Solvent Effects on Radical Polymerization of Vinyl Benzoate and Phenyl Methacrylate

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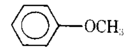
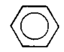
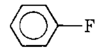
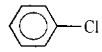
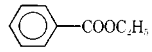
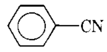
Received December 16, 1975

A number of papers have described the solvent effects on the radical polymerization of vinyl compounds.[1-14] Some of them have determined elementary reaction constants for styrene and methyl methacrylate in various solvents, indicating that a predominant factor of the solvent effects is the viscosity effect on the termination reaction. Termination rate constants were found to be almost inversely proportional to the viscosity of the medium and small solvent effects on the propagation rate constant were observed.[4-14] Complexation of the propagating radicals with solvents has been postulated for this minor solvent dependency of the propagation rate constants, but the observed variation was too small to be distinguished from the experimental error.

We wish to report herein the remarkable effect of aromatic solvents on the propagation rate constants of two vinyl compounds having opposite polar substituent. The monomers are vinyl benzoate and phenyl methacrylate, which were reported to obey normal kinetics.[15-18]

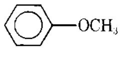
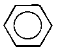
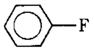
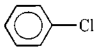
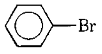
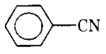
For the determination of the propagation rate constants (k_p) and the termination rate constants (k_t), k_p^2/k_t and k_p/k_t must be determined at the same temperature. The former values were determined from the polymerization rates and the initiation rates and the latter from the lifetimes of the propagating radicals. Since accurate initiation rates could not be determined by the inhibition method in photopolymerization, k_p^2/k_t was determined in polymerizations thermally initiated with 2,2′-azobis(isobutyronitrile) at 30 ± 0.001 °C. The polymerization rate was dilatometrically followed and was confirmed to be proportional to $[M]^{1.05-1.15}[C]^{0.47-0.53}$ for both monomers ($0.05\ M < [C] < 0.20\ M$ and $0.5\ M < [M] < 3.0\ M$). The initiation rates were determined by using 1,1-diphenyl-2-picrylhydrazyl or p-benzoquinone as inhibitor. Photopolymerizations were carried out with 2,2′-azobis(cyclohexane-1-carbonitrile) as initiator at 30 ± 0.001°, using an Ushio 250W high-pressure mercury lamp together with filters (Toshiba UV-DIC and IRQ-80) for 3650A. It was confirmed that photopolymerization rates of both monomers were proportional to $[M]^{1.00-1.10}$ $[C]^{0.50-0.53}$ ($2.00 \times 10^{-3}\ M < [C] < 2.00 \times 10^{-2}\ M$, $0.5\ M < [M] < 3.0\ M$). The average lifetime of the propagating radical was determined by the rotating sector

Table I
Rate Constants for Vinyl Benzoate Polymerization at 30 °C in Various Solvents

Solvents	$R_p \times 10^7$,[a] mol/(L s)	$R_i \times 10^9$,[a,b] mol/(L s)	$(k_p^2/k_t) \times 10^5$,[a] L/(mol s)	$(k_p/k_t) \times 10^7$[c]	$k_p \times 10^{-2}$, L/(mol s)	$k_t \times 10^{-8}$, L/(mol s)
	5.66 ± 0.12 (2)[d]	6.95 ± 0.12 (2)[d]	4.52 ± 0.13	4.40 ± 0.43 (2)[d]	1.06 ± 0.14	2.53 ± 0.63
	8.15 ± 0.13 (3)	7.68 ± 0.12 (2)	8.48 ± 0.18	4.61 ± 0.22 (4)	1.85 ± 0.08	4.02 ± 0.32
	9.14 ± 0.14 (3)	7.10 ± 0.16 (3)	11.5 ± 0.3	4.71 ± 0.15 (2)	2.45 ± 0.13	5.22 ± 0.48
	7.71 ± 0.13 (2)	7.81 ± 0.14 (2)	7.46 ± 0.19	4.48 ± 0.41 (2)	1.68 ± 0.18	3.83 ± 0.76
	3.55 ± 0.12 (2)	6.53 ± 0.15 (2)	1.90 ± 0.01	2.38 ± 0.38 (2)	0.69 ± 0.13	2.57 ± 0.72
	1.77 ± 0.10 (3)	8.78 ± 0.13 (3)	0.36 ± 0.02	1.10 ± 0.10 (2)	0.33 ± 0.03	2.99 ± 0.44
$CH_3COOC_2H_5$	10.71 ± 0.11 (3)	7.16 ± 0.16 (2)	15.7 ± 0.3	5.93 ± 0.44 (3)	2.67 ± 0.33	4.51 ± 0.65

[a] [Azobisisobutyronitrile] = 0.10 M, [monomer] = 1.01 M. [b] Inhibitor = *p*-benzoquinone. [c] From rotating sector method. [Cyclohexanecarbonitrile] = 3.15×10^{-3} M, [monomer] = 1.01 M. [d] The numbers in parentheses are the number of experiments.

Table II
Rate Constants for Phenyl Methacrylate Polymerization at 30 °C in Various Solvents

Solvents	$R_p \times 10^5$,[a] mol/(L s)	$R_i \times 10^8$,[a,b] mol/(L s)	$(k_p^2/k_t) \times 10^2$,[a] L/(mol s)	$(k_p/k_t) \times 10^4$[c]	$k_p \times 10^{-2}$, L/(mol s)	$k_t \times 10^{-6}$, L/(mol s)
	3.52 ± 0.03 (2)[d]	1.13 ± 0.03 (2)[d]	2.62 ± 0.06	1.14 ± 0.07 (2)[d]	2.30 ± 0.15	2.02 ± 0.22
	3.04 ± 0.04 (4)	1.55 ± 0.05 (3)	1.49 ± 0.04	0.85 ± 0.04 (4)	1.76 ± 0.08	2.06 ± 0.21
	2.90 ± 0.03 (2)	1.40 ± 0.03 (2)	1.50 ± 0.05	0.83 ± 0.04 (3)	1.80 ± 0.09	2.16 ± 0.19
	3.40 ± 0.04 (2)	1.31 ± 0.03 (2)	2.21 ± 0.05	0.99 ± 0.05 (2)	2.23 ± 0.11	2.26 ± 0.22
	3.91 ± 0.03 (2)	1.18 ± 0.03 (2)	3.24 ± 0.06	1.38 ± 0.05 (2)	2.35 ± 0.08	1.72 ± 0.11
	4.36 ± 0.03 (3)	1.25 ± 0.04 (2)	3.80 ± 0.08	1.40 ± 0.04 (2)	2.73 ± 0.08	1.96 ± 0.12

[a] [Azobisisobutyronitrile] = 0.10 M, [monomer] = 2.00 M. [b] Inhibitor = 1,1-diphenyl-2-picrylhydrazyl. [c] From rotating sector method. [Cyclohexanecarbonitrile] = 3.00×10^{-3} M, [monomer] = 2.00 M. [d] The numbers in parentheses are the number of experiments.

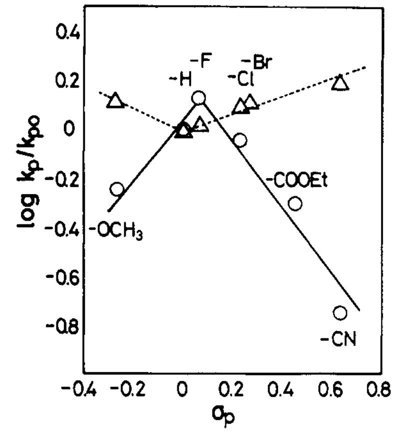


Figure 1. Correlation of propagation rate constants for vinyl benzoate and phenyl methacrylate with Hammett's σ_p of solvents: (○) vinyl benzoate; (△) phenyl methacrylate; k_{po}, propagation rate constants in benzene. Polymerization temperature, 30 ± 0.001 °C.

experiment. The precision of rate constants was expressed by the average deviation.

The results are shown in Tables I and II. The value of k_p for vinyl benzoate is largest in fluorobenzene and smallest in benzonitrile. To our knowledge, these variations in the rate constants with aromatic solvents seem to be the most remarkable ever reported in radical polymerization of vinyl compounds.[5-14] The solvent effects on k_p for phenyl methacrylate are opposite in trend to those observed for vinyl benzoate (Figure 1). These phenomena might be due to inverse polarity of the chain ends.[18,19] If these solvent effects mainly result from the polar participation of solvent in the transition state of the propagation reaction, the change of k_p with solvent should be correlated with the polarity of the solvent. No correlation was found between k_p and $1/\epsilon$ or $(\epsilon - 1)/(2\epsilon + 1)$, where ϵ is the dielectric constant of solvent. The relationship of k_p with Hammet σ_p values of substituents was shown in Figure 1. The k_p is shifted in the same direction by either donor or acceptor substituents. Since similar effects have been found in some radical reactions in which aromatic rings directly or indirectly participate,[19-21] the variation of k_p with σ_p suggests that a participation of the π system of solvent to the reactivity of the propagating radical must be taken into account. The possibility of copolymerization is ruled out by the reported evidences that the copolymerization of vinyl monomers with simple aromatic compounds did not take place at all.[22-26] One of the possible explanations for the solvent effect might be the differences in the chain transfer rates to solvent and/or the reinitiation rates by the resulting solvent radicals. It was found, however, that the solvent dependency of k_p did not correlate with the chain transfer constants to solvent.[27]

Another influence must be considered for the solvent effect. The fact that the polymerization rate of vinyl benzoate is far lower than that of vinyl acetate has been explained in terms of reversible complex formation between the propagating radical and aromatic ring.[26] The k_p for vinyl benzoate in ethyl acetate (Table I) is one fifth of that for vinyl acetate in bulk.[28] This fact indicates that the propagating radical of vinyl benzoate is stabilized by the aromatic ring, since methyl affinity for vinyl benzoate has been found to be similar to that for vinyl acetate.[26] Thus, influence of solvent might arise from the intermolecular reversible complex formation of the propagating radical with aromatic solvents. The decrease in k_p for vinyl benzoate in aromatic solvents compared to that in ethyl acetate also suggests that intermolecular complex formation of the propagating radical with solvents should be taken into account.

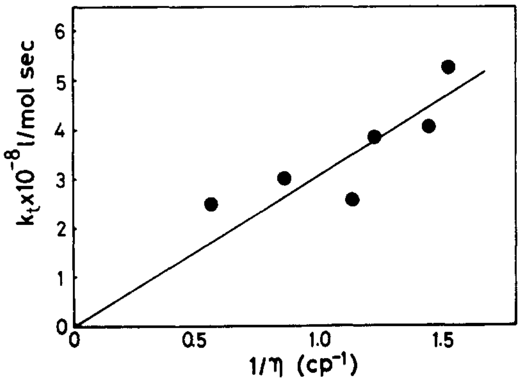


Figure 2. Termination rate constants for vinyl benzoate polymerization as a function of medium fluidity.

The termination rate constants are correlated in Figure 2 with the viscosities of the polymerization system, which are calculated from the viscosities of the constituents by assuming a linear relation between fluidity and volume composition. This result suggests that the termination reaction is diffusion controlled, as shown in the cases of styrene and methyl methacrylate.[5,8,10]

Interpretation of the solvent effect is being studied and will be published in another paper.

References and Notes

(1) G. Henrici-Olive and S. Olive, *Makromol. Chem.*, **68**, 219 (1963).
(2) G. Henrici-Olive and S. Olive, *Z. Phys. Chem.*, (*Frankfurt am Main*), **47**, 286 (1965).
(3) G. Henrici-Olive and S. Olive, *Z. Phys. Chem.*, (*Frankfurt am Main*), **48**, 35, 51 (1966).
(4) G. M. Burnett, W. S. Dailey, and J. M. Pearson, *Trans. Faraday Soc.*, **61**, 1216 (1965).
(5) C. H. Bamford and S. Brumby, *Makromol. Chem.*, **105**, 122 (1967).
(6) G. M. Burnett, G. G. Cameron, and B. M. Parker, *Eur. Polym. J.*, **5**, 231 (1969).
(7) G. M. Burnett, G. G. Cameron, and M. M. Zafar, *Eur. Polym J.*, **6**, 823 (1970).
(8) G. M. Burnett, G. G. Cameron, and S. N. Joiner, *J. Chem. Soc., Faraday Trans. 1*, **69**, 322 (1973).
(9) M. M. Zafar, *Makromol. Chem.*, **157**, 219 (1972).
(10) J. P. Fischer, G. Mucke, and G. V. Schulz, *Ber. Bunsenges. Phys. Chem.*, **73**, 154 (1969).
(11) J. P. Fischer and G. V. Schulz, *Ber. Bunsenges. Phys. Chem.*, **74**, 1077 (1970).
(12) M. M. Zafar and R. Mahmud, *Makromol. Chem.*, **175**, 2627 (1974).
(13) T. Yamamoto and T. Yamamoto, *J. Chem. Soc., Jpn.*, **92**, 1300 (1972).
(14) T. Yamamoto, T. Yamamoto, and T. Yamamoto, the 23rd Annual Meeting of the Society of Polymer Science, Japan, Tokyo, 1974, preprint p 140.
(15) A. Vrancken and G. Smets, *Makromol. Chem.*, **30**, 197 (1959).
(16) S. Banerjee and M. S. Muthana, *J. Polym. Sci.*, **37**, 469 (1959).
(17) K. Yokota, M. Kani, and Y. Ishii, *J. Polym. Sci., Part A-1*, **6**, 1325 (1968).
(18) M. Kinoshita, T. Irie, and M. Imoto, *Makromol. Chem.*, **110**, 47 (1967).
(19) T. Otsu, "Progress in Polymer Science", Vol. 1, M. Imoto and S. Onogi, Ed., Kodansha, Tokyo, 1971, pp 39–55.
(20) T. Yamamoto and T. Otsu, *Bull. Chem. Soc., Jpn.*, **40**, 2449 (1967).
(21) T. Yamamoto and T. Otsu, *J. Polym. Sci., Part A-1*, **6**, 49 (1968).
(22) J. W. Breitenbach, G. Billek, G. Faltlhansl, and E. Weber, *Monatsh. Chem.*, **92**, 1100 (1961).
(23) G. A. Mortimer and L. C. Arnold, *J. Am. Chem. Soc.*, **83**, 4986 (1961).
(24) G. Henrici-Olive and S. Olive, *Makromol. Chem.*, **51**, 236 (1962).
(25) H. C. Haas and H. Husek, *J. Polym. Sci., Part A*, **2**, 2297 (1964).
(26) G. F. Santee, R. H. Marchessault, H. G. Clark J. J. Kearny, and V. Stannett, *Makromol. Chem.*, **73**, 177 (1964).
(27) J. T. Clarke, R. O. Howard, and W. H. Stockmayor, *Makromol. Chem.*, **44/46**, 427 (1961).
(28) L. J. Young, "Polymer Handbook", 2nd ed, J. Brandrup and E. H. Immergut, Ed., Wiley, New York, N.Y., 1975, Chapter II, p 50.