Radical Ring-Opening Copolymerization of 2-Methylene 1,3-Dioxepane and Methyl Methacrylate: Experiments Originally Designed To Probe the Origin of the Penultimate Unit Effect

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ABSTRACT: Pulsed-laser polymerization experiments were conducted on the copolymerization of 2-methylene 1,3-dioxepane (MDO) and methyl methacrylate (MMA) at 40 °C. Reactivity ratios, based on the terminal model, were determined from copolymer compositional analyses as $r_{\mathrm{MDO}} = 0.057$ and $r_{\mathrm{MMA}} = 34.12$. The average propagation rate coefficients, $\langle k_p \rangle$, were determined for a number of feed compositions ranging from an MDO mole fraction of 0 to 0.916. It was not possible to obtain a $\langle k_p \rangle$ value for the homopolymerization of MDO as the PLP experiment was compromised by high chain transfer rates to polymer and monomer. The data were fitted to a number of copolymerization models, viz. the terminal and the explicit and implicit penultimate unit models and the bootstrap solvent dependence model. It was found that the terminal and penultimate unit models for copolymerization could not adequately describe the experimental results. A fit to a bootstrap model was successful, but the values obtained indicated a very large, unprecedented, partitioning effect.

Introduction

The pulsed-laser polymerization (PLP) technique[1] has now become firmly established as a powerful tool to measure propagation rate coefficients in free radical polymerization.[2,3] Several groups have extended PLP studies into copolymerization and terpolymerization reactions.[4−10] In nearly all cases observed so far, the terminal (or Mayo−Lewis) model fails to describe the experimental $\langle k_p \rangle$ and copolymer composition data simultaneously. Most workers now believe that the main shortcomings of the terminal model can be assigned to a strong penultimate unit effect on many copolymerization reactions, although opinions on the origin of the penultimate unit effect may be different. The theoretical framework that seems to have supplanted the terminal model is the implicit penultimate unit model (IPUE) developed by Fukuda and co-workers.[11] This model assumes that there is a substantial contribution from the γ-substituent (penultimate unit) which alters the reactivity but not the selectivity of the radical. As a consequence, the general penultimate model, as originally proposed by Merz et al.,[12] reduces to a set of much simpler mathematical equations. However, the general validity of this assumption, as justified in the stabilization energy model proposed by Fukuda et al.,[11] has been questioned in recent theoretical studies[13,14] which conclude that implicit penultimate unit effects can only occur under specific circumstances. Therefore, we believe that the general penultimate unit model (called the explicit penultimate unit model by Fukuda et al.)[15] provides in general a physically more realistic, though mathematically more complex, description of the chemical reaction kinetics. The task at hand is thus to provide experimental evidence for these penultimate unit effects and to determine situations in which the simplified model, i.e., the IPUE model, is applicable. Although this sounds trivial, such detailed studies have only been performed in a few specific cases, and the bulk of experimental data reported in the literature implicitly assume the validity of the IPUE model without testing this assumption.

The main problem in deciding among the various copolymerization models is that the composition and $\langle k_p \rangle$ values experimentally measured are not sensitive enough to allow for unequivocal discrimination. This was shown quite clearly by extensive studies on styrene (STY)−methyl methacrylate (MMA) copolymerization where even a large, careful experimental design did not permit model discrimination.[8,16] The challenge is therefore to design new experiments that will permit either a direct measure of the penultimate unit effect (negating the need for model fitting) or experiments that simplify the model fitting procedure by minimizing the number of fit parameters. In this study, we choose the latter approach, and the system we selected to investigate is the copolymerization of MMA with 2-methylene 1,3-dioxepane (MDO), a monomer that undergoes ring-opening in free-radical polymerization.

Radical ring-opening polymerization has been studied extensively by Bailey[17] and Endo.[18,19] Most previous studies have concentrated on the synthetic aspects of monomer and polymer syntheses, and there is very little kinetic and mechanistic data available in the literature. The radical ring-opening polymerization of MDO to yield polycaprolactone has been subject of a number of studies[17,18,20−22] which show that 100% ring-opening occurs at 25 °C and the mechanism shown in Figure 1 is generally assumed to be valid. The rate-determining step has been shown to be the bimolecular propagation step. The only previous work on copolymerization of MDO monomer has been restricted to monomer reactivity ratio measurements with styrene.[22]

The work described in this paper is the first attempt (to our knowledge) to measure propagation rate coefficients for the ring-opening polymerization of a cyclic

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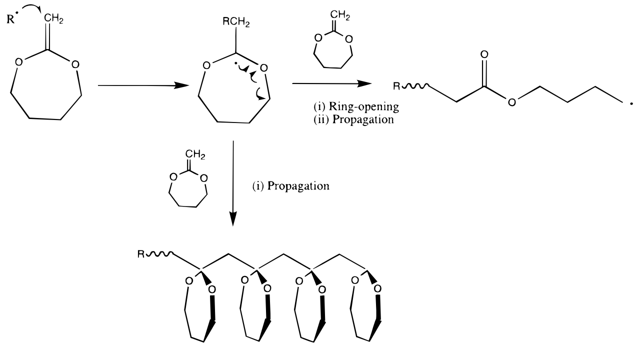

Figure 1. Scheme depicting the generally accepted mechanism for the radical ring-opening of MDO. The facile ring-opening reaction occurs exclusively at room temperature leading to the formation of polycaprolactone.

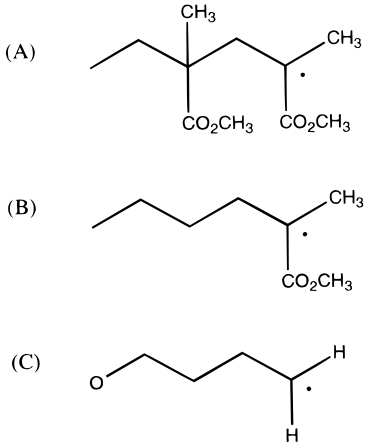

Figure 2. Chain end structures of the three radical types present in the system (assuming a negligible kinetic contribution from antepenultimate units). The MMA radical end group may be preceded by either another MMA unit (A) or a MDO (ethylene) unit (B). The MDO radical end group is always preceded by another ethylene-type unit (C).

ketene acetal. The specific experimental design was originally envisaged as an attempt to simplify copolymerization kinetics, so that the penultimate unit effect on propagation could be restricted to an influence on just one terminal-radical type in a copolymerization system. This is illustrated in Figure 2, which shows that the MMA terminal radical can have either a MMA or an ethylene penultimate unit. In contrast, the MDO terminal unit (defining a unit as consisting of two substituted carbon atoms in the polymer backbone, which for MDO is effectively an ethylene unit) always has the same preceding unit, viz. another ethylene unit. Therefore any penultimate unit effect which is observed may be attributed solely to the one on the MMA radical.

Experimental Section

Synthesis of MDO Monomer. MDO was synthesized in a two-step process via 2-bromomethyl-1,3-dioxepane (BMDO). Bromoacetaldehyde diethyl acetal (1 mol, 197.08 g), butane-1,4-diol (1 mol, 90.0 g), *p*-toluenesulfonic acid (1 g), and a trace of hydroquinone were refluxed in cyclohexane solvent for 5 h. Ethanol was removed as the reaction progressed. The BMDO was isolated by vacuum distillation at 0.02 mmHg (yield 71%). The BMDO (0.31 mol, 60 g) was cooled to 0 °C, and finely ground potassium hydroxide (0.36 mol, 20 g) and tetrabutylammonium bromide (TBAB) (0.5 g) were slowly added to the stirred mixture. The solution was maintained at 0 °C for 20 min and then allowed to warm to ambient temperature. The reaction mixture was then placed in an ultrasonic bath at 75 °C, and MDO was distilled into a collection flask containing potassium carbonate and potassium hydroxide pellets (yield, 28.5%). The product MDO obtained was found to contain some BMDO contaminant which we found difficult to remove. Therefore in all the PLP experiments detailed in this paper we corrected the MDO concentration to allow for a 6% contamination by BMDO (as found by NMR). For the CLD experiments we double-distilled the MDO and obtained a purity of 99% (by NMR). This matter is discussed further in the paper.

Pulsed-Laser Polymerization. The PLP procedure has been described in a number of our earlier publications[8,16,23] and will not be elaborated on here. All of the PLP data were obtained at 40 °C.

Chain Transfer to Monomer Experiments. The chain transfer to monomer constant was determined using the chain length distribution method (CLD).[24,25] A stock solution of azobisisobutyonitrile (AIBN) (0.0107 g) in MDO (0.976 g) was prepared. This stock solution was successively diluted with MDO to make a number of solutions with decreasing initiator concentrations. Each solution was degassed via freeze−thaw cycles and then placed in a thermostated oven at 40 °C. The resultant polymer was precipitated in methanol, redissolved in acetone, and reprecipitated in methanol prior to drying at 20 °C in vacuo.

SEC Analyses. Molecular weights were determined by SEC using tetrahydrofuran (THF) eluent at 1 mL min^{-1}. Four 5.0 μm bead columns (Polymer laboratories) were used in series (10^3, 10^4, 10^5, and 10^6 Å). Two detectors were used: a PL differential refractive index detector and a Viscotek model 250 differential viscometer.

NMR Analyses. ^{13}C and ^{1}H NMR spectra were recorded on a 300 MHz (Bruker ACF300) spectrometer using $CDCl_3$ (Aldrich) as solvent. These were used to determine both the composition of the copolymers and the extent of ring-opening in the MDO homopolymers. In all of the experiments conducted with MDO we found 100% ring-opening.

Results and Discussion

Determination of Mark−Houwink−Kuhn−Sakurada (MHKS) Parameters for PMDO in THF. Attempts were made to measure the MHKS parameters for PMDO using the polymers synthesized for chain transfer to monomer studies. The approach used has been described in earlier papers and utilizes SEC with online viscometric detection.[23,26,27] Ten different samples were subjected to MHKS analyses, and we observed considerable scatter in the MHKS plots. This scatter can be ascribed to the low molecular weights of the polymers, caused by the high chain transfer constant to monomer (vide infra) and branching originating from backbiting reactions.[20,28] Four of the 10 samples gave reasonably linear MHS plots and showed fair agreement, yielding MHKS parameters, $K = 23 \times 10^5$ dL·g^{-1} and $\alpha = 0.71$. To investigate the possible influence of branching on these polymers we used ^{1}H NMR in conjunction with assignments for branching reactions obtained for PMDO polymers.[20,28] Branching was found to be present at about one branch point for every 25 chain units. It therefore seems likely that these MHKS constants are subject to reasonable uncertainty.

Measurement of Chain Transfer to Monomer Constant, C_M, by The CLD Method. The CLD approach has recently been developed by Gilbert and coworkers,[24] founded on the precept that chain-length effects diminish if one determines the high-molecular weight slope of a molecular weight distribution which is plotted as the natural logarithm of the number distribution, $P(M)$, vs molecular weight.

$$\lim_{M\to\infty} P(M) = \text{constant} \times \exp\left(-\frac{\langle k_t\rangle[\mathrm{R}^\bullet] + k_{tr}[\mathrm{M}]}{k_p[\mathrm{M}]}\frac{M}{m_0}\right) \tag{1}$$

where $P(M)$ is the number of chains of molecular weight M, m_0 is the molecular weight of monomer, [M] and [R$^\bullet$] are the monomer and radical concentrations, respectively, k_{tr} and k_p are the rate coefficients for chain transfer to monomer and propagation, respectively, and $\langle k_t\rangle$ is the average termination rate coefficient. As the concentration of initiator is reduced, the radical concentration, and hence the rate of termination decreases. This eventually leads to the termination rate being insignificant compared to the chain transfer rate and so $\langle k_t\rangle[\mathrm{R}^\bullet] \ll k_{tr}[\mathrm{M}]$, allowing eq 1 to be simplified as

$$\lim_{M\to\infty,[\mathrm{I}]\to 0} P(M) = \text{constant} \times \exp\left(-C_\mathrm{M}\frac{M}{m_0}\right) \tag{2}$$

Thus in the limit of low initiator concentration, the chain transfer to monomer constant, C_M ($=k_{tr}/k_p$), can be determined from the slope of the molecular weight distribution, plotted as ln $P(M)$ vs M.

The results for MDO homopolymerization at 40 °C are given in Table 1 and a typical CLD plot is shown in Figure 3. From these experiments a C_M value of 1.7×10^{-2} can be obtained. This value contains some uncertainty due to the occurrence of chain transfer to polymer and backbiting, which lead to a narrowing of the high molecular weight side of the molecular weight distribution and hence a larger slope. However, we believe that our estimate is correct within a factor of about 3. It is noteworthy that the molecular weight distributions are much narrower than we would normally expect, and we have no current explanation for this, other than that some narrowing may be caused by branching. We are confident that the polydispersities we obtained are not caused by errors in the SEC analyses.

Using the obtained value for C_M and a homopropagation rate coefficient of 40 dm^3 mol^{-1} s^{-1} (vide infra), a value of ~0.1−0.7 dm^3 mol^{-1} s^{-1} is obtained for k_{tr}. This value is quite high compared to the k_{tr} values of MMA and styrene, which are about 2 orders of magnitude lower,[29,30] but is of comparable magnitude to the k_{tr} found for the acrylates[29,31] at the same temperature. The latter observation indicates that the value we obtained for C_M is indeed a realistic one. Comparison now of this C_M value with those obtained for MMA, styrene, and the acrylates, which all have C_M values around 5×10^{-5} at 40 °C, shows that this value is about 2−3 orders of magnitude larger. This is mainly caused by the fact that we have a combination of a large chain transfer and a small propagation rate coefficient, a situation that is similar to the one observed in α-methylstyrene.[30] The effect of such a high chain transfer constant to monomer is quite dramatic, as this value intrinsically limits the maximum obtainable molecular weight[32] which can be estimated from the simplified Mayo equation (i.e., average degree of polymerization $= C_\mathrm{M}^{-1}$). In the present situation the maximum obtainable number average molecular weight, M_n, can be estimated to lie between 7000 and 20000, which is indeed observed experimentally (see Table 1).

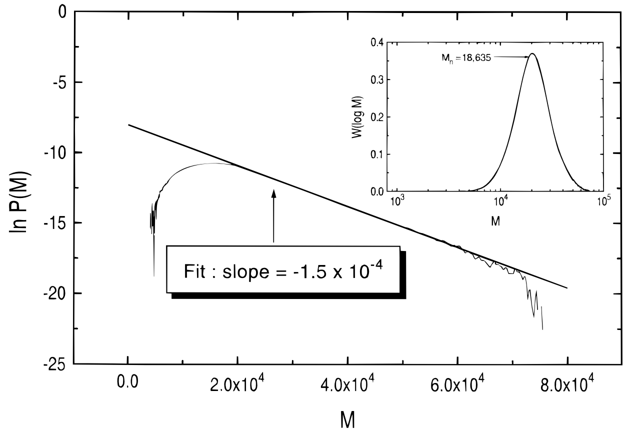

Figure 3. Typical ln $P(M)$ plot from which we derived C_M values for MDO. The inset shows the original SEC chromatogram ($W(\log M)$ vs M).

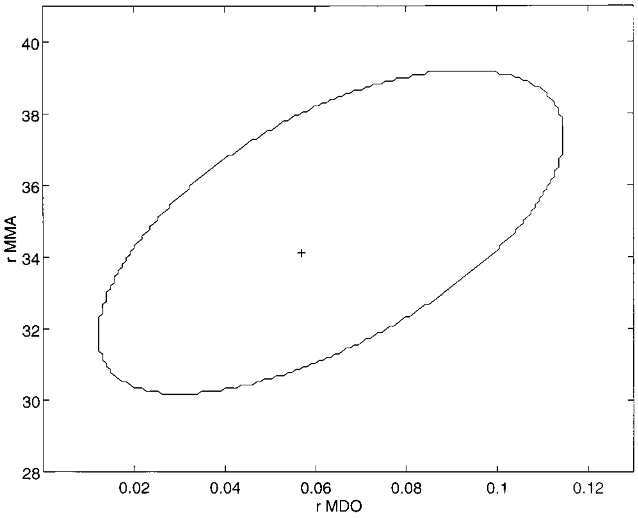

Figure 4. 95% confidence interval for the reactivity ratios of MDO with MMA.

Table 1. Experimental Conditions and Results for the CLD Measurements on MDO at 40 °C

AIBN concn (w/w %)	MDO (g)	polymerization yield (%)	$M_n \times 10^{-3}$	poly-dispersity	slope
9.60	0.7985	1.60	16.7	1.14	-1.3×10^4
1.42	0.9176	7.59	16.8	1.35	-4.7×10^4
0.15	0.9076	2.83	15.4	1.23	-2.4×10^4
0.012	1.5561	0.37	18.6	1.18	-1.5×10^4

Copolymer Composition. Copolymers were prepared from different monomer feed compositions using pulsed-laser polymerization (see following section), and each polymer was analyzed by ^{1}H NMR for compositional analysis. This was achieved by comparing the areas of the peak at 4.0 ppm [(CO)CH_2CH$_2$] of the MDO ester backbone with the peak at 3.6 ppm corresponding to [(CO)OCH_3] of the pendant MMA ester group. The composition data was fitted to the terminal copolymerization model using nonlinear regression, to yield estimates for the reactivity ratios, $r_\mathrm{MDO} = 0.057$ and $r_\mathrm{MMA} = 34.12$. A 95% joint confidence interval (JCI) for the reactivity ratios is given in Figure 4. In performing the regression and calculating the JCI, a constant relative error was assumed for the composition data. The only other reactivity ratios determined for MDO (to our knowledge) were measured by Bailey and coworkers[22] for the copolymerization of MDO with STY, yielding $r_\mathrm{MDO} = 0.021$ and $r_\mathrm{STY} = 22.6$. These values are broadly consistent with those obtained in this work, where neither radical has a propensity to react with the MDO monomer. A plot showing the experimental com-

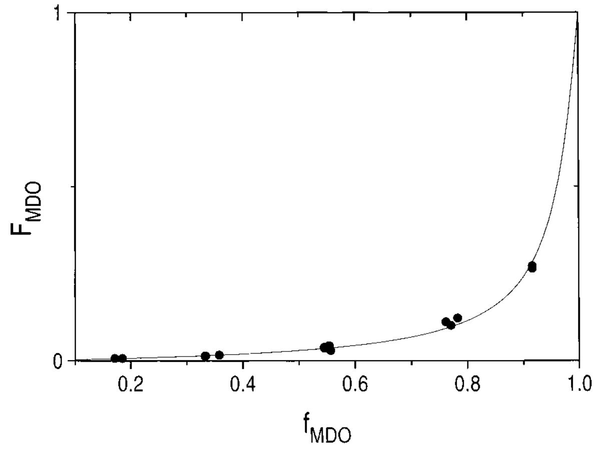

Figure 5. Plot of copolymer composition vs monomer feed composition for the copolymerization of MDO with MMA. The experimental data points are shown with the solid line predicted from the reactivity ratios assuming the terminal model.

position data and the terminal model fit is shown as Figure 5.

Pulsed-Laser Polymerization. The homo and average propagation rate coefficients were determined using eq 3,[1]

$$v = \langle k_p \rangle [M] t_f \tag{3}$$

where v is the chain length generated between two consecutive pulses (obtained from the inflection points of the primary peak of the linear scale molecular weight distributions), [M] is the monomer concentration, and t_f is the dark time between pulses. This expression is also valid for MDO ring-opening polymerization provided that the rate-determining step is the propagation step and the ring-opening process is extremely rapid. In the event that the ring-opening step takes significant time, then an alternative mathematical expression can be formulated for interpreting PLP experiments; however, in this case it is unnecessary, and eq 3 can be presumed to hold.

All of the PLP molecular weight distributions were measured by SEC against a PMMA calibration curve. This can be justified as the composition data indicate that MDO incorporation in the copolymer is extremely low even at a high feed content of MDO, and thus the uncertainty introduced by this simplified analysis is predicted to be low. The range of PLP experiments that was performed is shown in Table 2. All PLP experiments were run in replicate, varying pulse frequency and initiator concentration and type as recommended by the IUPAC guidelines for PLP experiments.[33,34]

Homopropagation Rate Coefficient of MDO. We were unsuccessful in obtaining a PLP molecular weight distribution for the homopolymerization of MDO which may not be regarded as too surprising following the results we obtained for the C_M value. However, the main problem with PLP of MDO proved to be the attainment of only trace amounts of polymer even after pulsing for 12 h in the laser beam. This problem may well be associated with initiation problems and is the subject of further scrutiny.

Table 2. Experimental Data for the PLP Experiments[a]

f_{MDO}	initiator	[I] (mmol/L)	mol/L	F_{MDO}	t_f (s)	M_{inf}	k_p (L/(mol/s))
0.000	benzoin	2.49	9.36	0	0.25	110500	471
0.000	AIBN	3.59	9.36	0	0.10	46600	497
0.172	benzoin	2.69	9.18	0.0067	0.25	110515	440
0.172	benzoin	2.69	9.18		0.25	101300	441
0.185	AIBN	2.65	9.17	0.0067	0.10	46020	458
0.333	benzoin	3.39	9.01	0.0137	0.10	45897	426
0.334	AIBN	4.65	9.01	0.0135	0.10	45068	420
0.358	benzoin	3.86	8.99	0.0162	0.25	116714	422
0.358	benzoin	3.86	8.99		0.25	95100	422
0.545	benzoin	3.90	8.80	0.0361	0.25	130015	392
0.545	benzoin	3.67	8.80	0.038	0.10	56543	418
0.554	benzoin	3.70	8.79	0.0425	0.10	57416	409
0.557	AIBN	4.71	8.79	0.0289	0.10	48722	394
0.762	benzoin	3.75	8.60	0.1105	0.10	78209	356
0.771	benzoin	4.20	8.59	0.1007	0.25	178536	344
0.783	benzoin	3.57	8.58	0.1214	0.10	82860	357
0.916	benzoin	3.60	8.46	0.2705	0.10	127818	315
0.916	benzoin	3.63	8.46	0.2632	0.25	339137	342

[a] The F_{MDO} data were obtained from NMR measurements of the copolymer composition, as described in the main text.

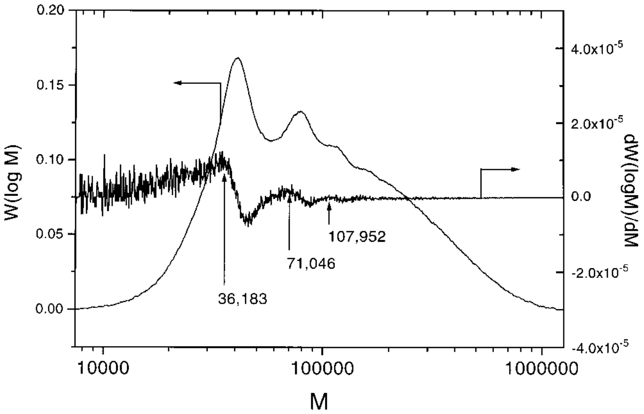

Figure 6. Typical PLP molecular weight distribution for the copolymerization $f_{MDO} = 0.76$. The differential plot is overlayed to emphasize the inflection points.

Average Copolymerization Propagation Rate Coefficients. All of the molecular weight distributions displayed characteristics typical of successful PLP experiments. A typical PLP distribution is shown in Figure 6 with the primary peak and higher overtones clearly evident. As our MDO contained some BMDO impurity we verified that BMDO as an additive has no detrimental effect on the PLP of MMA by deliberately dosing MMA with BMDO prior to several test experiments. These test runs verified that BMDO has no effect on the PLP experiment or the k_p of the MMA homopropagation. As shown in Table 2 the $\langle k_p \rangle$ values in the copolymerization steadily decrease as the concentration of MDO in the feed increases. In the following section we will attempt to explain these results in terms of current copolymerization models.

Copolymerization Model Fitting and Mechanistic Interpretation. The simplest copolymerization model is the terminal model, which assumes that the nature of the terminal unit of a polymer radical governs its reactivity in propagation reactions. The (low conversion) terminal model equation for predicting $\langle k_p \rangle$ is as follows:

$$\langle k_p \rangle = \frac{r_1 f_1^{\,2} + 2 f_1 f_2 + r_2 f_2^{\,2}}{(r_1 f_1 / k_{11}) + (r_2 f_2 / k_{22})} \tag{4}$$

f_1 and f_2 are the molar fractions of the monomers in the feed, and k_{11} and k_{22} are the homopropagation rate coefficients. In eq 4, there are four characteristic constants: two homopropagation rate coefficients (k_{ii})

and two monomer reactivity ratios (r_i), the latter are defined as follows:

$$r_i = \frac{k_{ii}}{k_{ij}} \tag{5}$$

It has long since been established that the terminal model description of copolymerization kinetics is not complete, and additional effects need to be included into this model in order to provide adequate predictions. As mentioned before, it seems to be generally accepted that these additional effects may be ascribed to penultimate unit effects, and models based upon this assumption indeed seem to provide adequate simultaneous descriptions of copolymer composition and copolymerization propagation kinetics. In the general penultimate unit model it is held that both the terminal and penultimate units influence the radical reactivity. Equations for the penultimate model are obtained by replacing the characteristic constants of the terminal model (that is, the monomer reactivity ratios, r_1 and r_2, and the homopropagation rate coefficients, k_{11} and k_{22}), by average quantities, defined as follows:

$$\bar{r}_i = r_i'\left(\frac{f_i r_i + f_j}{f_i r_i' + f_j}\right) \tag{6}$$

$$\bar{k}_{ii} = k_{iii}\left(\frac{r_i f_i + f_j}{r_i f_i + f_j/s_i}\right) \tag{7}$$

$$(i \neq j \text{ and } i, j = 1 \text{ or } 2)$$

In place of the four characteristic constants of the terminal model, there are eight characteristic constants in the penultimate model: the two homopropagation rate coefficients (k_{iii}), four monomer reactivity ratios (r_i and r_i') and two radical reactivity ratios (s_i). The monomer and radical reactivity ratios are defined as follows.

$$r_i = \frac{k_{iii}}{k_{iij}} \tag{8}$$

$$r_i' = \frac{k_{jii}}{k_{jij}} \tag{9}$$

$$s_i = \frac{k_{jii}}{k_{iii}} \tag{10}$$

$$(i \neq j \text{ and } i, j = 1 \text{ or } 2)$$

Fukuda et al.[35] simplified the penultimate model by setting the equality $r_I' = r_i$. They termed this mathematically simplified model the implicit penultimate unit model (IPUE),[15] and, under the condition that $r_i = r_i'$, the composition equation collapses to the terminal model form, with the penultimate unit effect only appearing in the $\langle k_p \rangle$ equation.

As many copolymerizations cannot be adequately described by the terminal model, but appear to obey the IPUE model,[35] we started our work by examining the fit of the experimental $\langle k_p \rangle$ data to both of these models. As discussed in the Introduction, if the chemistry of the penultimate model is correct, then we can ignore any penultimate effect on the MDO (ethylene) radical and set $s_1 = 1$. The remaining problem with describing the experimental data is the absence of an experimental value for the homopropagation rate coefficient for MDO. However, preliminary high level ab initio molecular orbital calculations on the five-membered analogue of MDO (containing a C_2H_4 link between the two oxygen atoms instead of a C_4H_8 link), yield the following estimate for k_p of this compound (which should be similar to the one for MDO)[36]

$$k_p \approx 1.0 \times 10^7 \exp\left(-\frac{30 \pm 5 \text{ kJ mol}^{-1}}{RT}\right) \tag{11}$$

To estimate the reliability of this expression we compared the calculation results with those obtained in an extensive theoretical study of the propagation reaction of ethylene. The obtained theoretical result for ethylene[37] is given in eq 12 and is in excellent agreement with the experimental value obtained by Schweer.[38]

$$k_p = 1.3 \times 10^7 \exp\left(-\frac{32.7 \text{ kJ mol}^{-1}}{RT}\right) \tag{12}$$

Comparing eqs 11 and 12, we may conclude that the homopropagation rate coefficient of MDO at 40 °C is similar to the one obtained for ethylene, i.e., about 40 $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. This conclusion is substantiated by comparing the homopropagation of MDO with the cross-propagation of an ethylene radical with vinyl acetate. An estimate for the propagation rate coefficient of the latter may be made by dividing the homopropagation rate coefficient of ethylene, by the corresponding monomer reactivity ratio with vinyl acetate;[39,40] this exercise also indicates a k_p value of around 40 $\text{dm}^{-3}\ \text{mol}^{-1}\ \text{s}^{-1}$.

Although we believe the value of 40 $\text{dm}^{-3}\ \text{mol}^{-1}\ \text{s}^{-1}$ to be correct within, at least, an order of magnitude, we applied a sensitivity analysis to evaluate the effect that this value has on the overall model fitting procedure. Parts a–e of Figure 7 show the predictions of the terminal and IPUE copolymerization models for a wide range of s_2 values in each of five different cases, corresponding to k_p values for MDO of 5000, 500, 350, 50, and 5 $\text{dm}^{-3}\ \text{mol}^{-1}\ \text{s}^{-1}$ (in all cases we set k_p for MMA at 480 $\text{dm}^{-3}\ \text{mol}^{-1}\ \text{s}^{-1}$ and $s_1 = 1$, as explained above). It is quite evident that neither model can describe the observed experimental data, and the difference is so large that uncertainties introduced by the SEC calibration are trivial.

Having established the failure of the terminal and IPUE models to describe the $\langle k_p \rangle$ data we decided to apply a full explicit penultimate unit model fit to the data. The model was fitted to the combined composition and $\langle k_p \rangle$ data and, depending upon the weighting of residuals, it was found that this model could describe either the composition data or the $\langle k_p \rangle$ data, but not both simultaneously. An example of the fit obtained when all of the residuals were weighted according to the size of the dependent variable (thereby assuming that the relative error was constant and making no other distinction between relative sizes of error in composition and $\langle k_p \rangle$ data) is shown in parts a and b of Figure 8. Also shown is the fit obtained with unweighted residuals (in which the fit to the $\langle k_p \rangle$ data dominates at the expense of the composition data). Clearly, the full penultimate model cannot describe the experimental observations.

The failure of the terminal and implicit/explicit penultimate models to simultaneously fit the composition

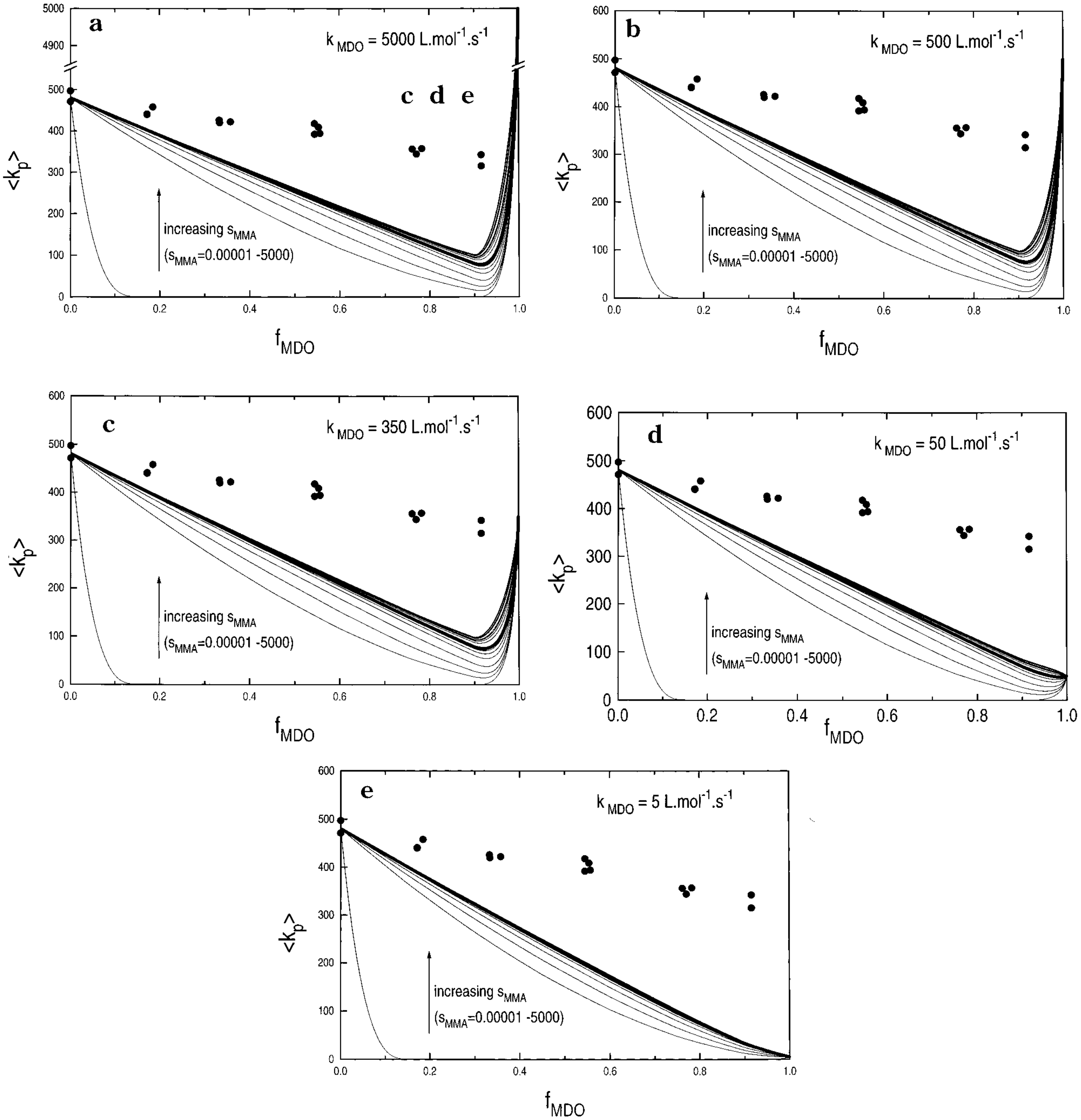

Figure 7. Predictions of the terminal and IPUE copolymerization models for a wide range of s_2 values in each of five different cases, corresponding to k_p values for MDO of (a) 5000, (b) 500, (c) 350, (d) 50, and (e) 5 dm^{-3} mol^{-1} s^{-1} (in all cases we set k_p for MMA at 480 dm^{-3} mol^{-1} s^{-1} and $s_1 = 1$, as explained in the main text). The terminal model prediction (corresponding to $s_2 = 1$) is shown in boldface. The experimental $\langle k_p \rangle$ values are shown as solid circles.

and $\langle k_p \rangle$ data can be rationalized as follows. The kinetic models in all cases mainly predict a dilution effect on the homopropagation rate coefficient of MMA with minor corrections for the small contribution from MDO radicals; i.e., the dominant reaction is the MMA homopropagation, and the MDO effectively behaves as an inert solvent. Under these circumstances, the terminal and penultimate models cannot predict propagation rates much higher than those caused by the dilution effect of an inert solvent in an MMA homopolymerization. The $\langle k_p \rangle$ values measured for this copolymerization are significantly higher than those expected if the MDO was mainly causing a dilution effect, and thus these copolymerization models cannot be fitted to the data.

It is clear from the above that models based on radical reactivity alone cannot explain the experimental data, as they basically describe a dilution effect on the main propagation event, the MMA homopropagation. As the overall propagation rate coefficients of the MMA−MDO copolymerization significantly exceed those expected under a dilution-effect model, it is conceivable that one of the following two situations is happening: either (1) the dilution effect is not as large as we expect, i.e., there is monomer partitioning between the reaction site and the bulk phase, or (2) the presence of MDO causes the homopropagation rate coefficient of MMA to exceed its assumed (bulk solution) value, which could be caused by some sort of complexation of the monomer molecules in solution.

First, we investigate the possibility of monomer partitioning between the bulk monomer phase and the radical center, which was called a bootstrap effect by

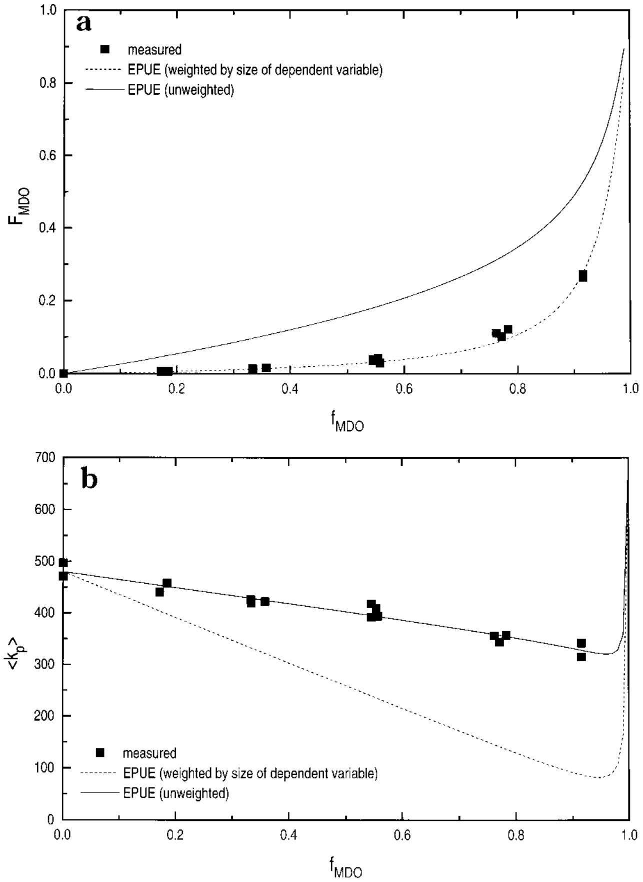

Figure 8. Plots showing the explicit penultimate unit model fit to the (a) composition and (b) $\langle k_p \rangle$ data. The solid line on both graphs corresponds to the fit obtained with unweighted residuals (in which the fit to the $\langle k_p \rangle$ data dominates at the expense of the composition data). The broken line in both plots shows the fits obtained by weighting the residuals according to the size of the dependent variable (thereby assuming that the relative error was constant and making no other distinction between relative sizes of error in composition and $\langle k_p \rangle$ data).

Harwood.[41] To estimate the degree of partitioning needed to account for the propagation rate coefficients observed in the MDO−MMA copolymerization, we fitted a version of the terminal bootstrap model simultaneously to the experimental composition data and average propagation rate coefficients.

In a bulk copolymerization, the bootstrap concept dictates that the relative fractions of the two monomers may differ between the bulk solution and the active chain end. In its simplest form, this form of monomer partitioning may be described by the following equilibrium expression:

$$\frac{f_1}{f_2} = K\left(\frac{f_{1b}}{f_{2b}}\right) \tag{13}$$

f_{1b} and f_{2b} are the bulk (measured) molar fractions of monomers 1 and 2 and K is an equilibrium constant. Using this expression to eliminate f_1 and f_2 from the (low conversion) terminal model composition and $\langle k_p \rangle$ equations, equations for the (low conversion) terminal bootstrap model may be derived:[8,42]

$$\frac{F_1}{F_2} = \left(\frac{Kf_{1b}}{f_{2b}}\right)\frac{r_1Kf_{1b} + f_{2b}}{r_2f_{2b} + Kf_{1b}} \tag{14}$$

$$\langle k_p \rangle = \left(\frac{1}{f_{2b} + Kf_{1b}}\right)\frac{r_1(Kf_{1b})^2 + 2Kf_{1b}f_{2b} + r_2f_{2b}^{\;2}}{(r_1Kf_{1b}/k_{11}) + (r_2f_{2b}/k_{22})} \tag{15}$$

As in the case of the EPUE model, we simultaneously fitted the bootstrap $\langle k_p \rangle$ and composition equations to their respective experimental data. Residuals were weighted according to the size of the dependent variable. The k_p for MMA was fixed at 480 dm^3 mol^{-1} s^{-1}. The parameters obtained ($r_{MDO} = 0.44$, $r_{MMA} = 6.81$, $k_{pMDO} = 2 \times 10^9$ dm^3 mol^{-1} s^{-1}, and $K = 0.17$) provided an adequate simultaneous fit to both data sets (see parts a and b of Figure 9). However, the enormously high k_{pMDO} value immediately renders this fit unrealistic, and so we repeated the model fitting with k_{pMDO} fixed at 50 dm^3 mol^{-1} s^{-1}. The parameters obtained also provided a reasonable fit to the data sets (see parts a and b of Figure 9), which could no doubt be improved if further corrections for a penultimate unit contribution and/or the possibility of K varying as a function of monomer feed, were included in the model.

Thus, the bootstrap model can simultaneously describe the experimental $\langle k_p \rangle$ and composition data. However, to achieve this, a very large partitioning effect (low K) is required. At first glance, this large partitioning effect is unprecedented and therefore seems unlikely. However, we are unable to discount it on the basis of current evidence, and we speculate that some partitioning is possible if we consider the electron density distribution around the two monomer molecules whereas the MMA molecule seems to be completely covered by an "electron cloud", the MDO molecule is only partly covered by such a "cloud". Furthermore, we should bear in mind that the basic bootstrap model is a vast simplification of all the possible solvent and PUE effects in any given copolymerization, and that, all possible "nonideal" effects are condensed into one single parameter, K. In summary, monomer partitioning is possible, but if this is happening, the simple bootstrap model description, yielding an extreme level of monomer partitioning, is not likely to be a realistic reflection of the true physical chemistry that is happening in this system.

The second option, i.e., an increase in the MMA homopropagation rate coefficient caused by the presence of MDO, is conceivable if some sort of complex participates in the propagation reaction of MMA. We can think of two different possibilities, i.e., a complexation of the radical center or the MMA monomer by MDO:

$$[\text{polymer}-\text{MMA}^{\bullet}\cdots\text{MDO}] + \text{MMA} \xrightarrow{k_p^{\text{complex 1}} > k_{p\text{MMA}}} [\text{polymer}-\text{MMAMMA}^{\bullet}\cdots\text{MDO}]$$

$$\text{polymer}-\text{MMA}^{\bullet} + [\text{MMA}\cdots\text{MDO}] \xrightarrow{k_p^{\text{complex 2}} > k_{p\text{MMA}}} \text{polymer}-\text{MMAMMA}^{\bullet} + \text{MDO}$$

These reactions can only lead to an increased propagation rate if the stabilization energy due to complexation of the reactants is more than compensated for by a similar stabilization of the transition state. Since we are not aware of the existence of any reliable information regarding these processes, other than the results of complicated fitting exercises, we decided to refrain from the application of complex-participation models[15] to the present system. However, just as in the case of possible monomer partitioning, this possibility cannot be discarded.

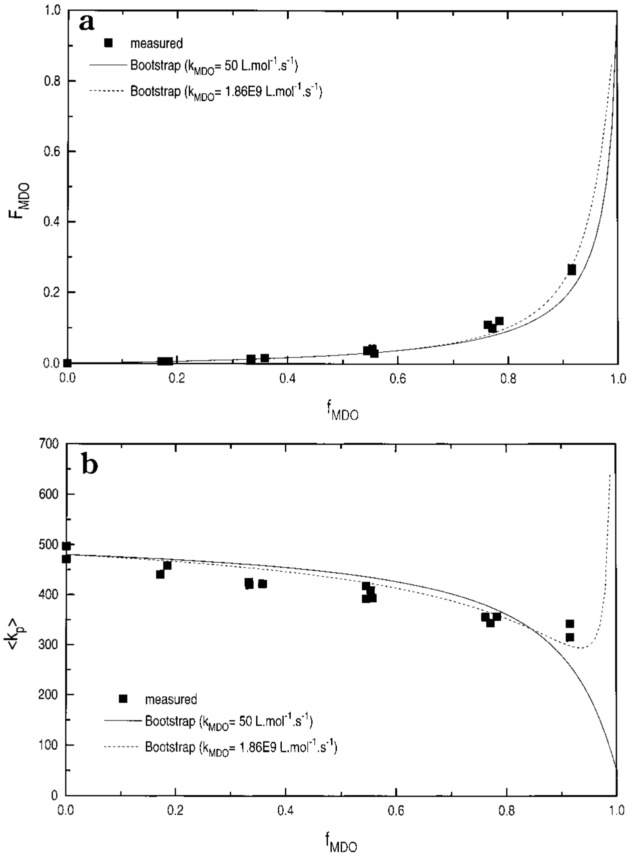

Figure 9. Plots showing the bootstrap model fits to the (a) composition and (b) $\langle k_p \rangle$ data. Residuals were weighted according to the size of the dependent variable. The k_{pMMA} was fixed at 480 dm^3 mol^{-1} s^{-1}. The broken line in both plots corresponds to a fit where k_{pMDO} was used as a fit parameter. The solid line shows the fits obtained when k_{pMDO} was fixed at 50 dm^3 mol^{-1} s^{-1}.

Free-Radical Mechanism? As this work indicates unusually narrow polydispersities in some instances and as we have found it impossible to fit a credible model to the observed copolymerization kinetics, it is worth reflecting on the nature of the chain carrier in these ring-opening reactions. Bailey[17] has indicated that in one particular case of "radical" ring-opening polymerization that the mechanism may in fact be concerted and that free radical intermediates are not generated. Subsequent work by Acar et al.[43] seemed to contradict this view and most researchers assume a radical mechanism is valid especially in recent times where many examples of addition—fragmentation radical mechanisms have been demonstrated.[44,45] We believe that the evidence is very strongly in favor of a radical chain propagation mechanism as in two recent papers by Jin and Gonsalves,[20,21] evidence is found for radical backbiting—consistent with observations for ethylene radical-type polymerization. We have also done steady-state polymerization experiments[28] that show a rate dependence on [I]$^{0.5}$ consistent with free radical initiation and bimolecular termination. It is also fairly convincing that, in the current work, reactivity ratios consistent with expectations based on radical chemistry are found and that pulsed-laser polymerization which is dependent on intermittent radical generation and termination (with all the attendant IUPAC consistency criteria[33,34]) was successful.

While none of these factors can prove unequivocally that a radical chain carrier is present, the weight of these factors indicates that the overwhelming weight of extant evidence is in favor of a radical intermediate.

Conclusions

The copolymerization of MDO and MMA cannot be described by the main theories developed for copolymerization based on radical reactivity. The experimental $\langle k_p \rangle$ and composition data can be fitted to a bootstrap model, but the model fit parameters seem unrealistic. We cannot discount nonideal solvation effects or complexation models which may be playing some role. Further clarification of the unusual results reported here is only possible if additional experiments such as studying the effect of a diluent and copolymerizations of MDO with other monomers are performed. These supplementary experiments are currently in hand.

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