*Asian Journal of Chemistry* Vol 3, No. 4 (1991), 360-366

# p-Nitrobenzyl Triphenyl Phosphonium Ylide as a Chain Transfer Agent for Copolymerisation of Methyl Methacrylate with Styrene

URVI BHATNAGAR, RITA VASISHTHA AND A. K. SRIVASTAVA*

*Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-*208 002, *India.*

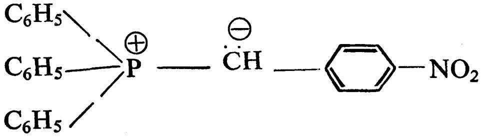
$\alpha$–$\alpha'$ Azobisisobutyronitrile initiated radical copolymerisation of methyl methacrylate and styrene in presence of p-nitrobenzyl triphenyl phosphonium ylide (p-NBTPY) using dimethyl sulphoxide as an inert solvent has been investigated dilatometrically at 60±0.1°C under nitrogen atmosphere. The ylide, p-NBTPY acts as a chain transfer agent and the ($C_{tr}$) value is 0·9. Various kinetic parameters have also been evaluated and a suitable mechanism has been proposed for the present system.

## INTRODUCTION

Among the wide variety of organic compounds, employed in polymer science, ylides occupy a special place, because of their unique applications as initiator[1,2], accelerator[3,4], retarder[5,6] and chain transfer agent[7,8]. A search of literature reveals that most of the recent reports are associated with application of nitrogen[9,10], sulphur[7,11] and arsenic[12] and rarely with phosphorus ylides[13]. We therefore undertook present work which shows that p-nitrobenzyl triphenyl phosphonium ylide could be successfully employed as a chain transfer agent for copolymerisation of methyl methacrylate with styrene.

## EXPERIMENTAL

Methyl methacrylate (MMA) (Robert Johnson make) and styrene (Sty) (Robert Johnson make) were washed with 4% NaOH solution followed by distilled water and then distilled under vacuum. Purified solvents and initiator $\alpha$–$\alpha'$ azobisisobutyronitrile (AIBN) recrystallised twice from methanol (m. pt. 102°C), were used. The ylide, p-NBTPY, having the following structure, was prepared *in situ* according to the method of McDonald and campbell[14].



The polymerisation runs were performed at 60±0.1°C using modified dilatometric apparatus[15] under an inert atmosphere of nitrogen for 2 hrs. The progress of reaction was monitored with the help of a cathetometer as meniscus movements (per unit volume per unit time). Copolymer, precipitated with acidified methanol and dried to a constant weight was treated with acetonitrile and cyclohexane to remove homopolymers. Finally the copolymer was dried to a constant weight to calculate percentage conversion. Over all rate of polymerisation ($R_p$) was calculated from the slope of linear portion of conversion-time plot (Fig. 1 a, b & c),

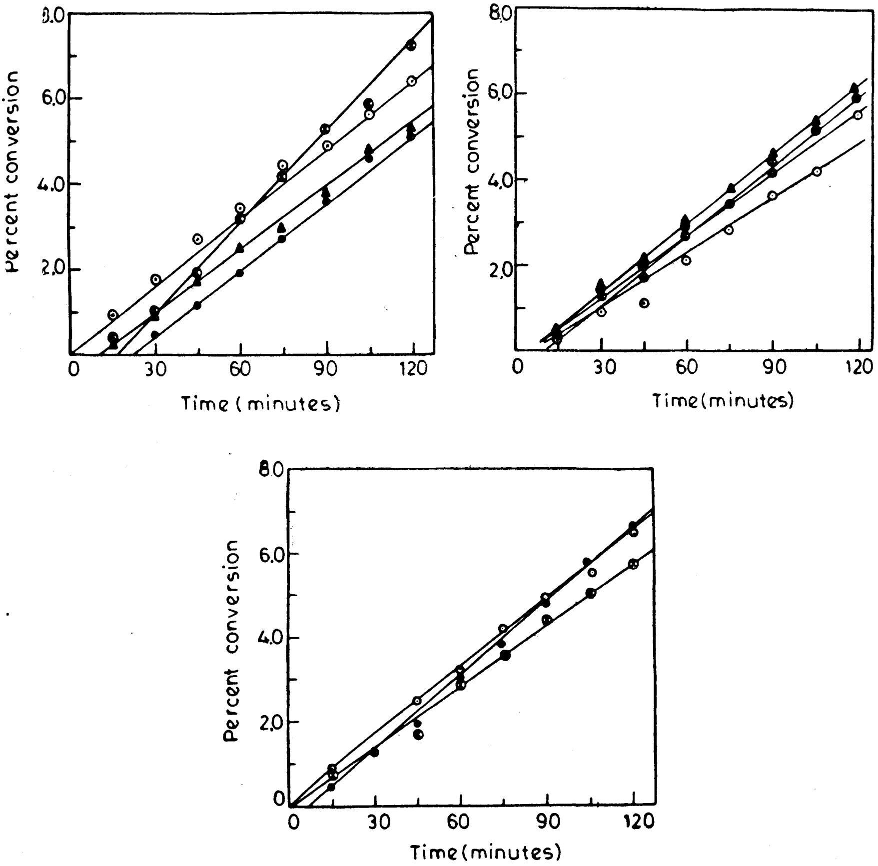


Fig. 1. A percentage conversion time plot for copolymerization of MMA and styrene (in mol $l^{-1}$) of p-NBTPY :

(a) ⊙ 0.00, ⊗ $4.2\times10^4$, ● $8.4\times10^4$, ▲ $12.6\times10^4$
(b) ⊙ $16.8\times10^4$, ⊗ $21.0\times10^4$, ● $25.2\times10^4$, ▲ $29.4\times10^4$
(c) ⊙ $33.6\times10^4$, ⊗ $37.8\times10^4$, ● $42.0\times10^4$

whereas [AIBN]=$3.04\times10^2$ mol $l^{-1}$; [MMA]=3.60 mol $l^{-1}$; [Sty]=1.73 mol $l^{-1}$; Time=2 hrs; Temperature=60±0.1°C.

The intrinsic viscosity ($\eta$) of the copolymer, determined in toluene at 32°C by using an Ubbelohde viscometer, was used to calculate viscosity average molecular weight ($\overline{M}_v$) using equation [16]

$$\eta = K\overline{M}_v^{\alpha}$$

$$\text{whereas } K = 8{\cdot}32 \times 10^{-5}$$

$$\alpha = 0{\cdot}75$$

## RESULTS AND DISCUSSION

No polymer was formed in the absence of AIBN which shows that ylide failed to initiate copolymerisation. The results of kinetic investigation of the copolymerisation of styrene and methyl methacrylate in the presence of ylide for fixed monomer ratio were presented in Table 1–4.

*Effect of [p-NBTPY]* : A study of Table 1, which summarizes the copolymerisation conditions and results of the kinetic investigations, reveals that p-NBTPY scarcely affected the rate of copolymerisation. However the average molecular weight ($\overline{M}_v$) of copolymer decreased gradually as [p-NBTPY] increased. Hence p-NBTPY acts as a chain transfer agent for the system. The chain transfer constant ($C_{tr}$) value, calculated from the slope of the plot between $1/\overline{P}_n$ against [p-NBTPY]/[M] is 0·9.

TABLE 1

EFFECT OF [p-NBTPY] ON COPOLYMERISATION OF MMA WITH STYRENE

| Run No. | [P-NBTPY] $\times 10^4$ mol $l^{-1}$ | Percentage (%) conversion | $R_p \times 10^5$ mol $l^{-1}s^{-1}$ | $\overline{M}v$ |
|---|---|---|---|---|
| 1. | 0 | 8.0 | 4.7 | 75,760 |
| 2. | 4.2 | 7.1 | 5.9 | — |
| 3. | 8.4 | 5.2 | 4.7 | 32,200 |
| 4. | 12.6 | 5.6 | 4.7 | — |
| 5. | 16.8 | 5.7 | 4.7 | 23,880 |
| 6. | 21.0 | 5.8 | 4.4 | 20.000 |
| 7. | 25.2 | 6.2 | 4.8 | 11,840 |
| 8. | 29.4 | 6.4 | 4.4 | — |
| 9. | 33.6 | 6.8 | 4.7 | — |
| 10. | 37.8 | 6.4 | 4.7 | — |
| 11. | 42.0 | 7.1 | 5.1 | 3,758 |

[MMA) = 3.60 mol $l^{-1}$; [Sty] = 1,73 mol $l^{-1}$; [AIBN] = $3.04 \times 10^{-2}$ mol $l^{-1}$; Temp. = 60°C; Time = 2 hrs

*Effect of [AIBN]* : The dependence of $R_p$ on [AIBN] was studied (Table 2) by varying [AIBN] from $1.82 \times 10^{-2}$ to $3.65 \times 10^{-2}$ mol $l^{-1}$ and keeping [p-NBTPY] ($21.0 \times 10^{-4}$ mol $l^{-1}$) and [monomer] constant. The order of reaction, calculated from the slope of the plot of log $R_p$ versus log [AIBN], is 0·5 (Fig. 2) as expected for ideal radical polymerization square root relationship.

$$R_p \propto [\text{AIBN}]^{0.5}$$

TABLE 2

EFFECT OF [AIBN] ON COPOLYMERISATION OF MMA WITH STYRENE IN PRESENCE OF (p-NBTPY)

| Run No. | [AIBN] $\times 10^{-2}$ mol $l^{-1}$ | Percentage (%) conversion | Rp $\times 10^{5}$ mol $l^{-1}.S^{-1}$ |
|---|---|---|---|
| 1. | 3.04 | 8.0 | 4.7 |
| 2. | 1.82 | 3.7 | 3.9 |
| 3. | 2.43 | 4.1 | 4.4 |
| 4. | 3.04 | 5.8 | 4.8 |
| 5. | 3.65 | 6.2 | 5.9 |

[MMA]=3.60 mol $l^{-1}$; [STY]=1.73 mol $l^{-1}$; [P-NBTPY]=$21.0 \times 10^{-4}$ mol $l^{-1}$; Time=2 hrs; Temp.=60°C

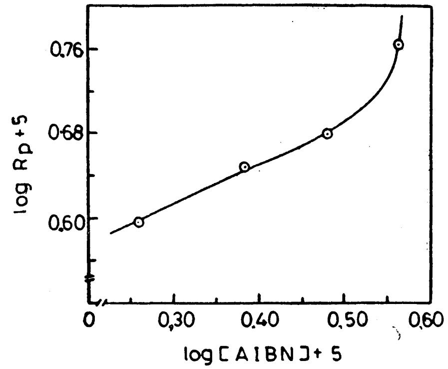


Fig. 2. Relationship between log AIBN Vs. log $R_p$ for the copolymerisation of MMA and styrene whereas [MMA]=3.60 mol $l^{-1}$; [Sty]=1·73 mol $l^{-1}$; [AIBN]=$3.04 \times 10^{-2}$ mol $l^{-1}$; [p-NBTPY]=$21.0 \times 10^{4}$ mol $l^{-1}$; Time=2 hrs. Temp.=60°C.

*Effect of* (*Methyl methacrylate*) : The effect of [MMA] on $R_p$ has been studied (Table 3) by varying [MMA] from 2.80 to 4.32 mol $l^{-1}$ whereas [styrene] and [p-NBTPY] are kept constant. It is noted that the $R_p$ is a direct function of [MMA]. A plot between log $R_p$ and log [MMA] (Fig. 3) gives an order of reaction with respect to MMA as unity as expected for radical copolymerisation. The $P_n$ of the copolymer increases with MMA.

TABLE 3

EFFECT of [MMA] ON COPOLYMERISATION OF MMA WITH STYRENE IN PRESENCE OF (p-NBTPY)

| Run No. | [MMA] mol $l^{-1}$ | Percentage (%) conversion | $R_p \times 10^5$ mol $l^{-1}$ $S^{-1}$ | $M_v$ |
|---|---|---|---|---|
| 1. | 2.80 | 4.6 | 3.68 | 12.760 |
| 2. | 3.60 | 5.8 | 4.80 | 20.000 |
| 3. | 4.32 | 6.6 | 5.60 | 70.470 |

[AIBN]$=3.04\times10^{-2}$ mol $l^{-1}$ [P-NBTPY]$=21.0\times10^{4}$ mol $l^{-1}$; [Sty]$=1,73$ mol $l^{-1}$; Time$=2$ hrs; Temp.$=60$°C.

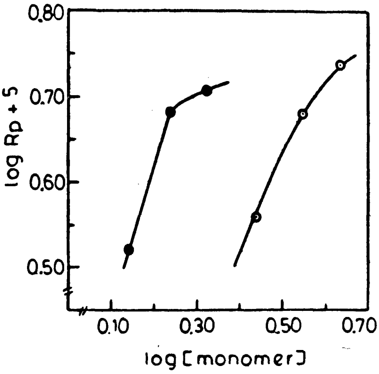
*Effect of* [*Styrene*] : The effect of styrene on the $R_p$ has been studied (Table 4) by varying [styrene] from 1.38 to 2.07 mol $l^{-1}$ while [MMA] and [p-NBTPY] are kept constant (Fig. 3). It is observed that styrene has a direct effect on $R_p$. The order of reaction with respect to styrene calculated from linear portion of plot between log $R_p$ log [Sty] is unity, as expected for radical copolymerisation. The $\overline{P}_n$ of the copolymer increases with [styrene].

TABLE 4

EFFECT OF [STYRENE] ON COPOLYMERISATION OF MMA WITH STYRENE IN PRESENCE OF (p-NBTPY)

| Run No. | [Styrene] mol $l^{-1}$ | Percentage (%) conversion | $Rp \times 10^5$ mol $l^{-1}S^{-1}$ | $M_v$ |
|---|---|---|---|---|
| 1. | 1.36 | 4.4 | 3.3 | 9,484 |
| 2. | 1.73 | 5.8 | 4.0 | 20,000 |
| 3. | 2.07 | 6.3 | 5.0 | 65,310 |

[A1BN]$=3{\cdot}04\times10^{-2}$ mol $1^{-1}$; [p-NBTPY]$=21.0\times10^{-1}$ mol $1^{-1}$; [MMA]$=3.60$ mol $l^{-1}$ Time$=2$ hrs; Temp$=60$°C.



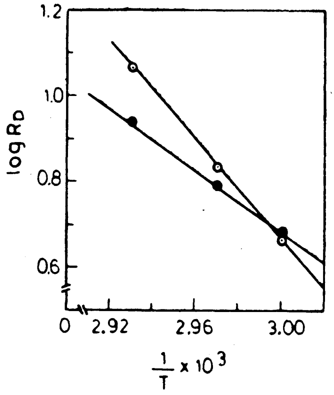


Fig. 3. Relationship between log [monomer] vs. log $R_p$ ;

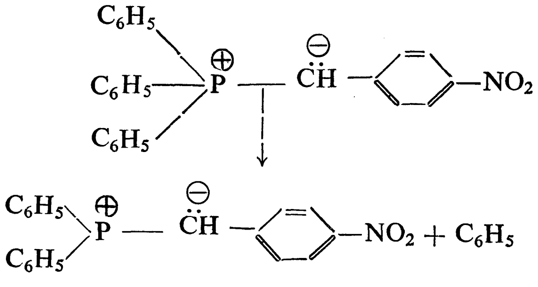
(a) ● is for [MMA]*. (b) ⊙ is for (Sty)**, whereas [Sty]$=1.73$ mol $l^{-1}$; [MMA]$=3.62$ mol $l^{-1}$; [AIBN]$=3.04\times10^{-2}$ mol $l^{-1}$ [p-NBTPY]$=21.0\times10^{4}$ mol $l^{-1}$; Time$=2$ hrs; Temp.$=60$°C.

Fig. 4. Relationship between 1/T vs. log $R_p$ for the copolymerisation of MMA and styrene :

⊙ is in the absence and ● in the presance of p-NBTPY ($31.0\times10^{4}$ mol $l^{-1}$). whereas [MMA]$=3.6$ mol $l^{-1}$; [Sty]$=1.73$ mol $l^{-1}$: [AIBN]$=3.04\times10^{-2}$ mol $l^{-1}$; Time$=2$ hrs, Temp.$=60$°C.

*Effect of Temperature* : The influence of temperature on the copolymer formation rate has been studied by carrying out the polymerisation at four different temperatures (55, 60, 63 and 65°C). The overall energy of activation ($\Delta E$) of the present system has been evaluated with the help of Arrhenius plot (Fig. 4) as 97.0 kJ $mol^{-1}$ and 87.0 kJ $mol^{-1}$ for the copolymerisation in the absence and presence of p-NBTPY, respectively.

*Mechanism* : Kondo *et al.*[11,13] have reported mechanism of polymerisation of vinyl monomers using triphenyl phosphonium ylide, tetrainitiators ylide and triphenyl sulphonium salts as photo initiators and proposed that these initiators undergo bond fission between the heteroatom and phenyl group on irradiation by a high pressure mercury lamp and the phenyl radicals produced participate in the initiation of polymerisation. From the structural similarities, it seems that the p-nitrbenzyl triphenyl phosphonium ylide (p-NBTPY) also undergoes similar fission and $Ph^{\cdot}$ is produced. This was confirmed by the GLC analysis of p-NBTPY solution in dimethyl sulphoxide, which confirms the presence of toluene in the system. Formation of toluene confirms the existence of phenyl radical in the present system. The various steps are outlined below :



## Characterisation of Copolymer

NMR of copolymer, prepared in the presence of p-NBTPY, showed appearance of phenyl protons as doublet at $7\tau$. The methoxy protons of methyl methacrylate appeared as singlet at 6 : $4\tau$. The methyl protons appeared as singlet at $9.1\tau$. This shows that in present case random copolymer is obtained[15].

## ACKNOWLEDGEMENT

Authors are thankful to Dr. A. K. Vasishtha, Director, Harcourt Butler Technological Institute, Kanpur for providing facilities.

## REFERENCES

1. R. Vasishtha and A. K. Srivastava, *British Polym. J.*, **82**, 53 (1990).
2. R. Vasishtha and A. K. Srivastava, *Indian J. Chem.*, **28**, 705 (1989)
3. R. Vasishtha and A. K. Srivastava, *J. Polym. Material*, **6**, 297 (1989).

4. S. Saini, A. K. Shukla and A. K. Srivastava, *Polym J.*, **17**, 1117 (1985).
5. P. Kumar, S. Saini,, A. K. Shukla, A. K. Srivastava, *Makromol. Chem., Rapid Commun.*, **7**, 149 (1986).
6. R. Vasishtha, P. Kumar, S. K. Awasthi, U. Bhatanagar and A. K. Srivastava, *Colloid and Polymer Sci.*, **268**, 645 (1990).
7. R. Vasistha and A. K. Srivastava, *Acta Polymerica*, **40**, 358 (1989).
8. R. Vaslshtha and A. K. Srivastava, *J. Polym.*, **21** 103 (1989).
9. P. Shukla and A. K. Srivastava, *Eur. Polym. J.*, **24**, 1115 (1988).
10. S. Saini, R. Vasishtha, P. Shukla and A. K. Srivastava, *Macromolecules*, **22**, 1025 (1989).
11. S. Kondo, M. Muramatsu Senga and K. Tsuda, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1187 (1984).
12. R. Vasishtha and A. K. Srivastava, *Polymer*, **31**, 150 (1990).
13. S. Kondo, Y. Kondo and K. Tsuda J. *Polymer Sci. Polym. Lett. Ed.*, **21**, 213 (1983).
14. R. N. McDonald, and T. W. Campbell, *J. Org. Chem.*, **24**, 1959 (1969).
15. A. K. Srivastava and B. N. Mathur, *Polymer*, **22**, 391 (1981).
16. J. Brandrup and E. H. I. Immergut, Polymer Hand Book, John Wiley & Sons, New York, PIV-22 (1966).

[*Received* : 26 August 1989; *Accepted* : 30 June 1990] AJC-199