10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization temperature = 65°C, polymerization time = 240 min.

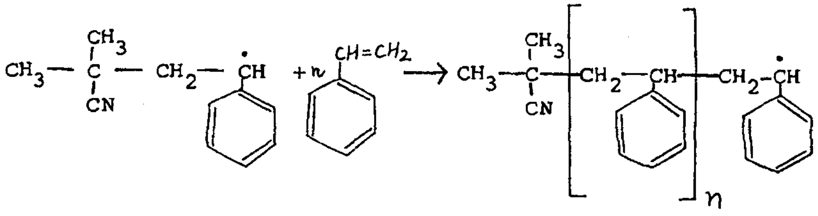
Therefore, it is concluded that the retarding effect of MNY is due to a decrease in the propagation rate. The overall value [8] of k_p^2/k_t, determined from the slope of the linear plot (Fig. 6) of polymerization rate versus inverse of average degree of polymerization, is 7.273×10^{-4} L/(mol·s).

Thus, it is concluded that MNY acts as a retarder for the radical polymerization of styrene without affecting its molecular weight.

Mechanism

The above kinetic studies show that the system attains the steady state and that $\overline{P}_n$ is unaffected by [MNY]. This suggests that MNY affects the propagation step in which it combines with the propagating chain to form radicals less reactive because of resonance stabilization. Therefore, the R_p falls as [MNY] increases.

(i)



Propagating chain

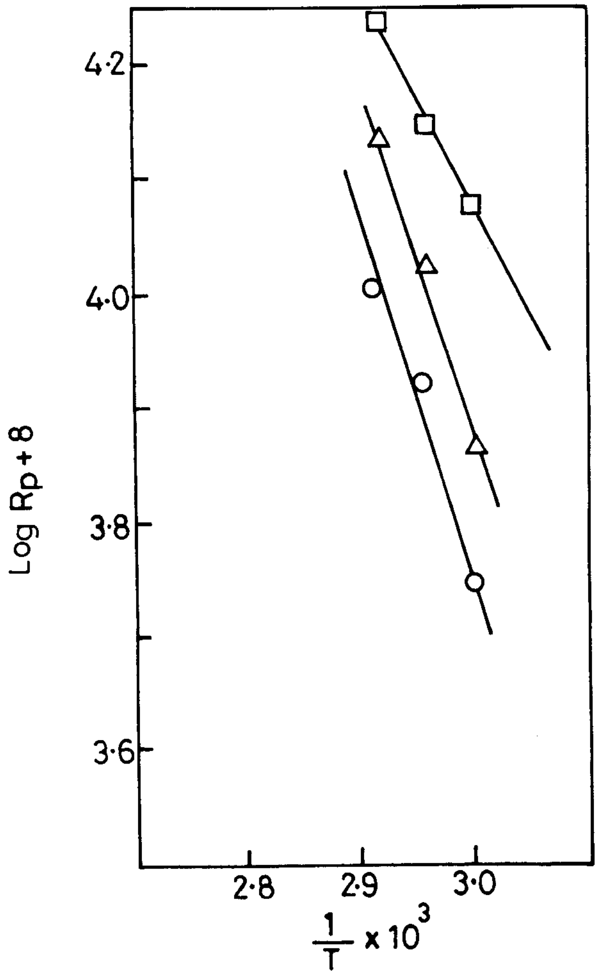


FIG. 2. Arrhenius plot. [MNY]: 2.90 × 10^{-7} mol/L (○), 1.45 × 10^{-7} mol/L (△), 0.0 mol/L (□). [STY] = 1.75 mol/L, [AIBN] = 6.10 × 10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization time = 240 min.

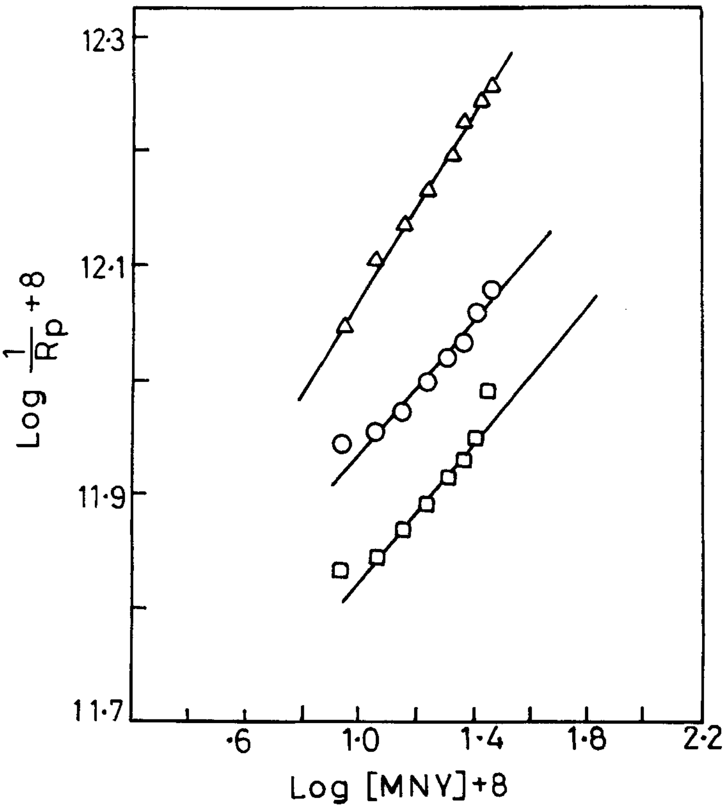


FIG. 3. Polymerization of styrene in the presence of methyl nitrile ylide: logarithmic plot of inverse of polymerization rate vs [MNY]. [STY] = 1.75 mol/L, [AIBN] = 6.10 × 10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization time = 240 min, polymerization temperature = 60°C (△), 65°C (○), 70°C (□).

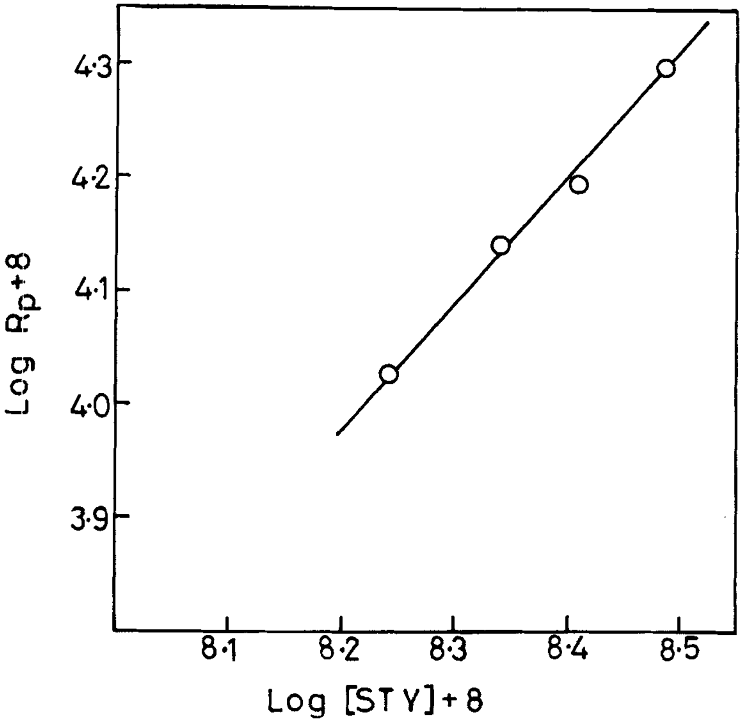


FIG. 4. Logarithmic plot of polymerization rate vs styrene concentration. [MNY] = 1.45 × 10^{-7} mol/L, [AIBN] = 6.10 × 10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization time = 240 min, polymerization temperature = 65°C.

TABLE 3. Effect of Solvent on the Polymerization of Styrene in the Presence of MNY Initiated by AIBN[a]

No.	Solvent	[Solvent], mol/L	Conversion, %	$R_p \times 10^5$ mol/(L·s)
1	Carbon tetrachloride	0.00	17.7	10.7
		0.99	17.0	10.3
		1.98	14.3	8.6
		2.98	9.1	5.5
2	Cyclohexane	0.00	17.7	10.7
		0.99	11.5	6.7
		1.99	9.0	5.4
		3.01	6.3	3.8
3	Tetrahydrofuran	0.00	17.7	10.7
		1.00	17.1	10.3
		1.99	17.4	10.5
		3.02	17.6	10.6
4	Dimethylsulfoxide	0.00	17.7	10.7
		0.99	16.7	10.1
		1.99	16.9	10.2
		3.03	17.0	10.3

[a] [STY] = 1.75 mol/L, [AIBN] = 6.10×10^{-2} mol/L, [MNY] = 1.45×10^{-7} mol/L, polymerization time = 240 min, polymerization temperature = 65°C.

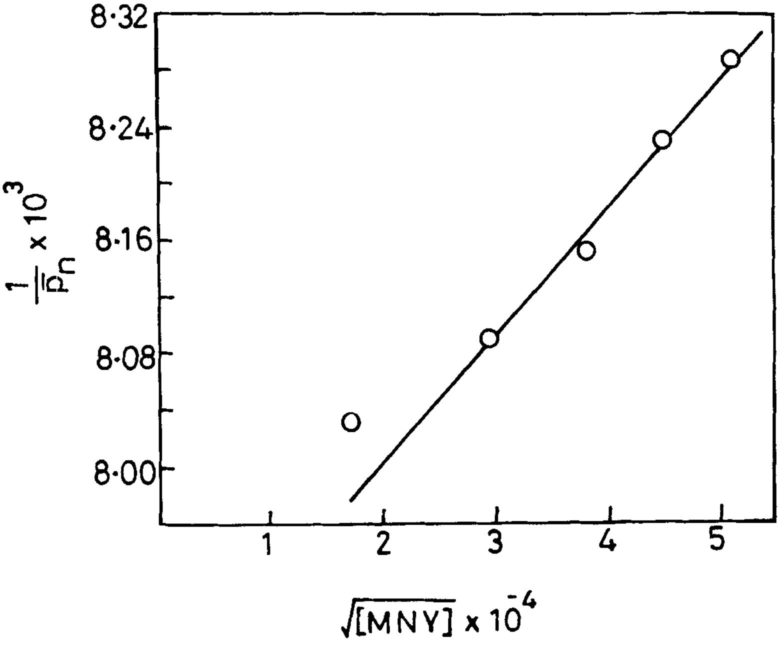


FIG. 5. Relation between inverse number-average degree of polymerization and square root of [MNY]. [STY] = 1.75 mol/L, [AIBN] = 6.10×10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization time = 240 min, polymerization temperature = 65°C.

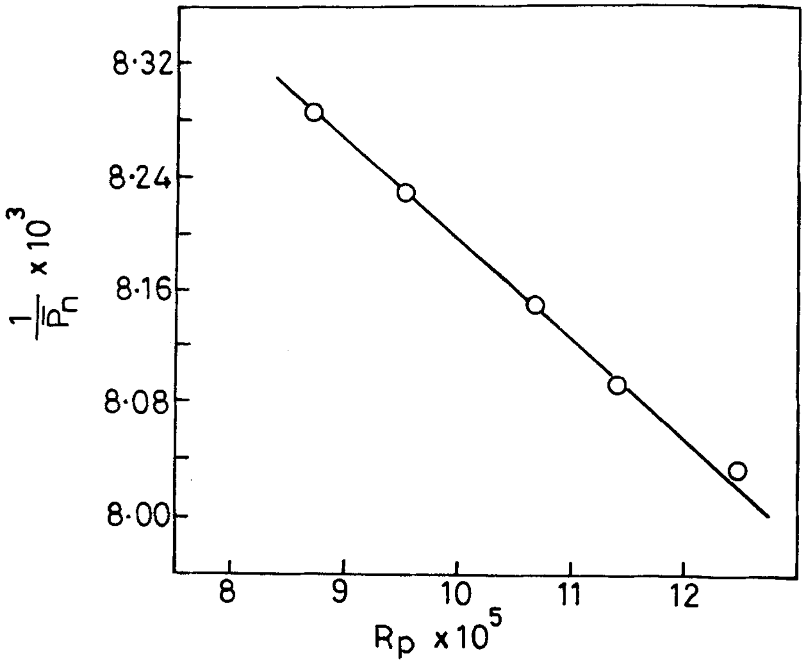
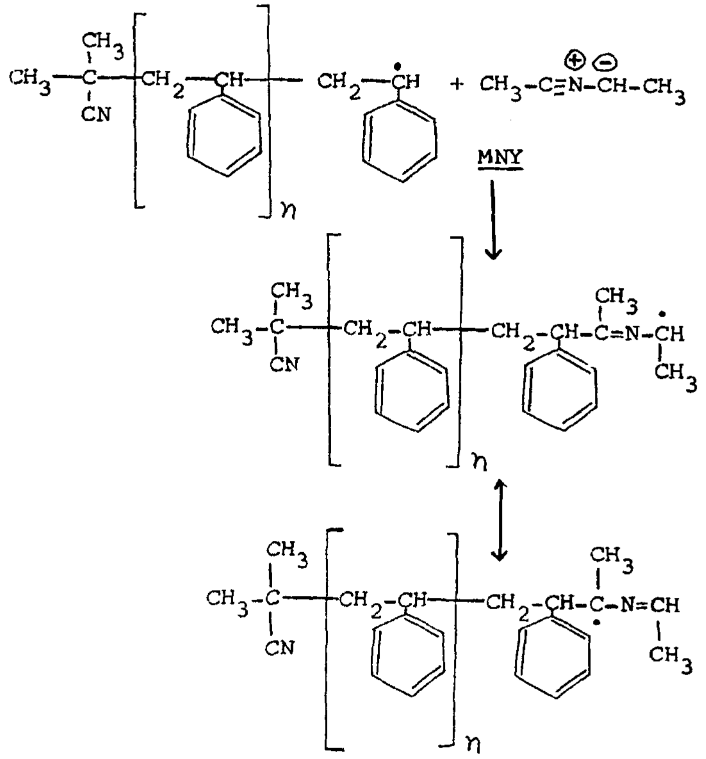


FIG. 6. Relation between inverse number-average degree of polymerization and polymerization rate. [STY] = 1.75 mol/L, [AIBN] = 6.10 × 10^{-2} mol/L, acetonitrile = 1.00 mL, polymerization time = 240 min, polymerization temperature = 65°C.

(ii)



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