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Free-radical propagation rate coefficients for hydroxyalkyl methacrylates and cyclohexyl methacrylate

Hou-Hsein Chu · Juan-Dan Wu

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Abstract Free-radical propagation rate coefficients (k_p) at 30°C for the homopolymerization of cyclohexyl methacrylate (CHMA), 4-hydroxybutyl methacrylate (HBMA), 2-hydroxypropyl methacrylate (HPMA), and 2-hydroxyethyl methacrylate (HEMA) were determined to be 1070, 917, 640, and 71.9 (L mol^{-1}s^{-1}), using the rotating-sector method. The k_p value increases rapidly, and the value of life time of free radicals (τ_s) increases smoothly with increasing the alkyl chain length in the hydroxyalkyl pendant group of the monomer. Values for the steady-illumination polymerization rate for CHMA, HBMA and HPMA are much larger than that for HEMA. Comparisons of k_p values from different sources were also made.

Key words cyclohexyl methacrylate · 2-hydroxyethyl methacrylate · 4-hydroxybutyl methacrylate · 2-hydroxypropyl methacrylate · propagation rate coefficient

Introduction

The determination of propagation rate coefficients (k_p) for certain monomers such as cyclohexyl methacrylate (CHMA), 4-hydroxybutyl methacrylate (HBMA), 2-hydroxypropyl methacrylate (HPMA), 2-hydroxyethyl methacrylate (HEMA) are quite important to both technology and academics. Either the lacking of available data or the existing of inconsistency among various source data leaves ample space for future exploiting.

Scattered propagation rate coefficient data are found for CHMA [1–5] in literature: ($k_p/k_t^{1/2}$)=0.185 (L/mol-s)$^{1/2}$ and ΔH=12.7 kcal/mol in solution polymerization at 44.1°C [2]; k_p of 1,190 (L/mol-s) in solution polymerization (using benzene as solvent) at 30°C, determined by using the rotating-sector technique [3]; k_p of 510 (L/mol-s) at 60°C from electron spin resonance (ESR) spectroscopic determination [4]; k_p of 260 (L/mol-s) obtained from emulsion polymerization at 50°C [5]; and k_p of 619, 930, 1,140 and 1,635 (L/mol-s) from the pulse-laser polymerization-size exclusion chromatograph (PLP-SEC) experiment [1] at 30, 40, 50, and 60°C, respectively.

There are propagation rate coefficient data for HEMA: k_p of 1,295, 1,986, 2,107, 3,367 and 3,963 (L/mol-s) at 30, 40, 50, 60 and 70°C, respectively, obtained from the PLP-SEC experiment [1]; k_p of 200 (L/mol-s) at 60°C, obtained from emulsion polymerization [6]; and ($k_p/k_t^{1/2}$) of 0.35 (L/mol-s)$^{1/2}$ by a steady photo-polymerization [7].

An analysis performed in an emulsion polymerization of 2-hydroxypropyl methacrylate (HPMA) estimated the propagation rate coefficient to be 4,200 (L/mol-s) at 80°C [8].

Valuable data for CHMA, HEMA, and HPMA have also been obtained by the PLP-SEC) technique [9, 10].

The PLP technique gained its appeal in the determination of k_p, due to that it allowed the direct determination of k_p from the chain-length distribution of a polymer prepared by periodic laser pulses. However, the weakness of the PLP technique [11] is that it experienced an extremely high variation of radical concentration in the course of one period, while the pseudostationary polymerizations were initiated by periodic laser pulses.

For the PLP data of acrylates published so far, consistent values of k_p were obtained only at temperatures below 30°C. This is attributed to the fact that the propagation rate is decreased by the occurrence of mid-chain radicals at higher

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H.-H. Chu (✉) · J.-D. Wu
Department of Chemical Engineering, Feng Chia University,
100 Wenhwa Rd.,
Taichung 407, Taiwan
e-mail: hhchu@fcu.edu.tw

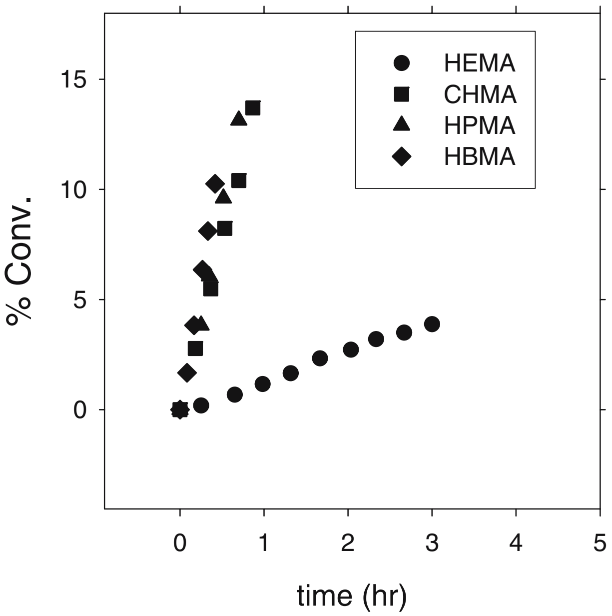

Fig. 1 Conversion-time curves for polymerizations under the steady-illumination without the rotating sector

temperatures, where transfer-to-polymer reaction is followed by slow re-initiation and β-scission [12].

It has been mentioned that the conventional technique of combining (k_p^2/k_t) and (k_p/k_t) data in the rotating sector technique was inappropriate since k_t is chain-length dependent [13–17] and the polydispersity of the terminating chain varied when the respective (k_p^2/k_t) and (k_p/k_t) data were measured. However, the rotating sector technique was considered competitive to the PLP method, if some care is taken with respect to the choice of experimental conditions.

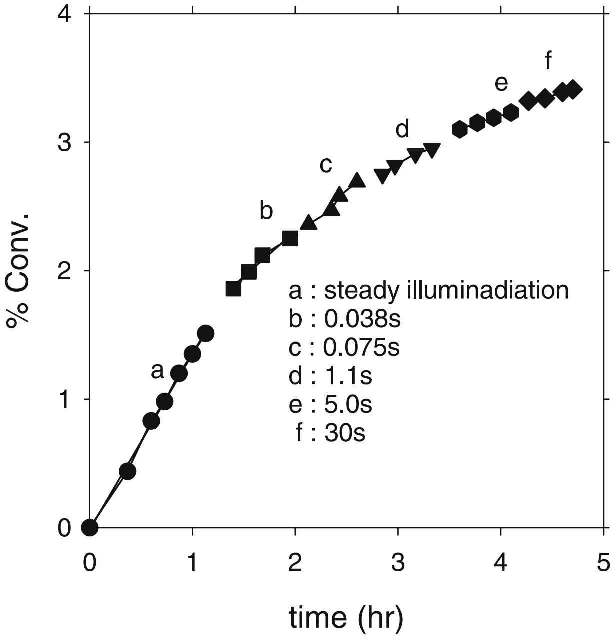

Fig. 2 Conversion-time curves of HEMA with varying illumination time

The situation improves in the chain-length dependent termination, such as : (a) for smaller rate of initiation, (b) for higher order points of inflection, (c) if termination is by combination, (d) if the role played by the shorter one of the two chains becomes less dominant [11].

In this study, the rotating sector technique was utilized in determining the k_p values for CHMA and the homologues of hydroxyalkyl methacrylates, such as HEMA, HPMA and HBMA. These data would provide crucial clues to reconcile the existing data.

Experimental

Materials and methods

Monomer, 2-hydroxyethyl methacrylate (HEMA, from Across Organics, purity > 96%) was purified by distillation under reduced pressure. Other monomers, such as cyclohexyl methacrylate (CHMA, from Tokyo Chemical Industry Co., Japan, purity = 96%), 2-hydroxypropyl methacrylate (HPMA, from Tokyo Chemical Industry Co., purity = 96.5%), and 4-hydroxybutyl methacrylate (HBMA, from Aldrich Chemical Company, 94% pure) were purified as follows: washed with the same volume of 5% aqueous sodium hydroxide solution, followed by distilled water, dried over anhydrous magnesium sulfate, distilled under reduced pressure in the presence of calcium hydride, and stored at −20°C until used. Both photoinitiator, 2,2′-diethoxy-acetophenoe (DEAP) and inhibitor, 4-methoxyphenol (MEHQ) were purchased from Tokyo Chemical Industry Co., and used as received.

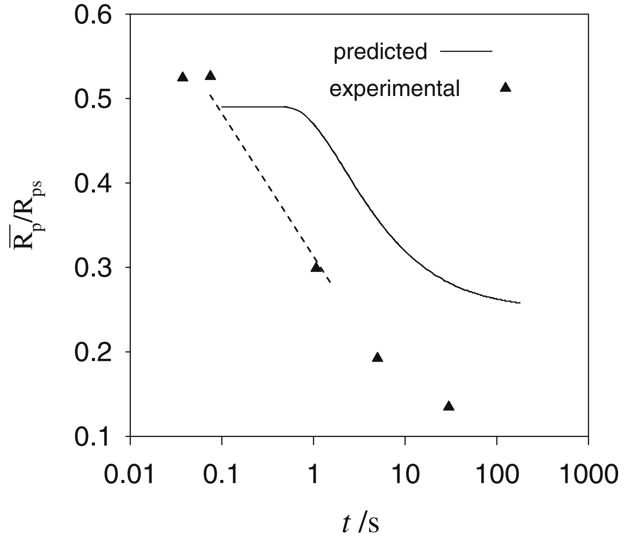

Fig. 3 Determination of the average lifetime of propagating radicals for HEMA at 30°C; $\overline{Rp}$= rate of polymerization at intermittent illumination time; t=intermittent illumination time (s); rate of dark to light = 3; [HEMA]=8.45 mol/L; [DEAP]=5.6×10^{-3} mol/L

Table 1 Kinetic data obtained in this study at 30°C

Monomer	$R_p \times 10^4$ (mol/L·s)	$R_i \times 10^7$ (mol/L·s)	Life time, τ_s (sec)	k_p (L/mol·s)	$k_t \times 10^{-7}$ (L/mol·s)
HEMA	0.321	4.74	0.111	71.9	8.56
CHMA	2.50	3.05	0.132	1070	9.30
HPMA	3.87	5.47	0.152	640	3.99
HBMA	4.34	4.31	0.172	917	4.02

Polymerization

The purified monomer (18 cm^3) and initiator (DEAP, 0.10 wt.− %) was mixed in a degas bottle, and after conducting cycles of freezing, degassing and thawing to remove oxygen, the mixture was transferred to dilatometer through a connected tygon tube. The dilatometer was then placed in a constant temperature bath (30±0.01°C). The light source was an ultraviolet (UV) lamp ("Blak-ray," model B-100AP, with a power of 100 W and a wavelength of 365 nm) and the light was focused into a parallel beam on the dilatometer in the bath. The distance between the light source and dilatometer was 40 cm, unless otherwise specified. The illumination intensity of UV light was determined by using a photometer (i.e., 1330 digital light meter, Tes Electrical Electronic Corporation, Taiwan). A disk was divided into eight equal sectors, and one sector in four was cut out (i.e., the dark-to-light ratio (*r*) was set to be three for the rotating sector). The disk, interposing between the light source and the dilatometer, was rotated with a small variable-speed motor.

The photopolymerization was conducted under the controlled illumination. The conversion can be obtained from the variation of the level in the dilatometer. At the end of the polymerization, the reaction mixture was short-stopped in a ten-fold volume of methanol in the presence of trace amount of 4-methoxyphenol (MEHQ) inhibitor and then vacuum-distilled at 50°C for at least 24 h until reaching the constant weight to check the final conversion.

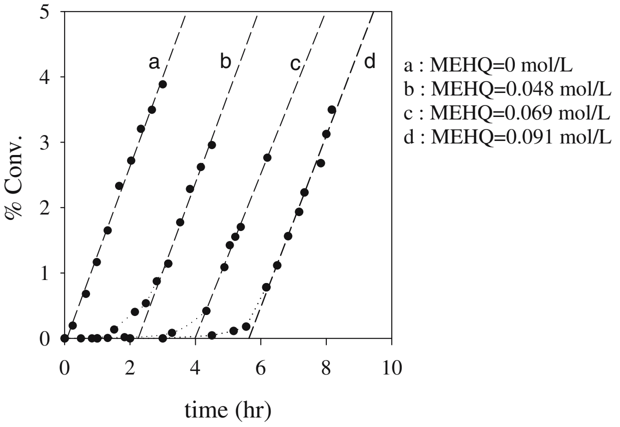

Fig. 4 Conversion-time curves of HEMA showing different induction periods for recipes containing different amounts of inhibitor (MEHQ)

Results and discussion

The photopolymerization in bulk has been conducted in this study for CHMA, HEMA, HPMA and HBMA, respectively. The polymerizations were stopped at low conversions to avoid the gel effect. The conversion-time curves for these monomers are shown in Fig. 1. It sounds that the HEMA has the lowest polymerization rate.

Investigation of k_p and k_t data by the rotating sector method

Analysis of the steady-state kinetic expression allows the determination of the ratio of k_p to k_t as (k_p^2/k_t), where the ratio is given as:

$$k_p^2 \Big/ k_t = 2R_p^2 \Big/ R_i[M]^2 \tag{1}$$

where R_p and R_i are the rate of propagation and initiation, respectively.

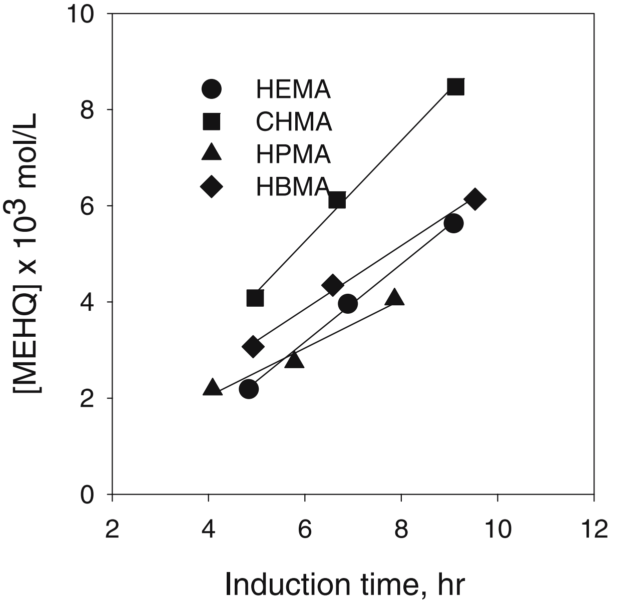

Fig. 5 Inhibitor concentration ([MEHQ]) vs. induction time for the bulk polymerization of each monomer at 30°C with DEAP initiator

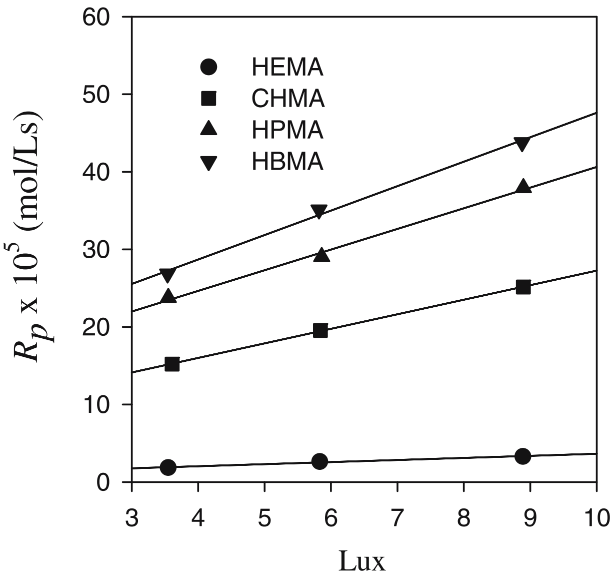

Fig. 6 Polymerization rate versus light intensity

The rotating sector technique makes it possible to decide the average lifetime (τ) of the kinetic chain, where τ is given as

$$\begin{aligned}\tau &= (\text{steady}-\text{state radical concentration})/\\ &\quad(\text{steady}-\text{state rate of radical disappearance})\\ &= [M\cdot]_s\Big/\left(2k_t[M\cdot]_s^2\right)\\ &= 1\big/\left(2k_t[M\cdot]_s\right)\end{aligned} \tag{2}$$

Substituting for $[M\cdot]_s$ in terms of the equation of $R_p=k_p[M]\,[M\cdot]_s$, the expression for τ becomes

$$\tau = \left(k_p[M]\right)\big/\left(2\,k_t\,R_p\right) \tag{3}$$

It is possible to calculate the ratio (k_p/k_t) by substituting values for T_s and R_p into Eq. 3. Thereafter, the individual constants of k_p and k_t can be obtained by comparing the ratio (k_p/k_t) with that of (k_p^2/k_t).

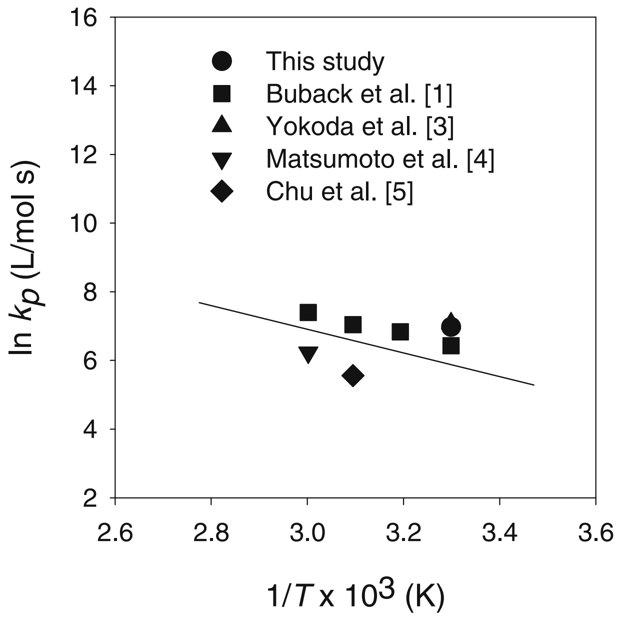

Fig. 7 Comparison of k_p data on the Arrhenius plot for CHMA polymerization

In each polymerization run, the rotating rate (i.e., deciding the period of illumination) of the rotating sector was varied in a way that the polymerization underwent different steps with different illumination period, as illustrated in Fig. 2. The average rate of polymerization $\left(\overline{Rp}\right)$ at intermittent illumination with the rotating sector for a particular duration "*t*" of the light period was compared with that of steady illumination without the rotating sector (*Rps*). The ratio of $\left(\overline{Rp}/Rps\right)$ (i.e., $[M\cdot]/[M\cdot]_s$) was then plotted against the period of illumination in log–log scale, for an example, HEMA being shown in Fig. 3. The τ value can be obtained by dividing the *t* value (i.e., the period of illumination) on the experimental fitting line with the *t* (i.e., *t* /τ) value on the predicted curve at the same altitude. The τ values obtained for monomers, thereafter, were listed in Table 1.

Table 2 Comparison of k_p data from different sources for CHMA

Temp. (°C)	% Conv.[a]	k_p / (L mol^{-1}s^{-1})	Source	Method
30	low	732±51	9	PLP-SEC
30	low	682±15	19	PLP-SEC
30	low	621±1.5	1	PLP-SEC
30	low	1,190	3	rotating sector (solution polymn.)
30	0–18.0	1,070	This study	rotating sector (bulk polymn.)
40	low	925±24	19	PLP-SEC
40	low	921±9.5	1	PLP-SEC
50	low	1,210±49	9	PLP-SEC
50	low	1,230±16	19	PLP-SEC
50	low	1,130±14	1	PLP-SEC
50	45–55	260	5	emulsion polymn.
60	low	1,590±13	19	PLP-SEC
60	low	1,620±13	1	PLP-SEC
60	0–20	510	4	ESR

[a] Percent conversion at which the data was determined

Table 3 Comparison of k_p data from different sources for HEMA and HPMA

Monomer	Temp. (°C)	% Conv.[a]	K_p / (L mol^{-1}s^{-1})	Source	Method
HEMA	30	4.1	1,295	1	PLP/SEC
	30	0–4.0	71.9	This study	rotating sector (bulk polymn.)
	60	3.4	3367	1	PLP/SEC
	60	45–55	200	6	emulsion polymn.
HPMA	30	0–12.0	640	This study	rotating sector (bulk polymn.)
	30	low	904	9	PLP/SEC
	80	45–55	4,200	8	emulsion polymn.
	80	low	2,910	9	PLP/SEC

[a] Percent conversion at which the data was determined

The initiation rate (R_i) was determined in terms of the ratio of initial inhibitor concentration to induction period. The detailed is referred to [18]. The induction period was measured at each run with different concentrations of inhibitor (MEHQ), where the intercept of the constant-rate line on the abscissa was taken as the induction period, as shown in Fig. 4. Data of the induction time were plotted against those of inhibitor concentration, as shown in Fig. 5. The initiation rate (R_i) was then calculated from the slope of each correlation line in Fig. 5. The R_i data are presented in Table 1.

The values of k_p and k_t can be calculated according to the procedure mentioned earlier, using Eqs. 1 and 3, and the results are shown in Table 1.

To investigate the effect of illumination intensity on the polymerization rate, the UV light source was set at different distances from the reactor to vary the intensity of the light that reaching the reactor. The polymerization rate is plotted against the light intensity in Fig. 6. The order dependence (x) of the polymerization rate (R_p) on the UV light intensity ($[L]$) (i.e., $R_p \sim [L]^x$) for each monomer was close to 0.5. The values are 0.46, 0.56, 0.51 and 0.53, for HEMA, CHMA, HPMA and HBMA, respectively. Note that Fig. 6 offers the relative reactivity among different monomers. This happens to provide valuable base for further comparison.

Hydroxyalkyl pendant group effect

As the homologous hydroxyalkyl methacrylates are concerned, the alkyl chain length in the hydroxyalkyl pendant group of the monomer may have an effect on the data of k_p and the life time of free radicals (τ_s). The k_p value increases rapidly, and the τ_s value increases smoothly with increasing the alkyl chain length in the hydroxyalkyl pendant group of the monomer, as shown in Table 1. In

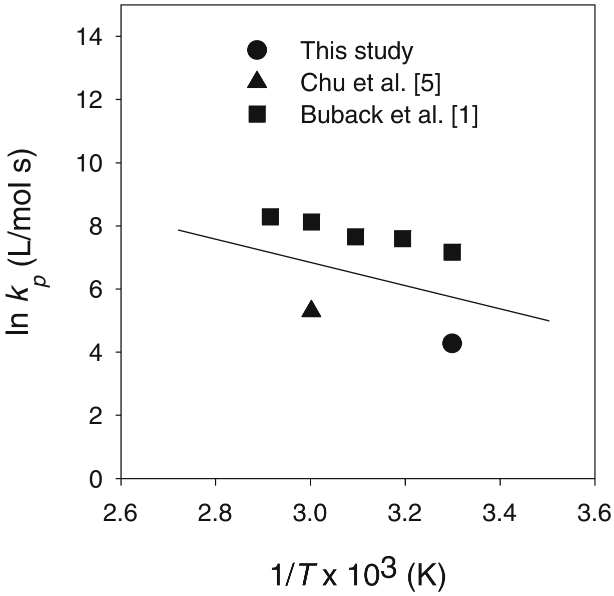

Fig. 8 Comparison of k_p data on the Arrhenius plot for HEMA polymerization

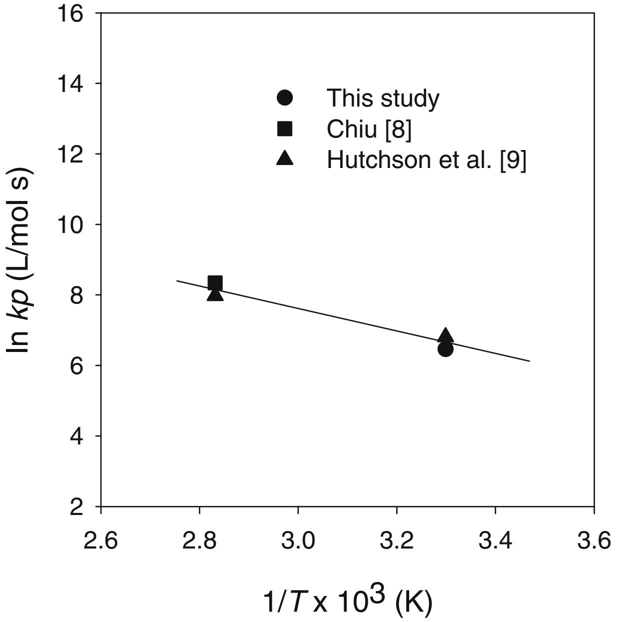

Fig. 9 Comparison of k_p data on the Arrhenius plot for HPMA polymerization

other words, the k_p value for each monomer follows a sequence as HEMA < HPMA < HBMA <CHMA . On the other hand, values for the steady-illumination polymerization rate for CHMA, HBMA and HPMA are much larger than that for HEMA, as shown in Figs. 1 and 6.

Values of k_p for CHMA [1, 3–5, 9, 19] and HEMA [1, 6, 8, 9] are shown in Table 2 and Fig. 7; and Table 3 and Fig. 8; respectively. The deviations of data between different sources could be quite significant, and could be attributed to factors, such as: difference in conversion where the data were determined, and difference in modes, which deciding the rate-determining steps (e.g., diffusion of radicals and monomers, partition of monomer in different phases, or spurs of radicals generated).

Our HEMA data gaining supports for the smaller *kp* data of HEMA from Figs. 1 and 6. Obviously, the steady-state polymerization rate data of HEMA are much smaller than other monomers.

Scarce literature data are available for HPMA and HBMA. There is no data for HBMA, but one for HPMA. The data for HPMA are compared in Table 3 and Fig. 9.

Conclusions

Using the rotating-sector method, the free-radical propagation rate coefficients (k_p) at 30°C for CHMA, HBMA, HPMA, and HEMA were determined. The k_p value increases rapidly, and the value of life time of free radicals (τ_s) increases smoothly with increasing the alkyl chain length in the hydroxyalkyl pendant group of the monomer. Values for the steady-illumination polymerization rate for CHMA, HBMA and HPMA are much larger than that for HEMA.

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