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Copolymerization Propagation Kinetics of Dimethyl Itaconate and Styrene: Strong Entropic Contributions to the Penultimate Unit Effect

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ABSTRACT: In this work, pulsed-laser polymerization has been utilized to measure average propagation rate coefficients, $\langle k_p \rangle$, in the bulk copolymerization reaction of dimethyl itaconate and styrene at 20 °C. The measured $\langle k_p \rangle$ values were substantially higher (up to a factor of 3) than those predicted by the terminal model. This unusual result is attributed to strong *entropic* penultimate unit effects on the DMI-terminal radicals. We discuss the significance of this result particularly for other copolymerization systems where there are large size differences between the monomers and for systems where the comonomer substituents are similar (for instance, acrylate–methacrylate pairs), where the enthalpic penultimate unit effect is diminished and the entropic effect may become observable.

Introduction

In 1985 Fukuda and co-workers¹ demonstrated the failure of the terminal model in the copolymerization of styrene (STY) and methyl methacrylate (MMA). In subsequent years, the failure of the terminal model was observed to be widespread, and a general consensus emerged that the penultimate unit is very important in influencing the rate of propagation.^{2–7} The precise physical chemistry of the penultimate unit effect became the subject of debate with models proposed emphasising the importance of both enthalpic and entropic influences.^{8,9} A recent review¹⁰ rationalized all the available experimental and theoretical evidence resulting in the conclusion that a number of factors, viz., polar interactions, radical stabilization effects, direct interactions, and entropic effects, are all important in determining the influence of penultimate and terminal units on propagation kinetics.

From an experimental perspective, in nearly all cases, the penultimate unit effect appears to be manifest in a reduction of the average propagation rate coefficient. This is consistent with the original theories of Fukuda and co-workers that penultimate unit effects act to stabilize the propagating radical.³ However, in a few cases where the comonomers bear similar substituents, for example, methyl methacrylate (MMA)/*n*-butyl acrylate⁷ and *p*-chlorostyrene/*p*-methoxystyrene,¹¹ then this stabilization is not observed. These results provide strong evidence that the overall *observed* penultimate unit effect in any given copolymerization originates from a combination of different contributions.

In an earlier paper¹² on the homopropagation of dimethyl itaconate (DMI) (**I**), we reported an activation energy for DMI comparable with that known for MMA (**II**). However, DMI propagates much slower at any given temperature because of a low pre-exponential factor consistent with the propagation of a “hindered” radical. One possibility that should be considered in certain polymerizations is that the origins of steric hindrance in homopropagation may involve both ter-

minal and penultimate units (so-called 1,3-interactions¹³). It may be surmised that penultimate unit effects in homopropagation should not be neglected. Therefore, in certain copolymerizations, we may be able to observe a “penultimate unit effect” that can be viewed (at least in part) as a “relief” of the actual penultimate unit effect present in homopolymerization. This “relief” effect by a differing penultimate unit has also been speculated upon previously⁸ for the hypothetical case of a penultimate effect solely consisting of entropic contributions in a copolymerization of two monomers of considerably different sizes. It was proposed that a small penultimate unit would speed up the addition of the large radical to a large monomer, leading to a radical reactivity ratio for the large monomer greater than unity.

This complex issue of the origin of *observed* penultimate unit effects in copolymerization is the subject of this paper.

Experimental Section

Materials. Dimethyl itaconate (DMI) [Aldrich, 99.6% purity (sic)] often contained substantial amounts of polymer. To obtain pure monomer for the experiments, the following steps were taken:

1. DMI/polyDMI was added to a solution of 95% MeOH and 5% distilled water. 4-*tert*-Butyl catechol was added to the solution to act as an inhibitor.

2. The polymer was removed, and the monomer was isolated using a rotary evaporator. The purity of the DMI monomer was monitored via NMR and FTIR.

The photoinitiators, benzoin (BZ) and 2,2'-azobisisobutyronitrile (AIBN), were recrystallized from ethanol. The GPC eluent, tetrahydrofuran (THF), was purchased from BDH (HiperSolv) and filtered twice through a commercial filtration system (Aldrich). Di-*tert*-butyl methylphenol (400 ppm) was added to the THF prior to use.

Polymerizations. Reaction cells (10 mm diameter × 60 mm height) were charged with monomer(s) and initiator, degassed using a flow of nitrogen for 5 min, and then sealed with rubber septa. The samples were allowed to equilibrate at the experimental temperature prior to laser exposure. All reactions were performed in bulk with conversion kept below 5%. The polymer was precipitated into methanol and then purified via a redissolution–reprecipitation technique using chloroform and methanol as the solvent and precipitant,

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respectively. The polymer was then dried under vacuum at room temperature until the attainment of constant weight.

A Continuum Surelite I-20 Nd:YAG pulsed laser system was used to generate a wavelength of 355 nm with a pulse energy range of 5–30 mJ and a beam diameter of 6 mm. Pulsing rates of between 0.3 and 2 Hz were used. Isothermal reaction conditions were maintained using a recirculating water bath including a feedback loop through a thermocouple attached to the side of the reaction cell. The experimental rig employed is very similar to that reported previously.¹⁴

Size Exclusion Chromatography (SEC). SEC analyses were performed on a modular system comprising of the following: GBC Instruments LC1120 HPLC pump operating at room temperature, an in-line ERC-3415 degasser unit, a SIL-10AD VP Shimadzu autoinjector with a stepwise injection control motor with an accuracy of $\pm 1 \mu\text{L}$, a column set which consisted of a PL 5.0 μm bead size guard column and a set of $3 \times 5.0 \mu\text{m}$ PL linear columns (10^3 , 10^4 , 10^5 \AA) and a DRI and DV (Viscotek Model 250) detector. Tetrahydrofuran (THF) was utilized as the continuous phase at a flowrate of 1 mL min^{-1} . Polymer analyte solutions were prepared with (accurately known) concentrations in the range 2–3 mg/mL, while sample injection volumes in the range 50–100 μL were used. Lower concentrations were used for the narrow standards, depending upon their molecular weights. Absolute molecular weights were obtained by combining the DV and DRI signals using PL Calibre software in conjunction with our own analysis software as described in a number of previous publications.^{15,16} The $\langle k_p \rangle$ data were interpolated from the inflection point molecular weights as discussed in many previous publications.^{17,18}

NMR Compositional Analysis. ^1H NMR spectra were recorded on a 300 MHz (Bruker ACF300) spectrometer using CDCl_3 (Aldrich) as solvent. The copolymer compositions were determined from the relative magnitude of aliphatic and aromatic areas of the spectra.

Copolymerization Models

In this section, we will provide a brief summary of copolymerization theory. For a more detailed account we refer the reader to an earlier review article.¹⁰

Terminal Kinetics. In this model, there are only four types of propagation reaction in the free-radical copolymerization of any two given monomers (M_1 and M_2):



From this assumption, Jenkel,¹⁹ Mayo and Lewis,²⁰ and Alfrey and Goldfinger²¹ derived an expression for the copolymer composition (F_1/F_2) as a function of the monomer feed fractions (f_1 and f_2) and the reactivity ratios (r_1 and r_2) of the monomers:

$$\frac{F_1}{F_2} = \frac{f_1 r_1 f_1 + f_2}{f_2 r_2 f_2 + f_1} \quad \text{where } r_i = \frac{k_{ii}}{k_{ij}} \quad i \neq j \text{ and } i, j = 1 \text{ or } 2 \quad (1)$$

Fukuda et al.¹ derived the following expression for the copolymerization propagation rate coefficient $\langle k_p \rangle$ under the terminal model:

$$\langle k_p \rangle = \frac{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}{[r_1 f_1/k_{11}] + [r_2 f_2/k_{22}]} \quad (2)$$

It is clear from eq 2 that the average k_p is solely dependent on the monomer feed composition, monomer reactivity ratios, and the homopropagation rate coefficients.

Penultimate Kinetics. In the presence of a penultimate unit effect, there are eight different types of propagation reactions to characterize:²²



From their eight different propagation rate constants, four different monomer reactivity ratios (r_i and r'_i) and two radical reactivity ratios (s_i) can be defined as follows:

$$r_i = \frac{k_{iii}}{k_{ijj}} \quad r'_i = \frac{k_{jii}}{k_{jij}} \quad s_i = \frac{k_{jii}}{k_{iii}} \quad \text{where } i \neq j \text{ and } i, j = 1 \text{ or } 2$$

These are used to calculate the adjusted parameters, \bar{r}_i and \bar{k}_{ii} :

$$\bar{r}_i = r'_i \left(\frac{f_i r_i + f_j}{f_i r'_i + f_j} \right) \quad \text{where } i, j = 1 \text{ or } 2 \text{ and } i \neq j \quad (3)$$

$$\bar{k}_{ii} = k_{iii} \left(\frac{r_i f_i + f_j}{r_i f_i + f_j/s_i} \right) \quad \text{where } i, j = 1 \text{ or } 2 \text{ and } i \neq j \quad (4)$$

These are used in place of r_i and k_{ii} in the terminal model expressions for composition (eq 1) and $\langle k_p \rangle$ (eq 2).

The *implicit penultimate model* was first suggested by Fukuda et al.¹ In this model, the following restriction is imposed:

$$r_i \left(= \frac{k_{iii}}{k_{ijj}} \right) = r'_i \left(= \frac{k_{jii}}{k_{jij}} \right) = \frac{k_{ii}}{k_{jj}} \quad \text{where } i \neq j \text{ and } i, j = 1 \text{ or } 2 \quad (5)$$

The penultimate unit effect is thus assumed to be absent from the monomer reactivity ratios, which are equivalent to their terminal model forms, and only to exist in the radical reactivity ratios (i.e., through values of $s_i \neq 1$). This implies that the magnitude of the penultimate unit effect on reactivity is independent of the type of monomer with which it is reacting (since the equality $k_{ii}/k_{iii} = k_{jii}/k_{ijj}$ follows directly from the assumption that $r_i = r'_i$). In other words, it is assumed that there is a penultimate unit effect on reactivity but not selectivity.

On the basis of the above assumption (i.e. eq 5), eq 3 collapses into

$$\bar{r}_i = r'_i \left(= \frac{k_{jii}}{k_{jij}} \right) = r_i \left(= \frac{k_{iii}}{k_{ijj}} \right) = \frac{k_{ii}}{k_{jj}} \quad \text{where } i \neq j \text{ and } i, j = 1 \text{ or } 2 \quad (6)$$

Fukuda later introduced a theoretical basis for his model,⁹ based on a hypothesis of strong penultimate unit effects on radical stability. This led to a prediction that the relationship given by eq 7 should hold:

$$r_1 r_2 = s_1 s_2 \quad (7)$$

Several different research groups have discovered the limitation of estimating individual s_1 and s_2 parameters from copolymerization $\langle k_p \rangle$ experimental data.^{2,23} The lack of precision in estimating these parameters has made the testing of eq 7 very difficult. However, in recent work on the copolymerization of substituted styrenes, eq 7 was found to be invalid.¹¹ Because of these practical problems, Fukuda et al.³ suggested a pragmatic approach of using a simplified implicit model with

the restriction $s_1 = s_2$. The physical reality of eq 7 was questioned in a subsequent paper by Heuts et al.,⁸ who argued that entropic effects are important in the rate coefficients and that there is no a priori reason these should cancel out or can be ignored in eq 7. Fukuda and co-workers²⁴ consequently introduced a modified implicit model encompassing these effects, leading to a more complex version of eq 7.

More recently, evidence has been accrued within our laboratory^{10,25–28} that the penultimate unit effect (PUE) is a general “umbrella” term for complex interactions involving the terminal and penultimate units (and antepenultimate units—diminishing in importance further from the reaction center) and the incoming monomer. They encompass radical stabilization energies, polar interactions, and entropic factors. However, formulating an appropriate working model for copolymerization remains problematic as the statistical uncertainty associated with model fitting experimental data to such a complex reaction scheme leads to meaningless parameter estimates.²³

Therefore, we have adopted the strategy of investigating the kinetic behavior of copolymerizations involving monomers with diverse structures in an attempt to rationalize patterns of behavior.

Results and Discussion

As discussed in the Introduction, the terminal model is known to fail in many copolymerization reactions. There is a general understanding that the penultimate unit (or γ -substituent) plays a major role in determining the propagation kinetics in free radical (co)polymerizations. The recent focus of our work has been to study copolymerization systems that demonstrate deviation (or in some cases compliance) from (with) the terminal model with the aim of developing a hypothesis that the influence of the penultimate unit is a complex issue with many contributory factors. These factors include polar interactions, radical stabilization effects, direct interactions, and entropic effects. These effects are operative in all copolymerization reactions: in some cases, one contribution dominates, and in other systems, two (or more) effects may well compound or nullify each other. Therefore, we have adopted a general strategy of using the terminal model as a starting point for kinetic analysis and then framing our discussion and analysis around the ability or failure of the model to explain our experimental observations.

Composition Measurements and Monomer Reactivity Ratios

The determination of terminal monomer reactivity ratios for the copolymerization of STY with DMI from composition data has been reported previously in a number of papers.^{29–31} There is poor agreement among the previous studies with r_{DMI} and r_{STY} falling in the ranges 0.12–0.25 and 0.32–0.59, respectively. This uncertainty can be attributed to a number of factors:

1. Difficulties with analysis of the copolymers exist. (A) A previous study utilized UV spectroscopy—accurate interpretation of the data would depend on the complete absence of monomer, and it would not be possible to verify this.

- (B) In many instances (at least on 10 separate occasions over a 3 year period), the DMI monomer we purchased was contaminated with substantial amounts of polyDMI. This seems to have been neglected in

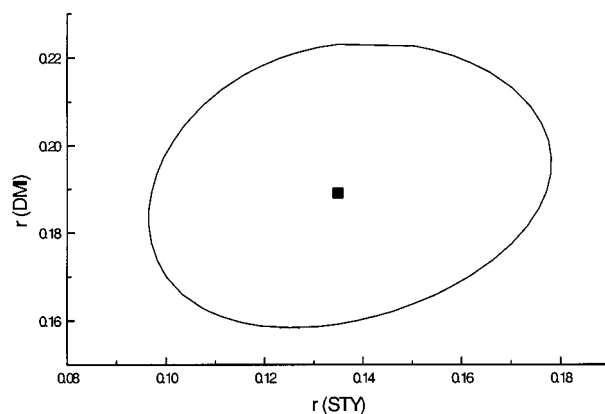


Figure 1. Plot of 95% joint confidence interval for the reactivity ratios of DMI and STY. Data were obtained by composition measurements and analyzed assuming the terminal model.

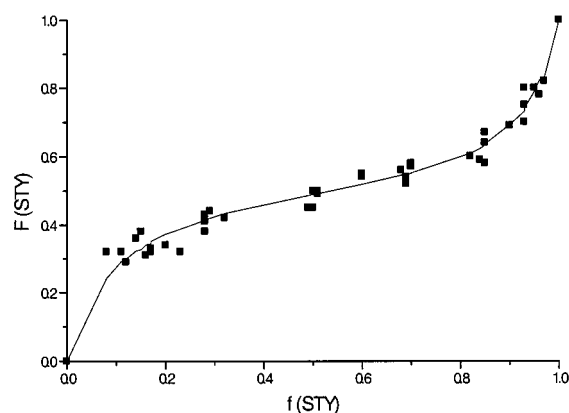


Figure 2. Copolymer composition data and the terminal model fit (solid line).

previous studies. This would lead to considerable errors in reactivity ratio determinations

2. The fact that individual reactivity ratios are not too sensitive to composition measurements and many combinations will often produce a similar prediction of composition. This is, of course, the reason the measurement of composition is a poor test of copolymerization mechanism.

3. The terminal model is probably an oversimplification of the mechanism and this may lead to (apparent) systematic errors.

In our work we utilized ¹H NMR spectroscopy and in some cases vinyl peaks indicative of some residual monomer, however, the contribution of monomer was never found to exceed 0.2% of any sample and so errors from this source are minimal in this work. Fitting of the terminal model to the composition data, using nonlinear regression, yielded values for the reactivity ratios r_{DMI} and r_{STY} of 0.19 and 0.14, respectively. The 95% joint confidence interval is depicted in Figure 1. The determination of this joint confidence interval (JCI) was performed by an F -test where the 95% probability F values were used.

A plot of f_{STY} vs F_{STY} is given in Figure 2 demonstrating the ability of the terminal model to describe the experimental composition data.

These reactivity ratios suggest that the STY–DMI pair exhibit a greater tendency toward cross-propagation than in STY–MMA (methyl methacrylate) copolymerization. However, we prefer not to overinterpret the significance of the specific reactivity ratio

Table 1. Relevant Data from the Pulsed-Laser Polymerization Experiments

$f(\text{DMI})$	$f(\text{STY})$	$[\text{M}]$	$[\text{I}],$ mmol/L	temp, °C	energy, mJ/pp	$T_i,$ s	convn, %	$M_{ip}(\text{STY})$	k_p from $M_p(\text{STY})$	M_p absolute	k_p from M_p absolute
0.00	1.00	8.70	27.6	20.0	26.2	2	0.4%	1.25×10^5	68.9	1.56×10^5	86.37
0.00	1.00	8.70	32.9	20.0	26.2	2	1.6%	1.26×10^5	69.5	1.43×10^5	78.96
0.04	0.96	8.63	27.2	20.0	26.7	2	1.1%	1.19×10^5	59.5	1.50×10^5	74.76
0.07	0.93	8.57	25.3	20.0	26.7	2	1.1%	1.17×10^5	59.6	1.28×10^5	64.96
0.07	0.93	8.57	32.0	20.0	26.7	2	1.3%	1.16×10^5	57.9	1.36×10^5	67.42
0.15	0.85	8.42	33.2	20.0	26.2	2	1.5%	1.14×10^5	55.4	1.34×10^5	65.02
0.15	0.85	8.41	27.4	20.0	26.2	2	1.6%	1.14×10^5	54.7	1.61×10^5	77.34
0.18	0.82	8.35	31.0	20.0	14	2	0.6%	6.7×10^3	3.2		
0.19	0.81	8.34	27.6	20.0	14	1	0.8%	5.4×10^4	51.8		
0.19	0.81	8.35	33.7	20.0	14	1	0.3%	5.4×10^4	51.1		
0.19	0.81	8.34	25.9	20.0	14	0.5	0.5%	2.8×10^4	53.7		
0.30	0.70	8.15	33.6	20.0	26.2	2	1.7%	1.11×10^5	53.8	1.43×10^5	68.73
0.32	0.68	8.12	27.6	20.0	26.2	2	1.5%	1.11×10^5	53.6	1.35×10^5	64.91
0.39	0.61	8.00	33.6	20.0	14	0.25	0.8%	1.5×10^4	58.7		
0.40	0.60	7.99	32.4	20.0	26.7	2	1.5%	1.11×10^5	54.0	1.31×10^5	63.63
0.40	0.60	7.99	31.3	20.0	26.7	2	1.3%	1.09×10^5	53.3	1.28×10^5	62.06
0.41	0.59	7.98	36.2	20.0	14	0.5	0.5%	2.8×10^4	55.0		
0.49	0.51	7.83	35.0	20.0	26.2	2	1.6%	1.09×10^5	53.0	1.39×10^5	67.64
0.50	0.50	7.82	31.3	20.0	26.2	2	1.3%	1.10×10^5	53.9	1.42×10^5	69.40
0.64	0.36	7.61	33.4	20.0	14	0.25	1.5%	1.5×10^4	56.6		
0.65	0.35	7.60	37.1	20.0	14	0.5	0.7%	2.7×10^4	51.9		
0.67	0.33	7.56	35.7	20.0	14	0.25	1.4%	1.5×10^5	58.0		
0.71	0.29	7.51	35.0	20.0	26.2	2	1.0%	1.03×10^5	51.0	1.27×10^5	62.82
0.72	0.28	7.49	35.8	20.0	26.7	2	1.2%	1.01×10^5	50.1	1.21×10^5	59.84
0.85	0.15	7.30	38.5	20.0	26.7	2	0.8%	7.9×10^4	39.6	9.6×10^4	47.60
0.86	0.14	7.30	33.4	20.0	26.7	2	0.9%	7.8×10^4	38.4	1.01×10^5	50.00
0.92	0.08	7.21	31.2	20.0	26.7	2	1.3%	5.2×10^4	25.6	6.7×10^4	33.03
1.00	0.00	7.11	37.2	20.0	26.2	2	1.3%	1.2×10^4	5.3	1.7×10^4	7.37
1.00	0.00	7.11	35.0	20.0	26.7	2	1.3%	1.2×10^4	5.2	1.67×10^4	7.40

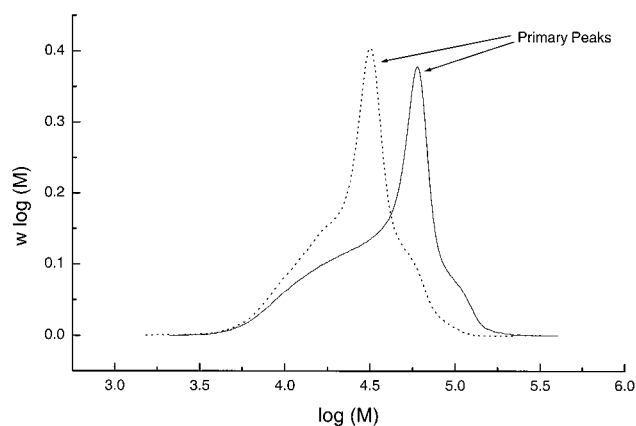


Figure 3. Molecular weight distributions obtained from selected pulsed-laser polymerization experiments. The comonomer feed composition $f_{\text{STY}} = 0.81$, and the laser flashing frequencies are 1 and 2 Hz.

values as we are only applying an approximate model. In broad terms one would expect a similar pattern of reactivity to the STY–MMA pair as DMI has strong structural similarities to MMA, with additional hindrance in the DMI radical that could enhance cross-propagation—this is indeed what we observe.

Pulsed-Laser Polymerization and Propagation Rate Coefficients. A range of PLP experiments was conducted across the comonomer compositional range. All of the polymerizations were restricted to low conversion. In Figure 3, several molecular weight distributions are shown. These distributions were obtained at one specific monomer feed composition and show the influence of the laser flashing frequency on the molecular weight distributions. It is evident that the laser is effecting control over the distributions. In all cases, we found that $\langle k_p \rangle$ data obtained at different flashing frequencies were in close agreement. However, for some compositions, we found it difficult to locate experimental

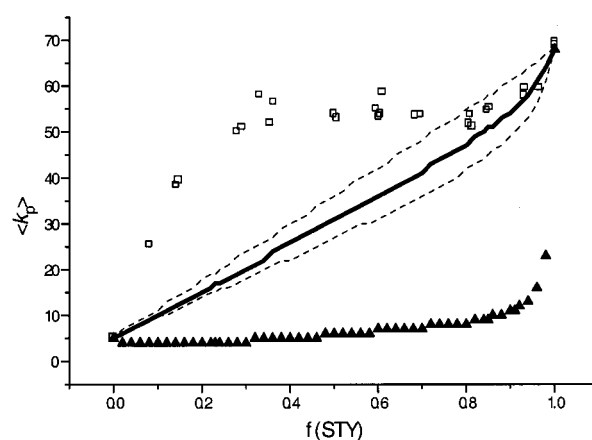


Figure 4. $\langle k_p \rangle$ data obtained using a polystyrene calibration of the SEC. The plot also shows the terminal model prediction (solid line) and the extent of variation in the terminal prediction when the extremes of the 95% confidence in r_1 and r_2 are taken into account (dashed lines). The prediction of the implicit penultimate unit model is shown (triangles) for the special restrictions that $r_1 r_2 = s_1 s_2$ and that $s_1 = s_2$.

conditions to generate molecular weight distributions with multiple peaks, and thus we could not use multiple peaks from a single experiment to perform a cross-check of the PLP experiments. In Figure 4, the $\langle k_p \rangle$ data are plotted against the mole fraction of styrene in the comonomer feed. Also shown are the predictions of the terminal model and the implicit penultimate model using the restrictions of eq 7 and assuming that $s_1 = s_2$. This implicit model prediction is only intended as a guide to the general form predicted for an implicit (enthalpic) radical stabilization model. In this figure, the $\langle k_p \rangle$ data were obtained by assuming a polystyrene calibration curve for the SEC analysis. The first striking observation is that the experimental values indicate $\langle k_p \rangle$ data that are substantially above the values predicted by the two models. A similar observation (though to a

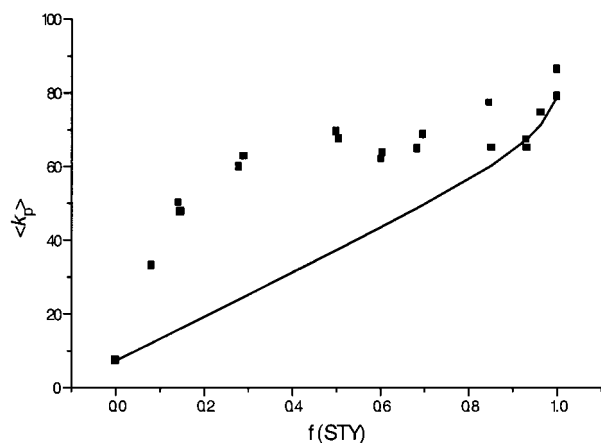


Figure 5. $\langle k_p \rangle$ data obtained using SEC/viscometry to obtain accurate molecular weight data. The plot also shows the terminal model prediction (solid line).

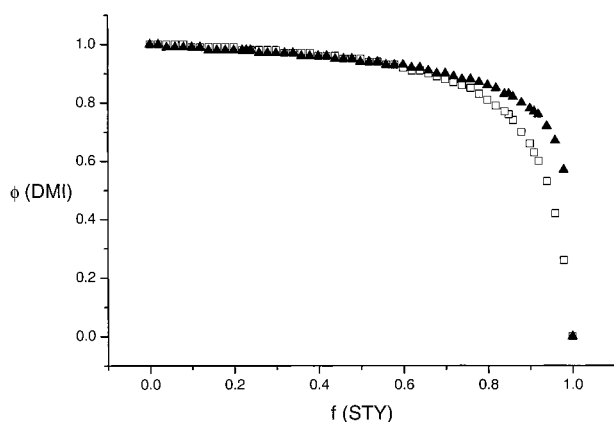


Figure 6. Calculated mole fraction of DMI-terminal radicals vs the mole fraction of styrene in the feed. Key: terminal model prediction (squares); implicit model prediction (triangles).

much lesser extent) has been noted previously in the copolymerization of butyl acrylate and methyl methacrylate by Hutchinson et al.⁷ In this earlier work,⁷ Hutchinson et al. found that a three parameter (penultimate) model provided a better description of the $\langle k_p \rangle$ data than the terminal model. However an accurate assessment of individual s_1 and s_2 values proved impossible. This problem is a general one and has been discussed in several other publications.²³ However, in this DMI-STY system, it is evident that the discrepancy between the experimental data and the terminal model prediction is the largest yet observed for a system where the $\langle k_p \rangle$ is higher than that predicted. To ensure that this observation is not an aberration caused by errors in the molecular weight analysis, we performed SEC with on-line viscometry on a number of the samples. These data are shown in Figure 5. As expected the scatter in the data increases—this reflects the fact that “true” experimental error is now being taken into account (the predominant error in PLP is in the molecular weight analysis—unfortunately this is not always acknowledged). Despite the increased error, it is plain that the same trend is manifest.

In what follows, we will argue that the factor causing the discrepancy between the terminal model and the experimental data is a penultimate unit effect largely originating in the pre-exponential factors of the copropagation reactions. In Figure 6 the calculated fraction of DMI radicals is plotted against the mole fraction

of styrene in the feed. The DMI radicals dominate as they are less reactive and therefore have longer lifetimes.

Despite the limitations of the reactivity ratios they can be used to provide some useful information. In this case the $r_1 r_2$ product of 0.03 indicates significant alternation, so many of the DMI radicals are likely to have a styrene unit as a penultimate group. If we focus on high feed concentrations of DMI we can see that this is where the discrepancy between the terminal model and the experimental $\langle k_p \rangle$ data is largest. For instance at a feed of 20 mol % styrene then the observed $\langle k_p \rangle$ is three times higher than the terminal prediction and ca. nine times higher than the implicit model prediction (with the restrictions already discussed). At these feed compositions ~95% of the radical population is DMI end groups and many of these will have a styrene penultimate group.

Therefore, the most likely explanation for an increase in $\langle k_p \rangle$ over the terminal model prediction is that DMI propagates faster with a styrene penultimate unit than if it has another DMI penultimate unit. The enthalpic penultimate unit effect is generally manifest as a radical stabilization effect that slows the average propagation rate. Therefore, we postulate that the increase in $\langle k_p \rangle$ is caused primarily by entropic factors. This type of kinetic behavior was predicted in an earlier paper where entropic effects on copolymerization were discussed extensively.⁸

We propose a hypothesis that the homopropagation kinetics of DMI are dominated by interactions between the terminal and penultimate groups resulting in a substantially reduced pre-exponential factor, A . It is already known that DMI propagates slowly compared with methyl methacrylate (MMA), and the cause is steric hindrance as measured by an A factor that is 1 order of magnitude lower for DMI ($10^{5.3}$ L/mol/s)¹² than for MMA ($10^{6.43}$ L/mol/s).³² However, the activation energies of MMA and DMI are similar.

The present copolymerization data suggest that if the DMI penultimate unit is replaced by a styrene unit then the propagation reaction proceeds much faster. This can be achieved if the steric congestion in the transition state for the addition of a DMI radical to another monomer is significantly alleviated by a styrene penultimate unit.

We will focus now on the copolymerization reactions with high feeds of styrene monomer. Figure 7 shows that the concentration of styrene radicals only becomes greater than 50% at very high (ca. 80%) styrene feed concentrations. Therefore it is difficult to assess the penultimate unit effect on styrene radicals, however, by analogy with the styrene/MMA copolymerization we would predict a small enthalpic stabilization effect.

Conclusions

In this work we measured the $\langle k_p \rangle$ in the copolymerization of styrene with DMI. We observe a significant increase in $\langle k_p \rangle$ above either the terminal or implicit penultimate unit predictions. We ascribe this to a strong entropic effect on DMI radical propagation where a DMI penultimate unit plays a large role in determining the pre-exponential factor for the reaction. When the penultimate unit is replaced by a monomer with less bulky substituents (e.g. styrene) then the DMI propagation rate is enhanced. It is likely that enthalpic penultimate

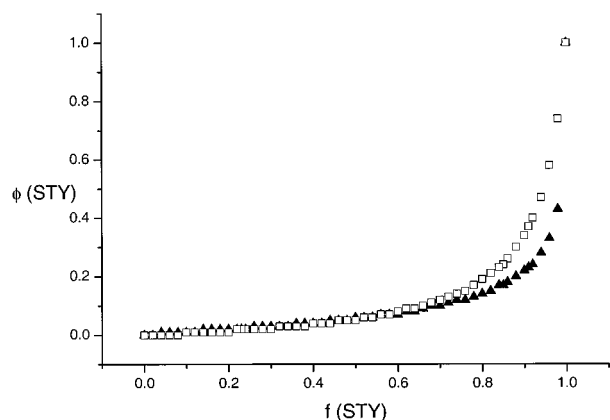


Figure 7. Calculated mole fraction of styrene-terminal radicals vs the mole fraction of styrene in the feed. Key: terminal model prediction (squares); implicit model prediction (triangles).

unit effects also play a role in this reaction but they are swamped by the large entropic effects. We predict on the basis of this work that any propagation reaction involving significant 1,3-interactions will have a significant entropic component to the penultimate unit effect. It is possible that the results reported by Hutchinson et al.⁷ for the copolymerization of a methacrylate and an acrylate can be explained using a similar hypothesis. This hypothesis, based on entropic considerations, has more credibility than an enthalpy based model for monomers bearing similar substituents (both ester groups) where the scope for enthalpic stabilization is minimal.

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