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CRITICALLY EVALUATED PROPAGATION RATE COEFFICIENTS IN FREE-RADICAL POLYMERIZATIONS: PART III. METHACRYLATES WITH CYCLIC ESTER GROUPS

(IUPAC Technical Report)

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Critically evaluated propagation rate coefficients in free-radical polymerizations: Part III. Methacrylates with cyclic ester groups

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Abstract: Propagation rate coefficients, k_p, as a function of temperature, are reported for bulk free-radical homopolymerizations of oxiranylmethyl, cyclohexyl, and benzyl methacrylate at ambient pressure and low conversion. The data were obtained from experiments combining pulsed-laser initiated polymerization and size-exclusion chromatography. The data determined from experiments carried out in independent laboratories obey the consistency criteria established for this technique. The rate coefficients for the three monomers are well represented by a single Arrhenius relation.

INTRODUCTION

Modeling and optimization of free-radical polymerization processes requires the knowledge of accurate individual rate coefficients for the reactions occurring during a polymerization. Pulsed laser-initiated polymerization (PLP) in conjunction with polymer analysis by size-exclusion chromatography (SEC) has proven to be a valuable technique to derive propagation rate coefficients k_p. The IUPAC Working Party on Modeling of Polymerization Kinetics and Processes has reported critically evaluated rate coefficient data for styrene [1,2] and alkyl methacrylates [1,3,4]. The present paper continues this series by reporting k_p values for monomers with cyclic ester groups: oxiranylmethyl methacrylate[*] (OMA), cyclohexyl methacrylate (CHMA), and benzyl methacrylate (BzMA). For each monomer, the rate coefficients have been independently measured in two laboratories.

In a series of papers [1–4], it has been established that the so-called PLP-SEC technique, first introduced by Olaj and coworkers [5,6], provides reliable rate coefficients for the propagation reaction if the data fulfill certain consistency criteria [2,7]. A typical experiment involves the irradiation of a mixture consisting of 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 [5] and in full agreement with extended simulation studies [8–12], the point of inflection on the low-molecular-weight side of the peak maximum of the molecular weight distribution (MWD) obtained via SEC provides a robust measure of L_0. From the known monomer concentration, c_M, the time t_0 between two subsequent laser pulses and from L_0, k_p is found according to eq. 1:

$$k_p = L_0 \cdot t_0^{-1} \cdot c_M^{-1} \tag{1}$$

For the methacrylates with cyclic ester groups considered in this report, SEC calibration is established via universal calibration using the Mark–Houwink constants given in the original references [9,10]. Only k_p data for BzMA provided by the group of Davis [11] are determined on the basis of absolute SEC calibration employing a multidetector SEC.

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[*]The traditional name for oxiranylmethyl is glycidyl.

RESULTS

The propagation rate coefficients for oxiranylmethyl and cyclohexyl methacrylate were measured by Buback et al. [10] and Hutchinson et al. [9]. Data for BzMA are provided by Zammit et al. [11] and Hutchinson et al. [9]. The data sets for OMA (46 experiments) and for CHMA (68 experiments) cover a temperature range from −10 to 110 °C and −0.4 to 110 °C, respectively. k_p values for BzMA (40 experiments) are reported for a temperature interval from 6.1 to 110 °C: The reactions are initiated with laser pulse repetition rates varied between 1 and 100 Hz, and different initiators, initiator concentrations, and laser pulse energies were used. For details, see the original publications [9–11]. For the three monomers, no systematic trend in k_p with initiator-derived primary free-radical concentration is seen. Further, k_p is not dependent on the laser pulse repetition rates used in the investigations. Thus, the reported k_p values are exclusively derived from MWDs that are in accordance with the consistency criteria put forward in an earlier publication [2].

The ambient pressure k_p values for CHMA and OMA are presented in Fig. 1. k_p data from different laboratories (indicated by different marker styles) are in good agreement for both monomers. The lines in both figures indicate best linear fits to the combined data sets for each monomer:

OMA: $$\ln[k_p/(\text{L·mol}^{-1}\text{·s}^{-1})] = 15.72 - 2792 \cdot (T/\text{K})^{-1} \tag{2}$$

$$(-20\ °\text{C} \leq T \leq 90\ °\text{C})$$

CHMA: $$\ln[k_p/(\text{L·mol}^{-1}\text{·s}^{-1})] = 15.88 - 2848 \cdot (T/\text{K})^{-1} \tag{3}$$

$$(-9\ °\text{C} \leq T \leq 90\ °\text{C})$$

Referring to the relation $\ln k_p = \ln A - E_A/RT$, eqs. 2 and 3 are associated with preexponential factors A of 6.7 and 7.9·10^6 L·mol^{-1}·s^{-1}, respectively. The activation energies E_A for k_p are 23.2 and 23.7 kJ·mol^{-1}, respectively. Statistical analysis of each k_p data set yields absolute errors of $\Delta\ln[A/(\text{L·mol}^{-1}\text{·s}^{-1})] = \pm 0.30$ and $\Delta E_A = \pm 0.8$ kJ·mol^{-1}.
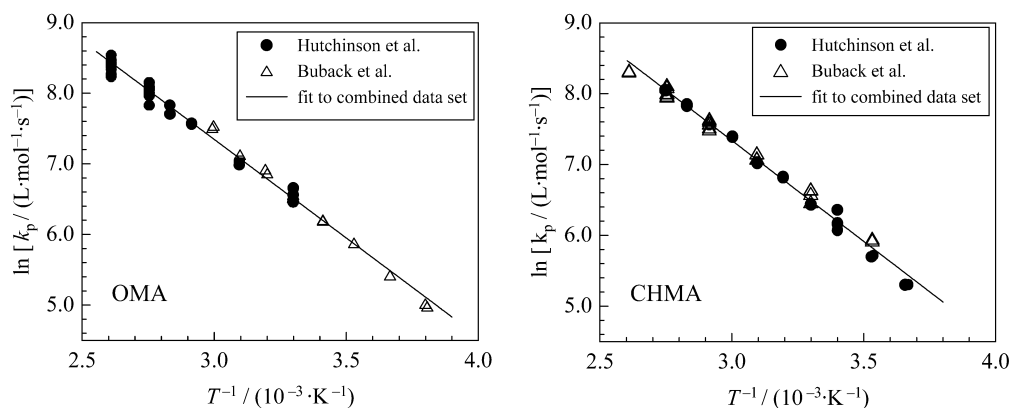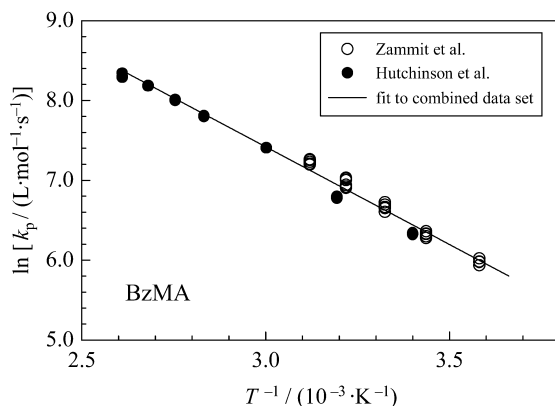

Fig. 1 Temperature dependence of the propagation rate coefficient for OMA (left) and CHMA (right) homopolymerizations at ambient pressure. The line represents a linear fit to the combined data sets for each monomer.

The k_p data for BzMA polymerizations are presented in Fig. 2. In contrast to the data for OMA and CHMA, a slight systematic deviation between the data sets from the two laboratories is seen. The deviation amounts to at most 26 %. In the original papers, it is discussed that the deviation originates from the different SEC calibration strategies applied. The line in Fig. 2 represents a best linear fit to the combined data set. The data are reasonably well fitted by the following equation:

BzMA: $\ln[k_p/(\text{L·mol–1·s–1})] = 14.77 - 2447 \cdot (T/\text{K})^{-1}$ (4)

$$(-9 \ ^\circ\text{C} \le T \le 90 \ ^\circ\text{C})$$

Absolute errors derived from statistical analysis are $\Delta\ln[A/(\text{L·mol}^{-1}\text{·s}^{-1})] = \pm 0.30$ and $\Delta E_A = \pm 0.9 \ \text{kJ·mol}^{-1}$. The Arrhenius parameters of k_p are $A = 2.6 \cdot 10^6 \ \text{L·mol}^{-1}\text{·s}^{-1}$ and $E_A = 20.3 \ \text{kJ·mol}^{-1}$.

Fig. 2 Temperature dependence of the propagation rate coefficient for BzMA homopolymerizations at ambient pressure. The line represents a linear fit to the combined data.

All k_p data reported for the three monomers under consideration are plotted as a function of temperature in Fig. 3. It is seen that all k_p values are overlapping and that there are no significant differences. The line in Fig. 3 gives the best fit to all k_p data for OMA, CHMA, and BzMA. For these monomers, the size of the ester group does not influence k_p. Equation 5 gives the Arrhenius relation for the combined data set:

OMA, CHMA, BzMA: $\ln[k_p/(\text{L·mol}^{-1}\text{·s}^{-1})] = 15.43 - 2684 \cdot (T/\text{K})^{-1}$ (5)

$$(-9 \ ^\circ\text{C} \le T \le 90 \ ^\circ\text{C})$$

Absolute errors derived from statistical analysis are $\Delta\ln[A/(\text{L·mol}^{-1}\text{·s}^{-1})] = \pm 0.20$ and $\Delta E_A = \pm 0.6 \ \text{kJ·mol}^{-1}$. The temperature dependence of k_p for the three monomers may be expressed by the Arrhenius parameters $A = 5.0 \cdot 10^6 \ \text{L·mol}^{-1}\text{·s}^{-1}$ and $E_A = 22.3 \ \text{kJ·mol}^{-1}$.

The small absolute errors for the Arrhenius parameters given in this report originate from the large number of data points and the very good reproducibility of the k_p values. The statistically derived errors, however, do not represent the true error of k_p. The major source of error for k_p values is the SEC calibration. For a detailed discussion on the importance of absolute SEC calibration, the reader is referred to ref. 4.

The 95 % confidence interval for the Arrhenius parameters of the combined k_p data set of OMA, CHMA, and BzMA is presented in Fig. 4. The confidence interval is generated using the method of ref. 12. In addition, the previously published 95 % confidence intervals of the Arrhenius parameters for k_p in MMA, BMA, and DMA homopolymerizations are given in Fig. 4. The nonoverlapping confidence intervals indicate that the k_p values of OMA, CHMA, and BzMA are distinctly different from those for the alkyl methacrylates. The confidence intervals contained in Fig. 4 suggest that the activation energies of k_p for methacrylates with an alkyl or a cyclic ester group are not significantly different, whereas the preexponential factor A is higher for the latter monomers. This observation is in agreement with the previously discussed family-type behavior of methacrylates with different ester sizes. The k_p values for
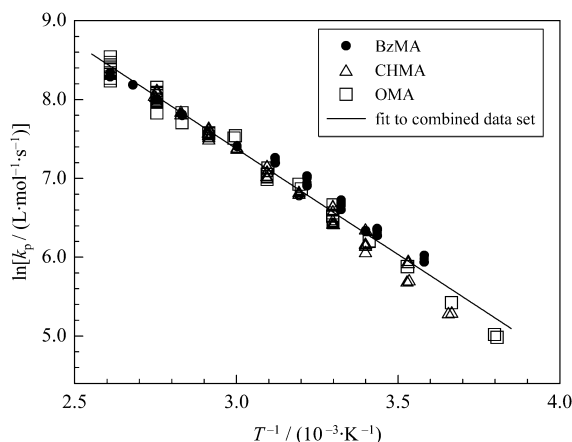
Fig. 3 Temperature dependence of the propagation rate coefficient for CHMA, OMA, and BzMA homopolymerizations at ambient pressure. The line represents a linear fit to the entire combined data set for OMA, CHMA, and BzMA.
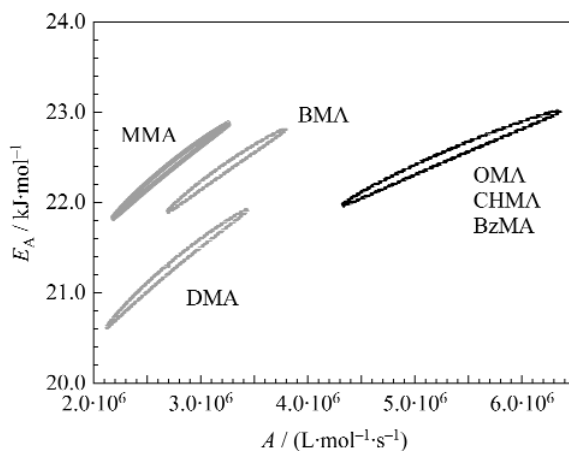
Fig. 4 95 % confidence intervals of the Arrhenius parameters (E_A and A according to eq. 6) for the fit of the combined data set of CHMA, OMA, and BzMA. The MMA data are from ref. 3, data for BMA and DMA are taken from ref. 4.

the methacrylates are dependent on the ester size, whereas the activation energies are not significantly different. In addition, the activation volume of k_p for all methacrylates is around -16 cm^3·mol^{-1} [13].

    A full paper on the propagation rate coefficients for methacrylates with a cyclic ester group will be published by the members of Project 2000-001-1-400, which will discuss SEC calibration issues in more detail.

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