NOTES

Radical Polymerization of *ortho-*, *meta-*, and *para-*Monobrominated Styrenes

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Relationships between structures and polymerizabilities of mono-substituted styrenes (*o*- and *p*-Cl; *m*- and *p*-OCH$_3$; *m*- and *p*-CN; *m*- and *p*-Br; *p*-CH$_3$) have been investigated.[1-7] However, there have been no reports on *o*-, *m*-, and *p*-substituent effects on the polymerization under the same conditions.

Poly(bromostyrene) and its copolymers are interesting because of their flame retarding properties.[8,9] There have been many reports on polymerizations of brominated styrenes.[1,3,10-15] Kinoshita *et al.*[1,3] describe the monomer reactivity ratios of *m*- and *p*-monobrominated styrenes (MBS) at 30°C in bulk condition. Cubbon *et al.*[10,11] and Koton *et al.*[12] reported the monomer reactivity ratios and time-conversion for dibromo- and 2,4,5-tribromostyrenes in bulk and benzene. Konigsberg *et al.*[13] investigated the anionic polymerization of *p*-MBS. The overall radical polymerization rate equations for MBS have not been described except for only one report on *p*-MBS at 30°C in bulk condition.[14]

This paper describes the differences of radical polymerizabilities and properties of the polymers among positional isomers for MBS.

EXPERIMENTAL

Materials

MBS (*o*-, *m*-, and *p*-MBS) (Aldrich Co.) were distilled under vacuum (bp 30°C/0.08 mmHg; *o*-MBS, *m*-MBS, *p*-MBS) to remove residual impurities and inhibitors. Three monomers were identified by GC and ^{1}H and ^{13}C NMR analysis.[15] Styrene (ST) and toluene were purified by the usual method. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol and chloroform.

Homopolymerization and Copolymerization

Radical homopolymerization and copolymerization were carried out in toluene with AIBN as an initiator in sealed tubes under nitrogen gas. The solution was cooled by liquid nitrogen and degassed under vacuum by the ordinary freeze-thaw technique. After polymerization, the solution was poured into a large amount of methanol to precipitate the polymers. The polymers were filtered, washed with methanol and dried *in vacuo* at 50°C. The compositions of the copolymers were determined by elemental analysis (Br).

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Measurements

The molecular weights of the polymers were measured by gel permeation chromatographic (GPC) analysis. The molecular weight calibration curve was obtained with polystyrene standards. Glass transition (T_g) and beginning of degradation temperatures (T_d) were measured by thermal mechanical analysis (TMA) and TG-DSC, respectively. Melting points of polymers (T_m) were observed directly.

RESULTS AND DISCUSSION

Homopolymerization

The homopolymerization rate equations of MBS were obtained at 60°C. The initial polymerization rates (R_p) were obtained at various monomer concentrations under constant AIBN concentration. R_ps were also obtained at various AIBN concentrations under a constant monomer concentration. The exponents of monomer concentration (m) were determined as 1.12—1.18 from the relation between $\log R_p$ and $\log[\text{MBS}]$ (where [MBS] is the monomer concentration), as shown in Figure 1. They were slightly higher than the value ($m=1$) of ordinary radical polymerization, and this agreed with the value for *p*-MBS reported previously.[14] It is thought that Br-group is a bulky functional group, but the m values were almost the same value among *o*-, *m*-, and *p*-MBS, as shown in Table I. This suggests that there may scarcely be difference of steric hindrance in the polymerizability of *o*-, *m*-, and *p*-MBS. All polymerizations proceeded in a homogeneous system. This

($m>1$) may be characteristic for MBS, and may result from some "cage effect".[16] That is, the initial radicals resulting by degradation of the initiator may be forced to react in a kind of cage formed from the monomer and the solvent. It has been reported[17] that the effect of monomer concentration on initiator efficiency would be expected at monomer concentrations below 10^{-1}—10^{-2} mol l^{-1}. In this experiment there is the possibility that initiator efficiency might be slightly lower than the general values (0.6 to 0.7) since monomer concentrations were relatively low (3.02, 1.59, 0.88, and 0.48 mol l^{-1}). This may be associated
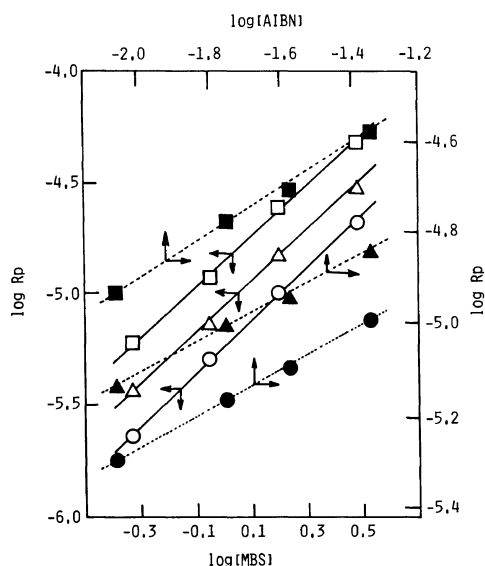

Figure 1. Effects of the MBS and AIBN concentrations on the rate of polymerization (R_p) in toluene at 60°C: [AIBN] = 8.8 mmol l^{-1}; (□) *o*-MBS, (△) *m*-MBS, and (○) *p*-MBS; [MBS] = 0.88 mol l^{-1}; (■) *o*-MBS, (▲) *m*-MBS, and (●) *p*-MBS.

Table I. Parameters of polymerization rate equations (R_p), overall activation energies (E) and frequency factors (A) for monobrominated styrenes

| Monomer | $R_p = k[\text{M}]^m[\text{AIBN}]^n$ (60°C) | | | E | A |
	m	n	k	kcal mol^{-1}	s^{-1}
o-MBS	1.12	0.49	1.37×10^{-4}	19.9	8.31×10^9
m-MBS	1.14	0.41	5.93×10^{-5}	18.7	1.04×10^8
p-MBS	1.18	0.43	4.47×10^{-5}	19.6	3.45×10^8

with the fact that the m values were slightly higher than 1.0. However, it was concluded that there were no differences among the m values for o-, m-, and p-MBS.

The exponents of AIBN concentration (n) were determined as 0.41—0.49 from the relation between $\log R_p$ and $\log[\text{AIBN}]$, as shown in Figure 1 and Table I. In the experiments the monomer concentration was 0.88 mol l^{-1}. Thus the initiator efficiency may be slightly lower than the general values.[17] Consequently, a definite conclusion could not be reached. But it is considered that the 1/2 power rule was satisfied among o-, m-, and p-MBS within an error of ± 0.07 and that there were few differences among n values for o-, m-, and p-MBS.

The order of polymerization rate constants (k) at 60°C was p-MBS $< m$-MBS $< o$-MBS, as shown in Table I. It is considered that k for o-, m-, and p-MBS can be elucidated by steric, resonance and polar effects. The steric effect may be neglected, as also noted for the effect of monomer concentration. The relation of polar effect for aromatic compound is generally expressed as m-Br $> p$-Br, according to the Hammett equation.[18] This order agrees with that $(p$-MBS $< m$-MBS) of k. The order for resonance effect is also expressed as o-Br $= p$-Br $> m$-Br, according to the Otsu and Yamamoto equation.[19] This order is not consistent with that for k. Consequently, the difference among k for o-, m-, and p-MBS may be contributed to the polar effect.

Polymerizations were performed at constant monomer and AIBN concentrations at 50, 60, 70, and 80°C. k at the temperature were calculated from the equations at 60°C for three monomers. Overall activation energies (E) of the polymerizations were obtained from the relation between $\log k$ and $1/T$, as shown in Figure 2. As can be seen from Table I, there is little difference among E for the positional isomers. The values are almost equal to those for ST and other ordinary vinyl monomers.
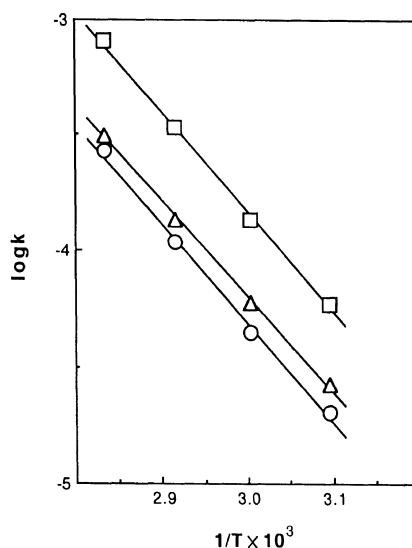

Figure 2. Relationship between $\log k$ and $1/T$ for the polymerization of MBS initiated by AIBN in toluene: [MBS] = 0.88 mol l^{-1}; [AIBN] = 8.8 mmol l^{-1}: ($\square$) o-MBS, ($\triangle$) m-MBS, and ($\bigcirc$) p-MBS.

Copolymerization

The copolymerizations of MBS (M_1) with ST (M_2) were performed in toluene at 60°C. The polymerizations were stopped within 20% conversion to polymers in order to calculate monomer reactivity ratios by changing the reaction time from 5 to 7 h. All copolymerizations proceeded homogeneously. Copolymer–composition curves are shown in Figure 3. Monomer reactivity ratios were determined according to the high conversion method reported by Tüdös et al,[20] and Alfley–Price[21] Q_1 and e_1 values were calculated assuming $Q_2 = 1.0$ and $e_2 = -0.8$ for ST. These values are shown in Table II.

The order $(o$- $> m$- $> p$-MBS) of the r_1 values was consistent with that of k for the homopolymerization. $1/r_2$, which indicate the reactivity of MBS against an attack by a polystyryl radical, were o-MBS (1.82) $> p$-MBS (1.69) $> m$-MBS (1.56). This order is different from that $(o$- $> m$- $> p$-MBS) of k for the homopolymerization. Consequently, in the copolymerizations, the resonance effect
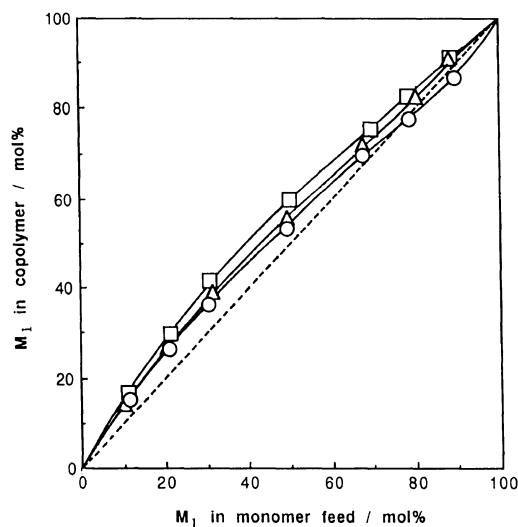
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Figure 3. Copolymer composition curves for MBS (M_1) and ST (M_2) in toluene at 60°C: [MBS]+[ST]=*ca.* 0.88 mol l^{-1}, [AIBN]=8.8 mmol l^{-1}; ($\square$) *o*-MBS/ST, ($\triangle$) *m*-MBS/ST, and ($\bigcirc$) *p*-MBS/ST systems.

Table II. Monomer reactivity ratios and Q_1, e_1 for monobromated styrenes (M_1) and styrene (M_2)

M_1	r_1	r_2	$1/r_2$	Q_1	e_1
o-MBS	1.31	0.55	1.82	1.15	−0.22
m-MBS	1.22	0.64	1.56	1.05	−0.30
p-MBS	0.79	0.59	1.69	0.84	0.08

may not be negligible. Q_1 of MBS (0.84—1.15) were similar to that ($Q=1.0$) of ST. e_1 of MBS (−0.30—0.08) was higher than that ($e=-0.8$) of ST. This may be understood from the fact that the density of a reactive double bond decreases because of the electron attracting Br-group.

Homopolymer and Copolymer Properties

Table III shows the properties for the *o*-, *m*-, and *p*-MBS polymers. The weight-average molecular weight ($\bar{M}_w$) linearly increased with MBS monomer concentration in the feed. The order of $\bar{M}_w$ for the polymers was expressed as *o*- > *m*- > *p*-MBS, and agreed with that of k for the polymerization. The order of T_g for

Table III. Properties of monobrominated styrene polymers

Polymer	$\bar{M}_w$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	T_g °C	T_m °C	T_d °C
Poly(*o*-MBS)	3.99[a]	1.84		203	325
	7.55[b]	1.44	117	207	
	14.6[c]	1.71	106		324
Poly(*m*-MBS)	3.03[a]	1.80		161	300
	5.27[b]	1.77	92		
	11.8[c]	1.56	93	175	310
Poly(*p*-MBS)	2.78[a]	1.72		192	
	5.10[b]	1.87	136		311
	10.2[c]	2.86	135	224	317

[a] [MBS]=0.88 mol l^{-1}, [AIBN]=8.8 mmol l^{-1}.
[b] [MBS]=1.59 mol l^{-1}, [AIBN]=8.8 mmol l^{-1}.
[c] [MBS]=3.02 mol l^{-1}, [AIBN]=8.8 mmol l^{-1}.

the polymers was *m*- < *o*- < *p*-MBS. Both T_m and T_d for poly(*m*-MBS) were lower than those for poly(*o*-MBS) and poly(*p*-MBS). $\bar{M}_w$ and T_d for the copolymers increased with MBS content. Thus the positional difference of Br-group in MBS affects not only polymerizability but also the properties of the polymers.

REFERENCES

1. M. Kinoshita and M. Nishigaki, *Kogyo Kagaku Zasshi,* **72**, 2332 (1969).
2. T. Okumoto, T. Takeuchi, and S. Tsuge, *Macromolecules,* **6**, 922 (1973).
3. M. Kinoshita and M. Imoto, *Kogyo Kagaku Zasshi,* **68**, 2454 (1965).
4. H. W. Melville and L. Valentine, *Trans. Faraday Soc.,* **51**, 1474 (1955).
5. R. H. Wiley and B. Davis, *J. Polym. Sci.,* **46**, 423 (1960).
6. D. Braun, G. Disselhoff, and F. Quella, *Colloid. Polym. Sci.,* **255**, 735 (1977).
7. C. Walling, E. R. Briggs, and K. B. Wolfstirn, *J. Am. Chem. Soc.,* **70**, 1537 (1948).
8. D. Alsheh and G. Marom, *J. Appl. Polym. Sci.,* **22**, 3177 (1978).
9. S. K. Braiman, *J. Fire Retard. Chem.,* **7**, 130 (1980).
10. R. C. P. Cubbon and J. D. B. Smith, *Polymer,* **10**, 479 (1969).
11. R. C. P. Cubbon and J. D. B. Smith, *Polymer,* **10**, 489 (1969).

12. M. M. Koton, T. M. Kiseleva, and F. S. Florinsky, *J. Appl. Chem. U.S.S.R.*, **26**, 625 (1953).

13. I. Konigsberg and J. J. Grodzinski, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 2649 (1983).

14. M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **86**, 217 (1965).

15. T. Sera, Y. Mabuchi, H. Inoue, Y. Oda, T. Okada, and H. Toita, *Nippon Kagaku Kaishi*, 633 (1992).

16. T. Otsu, "Kobunshi Gosei no Kagaku", Kagaku Dojin, Kyoto, 1989, p 74.

17. G. Odian, "Principles of Polymerization," 3rd ed, John Wiley & Sons, Inc., New York, N.Y., 1991, p 236.

18. L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 96 (1937).

19. T. Yamamoto and T. Otsu, *Chem. Ind.*, 787 (1967).

20. F. Tüdös, T. Kelen, T. F. Berzsnich, and B. Turcsanyi, *J. Macromol. Sci. Chem.*, **A10**, 1513 (1976).

21. T. Alfrey, Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).