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Propagation Rate Coefficients of Acrylate−Methacrylate Free-Radical Bulk Copolymerizations

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ABSTRACT: Copolymerization propagation rate coefficients, $k_{\mathrm{p,copo}}$, have been measured for the binary systems methyl acrylate (MA)−dodecyl methacrylate (DMA), butyl acrylate (BA)−methyl methacrylate (MMA), dodecyl acrylate (DA)−DMA, and DA−MMA at 40 °C and 1000 bar by the pulsed laser polymerization (PLP)−size-exclusion chromatography (SEC) technique. These acrylate−methacrylate systems are interesting because of the significant difference, by more than 1 order of magnitude, between the homopropagation rate coefficients of the two families. Reactivity ratios, r_i, are determined from monomer feed compositions and the NMR spectroscopically measured copolymer compositions. The resulting r_i values for the four acrylate−methacrylate copolymerizations agree within experimental accuracy. Moreover, these r_i data are surprisingly close to reactivity ratio data estimated from individual addition rate coefficients to MA and MMA, respectively, of appropriate small (meth)acrylate-type free radicals. Such addition rate coefficients have been determined via EPR in liquid solution by the Hanns Fischer group. The terminal model allows for excellent individual fits of composition and of $k_{\mathrm{p,copo}}$ for each of the four systems. The implicit penultimate unit effect (IPUE) model (and the explicit penultimate unit effect (EPUE) model) are capable of simultaneously fitting composition and rate data for the MMA−BA and DMA−MA systems whereas both models fail to provide a satisfactory representation of the two DA-containing systems. The data suggest that, with DA being one of the comonomers, individual propagation rate coefficients are not adequately described by consideration of only terminal and penultimate units at the free-radical terminus. On the other hand, ratioing individual propagation rate coefficients of free radicals with the same penultimate units seems to eliminate most of the impact of the penultimate units. For this reason the resulting and widely used “terminal model” reactivity ratios are reasonable and meaningful kinetic quantities although penultimate effects on the individual propagation rate coefficients undoubtedly operate.

Introduction

The quality of measuring propagation rate coefficients, k_{p}, of free-radical polymerizations has enormously improved with the advent of the pulsed laser polymerization (PLP)−size-exclusion chromatography (SEC) technique.[1,2] A significant number of homopolymerizations have been studied by this method,[4−7] with several of these investigations carried out up to high pressures.[8] Benchmark values of bulk k_{p} deduced from PLP−SEC have been collated for styrene,[9] methyl methacrylate,[10] and several other alkyl methacrylates[3,4,11] by the IUPAC Working Party “Modeling of Polymerisation Kinetics and Processes”. Because of significant technical and scientific interest, PLP−SEC studies need to be extended to copolymerization k_{p}. A few such experiments have already been carried out, on the styrene−methacrylate[1,12,13] styrene−acrylate,[14,15] and butyl acrylate−methyl methacrylate[16] systems. A comprehensive survey on the mechanism of the propagation step in free-radical copolymerization has recently been provided by Coote and Davis.[17] This article reports $k_{\mathrm{p,copo}}$ data from PLP−SEC and conventional techniques.

The simplest model to represent $k_{\mathrm{p,copo}}$ is the “terminal” model, in which it is assumed that propagation reactivity is solely determined by the monomer molecule and by the terminal unit at the free-radical chain end. In their pioneering work, Fukuda et al.[18] demonstrated that the terminal model mostly fails to describe copolymer composition and propagation rate simultaneously. As has been shown by Schweer,[19] the terminal model, however, allows for adequate separate fits of copolymer composition and of $k_{\mathrm{p,copo}}$ as a function of monomer feed composition. This procedure is, however, associated with the unfavorable situation of providing two sets of “terminal” reactivity ratios for a single system. Fukuda et al.[18] recommended the use of “penultimate” models in which both the terminal and penultimate units at the free-radical chain end are assumed to affect propagation kinetics. Two such models have been considered, the “implicit penultimate unit effect (IPUE)”[18] and the “explicit penultimate unit effect (EPUE)”[20] model. Aspects of both models are detailed in refs 16 and 17 and will not be reiterated here. The IPUE model assumes that both terminal and penultimate units affect free-radical reactivity, but selectivity is only determined by the terminal unit. This model has been successfully applied to simultaneously fitting copolymer composition and $k_{\mathrm{p,copo}}$ as a function of monomer feed composition

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for a wide variety of systems.[16,19] The EPUE model assumes that terminal and penultimate units of the free radical affect both reactivity and selectivity. Reference 17 addresses in great detail differences between IPUE and EPUE models and includes reaction barriers and frequency factors of associated reactions of small free radicals from various types of experiments and molecular orbital calculations. These authors recommend use of the EPUE model. From a chemical point of view, this suggestion is more than reasonable. Unfortunately, the EPUE model requires six reactivity ratio parameters (as compared to four such parameters with the IPUE model and to two reactivity ratios with the terminal model). Attempts to derive this considerable number of EPUE parameters from experimental data mostly yields indeterminate values. The argument that the evidence against the IPUE model is not (yet) strong enough to outweigh the enormous advantage of a reduced number of parameters thus is a strong one. Kinetic data for addition reactions of monomer molecules to suitable small free radicals may be used to estimate propagation rate coefficients of copolymerizations, a strategy that has already been applied by Fischer et al.[21,22] Absolute rate coefficients for such reactions of small radicals will not be a good measure of propagation rate of macroradicals because of major differences in preexponential factors. The activation energies of monomer addition to small and to large free radicals may, however, be very similar. This assumption has been tested recently for the copolymerization of ethene with methacrylates.[23] The data indicate that the temperature dependence of reactivity ratios may be estimated from differences in activation energy of the corresponding addition-to-monomer reactions of small free radicals.

To further advance the understanding of copolymerization kinetics, it appears mandatory to provide additional $k_{\mathrm{p,copo}}$ data. Studies into acrylate–methacrylate systems are of particular interest as the homopropagation rate coefficients of the two families differ significantly, by about 1–2 orders of magnitude.[4,16] Moreover, acrylates and methacrylates are widely used (co)-monomers. A first such study has been carried out by Hutchinson et al.[16] on the butyl acrylate (BA)–methyl methacrylate (MMA) system at 20 and 60 °C and ambient pressure. The same system has been investigated by Madruga and Fernandez-Garcia[24] without however using the PLP–SEC technique. The aim of the present paper is to provide PLP–SEC $k_{\mathrm{p,copo}}$ data for several alkyl acrylate–alkyl methacrylate systems—methyl acrylate (MA)–dodecyl methacrylate (DMA), dodecyl acrylate (DA)–dodecyl methacrylate (DMA), dodecyl acrylate (DA)–methyl methacrylate (MMA)—and to extend the data set for BA–MMA. The $k_{\mathrm{p,copo}}$ values will be determined for several monomer feed compositions at 40 °C and 1000 bar. The systems were chosen such as to contain acrylates and methacrylates of both small (methyl) and long (dodecyl) ester size. As the polymerizing mixtures are only weakly compressible in the 20–60 °C range, high-pressure conditions should not be associated with a change in propagation mechanism as compared to the situation at ambient pressure. An essential reason for selecting high-pressure conditions is that the $k_{\mathrm{p,copo}}$ data will additionally be used (in a forthcoming study) to deduce copolymerization termination rate coefficients, $k_{\mathrm{t,copo}}$, from single pulse (SP) experiments which yield the coupled parameter $k_{\mathrm{p,copo}}/k_{\mathrm{t,copo}}$. These so-called SP–PLP experiments are preferably carried out under high pressure where the signal quality is enhanced.

PLP–SEC experiments directly yield individual $k_{\mathrm{p,copo}}$ values. Equally spaced laser pulses are used to induce polymerization. The resulting polymeric product from reaction to fairly low degrees of monomer conversion is analyzed by SEC and points of inflection on the molecular weight distribution (MWD) are determined. From the degree of polymerization at the inflection points, L_i (with $i = 1, 2, 3, ...$), the propagation rate coefficient, k_p, is obtained via eq 1, where t is the time between

$$L_i = itk_\mathrm{p}c_\mathrm{M} \tag{1}$$

successive laser pulses and c_M is the (overall) monomer concentration. Points of inflection occur at positions iL_1, where L_1 is the degree of polymerization of the first such point of inflection (on the low molecular weight side of the MWD peak). The existence of “overtone” points of inflection ($i = 2, 3, ...$), at least of L_2 positioned at around $2L_1$, is an important consistency criterion for reliable k_p analysis via PLP–SEC.[9,10,16] The characteristic degrees of polymerization for copolymer samples are obtained by dividing the molecular weight at an inflection point, M_i, by the average molecular weight of the repeat unit of the particular copolymer, where M_1 and M_2 are the molecular weights of the individual repeat units (eq 2). Copolymer composition, F_1 and/or F_2, has

$$L_i = \frac{M_i}{F_1M_1 + F_2M_2} \tag{2}$$

to be measured, e.g., via elemental analysis or quantitative NMR, or may be deduced from the Lewis–Mayo equation[25] in cases where reactivity ratios are already known. The overall monomer concentration in the initial period of the copolymerization experiment, which is required for estimating $k_{\mathrm{p,copo}}$ from eq 1, may be estimated via eq 3, where ρ_mix is the density of the

$$c_\mathrm{M} = \frac{\rho_\mathrm{mix}}{f_1M_1 + f_2M_2} \tag{3}$$

comonomer mixture, which is calculated from the individual monomer densities assuming negligible excess volume, and f_1 and f_2 are the mole fractions of 1 and 2 in the monomer feed, respectively. The essential problem of accurate $k_{\mathrm{p,copo}}$ measurements via PLP–SEC relates to the precise copolymer molecular weight determination, in particular at the points of inflection. In the present study molecular weights were measured via universal SEC calibration which requires Mark–Houwink parameters, a and K. Such values have already been reported for the BA–MMA system.[16] The Mark–Houwink parameters for the MA–DMA, DA–DMA, and DA–MMA systems were determined at Polymer Standards Service (PSS, Mainz, Germany) on our samples.

The present paper reports copolymer composition and copolymerization k_p of several alkyl acrylate–alkyl methacrylate systems at 40 °C and 1000 bar, and analyzes the resulting data in terms of the terminal and penultimate unit models.

Experimental Section

Methyl acrylate (>99%, stabilized with 0.005 wt % hydroquinone monomethyl ether, Fluka Chemie), butyl acrylate (>99%, stabilized with 0.005 wt % hydroquinone monomethyl ether, Fluka Chemie), dodecyl acrylate (which was actually a mixture of 55 wt % DA and 45 wt % tetradecyl acrylate, Fluka Chemie), methyl methacrylate (>99%, stabilized with 0.005 wt % hydroquinone monomethyl ether, Fluka Chemie), and dodecyl methacrylate (DMA, ≈96%, Aldrich Chemie) were purified by distillation under reduced pressure in the presence of K_2CO_3. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Aldrich Chemie) was used without further purification at concentrations close to 5×10^{-3} mol·L^{-1}.

Preparation of the PLP Samples for SEC Analysis. Oxygen was removed from the monomer mixture by four cycles of freezing, degassing, and thawing. DMPA was added, and the solution was filled into an internal cell in a glovebox under an argon atmosphere. The internal cell,[26] consisting of a teflon tube and of two CaF_2 windows, was inserted into an optical high-pressure cell.[26] After reaching copolymerization temperature and pressure, sequences of evenly spaced laser pulses (each of about 20 ns width) were applied using an LPX 200 laser (Lambda-Physik), which was operated on the XeF line at 351 nm. The pulse repetition rate was varied between 40 and 100 Hz. The degree of monomer conversion was monitored via NIR spectroscopy in the 6000−6300 cm^{-1} range. For NIR analysis the optical high-pressure cell was removed from the irradiation assembly and introduced into the sample chamber of a BRUKER IFS 88 FT-NIR/IR spectrometer. The procedure of deriving monomer concentration from the NIR absorbance of C−H stretching modes, with the hydrogen atom being linked to the C═C double bond has been detailed elsewhere.[27] Total monomer conversion was always less than 3% which ensures applicability of eq 1. The monomer concentration used to estimate $k_{p,copo}$ was given by the arithmetic mean of the initial concentration and the NIR spectroscopically measured concentration after laser irradiation. The copolymerizations were carried out at different monomer mole fractions. The copolymer was precipitated in a methanol (p.a. grade, Fluka)−hydroquinone (99%, Aldrich) solution.

Molecular weight distributions were determined by SEC at the Polymer Institute of the Slovak Academy of Sciences in Bratislava and at the University of Göttingen. Both places used a Waters system (pump 515, DRI detector model 410) with PSS SDV 5 μm columns of pore sizes 10^5, 10^3, and 10^2 Å operated with tetrahydrofuran as the eluent at 30 °C and at a flow rate of 1 mL/min. Data acquisition and processing were carried out using the WinGPC 4 software (PSS, Mainz). The SEC setup was calibrated via narrow molecular weight (MW) polystyrene standards (PSS, Mainz) with MWs ranging from 400 to 2.18×10^6. The copolymer MWDs were obtained via universal calibration.[28] The investigations at PSS were carried out via the stripe method,[29−31] on samples from thermal copolymerizations at 80 °C/1 bar with AIBN (99%, Aldrich, recrystallized from di-*iso*propyl ether) as the initiator. The copolymer samples subjected to the calibration procedure are broad and encompass the range of molecular weights that occur in the PLP−SEC experiments. It is assumed that the difference in polymerization pressure and temperature, 80 °C/1 bar vs 40 °C/1000 bar, will not induce any major change in copolymer microstructure. Copolymer compositions were determined by ^{1}H NMR spectroscopy (see below). Table 1 summarizes the *a* and *K* parameters used in the present study. All data refer to SEC experiments with THF at 30 °C as the eluent. Mark−Houwink parameters for copolymer compositions that have not been investigated in the calibration studies at PSS were derived by linear interpolation between adjacent *a* and *K* values.

Preparation of the Samples for Quantitative ^{1}H NMR Analysis. The samples for ^{1}H NMR analysis of copolymer composition were prepared by pulsed laser experiments under the same temperature and pressure conditions, 40 °C and 1000 bar, as used in the PLP experiments. The copolymer was precipitated by adding methanol containing a small amount (0.02 wt %) of hydroquinone to prevent further polymerization. Residual monomer was removed by three redissolving and reprecipitation cycles in dichloromethane (Aldrich, 99.9%) and in methanol, respectively. The copolymer was dried for at least 24 h at room temperature. The ^{1}H NMR measurements of the copolymer were carried out in solution of tetrachloroethane-d_2 (99.9%, Deutero GmbH). The spectra were recorded on a Varian (Unity 300) 300 MHz spectrometer at 120 °C on solutions containing approximately 6 wt % copolymer.

Table 1. Mark−Houwink Parameters *a* and *K* Determined by the Stripe Method[29−31] at 30 °C Using THF as the Eluent for MMA−BA, DMA−MA, MMA−DA, and DMA−DA Copolymers[a]

F_{MMA} (MMA−BA)	*a*	*K* (mL·g^{-1})
0.000	0.700	0.012 20[16]
0.292	0.695	0.018 70[16]
0.538	0.706	0.016 90[16]
0.785	0.703	0.015 30[16]
0.903	0.711	0.010 50[16]
1.000	0.719	0.009 44[16]
F_{DMA} (DMA−MA)	*a*	*K* (mL·g^{-1})
0.000	0.696	0.016 80
0.500	0.727	0.011 70
0.618	0.753	0.006 88
0.929	0.735	0.005 97
1.000	0.736	0.004 95
F_{MMA} (MMA−DA)	*a*	*K* (mL·g^{-1})
0.000	0.585	0.0292[32]
0.154	0.758	0.004 75
0.291	0.742	0.005 81
0.462	0.806	0.002 88
0.500	0.795	0.003 62
0.673	0.784	0.005 51
0.857	0.739	0.009 57
1.000	0.719	0.009 44[16]
F_{DMA} (DMA−DA)	*a*	*K* (mL·g^{-1})
0.000	0.585	0.0292[32]
0.284	0.792	0.002 54
0.513	0.793	0.002 80
0.641	0.708	0.008 12
0.827	0.693	0.008 54
1.000	0.736	0.004 95

[a] Copolymer composition was determined by ^{1}H NMR spectroscopy.

Results and Discussion

There are two kinds of experimental results: (i) The ^{1}H NMR analysis yields copolymer composition, *F*, as a function of monomer feed concentration, *f*, and (ii) SEC analysis of the MWD of the copolymer from pulsed laser polymerization (PLP) provides propagation rate coefficients, $k_{p,copo}$.

Analysis of Copolymer Composition. The ^{1}H NMR spectrum of a DA−MMA copolymer measured in tetrachloroethane-d_2 solution at 120 °C is shown in Figure 1. The numbers assigned to the individual NMR resonances characterize the associated proton positions on the two types of repeat units: (I) = $-CH_2CH(COOC_{12}H_{25})-$ and (II) = $-CH_2C(CH_3)(COOCH_3)-$. The methacrylate mole fraction, F_{mac}, is deduced from the areas under peaks 3 (at 4.0 ppm) and 4 (at 3.7 ppm), which are due to the alkyl methylene protons in α-position to the oxygen atom (of DA units) and to the methyl group on the ester side chain (of MMA units), respectively. Along the same lines, the MA and DMA polymer content is deduced from resonances at 3.7 and 4.0 ppm, respectively. The composition analysis of DMA−DA copolymers is less straightforward because of overlapping ^{1}H NMR resonances.[33] Both monomeric units contribute to the α-methylene resonance at 4.0 ppm. Quantitative analysis has to include resonances 2 (at 1.1 ppm) and 6 (at 1.0 ppm). The overlap is associated

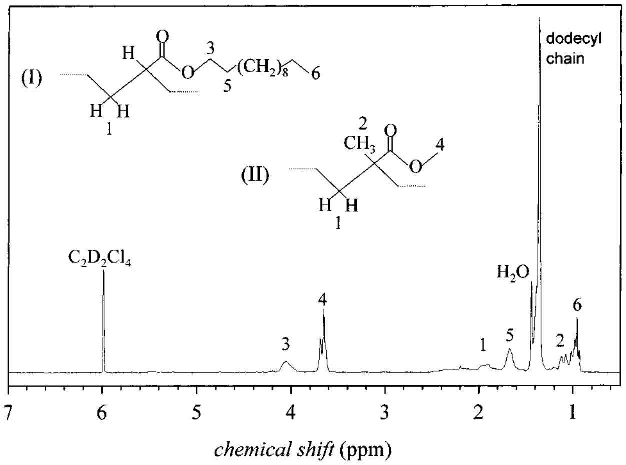

Figure 1. ^{1}H NMR spectrum of a MMA−DA copolymer with $F_{MMA} = 0.60$ synthesized at 40 °C and 1000 bar; I and II are the DA and MMA repeat units, respectively.

Table 2. Copolymer Methacrylate Contents Determined by ^{1}H NMR, F_{mac}, and Associated Monomer Feed Compositions, f_{mac}, for Copolymerizations of MMA−BA, DMA−MA, MMA−DA, and DMA−MA[a]

MMA-BA[16]		DMA−MA		MMA-DA		DMA-DA	
f_{mac}	F_{mac}	f_{mac}	F_{mac}	f_{mac}	F_{mac}	f_{mac}	F_{mac}
0.80	0.90	0.65	0.83	0.80	0.93	0.91	0.95
0.57	0.79	0.35	0.60	0.65	0.83	0.91	0.94
0.31	0.54	0.34	0.62	0.50	0.76	0.81	0.92
0.13	0.29	0.19	0.50	0.50	0.76	0.71	0.87
		0.10	0.31	0.37	0.60	0.71	0.85
		0.10	0.27	0.20	0.44	0.61	0.75
				0.20	0.42	0.61	0.79
				0.12	0.22		

[a] The MMA−BA data are from ref 16 and refer to ambient pressure and 50 °C whereas the other data are for 1000 bar and 40 °C.

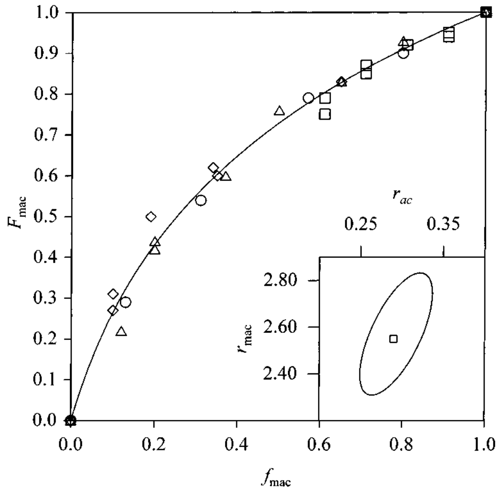

Figure 2. Lewis−Mayo plot for all copolymerization systems under investigation: MMA−BA (circles), DMA−MA (diamonds), MMA−DA (triangles), and DMA−DA (squares). The full line represents the fit of the entire data set to the Lewis−Mayo copolymerization equation (eq 4). With the exception of the MMA−BA data[16] for ambient pressure/50 °C, the composition data refers to 40 °C and 1000 bar.

Table 3. Reactivity Ratio Data, r_{mac} and r_{ac}, Obtained by Individually Fitting the MMA−BA, DMA−MA, and MMA−DA Composition Data, f_{mac} and F_{mac} in Figure 2, to Eq 4[a]

system	r_{mac}	r_{ac}
MMA−BA	2.55 ± 0.35	0.36 ± 0.08
DMA−MA	2.37 ± 0.50	0.21 ± 0.11
MMA−DA	3.26 ± 0.55	0.43 ± 0.11

[a] The limits of uncertainty are deduced from the extension of the individual 95% confidence intervals at the position of the optimum parameter set (see Figure 2).

with a higher uncertainty of F_{DMA} determination in the DA-rich region, below $f_{mac} = 0.5$. Composition data for this region will not be considered.

In Table 2, copolymer methacrylate contents, F_{mac}, deduced from ^{1}H NMR are listed together with the associated (methacrylate) monomer feed compositions, f_{mac}, for MMA−BA, DMA−MA, MMA−DA, and DMA−DA copolymerizations carried out to degrees of overall monomer conversion below 3%. With the exception of the MMA−BA data, which are the values reported by Hutchinson et al.[16] for copolymerization at 50 °C and ambient pressure, the f_{mac} and F_{mac} data refer to 40 °C and 1000 bar. The duplicate experiments in Table 2 demonstrate that the reproducibility of F_{mac} measurement is very satisfactory. The f_{mac} values which were determined by weighing are accurate to within ±1% and the F_{mac}'s are estimated to be accurate within ±5%.

Figure 2 plots the entire set of composition data from Table 2 in a single F_{mac} vs f_{mac} diagram. The composition data of the four acrylate−methacrylate copolymerizations are reasonably well fit by one curve. The particular type of acrylate and methacrylate monomer appears to have no significant influence on the F_{mac}-f_{mac} correlation. The difference in copolymerization pressure (ambient pressure for the MMA−BA system (circles) and 1000 bar for the other three systems) also does not seem to influence the F_{mac}−f_{mac} correlation. Throughout the entire composition range, the fraction of methacrylate polymerized, F_{mac}, exceeds the methacrylate monomer mole fraction, f_{mac}. This preference is most likely due to the higher stability of the radical formed upon the addition of a methacrylate monomer.

The full line in Figure 2 represents the fit of the entire data set to the Lewis−Mayo copolymerization equation (eq 4). The methacrylate and acrylate reactivity ratios

$$F_1 = \frac{r_1 f_1^{\,2} + f_1 f_2}{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}} \tag{4}$$

referring to the fitted line in Figure 2 are $r_{mac} = 2.55$ and $r_{ac} = 0.29$. The accuracy of these numbers is estimated from the extension of the associated 95% confidence interval at the position of the optimum parameter set to be $r_{mac} = 2.55 \pm 0.20$ and $r_{ac} = 0.29 \pm 0.04$. The confidence interval is shown in the lower right part of Figure 2.

Table 3 summarizes the reactivity ratios, r_{mac} and r_{ac}, that are obtained by individually fitting the composition data of the MMA−BA, MMA−DA, and DMA−MA systems. Because of the above-mentioned problem encountered in quantitative ^{1}H NMR analysis, the data for the DA−DMA system are too scarce to fit individually. Within the rather large uncertainty of the reactivity ratio data, these individual r_{mac} and r_{ac} values agree with the reactivity ratio numbers deduced from the overall fit. As is to be expected, the individual 95% confidence intervals overlap each other and are overlapping with the confidence interval obtained from the overall fit (Figure 2).

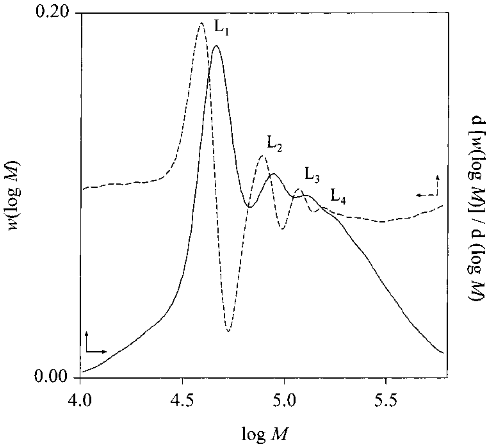

Figure 3. Experimental molecular weight distribution (full line) of a MMA−BA copolymer ($F_{\mathrm{MMA}} = 0.785$) produced at 40 °C and 1000 bar and associated first derivative curve (dashed line).

Analysis of Copolymerization k_p. Figure 3 shows the MWD (full line) and the associated first derivative curve (dashed line) of a BA−MMA copolymer ($F_{\mathrm{MMA}} = 0.785$) obtained at 40 °C/1000 bar by pulsed laser polymerization at a pulse repetition rate $\upsilon = 40$ Hz. The first derivative plot clearly exhibits four maxima, the positions of which yield the degrees of polymerization, L_1 to L_4, that allow the $k_{\mathrm{p,copo}}$ determination (see eq 1), although only L_1 was used for estimating $k_{\mathrm{p,copo}}$. Higher overtones, at least L_2, however, must occur to fulfill the consistency criterion for reliable PLP−SEC experiments.[9,10]

The experimental $k_{\mathrm{p,copo}}$ data for bulk polymerizations at 40 °C and 1000 bar are listed in Table 4, parts a−d together with the associated homopropagation values that were either measured in the present study or deduced from the literature. The homopropagation rate coefficients for MMA and DMA measured in the present study agree within ±20% with data from previous investigations.[10,11] The acrylate homopropagation rate coefficients were extrapolated from literature data measured at slightly lower temperature. The numbers for DA (39813 $\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$ at 40 °C/1000 bar) and for MA (28567 $\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$ at 40 °C/1000 bar) are estimated from ref 32. The homopropagation rate coefficient for BA (35596 $\mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}}$ at 40 °C/1000 bar) was estimated from the rate data presented in ref 5. These acrylate homopropagation rate coefficients are given in italics. Table 4, parts a−d also contains the methacrylate mole fractions of the initial mixture, f_{mac}, the densities of the monomer mixture prior to polymerization, ρ_{mix}, the pulse repetition rate, υ, and the molecular weight of the first point of inflection, M_{L1}, referring to universal calibration vs polystyrene standards.

Most experiments were carried out in duplicate. They yield $k_{\mathrm{p,copo}}$ values which agree within ±5%. Because of uncertainties associated with SEC calibration of copolymer molecular weight, the error in absolute $k_{\mathrm{p,copo}}$ may be as large as ±25%. The relative uncertainty of $k_{\mathrm{p,copo}}$ for a given copolymer system at constant p and T should not exceed ±15%.

As illustrated in Figure 4, in the MMA−BA and DMA−MA copolymerizations $k_{\mathrm{p,copo}}$ is almost constant at methacrylate concentrations above $f_{\mathrm{mac}} = 0.5$ and steeply increases at methacrylate mole fractions below $f_{\mathrm{mac}} = 0.2$ (toward the acrylate homopropagation value, k_p(ac), which exceeds k_p(mac) by more than 1 order of magnitude). The DA-containing systems, MMA−DA and DMA−DA, show a different type of composition dependence of $k_{\mathrm{p,copo}}$. Figure 5 shows that $k_{\mathrm{p,copo}}$ clearly increases with acrylate content also in the region above $f_{\mathrm{mac}} = 0.5$.

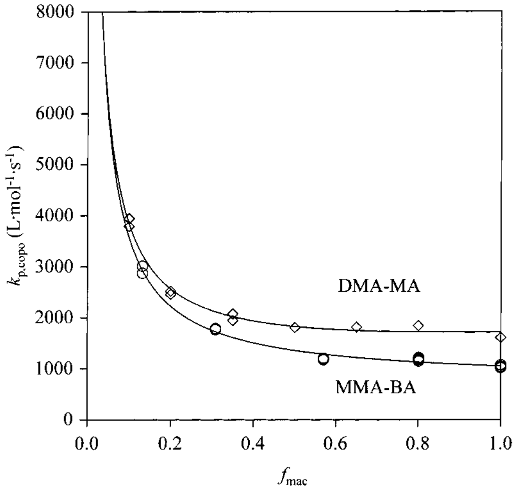

Figure 4. Experimental $k_{\mathrm{p,copo}}$ data for the systems MMA−BA (circles) and DMA−MA (diamonds) at 40 °C and 1000 bar.

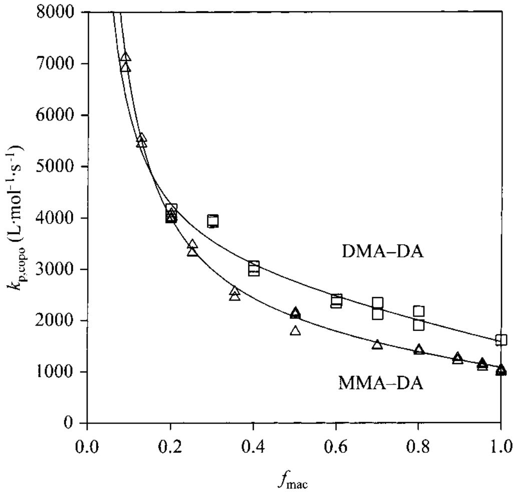

Figure 5. Experimental $k_{\mathrm{p,copo}}$ data for the systems MMA−DA (triangles) and DMA−DA (squares) at 40 °C and 1000 bar.

The kinetic data will now be analyzed in terms of the existing copolymerization k_p models. A brief overview of these models is given in ref 16. The terminal model expression correlates instantaneous monomer and copolymer compositions (eq 4); the reactivity ratios in this equation are defined as $r_i = k_{\mathrm{p}ii}/k_{\mathrm{p}ij}$, where $k_{\mathrm{p}ij}$ refers to the addition of monomer j to a free radical terminating in a unit derived from monomer i. The expression for copolymerization propagation rate coefficient, $k_{\mathrm{p,copo}}$, is shown in eq 5. The penultimate models, in addition,

$$k_{\mathrm{p,copo}} = \frac{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}}{(r_1 f_1/k_{\mathrm{p11}}) + (r_2 f_2/k_{\mathrm{p22}})} \tag{5}$$

specify the monomeric unit in the position penultimate to the free-radical site and use the propagation rate coefficients $k_{\mathrm{p}ijk}$. This extension increases the number of propagation rate coefficients to eight. By ratioing individual $k_{\mathrm{p}ijk}$'s, four reactivity ratios, r_{ij}, and two radical reactivity ratios, s_i, are obtained (eq 6). As shown

$$r_{ii} = \frac{k_{\mathrm{p}iii}}{k_{\mathrm{p}iij}}; \quad r_{ij} = \frac{k_{\mathrm{p}ijj}}{k_{\mathrm{p}iji}}; \quad s_i = \frac{k_{\mathrm{p}jii}}{k_{\mathrm{p}iii}} \tag{6}$$

by Fukuda et al.,[18] the terminal and penultimate reactivity ratios and propagation rate coefficients are related by the expressions in eqs 7 and 8. Expressions

$$\bar{r}_i = r_{ji}\frac{r_{ii}f_i + f_j}{r_{ji}f_i + f_j} \tag{7}$$

$$\bar{k}_{\mathrm{p}ii} = k_{\mathrm{p}iii}\frac{r_{ii}f_i + f_j}{r_{ii}f_i + f_j/s_i} \tag{8}$$

for copolymer composition and propagation rate in terms of the penultimate model are obtained by substituting these expressions into eqs 4 and 5, respectively.

Most of the systems that have been studied so far are adequately described by the implicit penultimate unit effect (IPUE) model, which assumes that $r_{11} = r_{21} = r_1$ and $r_{22} = r_{12} = r_2$. The IPUE model thus contains four parameters: r_1, r_2, s_1, and s_2. Only a few systems such as styrene/acrylonitrile,[34–36] and *p*-chlorostyrene/methyl acrylate[37] require consideration of the full penultimate scheme with six parameters: r_{11}, r_{21}, r_{22}, r_{12}, s_1, and s_2. This model is referred to as the explicit penultimate unit effect (EPUE) model.

As has been reported by Schweer for styrene–MMA,[19] both data sets, F_1 vs f_1 and $k_{\mathrm{p,copo}}$ vs f_1, may be remarkably well fitted to the associated terminal model expressions, eqs 4 and 5, respectively. The same observation has been made by Hutchinson et al.[16] for the MMA–BA system. The data from the present study also show this type of behavior. Figure 2 has already demonstrated that the compositions of the four acrylate–methacrylate systems are adequately represented by the terminal model expression. Figure 5 shows that the $k_{\mathrm{p,copo}}$ values are also nicely represented by the terminal model. The lines for the two DA-containing systems were obtained by fitting the experimental $k_{\mathrm{p,copo}}$ data to eq 5. For the other two systems, MMA–BA and DMA–MA, $k_{\mathrm{p,copo}}$ may also be nicely fitted to eq 5. This is illustrated for DMA–MA in Figure 6. The $k_{\mathrm{p,copo}}$ values are fitted by two procedures: (a) via the terminal model expression (eq 5) and (b) via the IPUE effect model by simultaneously fitting the $k_{\mathrm{p,copo}}$ and composition data. To give equal weight to the $k_{\mathrm{p,copo}}$ and the composition data in the simultaneous fitting procedure, the sum of squares of the deviations between measured and fitted values of $k_{\mathrm{p,copo}}$ and of composition is adjusted, by a factor applied to the $k_{\mathrm{p,copo}}$ data, to equal size. Each of these fits is represented by a full line. The complete overlap of these lines demonstrates that $k_{\mathrm{p,copo}}$ is equally well fit by applying the terminal model to $k_{\mathrm{p,copo}}$ alone or the IPUE model to both $k_{\mathrm{p,copo}}$ and composition data. As IPUE modeling works perfectly with DMA–MA and also with MMA–BA (see ref 16), we did not attempt to model these systems via the EPUE model. The two additional parameters associated with the EPUE treatment do not improve the representation of experimental $k_{\mathrm{p,copo}}$ further. Hutchinson et al.[16] already showed that EPUE modeling is not very rewarding for a system that is nicely fit by IPUE modeling.

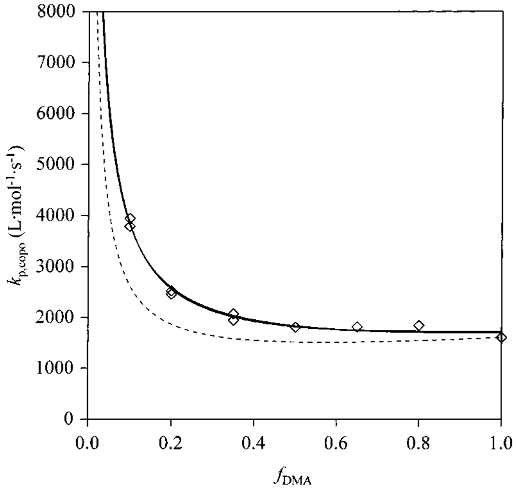

Figure 6. Experimental $k_{\mathrm{p,copo}}$ data for the system DMA–MA at 40 °C and 1000 bar. The two full lines represent fits of the terminal and the IPUE model as described in the text. The dashed line is a terminal model representation with the reactivity ratio data taken from the Lewis–Mayo fit to the composition data.

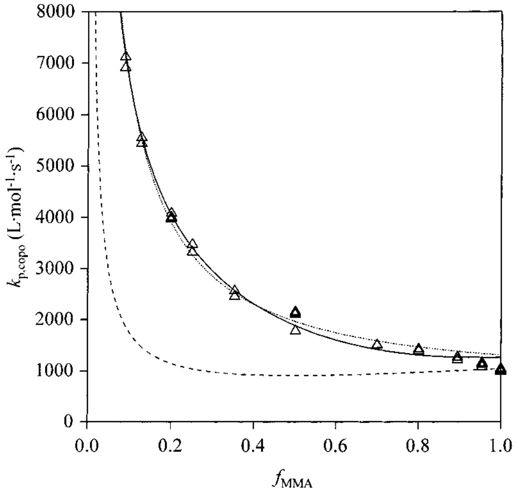

Figure 7. Experimental $k_{\mathrm{p,copo}}$ data for the system MMA–DA (triangles) at 40 °C and 1000 bar. The dashed line represents a terminal model fit with the reactivity ratios taken from the Lewis–Mayo fit to the composition data; the dotted line shows the IPUE model fit with simulated F_{mac} data deduced from the overall composition fit (Figure 2); the full line represents the associated EPUE model fit.

The dashed line in Figure 6, which results from calculating $k_{\mathrm{p,copo}}$ from the terminal model expression (eq 5) with r_1 and r_2 being taken from the terminal model fit of the associated F_{mac} vs f_{mac} data, demonstrates that the terminal model does not simultaneously fit rate and composition in the DMA–MA system. There is a clear discrepancy between calculated and experimental data. The deviation seen with DMA–MA (and also with MMA–BA[16]) is however minor compared to the situation with the two DA-containing copolymerizations, as illustrated by the dashed line in Figure 7 for $k_{\mathrm{p,copo}}$ of MMA–DA. The terminal model estimate of $k_{\mathrm{p,copo}}$ based on r_1 and r_2 values deduced from fitting F_{MMA} vs f_{MMA} (dashed line) is far from the experimental values.

Figure 7 also shows a simultaneous fit of the $k_{\mathrm{p,copo}}$ and composition data to the IPUE model (dotted line). The IPUE fitting is not satisfactory at high f_{mac}; the same is true for DMA–DA (not shown in Figure 7). The EPUE model has also been used for simultaneous nonlinear fitting of the $k_{\mathrm{p,copo}}$ and composition data. As expected, the EPUE fit (full line) represents $k_{\mathrm{p,copo}}$ (and

Table 4. Experimental $k_{p,copo}$ Data for Bulk Polymerizations at 40 °C and 1000 Bar[a]

(a) MMA− BA

f_{MMA}	ρ_{mix} (g·cm^{-3})	υ (Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})	f_{MMA}	ρ_{mix} (g·cm^{-3})	υ (Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})
1.000	0.965	40	24 547	1017	0.570	0.948	50	22 571	1191
1.000	0.965	40	25 100	1040	0.570	0.948	40	28 135	1187
1.000	0.965	40	25 900	1074	0.570	0.948	40	37 167	1176
0.801	0.957	50	23 096	1207	0.308	0.939	100	16 596	1767
0.801	0.957	50	22 568	1180	0.308	0.939	100	16 788	1787
0.801	0.957	40	29 094	1216	0.132	0.934	100	26 850	2876
0.801	0.957	30	36 653	1149	0.132	0.934	100	28 131	3013
0.570	0.948	50	22 833	1204	0.000				*35541*[5]

(b) DMA−MA

f_{DMA}	ρ_{mix} (g·cm^{-3})	υ (Hz)	M_{L1} (g·mol^{-1})	k_p(L·mol^{-1}·s^{-1})	f_{DMA}	ρ_{mix} (g·cm^{-3})	υ (Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})
1.000	0.924	100	14 853	1607	0.348	0.957	100	26 087	1242
0.799	0.930	100	18 570	1040	0.201	0.974	100	32 800	1300
0.645	0.937	100	19 667	1074	0.201	0.974	100	33 664	1422
0.645	0.937	100	19 667	1109	0.101	0.990	100	50 031	1455
0.496	0.945	100	21 102	1159	0.101	0.990	100	52 071	1529
0.348	0.957	100	24 483	1185	0.000				*28567*[32]

(c) MMA−DA

f_{MMA}	ρ_{mix} (g·cm^{-3})	υ(Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})	f_{MMA}	ρ_{mix} (g·cm^{-3})	υ(Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})
1.000	0.965	40	24 547	1017	0.501	0.895	90	17 242	2181
1.000	0.965	40	25 100	1040	0.501	0.895	60	21 419	1806
1.000	0.965	40	25 900	1074	0.354	0.885	60	29 694	2479
0.955	0.954	40	25 389	1109	0.354	0.885	60	31 026	2590
0.955	0.954	40	26 531	1159	0.251	0.880	40	62 239	3353
0.955	0.954	40	27 126	1185	0.251	0.880	40	65 031	3503
0.895	0.942	40	26 753	1242	0.200	0.877	90	33 830	4002
0.895	0.942	40	28 008	1300	0.200	0.877	70	43 800	4031
0.801	0.927	40	28 392	1422	0.200	0.877	70	44 680	4112
0.801	0.927	40	29 049	1455	0.128	0.874	100	44 248	5578
0.700	0.914	60	19 171	1529	0.128	0.874	100	43 383	5469
0.700	0.914	60	19 269	1537	0.090	0.872	100	56 541	6943
0.501	0.895	90	16 839	2130	0.090	0.872	100	58 266	7155
0.501	0.895	90	17 074	2160	0.000				*39813*[32]

(d) DMA−DA

f_{DMA}	ρ_{mix} (g·cm^{-3})	υ (Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})	f_{DMA}	ρ_{mix} (g·cm^{-3})	υ (Hz)	M_{L1} (g·mol^{-1})	k_p (L·mol^{-1}·s^{-1})
1.000	0.924	100	14 853	1607	0.402	0.891	100	26 458	2970
0.797	0.913	100	19 817	2171	0.299	0.885	100	35 039	3958
0.797	0.913	50	34 751	1904	0.299	0.885	100	34 692	3918
0.698	0.907	100	21 237	2341	0.201	0.880	100	36 761	4178
0.698	0.907	100	19 186	2115	0.201	0.880	100	36 056	4098
0.598	0.902	100	21 742	2411	0.098	0.874	100	42 833	4899
0.598	0.902	100	21 139	2344	0.098	0.874	100	44 843	5129
0.402	0.891	100	27 209	3054	0.000				*39813*[32]

[a] The acrylate homopropagation rate coefficients deduced from the literature are given in italics; f_{MMA} = MMA mole fraction of the initial monomer mixture, f_{DMA} = DMA mole fraction of the initial monomer mixture, ρ_{mix} = initial density, υ = pulse repetition rate, M_{L1} = molecular weight of the first point of inflection (referring to calibration against polystyrene standards).

composition) data better than IPUE modeling. The agreement between measured and EPUE-modeled data is, however, not perfect at high f_{mac}. Comparison with Figure 5 suggests that the EPUE fit is of poorer quality than that achieved by applying the (simple) terminal model to $k_{p,copo}$ alone.

Each of the various fitting procedures (which have been carried out via the nonlinear least squares procedure according to Levenberg−Marquardt[38]), yields reactivity ratio data. IPUE and EPUE modeling, in addition, provides radical reactivity ratios, s_i. The r values thus obtained are summarized in Table 5.

As already noted, the r_{mac} values of the various acrylate−methacrylate systems are close to each other, as are the r_{ac} data. The numbers for r_{mac} from fitting composition are in the range 2.7 ± 0.6 and for r_{ac} are in the range 0.32 ± 0.11. The reactivity ratio values from (simultaneous) IPUE modeling of composition and of $k_{p,copo}$ are also within these ranges, as are the $r_{mac,mac}$ and $r_{ac,ac}$ data from EPUE fitting. EPUE modeling has only been carried out for the MMA−DA system. The DMA−MA system has not been subjected to this procedure as IPUE modeling is already rather successful. DMA−DA was not EPUE-fitted as the information on compositions is too scarce for this system. For MMA−BA the EPUE parameters reported by Hutchinson et al.[16] are included in Table 5. The EPUE parameters illustrate the general problem which has already been pointed out by Coote and Davis,[17] that these parameters are partly indeterminate and/or are associated with large uncertainties.

The IPUE model affords for a satisfactory simultaneous representation of propagation rate and composition for the MMA−BA and DMA−MA copolymerizations and provides reasonable numbers for the methacrylate radical reactivity ratio, $s_{mac} \cong 2$, with s_{ac} however being indeterminate. EPUE modeling of the MMA−BA system yields numbers that are more or less consistent with

Table 5. Reactivity Ratios Obtained by Fitting the Experimental Composition and Propagation Rate Data of Acrylate−Methacrylate Copolymerizations to Different Models (See Text)[c]

		MMA−BA	DMA−MA	MMA−DA	DMA−DA
$F_{mac} - f_{mac}$ terminal	r_{mac}	2.55[a]	2.37	3.26	
model fit (eq 4)	r_{ac}	0.36[a]	0.21	0.43	
$k_{p,copo}$ terminal	r_{mac}	1.52	2.05	0.88	0.88
model fit (eq 5)	r_{ac}	0.44	0.37	0.53	0.21
IPUE fit	r_{mac}	2.47[b]	2.57	2.11	
	r_{ac}	0.38[b]	0.23	0.31	
	s_{mac}	2.06[b]	1.9	ind.	
	s_{ac}	ind.[b]	ind.	0.05	
EPUE fit	$r_{mac,mac}$	2.11 ± 0.40^{16}		2.80	
	$r_{ac,ac}$	0.56 ± 0.49^{16}		0.39	
	$r_{ac,mac}$	6.60 ± 24.5^{16}		0.52	
	$r_{mac,ac}$	0.60 ± 0.85^{16}		ind., high	
	s_{mac}	4.3^{16}		0.56	
	s_{ac}	ind.		ind., high	

[a] From data for ambient pressure and 50 °C.[16] [b] Fitting procedure was carried out by estimating F_{mac} for a given f_{mac} from eq 4 with $r_{mac} = 2.55$ and $r_{ac} = 0.29$. [c] ("ind." says that the value is indeterminate). If not stated otherwise, the data refer to 40 °C and 1000 bar.

the values from IPUE modeling. The expanded number of parameters is a disadvantage of EPUE modeling, at least from an application-oriented point of view.

For MMA−DA, where the IPUE model fails to provide an adequate simultaneous fit of the rate coefficient and composition data, also the EPUE analysis is not overly successful. The r_{ii} values are in the expected range, but the $r_{mac,ac}$, s_{mac}, and s_{ac} values are either difficult to understand ($s_{mac} < 1$) or are unrealistically high ($r_{mac,ac}$ and s_{ac}). Moreover, the fit of the experimental $k_{p,copo}$ data by the EPUE model is not satisfactory at high f_{mac} (see Figure 7). We do not know at the moment to which extent the experimental uncertainty and the limited number of available data, in particular of $k_{p,copo}$, contribute to this failure. With the exception of $r_{mac,mac}$ and $r_{ac,ac}$, detailed analysis of EPUE parameters does not appear to be overly rewarding.

In what follows, the entries in the upper part of Table 5 will be primarily addressed with particular emphasis on the reactivity ratios deduced from terminal model fitting of $k_{p,copo}$ via eq 5. This kind of information is available for all four systems with all these data referring to 1000 bar and 40 °C. A first point to be noted from these data is that with MA being the acrylate monomer, in DMA−MA, r_{mac} is relatively close to the methacrylate reactivity ratios obtained by terminal model fitting of the F_{mac}−f_{mac} data of the four systems under investigation. With the BA-containing system, MMA−BA, r_{mac} is clearly below the corresponding value obtained by fitting composition. This difference is consistent with what Hutchinson et al.[16] report for the terminal model fit of their ambient pressure/50 °C MMA−BA $k_{p,copo}$ data, $r_{mac} = 1.60 \pm 0.11$. Terminal model analysis of $k_{p,copo}$ for the two DA-containing systems yields even lower r_{mac} values. They are smaller than unity. That both r_{mac} values for the DA-containing systems are exactly the same ($r_{mac} = 0.88$) is certainly fortuitous. The significant lowering in r_{mac}, with increasing ester size of the acrylate monomer is, however, clearly backed by the experimental data.

One route to try to independently access reactivity ratio data, r_{mac} and r_{ac}, proceeds via estimates based on addition-to-monomer rate coefficients of free radicals. Fischer's group determined an extended series of such coefficients for reaction in liquid solution via EPR spectroscopy.[21,22] Among those radicals studied, the 2-(*tert*-butoxycarbonyl)-2-propyl radical, *t*-BuO−CO−C(CH$_3$)$_2^\bullet$, is rather similar to the free radical that occurs in methacrylate polymerization, whereas the *tert*-butoxy carbonylmethyl radical, *t*-BuO−CO−CH$_2^\bullet$, is similar to the propagating free radical that occurs in acrylate polymerization. The activation energy for the addition of the 2-(*tert*-butoxycarbonyl)-2-propyl radical to MMA (22.4 kJ·mol^{-1}) is the same as the experimental activation energy of MMA homopropagation. The rate coefficients, *k*, and associated activation energies, E_A, for the addition of the *tert*-butoxy carbonylmethyl radical and of the 2-(*tert*-butoxycarbonyl)-2-propyl radical to MA and to MMA in acetonitrile solution at ambient conditions are listed in the recent article by Fischer and Radom[39] and are summarized in Table 6.

Table 6. Addition Rate Coefficients, *k*, at Ambient Pressure and Temperature and Associated Activation Energies, E_A, for the Reaction of "Acrylate"-Type and "Methacrylate"-Type Free Radicals with MMA and MA

system	*k* (L·mol^{-1}·s^{-1})[21,22]	E_A (kJ·mol^{-1})[21,22]	*r*
t-BuO−CO−CH$_2^\bullet$			
+ MA	4.9×10^5	15.6	0.38
+ MMA	1.3×10^6	13.3	
t-Bu-O−CO−C(CH$_3$)$_2^\bullet$			
+ MMA	3710	22.4	3.23
+ MA	1150	25.3	

Assuming that these addition rate coefficients are suitable measures of homo- and cross-propagation rate of acrylate−methacrylate copolymerizations, the "terminal" reactivity ratios are $r_{mac} = 3.2$ and $r_{ac} = 0.38$. These numbers are remarkably close to those from terminal model fitting of the f_{mac}−F_{mac} data, and also to those obtained by simultaneous IPUE and/or EPUE modeling of $k_{p,copo}$ and of F_{mac} values measured as a function of methacrylate monomer content, f_{mac}. It should be noted that the *tert*-butoxy carbonylmethyl radical is not a perfect model for "acrylate" free radicals, and the reaction temperatures and pressures were not the same. Moreover, the enormous difference in size between the *tert*-butoxy carbonylmethyl radical or the 2-(*tert*-butoxycarbonyl)-2-propyl radical and the actual macroradicals will not be fully eliminated by the ratioing procedure in deducing r_{mac} and r_{ac} from the rate coefficients in Table 6.

The r_{mac} and r_{ac} values estimated from the addition rate coefficients for the *tert*-butoxy carbonylmethyl radical and the 2-(*tert*-butoxycarbonyl)-2-propyl radical reactions may be considered as some "terminal" reactivity ratios of free radicals that consist exclusively of the respective terminal unit. Inspection of the reactivity ratio data (Table 5) obtained by separate terminal model fitting of the $k_{p,copo}$ and composition data for the DA-containing systems reveals an important point: The set of r_{mac} and r_{ac} values estimated from the kinetic coefficients (Table 6) is clearly different from the reactivity ratio data deduced from terminal model fitting of $k_{p,copo}$, which clearly is another purely kinetic quantity, whereas it is close to the r_{mac} and r_{ac} data set obtained by terminal model fitting of composition. (The difference between the two r_{mac} values deduced for MMA−DA from the separate terminal model fits, to $k_{p,copo}$ and to composition, largely exceeds the limits of uncertainty. This is equivalent to saying that no reasonable simultaneous fit of both $k_{p,copo}$ and composition may be carried out via the terminal model.)

This puzzling behavior may be understood by considering the well-known terminal model expressions for copolymer composition and $k_{p,copo}$, eqs 4 and 5, respectively. Whereas copolymer composition is a function only of reactivity ratios, $k_{p,copo}$, in addition, depends on two individual propagation rate coefficients, k_{p11} and k_{p22}. The adequate fit of composition by the terminal model together with the rather satisfactory agreement of the associated r's with the r values deduced from rate coefficients of the corresponding small radicals (Table 6) strongly suggests that it is not the reactivity ratio data that is responsible for the failure of describing copolymerization kinetics. Reactivity ratios obviously are useful and important kinetic quantities, rather than adjustable parameters without any physical meaning. The difficulties met with simultaneously fitting composition and $k_{p,copo}$ appear to be due to the problems of taking the influence of penultimate units on individual homo- and cross-propagation rate coefficients properly into account.

The reason the "terminal model" reactivity ratios are relevant quantities, although penultimate units undoubtedly affect propagation rate, is seen in the ratioing procedure. Dividing homo- by cross-propagation rate coefficients for radicals terminating in the same units obviously eliminates most of the impact of the penultimate units on the resulting ratios and certainly also of units that are even further apart from the free-radical site. The failure of the terminal model to simultaneously fit propagation rate and copolymer composition demonstrates that penultimate effects are operative in the overwhelming majority of systems studied so far. The influence of penultimate units is adequately taken into account with most binary copolymerization systems by introducing the radical reactivity ratios, s_1 and s_2, as two additional parameters, by using the IPUE model. Considering kinetics, the success of the IPUE model is thus due to: (a) an effective elimination of penultimate unit contributions by the ratioing of rate coefficients of radicals with the same terminal and penultimate unit, which results in $r_{11} = k_{p111}/k_{p112} \cong r_{21} = k_{p211}/k_{p212}$, and (b) to the parameters $s_1 = k_{p211}/k_{p111}$ and $s_2 = k_{p122}/k_{p222}$ adequately accounting for the penultimate unit effect.

Why are not the copolymerization systems containing DA satisfactorily fit by the IPUE model, and why does not the EPUE model with two more parameters adequately fit both composition and propagation rate? Homopropagation studies of acrylates demonstrate that k_p increases with larger ester size.[5,32] This effect is presumably due to an increase in free-radical reactivity rather than to a rate enhancement induced by the acrylate monomer. The similar activation energies of acrylate homopropagation rate coefficients, k_p, suggest that entropic effects should primarily affect reactivity of the acrylate free radical. Such contributions may originate from units beyond the penultimate one. Consequently, even replacing the IPUE modeling by EPUE simulation will not help in cases where free-radical reactivity is influenced by "pen"-penultimate units.

It should be noted again, that the terminal model applied to $k_{p,copo}$ alone allows for a very reasonable fit. Inspection of eq 5 suggests that the surprisingly low values of r_{mac} in fitting the DA-containing systems and also the reduced (as compared to r_{mac} from composition analysis) value for r_{mac} of the BA-containing system (Table 5) may be due to a "pen"-penultimate-unit-induced enhancement of $k_{p,copo}$. During fitting this enhancement translates into the observed lowering of r_{mac}. The impact on r_{mac} is larger than that on r_{ac} as the $k_{p,copo}$ effect is seen in the methacrylate-rich composition range and as k_p(mac) is significantly below k_p(ac), which further enhances the importance of the methacrylate term in the denominator of eq 5. The DA-containing systems appear to be special in that the impact of DA units on free-radical reactivity cannot be fully accounted for by the IPUE and EPUE models which in addition to terminal units only consider penultimate units. A quantitative understanding of this effect will certainly also assist the interpretation of homopropagation rate coefficients within the (meth)acrylate families.

It appears to be a matter of priority to address the issue of propagation rate in both homo- and copolymerization in more detail. The data basis of highly accurate $k_{p,copo}$'s needs to be expanded to allow for model discrimination and for safely deciding whether an unsatisfactory fit of $k_{p,copo}$ data is due to a failure of the model or to insufficient data quality. Improving and extending kinetic models is another important task. The remarkable success of eq 5 to fit $k_{p,copo}$ suggests that, in addition to extending complex models, also simple expressions should be considered and perhaps be modified.

Conclusions

Copolymerization k_p and copolymer composition of several binary acrylate−methacrylate systems have been studied. The results clearly demonstrate the importance of penultimate unit effects on free-radical reactivity. The terminal model is not capable of simultaneously fitting the $k_{p,copo}$ and composition data, but adequately fits these two quantities individually. With the MA−DMA and BA−DMA systems, the IPUE model satisfactorily fits the rate and composition data simultaneously, whereas for the two DA-containing systems, DA−MMA and DA−DMA, neither the IPUE nor the EPUE model allows for overly convincing simultaneous fits. Reactivity ratios estimated from literature addition rate coefficients to MA and MMA of appropriate small (meth)acrylate free radicals agree well with reactivity ratios deduced for the four systems of the present study by the conventional Lewis−Mayo method. This suggests that the widely used terminal model reactivity ratios r_i are reasonable and meaningful kinetic quantities. The applicability of terminal r_i values to penultimate-type systems is probably due to the elimination of most of the impact of penultimate units on the reactivity ratios by the ratioing procedure. Thus, the IPUE r_{ii} and r_{ji} are close to each other as are r_{jj} and r_{ij}. Accordingly, the

IPUE model, which uses only two reactivity ratios, r_i and r_j, and the radical reactivity ratios, s_i and s_j, works remarkably well in the majority of systems. In cases where the IPUE model fails to simultaneously fit both rate and composition, the EPUE model may perform better. It appears, however, that such failure often results from influences of "pen"-penultimate units on free-radical reactivity. The EPUE model obviously cannot account for such effects which seem to operate, e.g., in the DA-containing systems of this study.

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