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SUBCOMMITTEE ON MODELING OF POLYMERIZATION KINETICS AND PROCESSES*

CRITICALLY EVALUATED RATE COEFFICIENTS FOR FREE-RADICAL POLYMERIZATION PART 6: PROPAGATION RATE COEFFICIENT OF METHACRYLIC ACID IN AQUEOUS SOLUTION**

(IUPAC Technical Report)

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Critically evaluated rate coefficients for free-radical polymerization
Part 6: Propagation rate coefficient of methacrylic acid in aqueous solution

(IUPAC Technical Report)

Abstract: Critically evaluated propagation rate coefficients, k_p, for free-radical polymerization of methacrylic acid, MAA, in aqueous solution are presented. The underlying k_p values are from two independent sources, which both used the IUPAC-recommended technique of pulsed-laser-initiated polymerization (PLP) in conjunction with molar mass distribution (MMD) analysis of the resulting polymer by size-exclusion chromatography (SEC). Different methods of measuring the MMD of the poly(MAA) samples have, however, been used: (i) direct analysis via aqueous-phase SEC and (ii) standard SEC with tetrahydrofuran as the eluent carried out on poly(methyl methacrylate) samples obtained by methylation of the poly(MAA) samples from PLP. Benchmark k_p values for aqueous solutions containing 15 mass % MAA are presented for temperatures between 18 and 89 °C. The Arrhenius pre-exponential and activation energy of k_p at 15 mass % MAA are 1.54×10^6 L mol^{-1} s^{-1} and 15.0 kJ mol^{-1}, respectively. Also reported are critically evaluated k_p values for 25 °C over the entire MAA concentration range from dilute aqueous solution to bulk polymerization.

Keywords: pulsed-laser polymerization; methacrylic acid; kinetics; free-radical polymerization; size-exclusion chromatography; IUPAC Polymer Division.

INTRODUCTION

Pulsed-laser-initiated polymerization (PLP) in conjunction with size-exclusion chromatography (SEC), according to the procedure introduced by Olaj et al. [1], has become the IUPAC-recommended method of choice for measuring reliable propagation rate coefficients, k_p [2]. Critical evaluation of k_p data from PLP–SEC experiments performed in several laboratories worldwide resulted in a series of papers which report benchmark values of k_p for styrene [3], methacrylate monomers [4–6], and butyl acrylate homo-polymerizations [7]. The underlying k_p data have been deduced from experiments in which different PLP and SEC set-ups have been used for one and the same monomer. The resulting reliable propagation rate coefficients provide an improved understanding of propagation in free-radical bulk polymerizations. Accurate k_p data are also required for deducing termination and transfer rate coefficients from experimentally accessible coupled parameters, such as k_t/k_p and k_{tr}/k_p [8]. Due to the enormous technical relevance of polymerization in aqueous phase, there is an urgent demand also for reliable rate coefficients of free-radical polymerizations in aqueous solution. Aqueous-phase PLP–SEC experiments suffered from difficulties associated with accurately measuring the molar mass distribution (MMD) of water-soluble polymers. Further problems resulted from propagation in aqueous phase being very fast, which is particularly true for acrylic acid [9]. First PLP–SEC results for aqueous-phase polymerizations were published in 2000 [10]. Since then, k_p data from PLP–SEC were provided for methacrylic acid (MAA) [10,11], acrylic acid [10,12–14], N-isopropylacrylamide [15], and acrylamide [16].

Within the early PLP–SEC studies into aqueous-phase k_p, MMD analysis was carried out using conventional SEC with tetrahydrofuran (THF) as the eluent and styrene-divinylbenzene as the SEC-column material [10,15]. Prior to such MMD analyses on MAA polymers, the polymeric material has to be converted, by a polymer modification (methylation) reaction, into the associated hydrophobic MAA methyl ester compound [10]. In more recent PLP–SEC investigations, MMDs were deduced from aqueous-phase SEC [11–14,16]. Taking MAA k_p in aqueous phase as an example, the present report aims at critically evaluating data obtained by PLP in conjunction with either conventional THF-phase SEC [10] or aqueous-phase SEC for MMD analysis [11].

Within the PLP–SEC technique, k_p is determined via eq. 1 [1]

$$L_i = i \cdot k_p \cdot c_M \cdot t_0 \qquad\qquad i = 1, 2, 3, \ldots, \qquad\qquad (1)$$

L_1 is the degree of polymerization at the point of inflection on the low molar mass side of the MMD peak. L_1 is identified with the number of propagation steps occurring in the preselected time interval t_0 between two successive laser pulses. c_M is monomer concentration, which is determined as the arithmetic mean of monomer concentrations before and after applying a sequence of laser pulses in the initial polymerization period. Higher-order inflection points, L_2, L_3, …, result from preferential termination of radicals that have grown over time intervals $2 \times t_0$, $3 \times t_0$, …. The following IUPAC-recommended consistency criteria need to be met [3] in order to demonstrate the reliability of k_p values: The ratio of inflection point positions L_1/L_2 should be close to 0.5, and k_p should be independent of pulse energy, of pulse repetition rate, and of photoinitiator concentration. The MAA k_p data from refs. [10] and [11], which are underlying the critical evaluation presented here, meet these requirements. Details of the experiments may be found in the original literature, with special emphasis on the MMD analysis via THF-phase SEC on products from methylation of polyMAA [10], and via aqueous-phase SEC calibrated against narrow poly(MAA) standards [11]. The data refer to polymerization of non-ionized MAA that is to MAA dissolved in water without taking any additional measure of affecting the pH. The present study has been carried out within the framework of the IUPAC Polymer Division Subcommittee on the Modeling of Polymerization Kinetics and Processes.

RESULTS

PLP experiments in conjunction with THF-phase SEC [10]

k_p values of MAA in aqueous phase at 25 °C were determined at concentrations from 1.7 to 9.3 mol L^{-1} (15 to 80 mass %) using an XeF excimer laser of 50 mJ energy per pulse and 2,2-dimethoxy-2-phenyl-acetophenone (DMPA) as the photoinitiator at concentrations between 1 and 2 mmol L^{-1}. The individual values of the 17 experiments are listed in Table 3 of ref. [10]. Another 17 experiments were carried out at fixed concentration of 15 mass % MAA in water and temperatures from 18 to 89 °C (see Table 1 in ref. [10]). A pulse repetition rate of 20 Hz was used within most of the experiments. Poly(MAA) was esterified to poly(methyl methacrylate), [poly(MMA)], by methylation with diazomethane. The poly(MMA) samples were analyzed via THF-phase SEC with styrene-divinylbenzene columns (Polymer Laboratories) calibrated against narrow poly(MMA) standards.

The MMDs exhibit a pronounced PLP structure. From the associated first-derivative curves, the positions of the first and second inflection points, L_1 and L_2, respectively, are clearly identified. L_2 is positioned at about twice the value of L_1. Additional experiments at two pulse repetition rates, 30 and 40 Hz, demonstrated that also the consistency criterion referring to k_p being independent of the specific selection of the time interval between successive pulses is fulfilled.

PLP–SEC experiments in conjunction with aqueous-phase SEC [11]

The experiments covered the entire range of MAA concentration between 1 and 100 mass %. The polymerization temperatures were varied from 20 to 80 °C. Out of this extended data set, only data from experiments at the conditions selected for the measurements in [10] are considered. These data are from 43 experiments at 25 °C and widely varying MAA concentrations in aqueous solution (Table 1 in [11]) and from 15 experiments at 15 mass % MAA and temperatures between 20 and 80 °C (Tables 2 and 3 in [11]). The polymerizations were carried out using an excimer laser of 10 mJ energy per pulse, mostly operated at a pulse repetition rate of 20 Hz, with a few control experiments being run at 10 or 40 Hz under otherwise identical polymerization conditions. Depending on MAA concentration and polymerization temperature, DMPA concentrations between 0.1 and 13.3 mmol L^{-1} were used. MMDs of poly(MAA) were obtained by using aqueous-phase SEC employing Suprema columns (PSS, Mainz) and an aqueous eluent at pH 9. The first-derivative curves of the MMDs allow for unambiguous identification of the primary and secondary points of inflection. L_1/L_2 is close to 0.5, and the k_p values determined under otherwise identical conditions are independent of DMPA concentration, of the number of applied pulses, and of pulse repetition rate. The PLP–SEC experiments thus fulfill the consistency criteria. Therefore, the resulting k_p data may be considered reliable.

Critical evaluation and benchmarking of MAA k_p values measured as a function of monomer concentration at 25 °C

Shown in Fig. 1 are the k_p values from [10] and [11] for 25 °C. A significant drop in k_p is seen toward increasing MAA concentration. Given on the lower abscissa are molar concentrations of MAA, whereas the upper abscissa denotes MAA concentrations in mass %. The data from the two fully independent series of experiments are in very close agreement, which is very satisfying, as the crucial part of the experiment, the MMD determination, has been performed according to two distinctly different SEC procedures. This agreement indicates that (i) methylation of poly(MAA) to yield poly(MMA) is not ac-
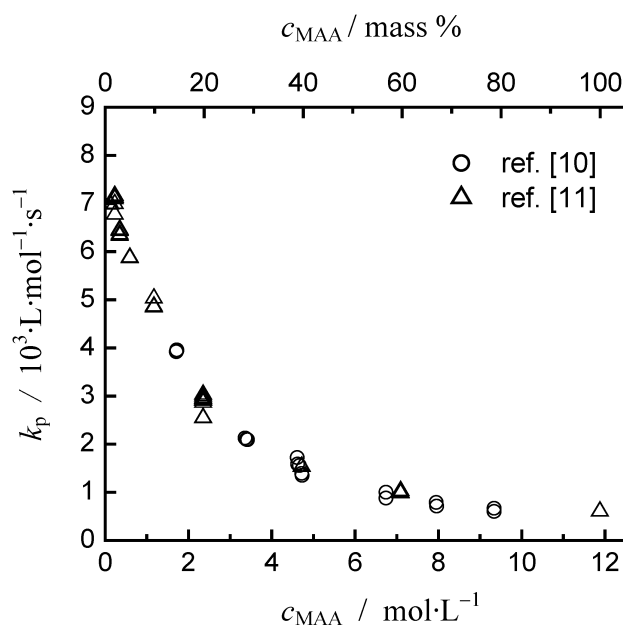

Fig. 1 Dependence on MAA concentration of the propagation rate coefficient, k_p, of MAA in aqueous solution at 25 °C [10,11].

companied by side reactions which affect the degree of polymerization, and that (ii) aqueous-phase SEC with poly(MAA) calibration and separation of poly(MAA) on Suprema columns is of similar quality as conventional THF-phase MMD analysis of poly(MMA) samples (from methylation) via poly(MMA) calibration and separation on styrene-divinylbenzene columns. These findings may, however, not be generalized. Within PLP–SEC studies into acrylic acid k_p, the esterification route may run into problems because of side reactions during polymer modification of poly(acrylic acid) samples which affect the MMD [12].

Critical evaluation and benchmarking of MAA k_p as a function of temperature for aqueous solutions containing 15 mass % MAA

The combined k_p data set for various temperatures and 15 mass % MAA [10,11] is shown in Fig. 2. Again, very satisfactory agreement of the data from the two different PLP–SEC procedures is obtained, which strongly suggests that the obtained k_p values are reliable. The nice agreement of the two individual data sets justifies common Arrhenius fitting of the entire set of k_p data for 15 mass % MAA. The resulting solid line in Fig. 2 provides an adequate representation of the data with the exception of the two k_p values at the lowest experimental temperature. The Arrhenius expression is given in eq. 2:

$$\ln [k_p/(\text{L mol}^{-1} \text{ s}^{-1})] = (14.3 \pm 0.2) - (1801 \pm 43) \cdot (\text{K}/T) \tag{2}$$
$$(15 \text{ mass \% MAA}; 18 \leq \theta/°\text{C} \leq 89; 291 \leq T/\text{K} \leq 362)$$

The associated activation energy and pre-exponential factor are $E_A = 15.0 \text{ kJ mol}^{-1}$ and $A = 1.54 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. The corresponding numbers from least-squares fitting of the individual data sets are: $E_A = 15.3 \text{ kJ mol}^{-1}$ and $A = 1.72 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ (for the data from [10]) and $E_A = 14.5 \text{ kJ mol}^{-1}$ and $A = 1.33 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ (for the data from [11]).
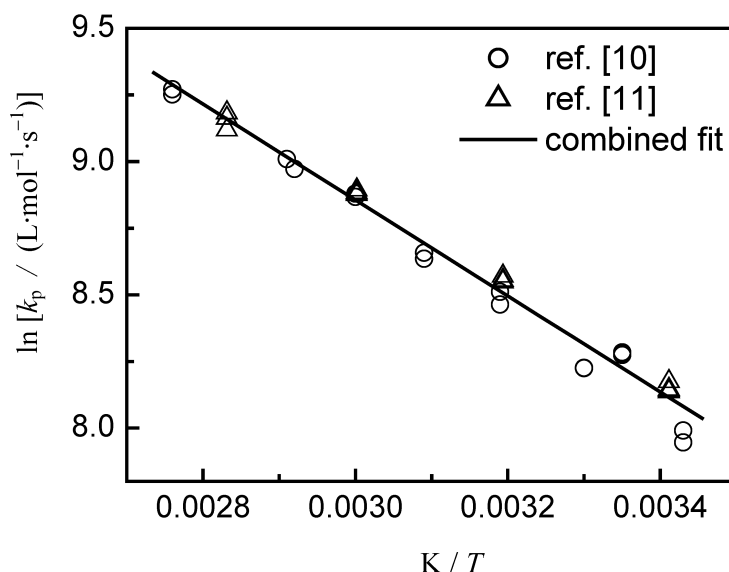

Fig. 2 Arrhenius plot of the propagation rate coefficients, k_p, for 15 mass % MAA polymerized in aqueous solution. The straight line represents the least-squares fit to the combined data set [10,11].

The uncertainties in the experimental k_p and T values are taken into account by estimating 95 % joint confidence intervals for E_A and A [17]. The confidence ellipsoid, which is obtained by a nonlin-

ear least-squares routine assuming constant relative errors in k_p and T, is presented in Fig. 3. The symbol (o) indicates the best estimate for A and E_A. The activation energy for aqueous-phase polymerization of 15 mass % MAA is significantly below the ones reported for bulk MAA ester polymerizations, which are in the range 21.0 to 23.4 kJ mol^{-1} [5,6]. Studies into the temperature dependence of MAA k_p in aqueous phase within a wide range of monomer concentrations (even including bulk polymerization) reveal that the lower activation energy applies to the entire range of MAA concentrations. The enormous variation of k_p as a function of MAA concentration is essentially due to changes of the pre-exponential factor. The significant drop toward increasing MAA content is assigned to hindrance of internal rotational motions of the transition structure by strong hydrogen-bonded interactions between the carboxylic acid groups. This aspect is discussed in detail elsewhere [11].
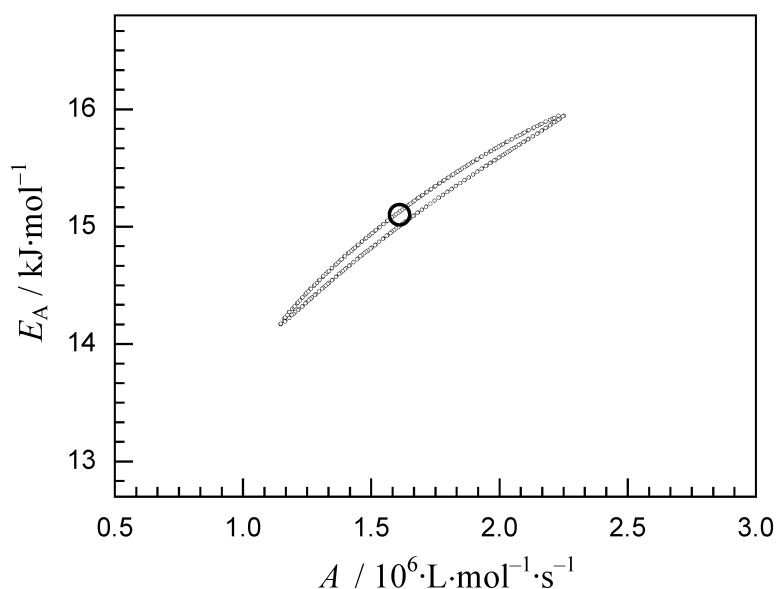

Fig. 3 95 % joint confidence interval for the Arrhenius parameters of MAA k_p in 15 mass % aqueous solution. The symbol (○) indicates the best estimate of activation energy and pre-exponential factor.

The excellent agreement of the aqueous-phase MAA k_p solution data from independent studies at 15 mass % monomer [10,11] strongly suggests that both procedures provide reliable data. In [11], k_p has been determined for a wide range of MAA concentrations with all these data obtained by the same method as has been used for deducing the 15 mass % data. Thus, there is good reason to assume that the entire body of data reported in [11] may be considered reliable. This assumption is supported by the perfect match of the bulk k_p data contained in [11] with the associated literature data reported by Beuermann et al. [18].

CONCLUSION

Within this first benchmark paper on free-radical polymerization rate coefficients in solution, critically evaluated k_p data for 15 mass % MAA in aqueous phase are presented. Also given are critically evaluated data for aqueous-phase k_p as a function of MAA concentration at 25 °C. Excellent agreement is seen of k_p data obtained by applying two different strategies which essentially differ in that the MMD distributions of the poly(MAA) samples from PLP are either determined by direct aqueous-phase SEC or by conventional THF-phase SEC on the methyl-esterified product samples. Within further activities

of the IUPAC Polymer Division Subcommittee on Modeling of Polymerization Kinetics and Processes, benchmark values will be presented for aqueous-phase k_p of partially or fully ionized MAA and of other water-soluble monomers.

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