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CRITICALLY-EVALUATED PROPAGATION RATE COEFFICIENTS IN FREE RADICAL POLYMERIZATIONS—II. ALKYL METHACRYLATES

(Technical Report)

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Critically-evaluated propagation rate coefficients in free radical polymerizations—II. Alkyl methacrylates (Technical Report)

Abstract: Propagation rate coefficients, k_p, with confidence ellipses of the Arrhenius parameters, are reported for bulk free-radical homopolymerizations of *n*-butyl and *n*-dodecyl methacrylate at ambient pressure and low conversion. The data which are from independent experiments in two laboratories, were obtained by the pulsed-laser polymerization / size-exclusion chromatography method. They obey the consistency criteria established for this technique. Plotting the *n*-butyl and *n*-dodecyl methacrylate k_p data together with the benchmark k_p values for methyl methacrylate and recent data for four other linear and branched alkyl methacrylates clearly shows a pronounced family-type behaviour of alkyl methacrylate k_p.

INTRODUCTION

Modeling of free-radical polymerization processes rests upon the availability of accurate rate coefficient data, but even for rather common monomers widely diverging values are reported for ostensibly the same conditions. This Working Party aims at providing critically evaluated rate coefficient data for monomers of technical and scientific relevance. These activities bore first fruit in producing, through international collaboration, reliable propagation rate coefficients, k_p, for the ambient pressure homopolymerizations of styrene (refs. 1, 2) and of methyl methacrylate (refs. 1, 3). The present paper continues this series by reporting k_p values for *n*-butyl methacrylate (BMA) and *n*-dodecyl methacrylate (DMA) which have been independently measured in two laboratories (refs. 4, 5). For ethyl methacrylate (EMA) and for the branched alkyl methacrylates (isobutyl, isodecyl, and 2-ethylhexyl methacrylate) at present only PLP-SEC data from one laboratory (ref. 5) are available. These data lie well within the range of k_p values for MMA, BMA, and DMA. Therefore they are deemed reliable.

It has been established (refs. 2, 3, 6) that the method of choice for determining the propagation rate coefficient is pulsed-laser-induced polymerization (PLP) in conjunction with analysis of the resulting polymer by size-exclusion chromatography (SEC), provided that the data fulfill certain consistency criteria (ref. 2, 7). The PLP-SEC technique which traces back to Olaj and coworkers (refs. 8, 9) involves the irradiation of a system containing monomer and photoinitiator by an evenly spaced sequence of laser pulses. Each pulse generates a large population of small free radicals which initiate polymerization. A significant fraction of these free radicals is terminated by radicals originating from the subsequent laser pulse resulting in polymer molecules of a characteristic degree of polymerization L_0. According to the original suggestion (ref. 8) and in full agreement with extended simulation studies (refs. 10 - 12), L_0 is best identified with the point of inflection on the low molecular weight side of the peak maximum of the molecular weight distribution (MWD) obtained via SEC. From the known monomer concentration, c_M, the laser pulse repetition rate, ν_{rep}, and from L_0, k_p is found according to Eq. (1):

$$k_p = L_0 \cdot \nu_{rep} \cdot c_M^{-1} \tag{1}$$

In contrast to the earlier publications for styrene (ref. 2) and MMA (ref. 3) which are based on SEC calibration with narrow distributed standards of polystyrene and poly(methyl methacrylate), respectively, for the higher alkyl methacrylates of this report molecular weight analysis proceeds via universal SEC calibration using the Mark-Houwink constants given in the original references (refs. 4, 5).

RESULTS

Propagation rate coefficients from PLP-SEC for the bulk polymerization of *n*-butyl methacrylate and *n*-dodecyl methacrylate have been measured by the Wilmington (ref. 5) and the Göttingen (ref. 4) groups. The combined data set for BMA (59 experiments) extends over the temperature range -20 to 90°C, the DMA data (from 75 experiments) are for temperatures from -9 to 90°C. Laser pulse repetition rate was varied between 4.5 and 25 Hz, and different initiators, initiator concentrations, and laser pulse energies were used. No systematic trend in k_p with pulse repetition rate or with the concentration of initiator-derived primary free radicals is seen. The reported k_p values are exclusively derived from MWDs that are in accord with the consistency criteria put forward in an earlier publication by this Working Party (ref. 2). The ambient pressure k_p values for BMA and DMA are presented in Fig. 1. For both monomers the data sets from the two laboratories (indicated by different marker styles) are in excellent agreement. The lines in Fig. 1 indicate best fits to the combined data sets:

$$\text{BMA: } \ln\left[k_p / \left(\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\right)\right] = 14.79 - 2638\cdot(T/\text{K})^{-1}; \quad (-20°\text{C} \le T \le 90°\text{C}) \tag{2}$$

$$\text{DMA: } \ln\left[k_p / \left(\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\right)\right] = 14.71 - 2536\cdot(T/\text{K})^{-1}; \quad (-9°\text{C} \le T \le 90°\text{C}) \tag{3}$$

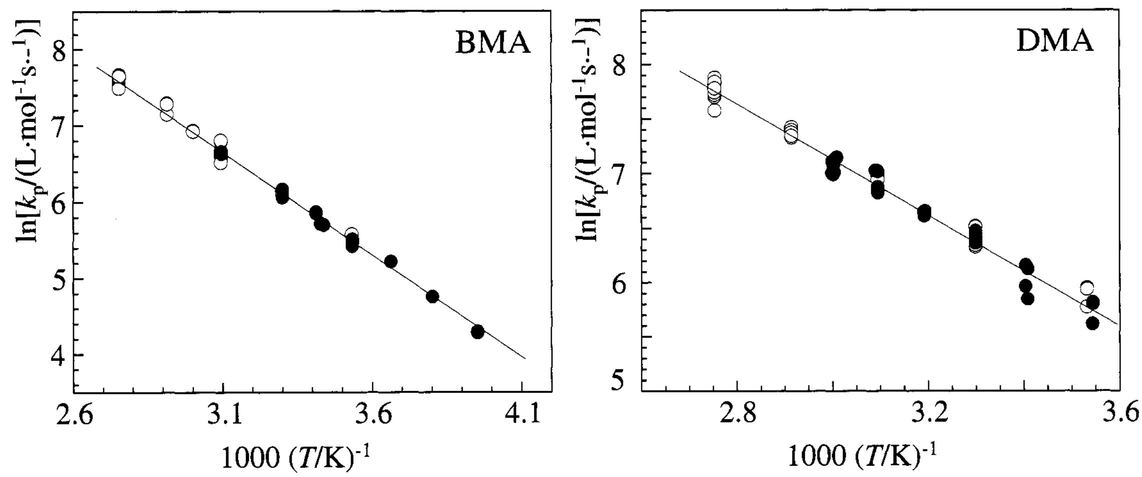

Fig. 1 Arrhenius plots of propagation rate coefficients for *n*-butyl (BMA) and *n*-dodecyl (DMA) methacrylates at ambient pressure. Filled circles: data from Buback et al. (ref. 4); open circles: data from Hutchinson et al. (ref. 5).

For BMA and DMA the 95% confidence intervals of the Arrhenius parameters, referring to Eq. (4), are presented in Fig. 2 together with the corresponding data for MMA from ref. 3.

$$k_p = A\cdot\exp\left(-E_A / \text{R}\cdot T\right) \tag{4}$$

The confidence intervals are generated according to the procedure devised by van Herk (ref. 13). They are clearly non-overlapping for the three monomers. The data show that the k_p values of these monomers are distinctly different. It should, however, be noted that the change in k_p associated with ester size is relatively small and that it is the high precision of PLP-SEC experiments which allows to quantitatively study such minor effects. It remains to be elucidated whether these changes can be assigned to either the pre-exponential factor, A, or to the activation energy, E_A, or whether both A and E_A vary with the size of the ester group.

Results for k_p of ethyl (EMA), isobutyl (iBMA), isodecyl (iDMA), and 2-ethylhexyl methacrylate (EHMA) have only been provided by Hutchinson et al. (ref. 5). As this data has not yet been confirmed by independent experiments in other laboratories, Arrhenius equations will not be presented here. Arrhenius plots of the entire set of linear and branched alkyl methacrylates are, however, given in Fig. 3.

k_p is virtually identical for the three alkyl methacrylates with larger ester size (EHMA, iDMA, DMA). k_p decreases toward smaller size of the ester group. This effect becomes particularly clear by comparing methyl, butyl, and dodecyl methacrylate. In spite of this small but significant effect, a pronounced family-type behaviour of alkyl methacrylate k_p is demonstrated by the results in Fig. 3.

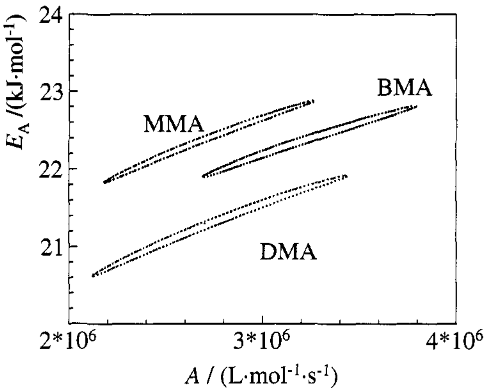

Fig. 2 95% confidence intervals of Arrhenius parameters (E_A and A according to Eq. (4)) for MMA, BMA and DMA. The MMA data are from ref. 3.

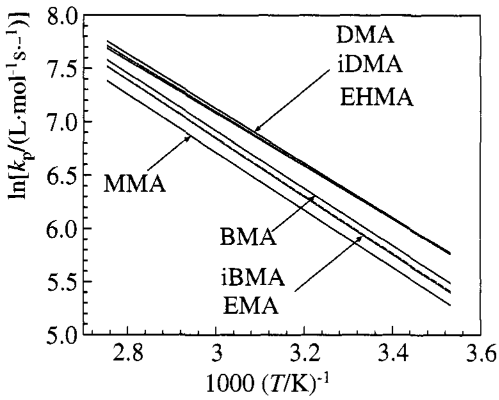

Fig. 3 Arrhenius plots of propagation rate coefficients for several linear and branched alkyl methacrylates. The lines for BMA and DMA correspond to Eqs. (2) and (3), respectively. The Arrhenius line for MMA is from ref. 3. All other data are from Hutchinson et al. (ref. 5).

Further independent investigations into k_p of these and several other methacrylates are underway. They will be included in an extended benchmark paper on methacrylate k_p.

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