

NOTES

***p*-Bromophenacyldimethylsulphonium Ylide as a Chain Transfer Agent for Polymerization of *N*-Vinylpyrrolidone and Methyl Methacrylate**

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Reports regarding applications of nitrogen ylides,¹⁻⁴ as initiators or accelerators for the homo- and copolymerization of vinyl monomers have appeared in the last five years in various polymer journals. Kondo *et al.*⁵⁻⁶ have prepared some poly(vinyl sulphonium) ylides. Thus, papers regarding applications of ylides containing sulphur as a hetero atom in the field of polymer science are few. Therefore, we have undertaken the present work to explore possible applications of sulphur ylide, *viz.* *p*-bromophenacyldimethylsulphonium ylide (*p*-BPDSY), in the field of polymers.

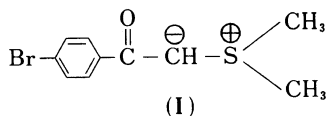
EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was washed with 4% NaOH solution and distilled water, and finally distilled under vacuum. *N*-Vinylpyrrolidone (*N*-VP) was used without further purification. Purified solvents were used. The initiator α,α' -azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol (mp 102°C) before use.

p-BPDSY, having the following structure

(I), was prepared according to the method of Ratts and Yao.⁷



Polymerization

The polymerization was performed at 60°C ± 0.01 using modified dilatometric apparatus⁸ under an inert atmosphere of nitrogen for 50 minutes in case of *N*-VP and for 90 minutes in case of MMA. The progress of the reaction was monitored with a Cathetometer for meniscus movement (per unit volume per unit time). Poly(*N*-VP) and poly(MMA), precipitated with carbon tetrachloride and acidified methanol, respectively, were dried to constant weight.

Intrinsic Viscosity

The intrinsic viscosity [η] of poly(*N*-VP) and poly(MMA) at 30°C using Ubbelohde viscometer was determined in methanol and benzene, respectively. The \bar{M}_v of the former and

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\bar{P}_n of the latter polymers were calculated using eq 1⁹ and 2,¹⁰ respectively.

$$[\eta]_{\text{MeOH}} = 2.3 \times 10^{-2} \times \bar{M}_v^{0.65} \quad (1)$$

$$\log \bar{P}_n = 3.342 + 1.13 \log[\eta] \quad (2)$$

RESULTS AND DISCUSSION

A study of Table I, which summarizes the polymerization conditions and results of the kinetic investigation of polymerization of *N*-VP and MMA, reveals that *p*-BPDSY scarcely affected the rate of polymerization. The molecular weight of polymers decreased gradual-

ly as [*p*-BPDSY] increased. Hence *p*-BPDSY seems to act as a chain transfer agent for the polymerization of *N*-VP and MMA. The C_{tr} value, calculated from the slope of the plot of $1/\bar{M}_v$ against [*p*-BPDSY] (Figure 1) for polymerization of *N*-VP is 0.83. Similarly, the slope of the plot between $1/\bar{P}_n$ against [*p*-BPDSY] for polymerization of MMA, (Figure 2) gives C_{tr} as 12.5×10^{-2} . The C_{tr} values¹¹ of tetramethylsilane, mono- and dichlorosilane for polymerization of MMA are 0.13×10^{-3} , 0.22×10^{-3} and 0.245×10^{-3} , respectively.

Table I. Polymerization of *N*-vinylpyrrolidone and methyl methacrylate in the presence of *p*-bromophenacyldimethylsulphonium ylide in benzene at 60°C^a

| Run No. | [<i>p</i> -BPDSY] × 10 ³ mol l ⁻¹ | <i>N</i> -Vinylpyrrolidone | | Methyl methacrylate | |
|---------|---|-------------------------------------|-------------|-------------------------------------|-------------|
| | | $R_p \times 10^4$ | \bar{M}_v | $R_p \times 10^4$ | \bar{P}_n |
| | | mol l ⁻¹ s ⁻¹ | | mol l ⁻¹ s ⁻¹ | |
| 1 | 0 | 6.73 | 33,270 | 1.93 | 912 |
| 2 | 1.45 | 6.10 | 28,280 | 1.76 | — |
| 3 | 2.91 | 5.67 | — | 1.87 | 750 |
| 4 | 4.37 | 5.46 | 15,160 | 1.87 | 585 |
| 5 | 5.82 | 6.44 | 15,160 | 1.69 | — |
| 6 | 7.28 | 5.88 | — | 1.74 | — |
| 7 | 8.74 | 6.35 | 10,070 | 1.70 | 500 |
| 8 | 10.1 | 5.34 | — | 1.79 | — |
| 9 | 11.6 | 5.78 | 8,127 | 1.85 | 438 |
| 10 | 13.1 | 5.33 | — | 1.73 | 396 |
| 11 | 14.5 | 5.17 | — | 1.82 | 357 |

^a [AIBN] = 4.76×10^{-2} mol l⁻¹; [MMA] = 2.81 mol l⁻¹; [*N*-VP] = 2.92 mol l⁻¹; polymerization temperature = 60°C.

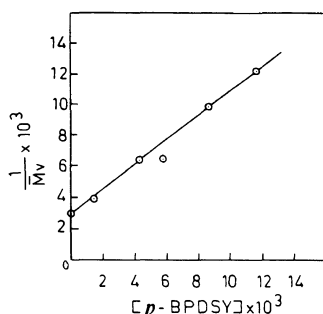


Figure 1. Relationship between $1/\bar{M}_v$ and the concentration of *p*-BPDSY for *N*-VP.

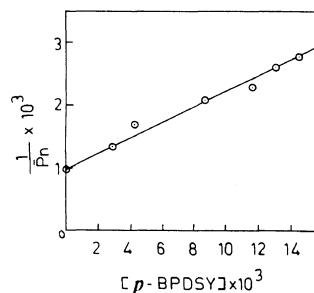
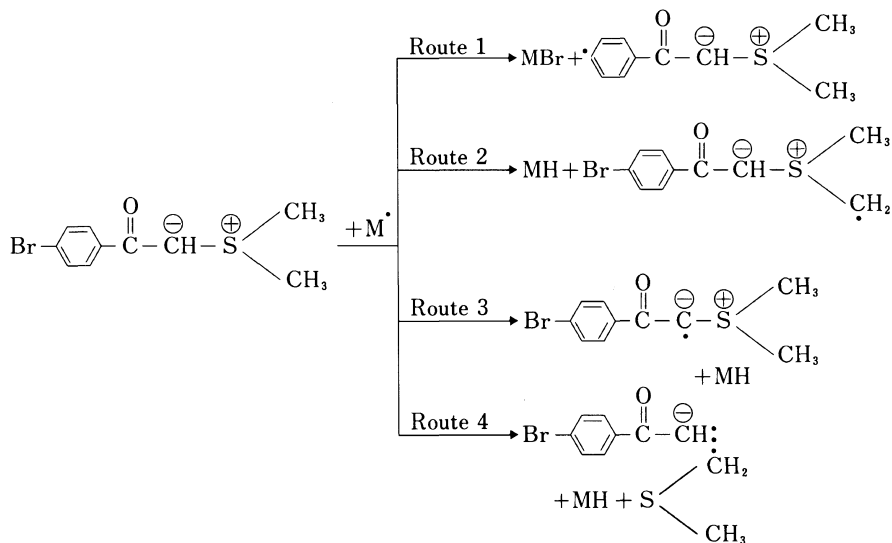


Figure 2. Relationship between $1/\bar{P}_n$ and the concentration of *p*-BPDSY for MMA.

MECHANISM

There are four possible ways by which *p*-

bromophenacyldimethylsulphonium ylide acts as a chain transfer agent.



Element analysis of the polymers showed the absence of bromine in the polymer which excludes route 1. In routes 2 and 3, radicals formed are less reactive and hence, the R_p would have been highly affected in the presence of sulphur ylide. But it is clear from the table that R_p is hardly affected and therefore, routes 2 and 3 are not possible. Based on the above, route 4 should be the best route to explain the chain transfer reaction mechanism.

CONCLUSION

On the basis of the above evidence, it is clear that *p*-BPDSY acts as a chain transfer agent for both monomers, but more effectively for MMA than for *N*-vinylpyrrolidone.

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