Free-Radical Propagation Rate Coefficients of Dodecyl Methacrylate Deduced from Electron Spin Resonance Experiments

Michael Buback* and Christopher Kowollik

Institut für Physikalische Chemie, Georg-August-Universität Göttingen, Tammannstr. 6,
D-37077 Göttingen, Germany

Mikiharu Kamachi* and Atsushi Kajiwara

Department of Macromolecular Science, Graduate School of Science, Osaka University,
Toyonaka, Osaka 560-0043, Japan

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ABSTRACT: Propagation rate coefficients (k_p) for the free-radical polymerization of dodecyl methacrylate (DMA) in solution in toluene have been measured via electron spin resonance (ESR) spectroscopy in the temperature range 0 to 50 °C. The polymerization is photochemically induced at different initiator concentrations of di-*tert*-butyl peroxide (DTBP). Free-radical concentration under steady-state conditions is deduced from double integration of the well-resolved ESR spectra, consisting of 13 lines in the initial period of the polymerization reaction and 9 lines at enhanced degrees of monomer conversion. The k_p values from ESR analysis are in excellent agreement with the corresponding data from pulsed laser polymerization (PLP)/size-exclusion chromatography (SEC), the IUPAC-recommended procedure for reliable k_p measurement. The activation energy associated with the ESR k_p data, $E_A = 21.7 \pm 2.0$ kJ mol^{-1}, is in full agreement with E_A (k_p) results from recent PLP−SEC studies.

Introduction

The measurement of propagation rate coefficients (k_p) has been revolutionized by the introduction of pulsed laser polymerization−size-exclusion chromatography (PLP−SEC),[1] which is now the IUPAC−recommended procedure for reliable k_p determination. Benchmark data for styrene[2] and for methyl methacrylate[3] have been derived by this technique, which has also been used to measure k_p for other methacrylates[4−7] and several acrylates.[8−11] Reliable k_p data should also be available by direct determination of the concentration of propagating free radicals, c_R, via electron spin resonance (ESR) spectroscopy accompanied by measurement of the overall polymerization rate. Calculation of k_p then proceeds via either the differential (eq 1) or the integrated (eq 2) polymerization rate expression:

$$r_0 = -(dc_M/dt) = k_p c_R c_M \qquad (1)$$

where r_0 is the overall polymerization rate and c_M is the monomer concentration, or

$$\ln(c_{M,1}/c_{M,2}) = k_p c_R (t_2 - t_1) \qquad (2)$$

where $c_{M,1}$ and $c_{M,2}$ are the monomer concentrations at reaction times t_1 and t_2, respectively.

Inspection of the literature, however, shows that k_p values derived from ESR are in poor agreement with k_p from PLP−SEC measurements.[2,6,12−18] Addressing this dicrepancy and trying to derive k_p values that are independent of the experimental procedure used for their determination became a matter of priority. Extended theoretical and experimental work by members of the IUPAC Working Party "Modeling of Polymerization Kinetics and Processes" demonstrated that the PLP−SEC technique should yield reliable k_p, provided already established consistency criteria are met. Thus further work has been directed toward testing and improving the ESR procedure. Kajiwara and Kamachi[13] succeeded in significantly improving the quality of ESR signals by using optimized ESR cavities and by properly selecting initiator type, initiator concentration, and irradiation intensity during photodecomposition of the initiator.

In an attempt to resolve the disagreement between k_p data from PLP−SEC and from ESR, Tonge et al.[19] studied styrene free-radical polymerization. By careful analysis, these authors identified potential sources of error that could disturb or even invalidate ESR measurement of c_R. They showed that consistency of PLP−SEC and ESR k_p data may be achieved by proper selection of experimental conditions. Particular problems arise if the initiator concentration is either too large, which leads to the formation of rather short free radicals with an atypical (too high) k_p, or too small, which reduces the ESR signal-to-noise ratio. Styrene seems not to be the optimum candidate for quantitatively comparing the potential of PLP−SEC and ESR techniques for k_p measurement; the styrene k_p is relatively low, such that a fairly large fraction of short free radicals is produced. In the present paper, we used ESR to study dodecyl methacrylate (DMA), which has a relatively high k_p, exceeding the styrene k_p at ambient pressure and temperature by a factor of ~4.5. Thus the problem of the propagating free-radical chain-length is being too short should be largely reduced. Moreover, the k_p of DMA is accurately known from recent PLP−SEC experiments.[7,20]

Experimental Section

ESR spectra were recorded on a JEOL JES RE-X2 spectrometer operating in the X-band at a 100-kHz modulation field and a microwave power of 1 mW. A TE$_{011}$-mode cavity equipped with a focusing lens for UV

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* To whom correspondence should be addressed.

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irradiation was used. Temperature was controlled by a JEOL DVT2 variable-temperature unit. The spectra were recorded over a magnetic field range of 7.5 mT with a time constant of 0.1 s. Total sweep time (to measure one ESR spectrum) varied between 4 and 16 min, depending on reaction conditions. During each polymerization experiment, several spectra were recorded and the (steady-state) c_R values were obtained from the individual ESR spectra by double integration. To deduce absolute free-radical concentrations, ESR spectra of precisely known amounts of 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) dissolved in a DMA/toluene mixture (as used in the polymerizations) were measured at polymerization temperature prior to each experiment. ESR investigations of highly polar media such as pure methacrylates, are not easy, as (e.g.) the resonance frequency is not easily obtained. For this reason the DMA polymerizations were carried out in solutions of toluene (65 mol %) corresponding to 30 wt % toluene or to an initial DMA concentration of 2.1 mol L^{-1}.

The DMA/toluene reaction mixture containing the photoinitiator di-*tert*-butyl peroxide (DTBP) in concentrations between 0.034 and 0.14 mol L^{-1} was introduced into a 0.5-cm (o.d.) ESR sample tube in an argon atmosphere. UV irradiation was provided by a 500-W ultra-high-pressure mercury lamp (Ushio USH-500D) positioned ~15 cm from the tube.

We used SEC of the reaction mixture after preselected polymerization times t to estimate r_0. SEC analysis was carried out in tetrahydrofuran (THF) solution on a TOSOH CCP & 8010 instrument equipped with TSK columns and both a UV and a refractive index detector.

DMA, (Wako Chemicals) was distilled under reduced pressure in the presence of K_2CO_3 to remove the inhibitor hydroquinone monomethyl ether. Toluene (Aldrich, 99%) and DTBP (Wako, 99%) were purified by distillation prior to use. TEMPO (99%, Nacalai-Tesque, Japan) was purified by recrystallization from hexane.

Steady-state free-radical concentration and r_0 were determined in separate experiments; the respective initial reaction mixtures, however, were taken from the same stock solution. Experiments were performed at temperatures between 0 and 50 °C. The temperature range is limited at lower T because of solidification and at higher T because of the polymerization proceeding too quickly for precise measurement of r_0 under optimum conditions of initiator and monomer concentration. The experimental setup is presented in more detail elsewhere[19] and thus will not be reiterated here.

Results and Discussion

An experimental ESR spectrum of the propagating free-radical recorded during a DMA solution polymerization (at 30 wt % toluene) is shown in Figure 1.

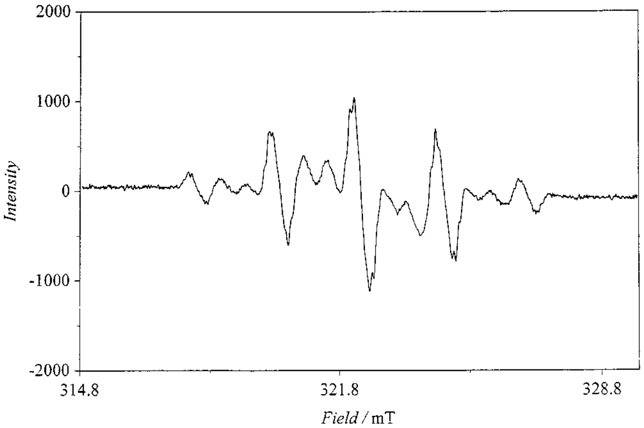

Figure 1. ESR spectrum of the propagating free radical in a DMA solution polymerization (with 30 wt % toluene) at 20 °C with an initial initiator (DTBP) concentration of 0.11 mol L^{-1}.

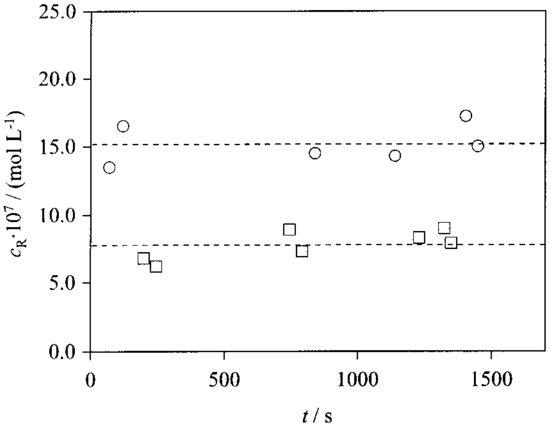

Figure 2. Free-radical concentration, c_R, plotted vs reaction time, t, for DMA solution polymerizations at $c_{DTBP,0} = 0.14$ mol L^{-1} and 40 °C (open circles) and at $c_{DTBP,0} = 0.034$ mol L^{-1} and 0 °C (open squares). The dashed lines indicate the arithmetic mean values of free-radical concentrations, $<c_R>$, for each polymerization experiment.

The polymerization was run at 20 °C and an initial DTBP concentration of 0.11 mol L^{-1}. The ESR spectrum was measured between $t = 0$ and $t = 480$ s, with the UV lamp that induces initiator photodecomposition being turned on at $t = 0$. Monomer conversion during the scanning of this particular ESR spectrum increased from 0 to 25% (see below). The 13-line ESR signal is typical for alkyl methacrylate free radicals in the initial polymerization period. The shape of the spectrum does not vary significantly with temperature but clearly changes at higher degrees of monomer conversion. Above 40% monomer conversion, the ESR signal consists of a 9-line spectrum. The gradual transition from a 13-line to a 9-line spectrum has already been reported.[21] This change is assigned to an enhanced hindrance in mobility of the propagating free radical upon increasing conversion. The shape of the ESR signal (9 or 13 lines) may be considered immaterial with respect to the quantitative analysis of c_R.

The well-resolved 3-line ESR spectrum of TEMPO is generally agreed to provide an excellent calibration standard for quantitative determination of c_R. By recording the TEMPO reference signal at each polymerization temperature (in a DMA/toluene solution as was used in the polymerization experiments and within the same ESR tube and ESR cavity but without irradiation), the value for c_R in DMA polymerization is found by direct ratioing of the sample and the reference (TEMPO) ESR signals after double integration. Steady-state values for c_R, during DMA solution polymerization at 0 °C and at an initial DTBP concentration ($c_{DTBP,0}$) of 0.034 mol L^{-1} and at 40 °C and $c_{DTBP,0} = 0.14$ mol L^{-1}, are plotted vs reaction time in Figure 2.

There is some indication of a weak increase in c_R as t increases. This effect may, however, be due to a minor variation in sample polarity during polymerization, resulting in a slight modification of the sensitivity of the ESR cavity. The (potential) change in c_R during a single polymerization experiment occurs within the

Table 1. Summary of Reaction Conditions and Experimental Results from ESR Investigations into k_p of DMA

T, °C	$c_{\mathrm{DBP},0}$, mol L^{-1}	$<c_R>$, mol L^{-1} × 10^{-7}	$k_p<c_R>$, s^{-1}	k_p, L mol^{-1} s^{-1}
0	0.10	14.6	0.00038	260
10	0.10	15.1	0.00049	321
10	0.13	15.0	0.00050	333
20	0.11	15.6	0.00072	462
20	0.11	15.6	0.00065	417
30	0.14	16.7	0.00094	563
40	0.14	15.4	0.00110	714
40	0.12	16.5	0.00130	789
0	0.034	7.8	0.00016	205
20	0.034	8.2	0.00030	366
50	0.034	7.9	0.00086	1089

limits of experimental accuracy for c_R determination (estimated as ± 15%). Thus for each experiment at constant temperature and, of course, identical $c_{\mathrm{DTBP},0}$, an arithmetic mean value, $<c_R>$, is derived from the individual ESR measurements of c_R. The mean values for the two experiments are plotted as dashed lines in Figure 2. That the c_R remains approximately constant during each polymerization indicates that the consumption of initiator during the conversion range covered in the experiments is small. This finding is also supported by the r_0 data (see below).

Summarized in the third column of Table 1 are the $<c_R>$ data for the entire set of polymerization experiments carried out in the present investigation. The last three entries, for $c_{\mathrm{DTBP},0} = 0.034$ mol L^{-1}, and those for $c_{\mathrm{DTBP},0}$ levels in the narrow range between 0.10 and 0.14 mol L^{-1} demonstrate that temperature has no significant influence on $<c_R>$. Because the steady-state c_R value should be determined by parameters of the initiation and termination process, this result is not unexpected: (i) The photoinitiation process should be independent of temperature, and (ii) the termination rate coefficient should be associated with a very small activation energy.

For the two experiments illustrated in Figure 2, $<c_R>$ differs by a factor of ~2. This is what would be expected for steady-state free-radical polymerizations when $c_{\mathrm{DTBP},0}$ differs by a factor of ~4 (in cases where $<c_R>$ is not significantly varied with temperature). This finding provides additional support for the reliability of the ESR analysis of c_R.

The second piece of experimental information that needs to be available for k_p determination is r_0 (or monomer concentration vs time profiles). These data were derived from independent polymerization runs using the same stock solution as that in the corresponding ESR study. Monomer conversion is obtained from SEC measurement of samples taken from the polymerizing system at preselected reaction times t. The SEC traces show three clearly separated peaks for polymer, monomer, and solvent, respectively. For each of the components, the area under the SEC signal is proportional to component concentration (verified by NMR). The degree of monomer conversion was deduced from the ratio of integrated SEC signals (areas) for monomer and polymer. The SEC analysis, in addition, allows estimating polymer molecular weights. Typical weight-averaged degrees of polymerization ~300 were obtained, which demonstrates that the dominant propagating free radicals had sizes clearly above the oligomer level.

In Figure 3 are plotted the conversion data obtained from SEC analysis in terms of the natural logarithm of inverse relative monomer concentration, $c_{M,0}/c_M(t)$, vs t. Figure 3a shows the data at higher $c_{\mathrm{DTBP},0}$ (0.10 to 0.14 mol L^{-1}) for polymerization temperatures between 0 and 40 °C. Figure 3b shows the data for $c_{\mathrm{DTBP},0} = 0.034$ mol L^{-1} and temperatures between 0 and 50 °C. The data points from each experiment nicely fit a straight line. According to eq 2, the slope of the individual lines may be identified with the product term $k_p<c_R>$. The linear dependencies in Figure 3 are consistent with the view that c_R remains approximately constant during each polymerization (at least within the conversion range under investigation). For almost all reaction conditions, duplicate runs were performed and the resulting $\ln(c_{M,0}/c_M(t))$ vs t data (not shown, to avoid overloading Figure 3) were in perfect agreement with the results displayed in Figure 3.

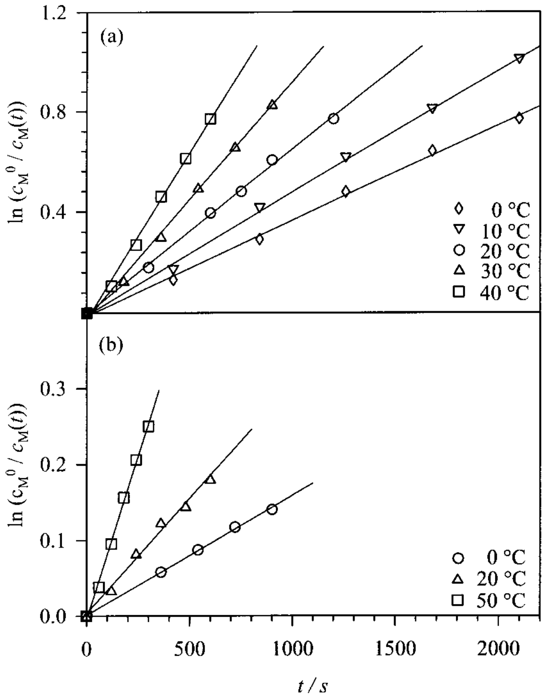

Figure 3. Plots of relative monomer concentration (see text) vs reaction time for DMA solution polymerizations at different temperatures and at two levels of initiator concentration: (a) $c_{\mathrm{DTBP},0}$ is between 0.10 and 0.14 mol L^{-1} (see Table 1); (b) $c_{\mathrm{DTBP},0}$ = 0.034 mol L^{-1}.

The $k_p<c_R>$ values derived from the slopes of the straight lines in Figures 3a and 3b, summarized in the fourth column of Table 1, are estimated to have an accuracy of ±3%. From $<c_R>$ and $k_p<c_R>$ we easily calculate the propagation rate coefficient k_p, given in the last column of Table 1. Based on the error estimates for $<c_R>$ and $k_p<c_R>$, the k_p values from our ESR analysis are assumed to be accurate within ±18%.

In Figure 4 the k_p data from ESR are plotted with recently reported PLP−SEC values[7,20] for bulk k_p. Excellent agreement of the entire data material is seen with no indication of any systematic discrepancy between k_p values derived from the two techniques. The slight difference in ESR k_p at the different values for c_R at 0 and 20 °C in Table 1 is within the limits of experimental accuracy. Moreover, k_p at 50 °C and low initiator concentration ($c_{\mathrm{DTBP},0} = 0.0034$ mol L^{-1}) is above the k_p values from PLP−SEC measurement (and above the fitted line in Figure 4), whereas the 0 and 20 °C data for the same $c_{\mathrm{DTBP},0}$ are below the line. The straight line in Figure 4 is a fit only to the ESR data of

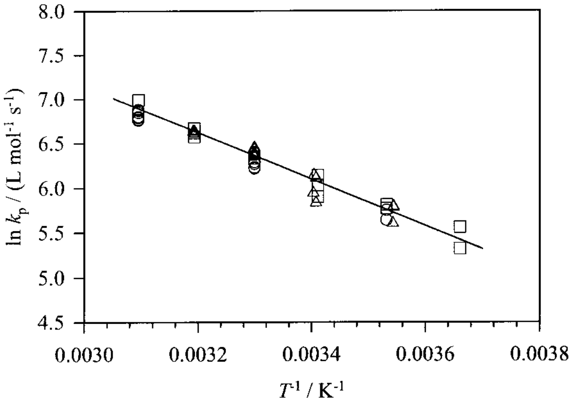

Figure 4. Temperature dependence of the DMA propagation rate coefficient k_p at ambient pressure. Squares: ESR data from this work, fitted by the straight line corresponding to eq 3. Also included are the recent PLP−SEC data for DMA bulk polymerization of Hutchinson et al.[20] (circles) and Buback et al.[7] (triangles).

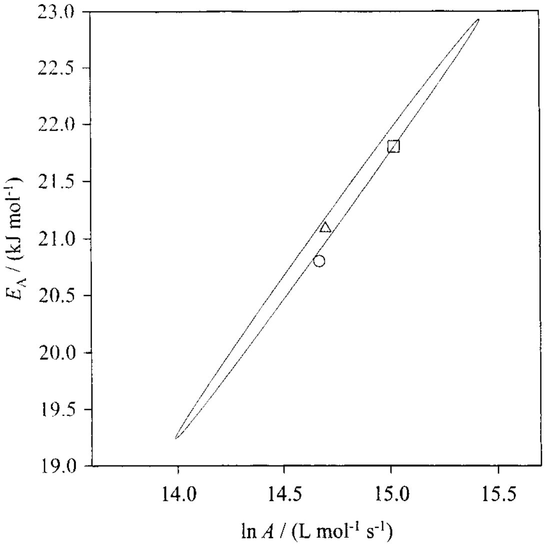

Figure 5. Confidence ellipsoid of Arrhenius parameters, E_A and A, of k_p (DMA) for the PLP−SEC data of Buback et al.[7] The triangle corresponds to the optimum value of this data set, whereas the circle and the square represent the optimum E_A, A values of the PLP−SEC data from Hutchinson et al.[20] and of the present ESR k_p values, respectively.

the present work, resulting in the following Arrhenius expression:

$$\ln [k_p/(\text{L mol}^{-1}\ \text{s}^{-1})] = 14.96 - 2605\ (T/\text{K})^{-1} \quad (3)$$

$$(0 \leq \text{temperature}/°\text{C} \leq 50)$$

The activation energy, E_A, associated with eq 3 is 21.7 ± 2.0 kJ mol^{-1}, which, as is to be expected from Figure 4, fully agrees with the corresponding E_A (k_p) reported for DMA by Hutchinson et al.[20] and by Buback et al.[7]: 20.8 ± 0.3 and 21.1 ± 2.1 kJ mol^{-1}, respectively. The preexponential factors, associated with the rate expression $\ln[k_p/(\text{L mol}^{-1}\ \text{s}^{-1})] = \ln A - E_A/(RT)$, are $\ln A/(\text{L mol}^{-1}\ \text{s}^{-1}) = 14.96$ (this work), 14.67,[20] and 14.71.[7]

It has become standard practice to represent Arrhenius plots via 95% joint confidence intervals of Arrhenius parameters in the manner described by van Herk.[22] Shown in Figure 5 is the confidence ellipsoid associated with the PLP−SEC k_p data reported by Buback et al.,[7] with the triangle indicating the most probable combination of Arrhenius parameters (E_A, A) of this data set. The two other symbols (open circle and square) represent the most probable set of E_A and A parameters for the PLP−SEC data of Hutchinson et al.[20] and for the ESR data of the present work, respectively. The confidence ellipsoids of the two latter data sets, not shown in Figure 5, differ significantly in size; the data of Buback et al. comprise a large number of experiments, resulting in an ellipsoid smaller than the one plotted in Figure 5, whereas the relatively few ESR experiments of the present study (Table 1) yields a fairly extended ellipsoid. Even without showing the ellipsoids around the individual optimum values, the results in Figure 5 convincingly demonstrate that the k_p values from ESR and PLP−SEC are in very satisfactory agreement.

The ESR data have been measured on DMA solutions containing toluene at 30 wt %, whereas the PLP−SEC data are for bulk polymerization. This difference should not invalidate the comparison shown in Figure 5, given that the PLP−SEC experiments on methyl methacrylate in both bulk and solution (in toluene and butanone) provided no indication of a solvent dependence of k_p, at least in these solvents.[23] As with the PLP−SEC data, access to independent ESR results from at least two groups is desirable. For DMA, only a single ESR k_p value (at 60 °C) has been reported, by Matsumoto and Mizuta.[24] Their result is ~55% less than the k_p we estimate for polymerization at 60 °C with eq 3. Thus it would be extremely useful to carry out further experiments with significant variations of initiator type and initiator concentration to improve the knowledge about potential shortcomings of ESR experiments. Obviously, the ESR studies should be extended to other monomers, particularly to other methacrylates. Moreover, studies of k_p as a function of conversion, up to high polymer contents, should be carried out. Such investigations cannot be performed with PLP−SEC measurements, which are restricted to kinetic analysis at low conversion.

Conclusion

The present study shows that by careful selection of experimental conditions, reliable k_p values are accessible from ESR experiments. Particular attention needs to be paid to the size of the steady-state free-radical concentration, which should be in an intermediate range. The type of initiator also seems to be important; we found DTBP to be a good choice. Additional studies should check whether the particular propagating free-radical is the single free-radical species in the system. This point is of special importance in photochemically induced polymerizations, where in addition to the photoinitiator, the monomer also may be excited.

As has been realized in the thorough study by Tonge et al.,[19] the experimental conditions must be such that the majority of propagating radicals are large enough to avoid determination of atypically high k_p values, which are known to occur with free radicals of short chain-length. Because of this limitation, studies into higher-k_p monomers may be advantageous (unless polymerization rates become too fast for precise determinations of monomer conversion vs time profiles). Moreover, one should check that high-molecular-weight material is indeed produced.

With these caveats in mind, we see no reason why reliable k_p values should not be available from ESR for a variety of monomers. The data of the present investigation appear to be of similar quality as those derived from PLP−SEC.

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