Measurement of Free-Radical Propagation Rate Coefficients for Ethyl, Butyl, and Isobutyl Methacrylates by Pulsed-Laser Polymerization

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Received December 13, 1994; Revised Manuscript Received March 10, 1995[⊗]

ABSTRACT: Propagation rate coefficient (k_p) values have been measured for monomers in the methacrylate family—ethyl (EMA), *n*-butyl (BMA), and isobutyl (*i*-BMA)—using pulsed-laser polymerization combined with gel permeation chromatography (GPC). Molecular weight calibrations were verified using both commercial polymer standards and GPC viscometry. Covering the temperature range of 10–90 °C, the k_p results are well fit by the Arrhenius relationship and are compared to previous determinations for methyl methacrylate (MMA). A definite increase in k_p is observed when progressing from MMA to EMA to BMA, with k_p differences between BMA and *i*-BMA slight.

Introduction

The pulsed-laser polymerization (PLP) technique is a direct and reliable method for estimating free-radical propagation rate coefficients (k_p) from molecular weight distributions (MWDs).[1–3] The technique involves the exposure of a monomer system with photoinitiator to laser flashes which generate a periodic profile of polymer radicals. Between flashes, the radical concentration decreases due to radical–radical termination. At the end of the period between flashes (t_0), the radicals which have escaped termination have propagated to an average chain length P_0. This chain length is given by the simple equation:

$$P_0 = k_p[\mathrm{M}]t_0 \qquad (1)$$

where [M] is the monomer concentration. When the next flash arrives, these radicals are exposed to a high concentration of newly generated radicals, which leads to a greatly increased probability for their termination. Thus, the formation of dead polymer molecules with length close to P_0 is favored. With a measure of P_0, k_p can be calculated from eq 1. With proper analysis, a single PLP experiment not only yields a direct estimate of k_p but also provides consistency checks as to the validity of the estimate.[3]

Our previous efforts have resulted in the determination of k_p values for methyl methacrylate (MMA), styrene, chloroprene, and vinyl acetate by PLP.[3,4] This paper summarizes recent measurements for other monomers in the methacrylate family—ethyl (EMA), *n*-butyl (BMA), and isobutyl (*i*-BMA).

Experimental Section

The experimental setup has been described in our previous work.[3] A Quanta-Ray pulsed DCR11 Nd:YAG laser with a harmonic generator is used to generate light of wavelength 355 nm at a pulse energy of 70 mJ/pulse and a half-height pulse width of 6 ns. All experiments are run with a pulse repetition rate of 10 Hz (t_0 = 0.1 s) for a total time sufficient to allow 0.5–1.5% conversion of the 4-mL monomer sample to polymer. The methacrylate monomers and benzoin photoinitiator (concentration of 1 mmol/L) were obtained from Aldrich Chemical and used as received. Experiments for all systems covered a temperature range of 10–90 °C.

Table 1. Mark–Houwink Coefficients

monomer	K (dL/g)	a
styrene	1.60×10^{-4}	0.706
EMA	1.549×10^{-4}	0.679
BMA	0.501×10^{-4}	0.758
***i*-BMA**	0.501×10^{-4}	0.758

After polymerization, the samples were directly diluted with tetrahydrofuran (THF) to polymer concentrations of 0.1–0.3%. Analysis was performed at 30 °C on a GPC system consisting of a Waters pump (Model 590), Waters autosampler (WISP 712), two Shodex columns (KF80M), and a Waters differential refractometer (Model 410). PEMA and PBMA analyses were based upon universal calibration using narrow-distribution polystyrene standards (MW ranging from 500 to 8.5 × 10^6) and known Mark–Houwink (M–H) coefficients;[5] the PBMA constants were also used for the analysis of P*i*-BMA. Values are summarized in Table 1.

Accurate GPC calibration is essential for estimation of k_p. Much attention was paid to this issue because of the differences between the EMA and BMA k_p measurements reported in this work and other literature values obtained by the PLP method.[6] (See the Results section.) Broad MW standards, obtained from Scientific Polymer Products, Inc. (SPP), were run to check the calibration. As shown in Table 2, the GPC values calculated according to universal calibration show excellent agreement with the primary M_n (measured by membrane osmometry) and M_w values (light scattering) reported by the supplier.

To further validate the calibration, the SPP polymer standards were also analyzed by GPC viscometry. The samples were run in THF at 35 °C on a Waters 150CV, modified to eliminate distortion of the viscosity chromatogram caused by a pressure drop across the refractometer; narrow fraction polystyrene standards were used to develop the primary calibration. Data were reduced using the Waters "Expert Ease" CV software. The M_n and M_w results, calculated from the direct measurement of polymer viscosity without the use of M–H calibration constants, are also reported in Table 2. Agreement between the GPC viscometry results and the values supplied by SPP is quite good. The only MW average not in good agreement is the M_n value of the BMA polymer standard. This mismatch is believed to be the result of a low molecular weight tail, which is not captured accurately by the analysis software as it extrapolates the viscometer data to the low-MW region. The PBMA M_w value, however, shows good agreement, as do both averages for the P*i*-BMA standard.

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1995.

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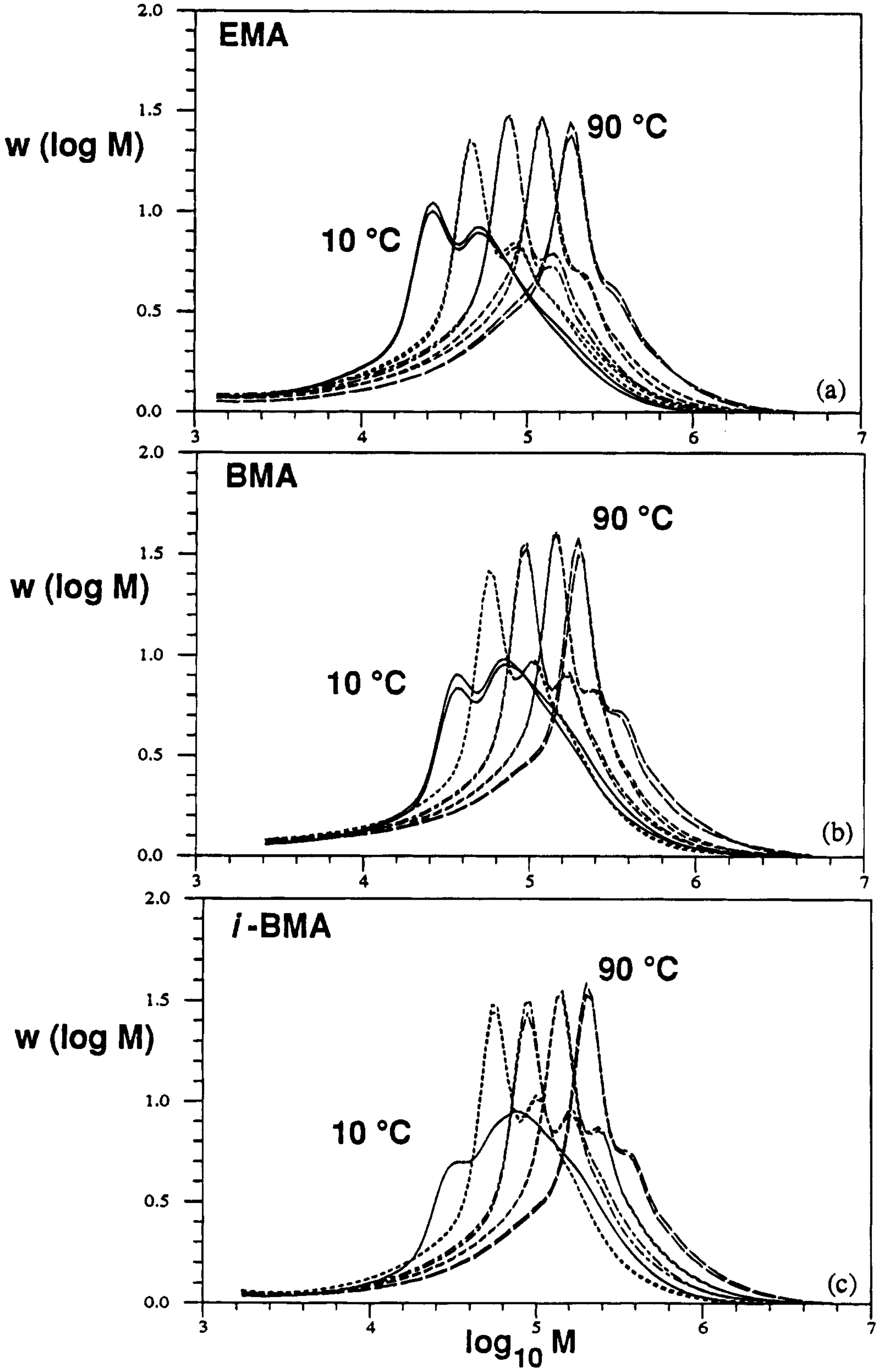

Figure 1. Molecular weight distributions produced by pulsed-laser polymerization at 10 Hz, with temperature varying from 10 to 90 °C in 20 °C intervals for (a) EMA, (b) BMA, and (c) *i*-BMA. MWDs progress from left to right with increasing T, with duplicate samples at each condition..

The GPC viscometry results validate the primary M_n and M_w values reported by SPP for their PEMA, PBMA, and P*i*-BMA standards. Since the averages calculated using universal calibration are also in excellent agreement, it can be concluded that the M–H coefficients measured by Samay *et al.*[5] are accurate. Thus, the k_p values calculated from the MWDs of the pulsed-laser generated polymer samples can be reported with confidence.

To analyze the experimental data, it is necessary to transform the GPC data from a mass MWD on a logarithmic scale to a number distribution on a linear scale. As described previously,[3] this is a two-step process. The relationship between a linear and log scale distribution is given by:

$$w(\log M) = \ln(10) M w(M) \tag{2}$$

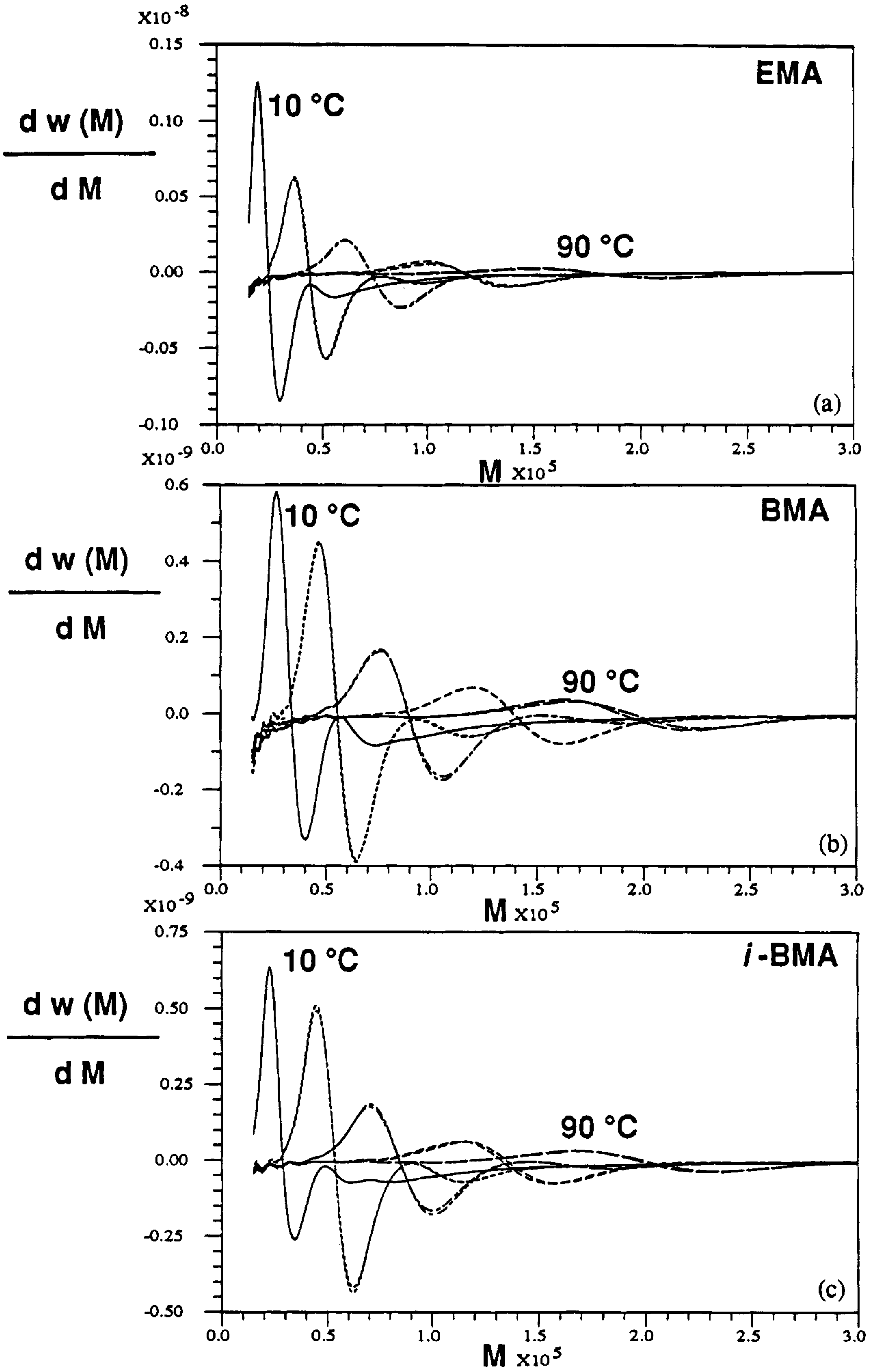

Figure 2. Derivative plots for curves of Figure 1, as calculated from the *w(M)* distributions.

where $w(\log M)$ is the weight differential of chain molecular weight M on a logarithmic plot, and $w(M)$ is the weight differential of chain molecular weight M on a linear plot. The final transformation to a number differential curve is performed according to the relationship

$$f(M) \sim w(M)/M \qquad (3)$$

$w(\log M)$ and $w(M)$ are normalized so that the area under the MWD is unity; $f(M)$ is not normalized. Inflection points are obtained by fitting the experimental MWD with cubic smoothing splines, followed by differentiation of the splines. Inflection points from the $w(M)$ and $f(M)$ distributions show good agreement, as tabulated in the Results section. In accordance with theory,[1] the inflection point from the derivative plot of

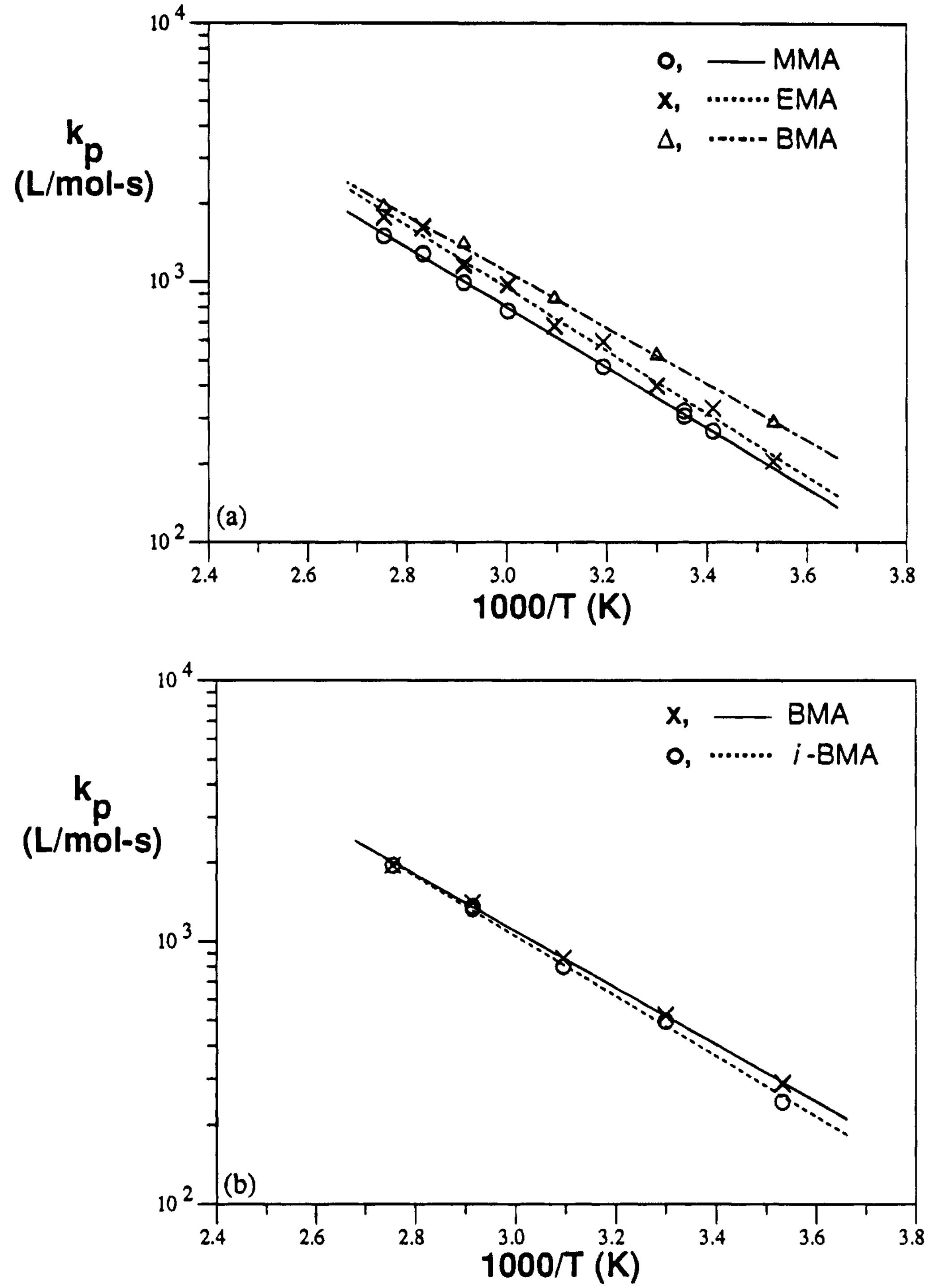

Figure 3. Arrhenius plots of k_p for (a) MMA,[3] EMA, and BMA and (b) BMA and *i*-BMA.

Table 2. Verification of GPC Calibrations Using Commercial Broad MW Standards

	primary values		universal calibration		GPC viscometry	
monomer	M_n	M_w	M_n	M_w	M_n	M_w
EMA	1.26×10^5	3.40×10^5	1.33×10^5	3.32×10^5	1.21×10^5	3.33×10^5
BMA	7.35×10^4	3.20×10^5	7.40×10^4	3.01×10^5	9.60×10^4	3.11×10^5
***i*-BMA**	1.40×10^5	3.00×10^5	1.36×10^5	3.12×10^5	1.42×10^5	3.26×10^5

the $f(M)$ distribution is used to calculate k_p from a rearranged form of eq 1:

$$k_p = \frac{M_0}{1000 \varrho t_0} \qquad (4)$$

where M_0 is the polymer MW at the inflection point, k_p has units of L/mol·s, and monomer density ϱ has units of g/cm^3. Monomer densities were obtained from the DIPPR database; these estimates showed good agreement with measurements for BMA[7] and EMA[8] at 30 °C, as well as recently reported BMA values by Bergert *et al.*[9]

Results

GPC MWDs for EMA, BMA, and *i*-BMA pulsed in the temperature range of 10–90 °C are shown as Figure 1,

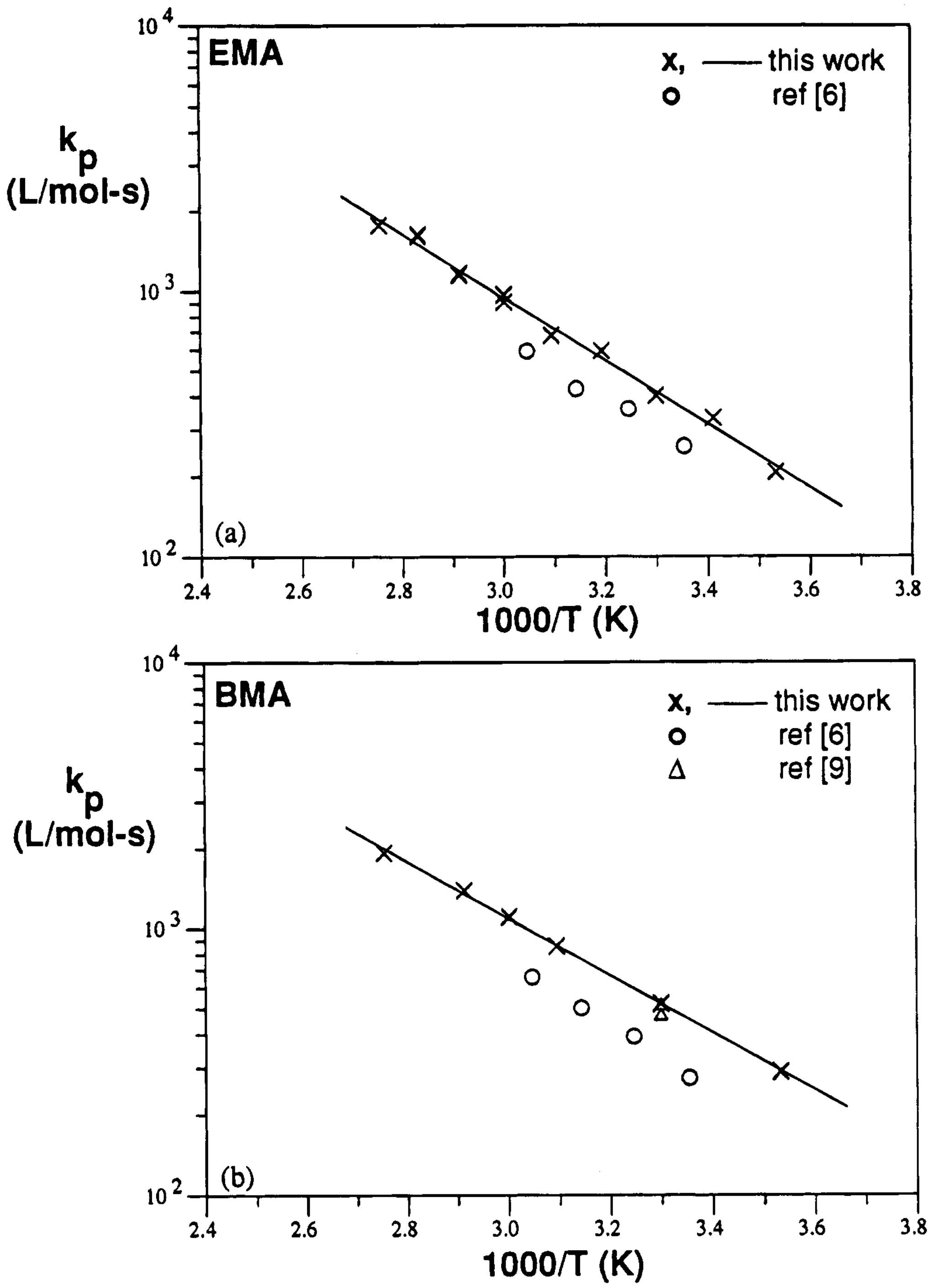

Figure 4. Comparison with other PLP k_p data from the literature for (a) EMA and (b) BMA.

with corresponding derivative plots (from $w(M)$ distributions) shown on Figure 2. Duplicate experiments were performed at each temperature; agreement among each pair is excellent. All of the samples showed excellent MWD traces, with clear, well-defined primary inflection points and observable secondary inflection points at twice the molecular weight. The complete results—inflection points and k_p estimates—are contained in Tables 3–5.

The k_p values have been used to create the Arrhenius plots shown as Figure 3. Results for MMA are taken from our previous work.[3] Figure 3a shows the increase in k_p observed in the progression from MMA to EMA to BMA, while Figure 3b examines differences between BMA and *i*-BMA. Linear regression of the data sets gives the following relations, with k_p in units of L/mol·s and T in K:

MMA:[3] $$\ln(k_p) = (14.69 \pm 0.11) - (2669 \pm 34)/T \tag{5}$$

EMA: $$\ln(k_p) = (15.11 \pm 0.17) - (2753 \pm 55)/T \tag{6}$$

BMA: $$\ln(k_p) = (14.41 \pm 0.09) - (2472 \pm 29)/T \tag{7}$$

i-BMA: $$\ln(k_p) = (14.72 \pm 0.13) - (2590 \pm 42)/T \tag{8}$$

Table 3. Inflection Points and k_p Estimates for EMA

T (°C)	ϱ (g/cm^3)	M_0 from weight MWD	M_0 from number MWD	k_p (L/mol·s)
10	0.9215	19 500	19 000	206
		19 500	19 000	206
20	0.9125	30 750	30 000	329
		30 750	30 000	329
30	0.9034	36 500	36 000	399
		36 750	36 250	401
40	0.8942	54 250	52 750	590
		54 000	52 750	590
50	0.8848	60 500	59 500	673
		60 750	60 000	678
60	0.8752	85 250	84 500	966
		86 250	85 250	974
		80 000	79 250	906
		81 000	79 500	908
70	0.8654	100 000	99 250	1147
		101 750	101 500	1173
80	0.8555	141 500	139 750	1634
		139 000	137 500	1607
90	0.8453	150 250	149 250	1766
		150 500	150 000	1775

Table 4. Inflection Points and k_p Estimates for BMA

T (°C)	ϱ (g/cm^3)	M_0 from weight MWD	M_0 from number MWD	k_p (L/mol·s)
10	0.9041	27 000	26 250	290
		26 750	26 000	288
30	0.8861	46 750	46 000	519
		47 000	46 500	525
50	0.8676	76 250	74 500	859
		76 000	74 250	856
60	0.8582	97 000	95 500	1113
		96 000	94 750	1104
70	0.8486	120 500	118 250	1393
		120 000	118 500	1396
90	0.8290	166 250	159 750	1927
		166 250	159 750	1927

Table 5. Inflection Points and k_p Estimates for *i*-BMA

T (°C)	ϱ (g/cm^3)	M_0 from weight MWD	M_0 from number MWD	k_p (L/mol·s)
10	0.9041	24 300	22 750	252
30	0.8861	44 750	43 750	494
		44 750	44 000	497
50	0.8676	70 500	69 500	801
		70 500	69 000	795
70	0.8486	116 000	114 750	1352
		114 000	112 000	1320
90	0.8290	169 000	159 750	1927
		166 750	159 750	1927

Although there is a definite increase in k_p values going from MMA to EMA to BMA, it is not reflected in consistent trends for the fitted Arrhenius pre-exponential factors and activation energies. The k_p values for BMA and *i*-BMA are similar, with a possible difference in the activation energies. Additional methacrylate systems are being studied to further examine the relationship between k_p and monomer structure.

It is puzzling to note that these results are not in agreement with the PLP results reported by Davis *et al.* for EMA and BMA in the range of 25−55 °C.[6] As shown in Figure 4, our k_p values are 30−50% higher. This mismatch is surprising, since k_p estimates for styrene and MMA from the two research labs show good agreement.[3,6] Thus, it is probable that the differences for the EMA and BMA, systems are a result of GPC calibration. The multiple calibration checks outlined in the Experimental Section were an attempt to explain the differences illustrated by Figure 4. Although no definite conclusion can be made as to the cause of the mismatch, the calibration checks performed during this effort give us confidence in our data analysis and reported results. Our data for BMA at 30 °C are in good agreement with recently reported values by Bergert *et al.*,[9] also obtained using the PLP technique; these data points are also shown on Figure 4.

Conclusions

Pulsed-laser techniques allow for the robust and direct measurement of k_p for free-radical polymerization systems. However, the accuracy of the technique is directly dependent on the accuracy of the underlying GPC calibration. As PLP is employed to examine a wider range of monomer and comonomer systems, documentation of GPC techniques and calibration checks becomes more essential. For the monomer systems reported in this paper, GPC calibrations were checked through the use of commercial polymer standards and GPC viscometry.

After verification of GPC calibration, k_p values for a monomer can be quickly and accurately determined over a wide temperature range. The results for EMA, BMA, and *i*-BMA, measured in the range of 10−90 °C, are well fit by the Arrhenius relationship. A definite increase in k_p is observed when progressing from MMA to higher homologues in the series, but the difference between BMA and *i*-BMA is too small to judge the significance. The data reported in this paper are the first step in a larger effort to examine how k_p varies with monomer structure, with the ultimate goal of developing models for prediction of radical-monomer propagation rate coefficients.

Acknowledgment. The authors thank F. W. Bailey and R. Prybolsky for their excellent work during the production and analysis of the PLP samples.

References and Notes

(1) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(2) Buback, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 851.

(3) Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410.

(4) Hutchinson, R. A.; Richards, J. R.; Aronson, M. T. *Macromolecules* **1994**, *27*, 4530.

(5) Samay, G.; Kubin, M.; Podesva, J. *Angew. Makromol. Chem.* **1978**, *72*, 185.

(6) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1990**, *23*, 2113.

(7) Burnett, G. M.; Evans, P.; Melville, H. W. *Trans. Faraday Soc.* **1953**, *49*, 1096.

(8) Yokota, K.; Kani, M.; Ishii, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *6*, 1325.

(9) Bergert, U.; Buback, M.; Heyne, J. *Macromol. Rapid Communication*, submitted for publication.

MA946190D