

SHORT COMMUNICATION

Study on the Dual Nature of the Propagating Radical of Methyl Methacrylate

Mikiharu KAMACHI, Der Jang LIAW, and Shun-ichi NOZAKURA

*Department of Polymer Science, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan.*

(Received March 20, 1978)

KEY WORDS Methyl Methacrylate / Propagating Radical / Phenyl Methacrylate / Copolymerization / Fineman—Ross Equation / Hammet Equation /

Research on the ability of a free radical to form a charge-transfer complex with organic molecules is one of the recent problems in radical reactions.¹ In previous papers,²⁻⁵ we reported that the effect of aromatic solvents on the radical polymerization of vinyl compounds was ascribed to a charge-transfer complex between the propagating radical and aromatic solvents. The propagating radical of methyl methacrylate (MMA) having an electron-withdrawing group on the side chain was assumed to be an electron-acceptor from aromatic solvents. Several papers have been published on the nature of the propagating radical of MMA.⁶⁻¹⁰ Some of these show that the radical is electron-poor⁸⁻⁹ and the other shows that the radical is electron-rich.¹⁰ In order to confirm whether or not these unexpected opposite observations are correct, further information has to be added on the nature of the poly(MMA) propagating radical. We will report here on the copolymerization of MMA with phenyl methacrylate (PhMA) and *p*-substituted PhMA (*p*-X-PhMA) and discuss the nature of the poly(MMA) radical.

Phenyl methacrylate was prepared as described in a previous paper.³ *p*-Tolyl methacrylate (*p*-CH₃-PhMA), *p*-chlorophenyl methacrylate (*p*-Cl-PhMA), *p*-methoxyphenyl methacrylate (*p*-CH₃O-PhMA) and *p*-acetylphenyl methacrylate (*p*-CH₃-CO-PhMA) were prepared by a reaction of corresponding phenols with methacryloyl chloride.³ *p*-Cl-PhMA and *p*-CH₃-PhMA were purified by the same method as PhMA;³ bp 142—143°C (23 mm) [lit.¹¹ bp 142—146°C (23 mm)] and 81°C (1

mm) [lit.¹² bp 82°C (1—2 mm)], respectively. *p*-CH₃O-PhMA was purified by recrystallization from ethyl alcohol and *p*-CH₃CO-PhMA from methyl alcohol until colorless crystals were obtained; mp 63°C (lit.¹³ 63—64°C) and mp 91°C (lit.¹² 90.5—92.0°C) respectively. MMA, benzene and 2, 2'-azobisisobutyronitrile (AIBN) were purified as previously described.^{3,14}

Solution copolymerization was carried out in benzene at 60±0.01°C in a sealed tube, using AIBN (6.1×10⁻³ mol/l) as an initiator. The mixture was degassed by a freezing and thawing method three times and sealed off under vacuum. (<10⁻⁵ mmHg) After the required polymerization time, the resulting copolymer was obtained by pouring the contents of the tube into a large amount of methanol. The copolymer was purified several times by a benzene—methanol system and then dried by freeze-drying. The monomer conversions did not exceed 7%. The composition of copolymers was determined by carbon analysis for the copolymers of *p*-CH₃O-PhMA, *p*-CH₃-PhMA, *p*-CH₃CO-PhMA or PhMA and by chlorine analysis for the copolymers of *p*-Cl-PhMA. The monomer reactivity ratio was calculated by using the Fineman—Ross equation,

The monomer reactivity ratios (*r*₁ and *r*₂) thus obtained are shown in Table I together with *Q* and *e* values for *p*-X-PhMA, calculated by assuming *Q*=0.74 and *e*=0.40 for MMA.¹⁵ The error of monomer reactivity ratios evaluated is very small as shown in Table I. All of the reactivity ratios *r*₁ are smaller than unity, indicating that

Table I. Monomer reactivity ratios for MMA (M_1)— p -X-PhMA (M_2) copolymerization and Q_2 , e_2 values for p -X-PhMA

X in X-PhMA	r_1	r_2	$1/r_1$	Q_2^a	e_2^a
p -OCH ₃	0.719±0.007	1.19 ±0.041	1.39	1.20	0.79
p -CH ₃	0.587±0.008	1.28 ±0.031	1.70	1.56	0.93
H	0.554±0.010	0.991±0.040	1.80	1.84	1.21
p -Cl	0.538±0.003	1.08 ±0.023	1.86	1.30	1.14
p -COCH ₃	0.471±0.004	0.672±0.025	2.12	2.41	1.47

^a Calculated with $Q_1=0.74$, $e_1=0.40$ for methyl methacrylate (M_1).

PhMA and p -X-PhMA have higher reactivity than MMA toward the poly(MMA) radical. The larger reactivity of PhMA or p -X-PhMA may be ascribed to the larger resonance of their π -electron system. The relative reactivities ($1/r_1$) of p -X-PhMA toward the poly(MMA) radical are plotted by using the ordinary Hammett equation

$$\log(1/r_1) = \rho\sigma_p + \text{constant}$$

where σ_p is the Hammett substituent constant and ρ is a reaction constant. The result is shown in

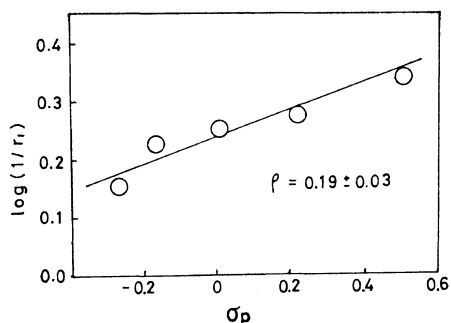


Figure 1. Correlation between relative reactivities of p -X-PhMA toward poly(MMA) radical and Hammett σ_p constants of substituent.

Figure 1. From this figure a linear relationship with a slope of small positive values ($\rho=0.19$) was obtained. The MMA growing end has electronegative feature to phenyl methacrylate derivatives, being consistent with the results obtained from its copolymerization with various kinds of alkyl methacrylates.¹⁰ This result is not consistent with that obtained from copolymerization of MMA with p -substituted styrene⁶⁻⁸ and phenyl vinyl sulfide⁹ since negative ρ values have been shown in both the copolymerizations. This phenomenon suggests that the sign of ρ value depends on the

nature of comonomers. When comonomers having negative e values such as styrene and phenyl vinyl sulfide are used, the poly(MMA) radical seems to behave as electropositive. On the contrary, this radical is electronegative for phenyl methacrylate and its derivatives with positive e values. This phenomenon may be ascribed possibly to the ability of a free radical to gain or lose an electron.¹⁶ Thus, we are led to the conclusion that the poly(MMA) radical can be either an electron-donor or an electron-acceptor to the comonomers according to the electron density of their double bonds.

Previously we explained the solvent effect on the radical polymerization of vinyl compounds in aromatic solvents by the formation of donor-acceptor complexes of their propagating radicals with solvents.²⁻⁵ In our explanation, the radical behaved as an electron-donor as well as an electron-acceptor. The observed nature of the poly(MMA) radical supports the explanation for the aromatic solvent effect.

REFERENCES

1. A. Tkáč, K. Veselý, and L. Omelka, *J. Phys. Chem.*, **75**, 2575 (1971).
2. M. Kamachi, J. Satoh, D. J. Liaw, and S. Nozakura, *Macromolecules*, **10**, 501 (1977).
3. M. Kamachi, D. J. Liaw, and S. Nozakura, *Polym. J.*, **9**, 307 (1977).
4. M. Kamachi, J. Satoh, and S. Nozakura, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
5. M. Kamachi, D. J. Liaw, and S. Nozakura, *Polym. Prepr., Jpn.*, **25**, 611 (1976).
6. C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).
7. C. Walling, D. Seymour, and K. B. Wolfstirn, *J. Am. Chem. Soc.*, **70**, 1544 (1948).
8. T. Otsu, *Kogyo Kagaku Zasshi*, **70**, 1854 (1967).
9. K. Tsuda, S. Kobayashi, T. Otsu, *J. Polym. Sci.*,

The Dual Nature of the Poly(MMA) Radical

- Part A-1*, **6**, 41 (1968).
10. K. Yokota, M. Kani, and Y. Ishii, *J. Polym. Sci., Part A-1*, **6**, 1325 (1968).
 11. S. Patai, M. Bentov, and M. E. Reichamann, *J. Am. Chem. Soc.*, **74**, 845 (1952).
 12. T. Otsu, T. Ito, Y. Fujii, and M. Imoto, *Bull. Chem. Soc. Jpn.*, **41**, 204 (1968).
 13. M. M. Koton, T. A. Sokolova, M. H. Savitskaia, and T. M. Kiseleva, *Zh. Obshch. Khim.*, **28**, 417 (1958).
 14. M. Kamachi, M. Kohno, D. J. Liaw, and S. Katsuki, *Polym. J.*, **10**, 69 (1978).
 15. L. J. Young, "Polymer Handbook" 2nd ed., J. Brandrup and E. H. Immergut, Ed., John Wiley, New York, N. Y., 1975, Chapter 11, p 401.
 16. M. Szwarc, *J. Macromol. Sci.-Chem.*, **A6**, 876 (1972).