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Radical copolymerisation propagation kinetics of methyl ethacrylate and styrene

L.M. Morris, T.P. Davis*, R.P. Chaplin

School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney 2052, NSW, Australia

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Abstract

Pulsed-laser polymerisation has been used to investigate the radical copolymerisation kinetics of styrene with methyl ethacrylate. Experiments were conducted over the temperature range 30–80°C. The results for copolymer composition and the average propagation rate coefficients, $\langle k_p \rangle$, can be interpreted using terminal model kinetics. It is argued that the primary factor influencing the copolymerisation $\langle k_p \rangle$ data is the sterically hindered methyl ethacrylate radicals and this steric effect swamps any enthalpic penultimate unit effect which may be expected to play a role in the copolymerisation reaction. The terminal model reactivity ratios are a strong function of temperature and this reflects the importance of depropagation reactions at higher temperatures and lower concentrations of methyl ethacrylate. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Copolymerisation; Hindered radical; Pulsed-laser

1. Introduction

The nature of the α-substituent of a vinyl monomer has been shown to play an important role in the kinetics of radical polymerisation. This can be illustrated by comparing styrene (STY), which readily polymerises to high molecular weight, with α-methyl styrene (AMS) which propagates slowly to low limiting molecular weights. The main source of the low propagation rate (k_p) of AMS is steric hindrance in the transition state as indicated by a low pre-exponential factor (A) in the Arrhenius relationship for propagation [1]. As k_p is low, transfer to monomer becomes an important kinetic event that dominates the chain stopping process, thereby limiting the maximum attainable molecular weight [2]. In addition, there is a low ceiling temperature in AMS, originating in thermodynamics (1,3 interactions leading to a low $-\Delta H$) — this can cause depropagation at elevated temperatures and low monomer concentrations [3]. The relatively high transfer to monomer in AMS can be exploited industrially to manufacture co- and ter-oligomers without the requirement for added chain transfer agent. Thus, there is an increasing awareness that monomers that are hindered to propagation (radical addition) but not transfer (normally H-abstraction) have considerable commercial utility.

Methyl ethacrylate (MEA) may be considered as a sterically hindered version of methyl methacrylate and thus the MEA–MMA monomer pair may be analogous in its comparative kinetic behaviour to the STY–AMS monomer pair. Pennelle et al. [4] have shown that MEA has a ceiling temperature of 82 ± 2°C and the k_p of MEA has been measured by ESR to be 8.6 l mol^{-1} s^{-1} at 60°C [5].

It is now common knowledge that the terminal model fails to predict the propagation reaction in most copolymerisation systems [6,7]. Of particular relevance to the current work is the existing database on the copolymerisation of STY with MMA. This system, originally studied by Fukuda et al. [8] has been the subject of extensive PLP studies [9–12]. Fukuda et al. [13] interpreted the failure of the terminal model in terms of a penultimate unit effect on the radical stability. More recent work [6,14–16] has led to the hypothesis that a large radical stabilisation effect is always accompanied by polar interactions and therefore the terminal model is generally invalid in most systems. From a physical chemistry standpoint the basic consideration is the presence (or absence) of specific interactions among the terminal, penultimate and incoming monomer groups [17] — in this case the ester and phenyl groups interacting. As these chemical groups are present in both the STY–MMA and STY–MEA copolymerisations then some similarity in

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* Corresponding author. Tel.: +61-2-9385-4371; fax: +61-2-9385-6250.
E-mail address: t.davis@unsw.edu.au (T.P. Davis).

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copolymerisation behaviour would be predicted. Moreover, in the copolymerisation of STY with MEA, two further (at least) complications arise. Firstly, a strong entropic effect on radical addition reactions involving the hindered MEA radical and secondly a concomitant depropagation reaction which may also play a role under certain experimental conditions. The copolymerisation behaviour of MEA has not been thoroughly investigated and should prove to be of interest in both an academic and applied industrial context. This paper describes the results of a study on the copolymerisation propagation kinetics of STY with MEA utilising pulsed-laser polymerisation (PLP).

2. Experimental

2.1. Materials

STY(Aldrich), was purified by elution through basic alumina. Benzoin (BZ) was purified by recrystallisation from methanol. Diethylamine (Aldrich), dimethyl ethyl malonate (Fluka) and formaldehyde solution (BDH) were used without further purification.

2.2. Synthesis of MEA

2.2.1. Preparation of methyl ethylmalonic acid [18]

A solution of dimethyl ethylmalonate (197.53 g, 1.23 mol) in dry methanol (250 ml) was cooled in an acetone–dry ice bath. A cooled solution of potassium hydroxide (82.96 g, 1.48 mol) in dry methanol (500 ml) was added drop-wise over a period of 30 min. The reaction mixture was then stirred at ~0°C for 4 h. The methanol was then removed from the reaction mixture under vacuum, yielding a white solid, which was subsequently dissolved in distilled water (300 ml). Hydrochloric acid (3 M) was then added inducing the formation of a separate oil phase (approx. pH 1–2). The resulting organic layer was separated from the aqueous phase and extracted using ether (3 × 100 ml). The combined ether layers were combined and dried with anhydrous magnesium sulphate. The ether was evaporated to afford 120.49 g of methyl ethylmalonic acid (67%).

2.2.2. Preparation of methyl ethacrylate [4]

Methyl ethylmalonic acid (60.09 g, 0.37 mol) was cooled to 10°C. Diethylamine (31.45 g, 0.43 mol) was then added dropwise and the agitated reaction mixture was maintained at 10°C for 3 h. Formaldehyde solution (55.04 g, 40 wt% in water) was added and the stirred solution was left at room temperature for six days. A solution of potassium carbonate (9.57 g in 50 ml water) was added to the reaction mixture, followed by extraction into ether (3 × 200 ml). The organic phase was then washed successively with aqueous sulphuric acid (4.25 M, 200 ml) and water (200 ml) and then dried over anhydrous sodium sulphate. The ether was removed under vacuum and the resulting product was distilled under reduced pressure (b.p. 88–91°C, 50 mmHg) to afford MEA (20.80 g, 49%).

2.3. Polymerisations

Monomer mixtures at various feed ratios of MEA and STY (total mass ~1 g) were mixed with BZ prior to charging to Pyrex ampoules (3 ml). Oxygen was removed from the reaction mixtures by purging with nitrogen and then sealing. Polymerisations were carried out in a Nd-YAG laser at 355 nm at pulse frequencies ranging from 0.5 to 20 Hz at temperatures of, 30, 50, 60, 70, and 80°C. The equipment and general polymerisation procedures have been described in a number of prior publications [12,19]. The polymerisation reactions were terminated by removing the ampoules from the laser beam and precipitating the contents into methanol. The polymer samples were then dried to constant mass in vacuo at 40°C.

2.3.1. Size exclusion chromatography analysis

Molecular weight distributions were determined by size exclusion chromatography using a Shimadzu LC-10AT Liquid Chromatograph pump, a Shimadzu SIL-10A Autoinjector, a column set consisting of a Polymer Laboratories (PL) 3.0 μm bead-size guard column (50 × 7.5 mm) followed by three linear PL columns (10^5, 10^4 and 10^3) (300 × 7.5 mm) and a Shimadzu RID-10A Refractive Index Detector. Tetrahydrofuran (BDH, HPLC grade) was used as the eluent at 1 ml/min. Calibration of the SEC equipment was carried out with narrow poly(methyl methacrylate) and poly(styrene) standards (Polymer Laboratories, molecular weight range: 200–6.886×10^5). Poly(methyl methacrylate) standards have been used in the absence of narrow polymethyl ethacrylate standards. The calibration curves used in the molecular weight analysis of the copolymers were based on the weighted average of the measured polystyrene and polymethyl methacrylate curves, generated by the below relationship.

$$\log M = F_{\mathrm{MEA}}(\log M_{\mathrm{MMA}}) + F_{\mathrm{STY}}(\log M_{\mathrm{STY}}) \tag{1}$$

where M_{MMA} and M_{STY} are the molecular weights given by the *poly*-MMA and *poly*-STY calibration curves and F_{MEA} and F_{STY} are the molar fractions of MEA and STY in the polymer sample. In these analyses we have assumed that the hydrodynamic volumes of the copolymers can be given as a weighted average of the homopolymers. This assumption is not always valid as previously explained by Goldwasser and Rudin [20]. However, this assumption *was* found to be valid for the copolymer molecular weight analyses of STY with AMS [1] and STY with MMA [12] in previous work. Possible uncertainties introduced by this approximation are discussed later in the paper.

2.4. NMR analyses

All samples were dissolved in tetrahydrofuran (THF) and

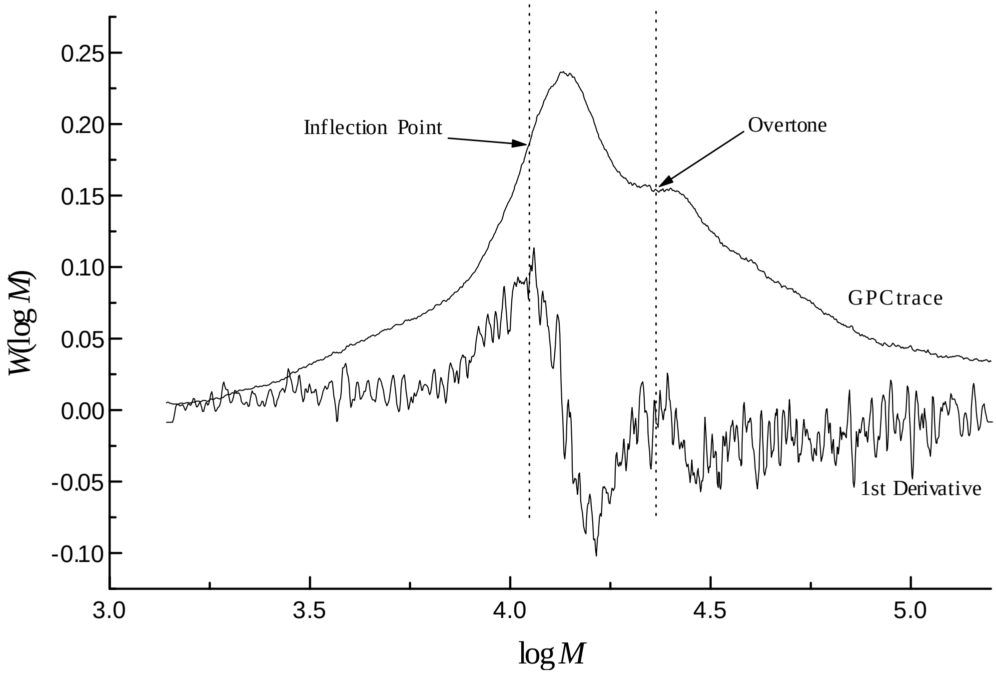


Fig. 1. Molecular weight distribution, W(logM) and first derivative from pulsed laser polymerisation at 60°C, $t_f = 0.05$ s, $f_{MEA} = 0.1059$.

reprecipitated in methanol prior to ^{1}H NMR analysis. All spectra were acquired on a Bruker ACF-300 instrument recording at 25°C. Samples were analysed as solutions in deuterated chloroform. The molar fraction of styrene in the copolymers was calculated from the total integrals of the aromatic and aliphatic regions of the spectra.

3. Results

3.1. PLP experimental data (propagation rate coefficients)

The average propagation rate coefficient, $\langle k_p \rangle$, is calculated from the degree of polymerisation, ν, at the low molecular weight inflection point of the molecular weight

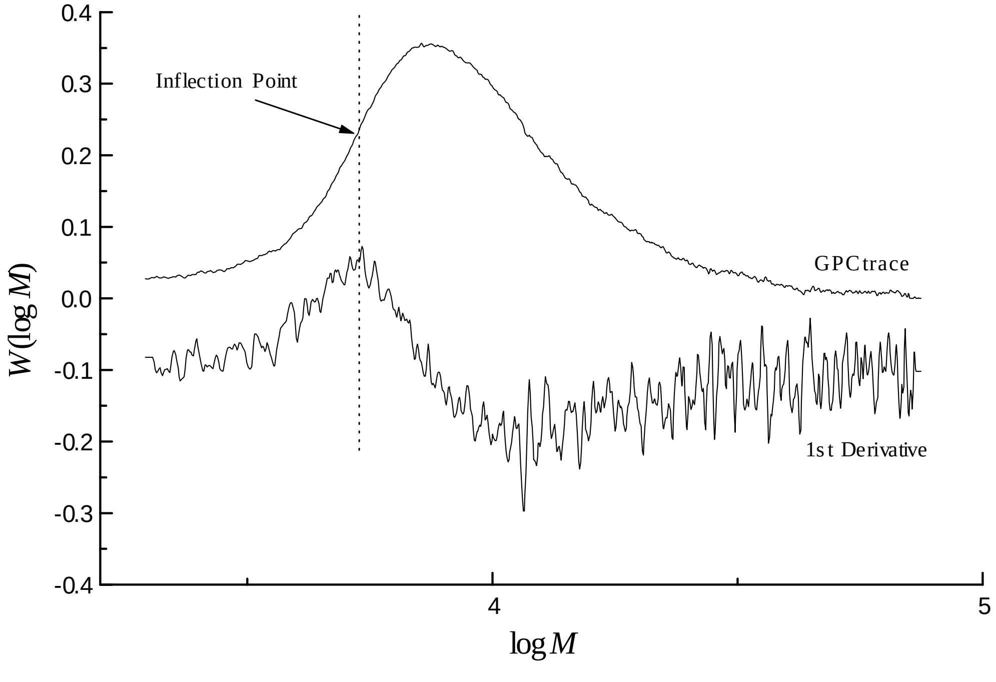


Fig. 2. Molecular weight distribution, W(logM) and first derivative from pulsed laser polymerisation at 60°C, $t_f = 0.05$ s, $f_{MEA} = 0.6698$. Note the absence of an overtone peak and the broad maxima on the derivative trace.

Table 1
Results of PLP experiments at 30°C

f_{MEA}	[In] (m mol l^{-1})	t_f (s)	No. of laser flashes	ν_{inf}		$\langle k_p \rangle$ (l mol^{-1} s^{-1})
				Primary	Overtone	
0	9.95×10^{-3}	0.5	4800	475	958	110
0	8.46×10^{-3}	0.25	4800	237	476	109
0.0988	7.16×10^{-3}	0.5	5400	340	676	79
0.1146	8.78×10^{-3}	0.25	6000	165	329	77
0.1842	7.11×10^{-3}	0.5	5400	271	467	64
0.1883	5.94×10^{-3}	0.25	7440	136	388	64
0.3858	8.92×10^{-3}	0.5	6000	180	360	43
0.3793	7.54×10^{-3}	0.25	7200	92	186	44
0.5839	7.63×10^{-3}	0.5	7200	122	252	30
0.5742	1.19×10^{-2}	0.25	10800	63	133	31
0.6820	7.33×10^{-3}	0.5	8400	96	204	23
0.6667	1.02×10^{-2}	0.25	12 000	60	113	29

distribution (MWD) produced from the PLP experiment via the following equations [21,22]:

$$\langle k_p \rangle = \frac{v}{[M]_{co} t_f} \tag{2}$$

$$v = \frac{M_{inf}}{m_{co}} \tag{3}$$

$$[M]_{co} = \frac{1000}{\dfrac{f_{MEA} m_{MEA}}{\rho_{MEA}} + \dfrac{f_{STY} m_{STY}}{\rho_{STY}}} \tag{4}$$

$$m_{co} = F_{MEA} m_{MEA} + F_{STY} m_{STY} \tag{5}$$

where M_{inf} is the molecular weight at the inflection point, m_{co} the average molecular weight of the repeat unit in the polymer, m_{MEA} and m_{STY} the molecular weights of MEA (114.14 g mol^{-1}) and STY (104.15 g mol^{-1}) respectively, F_{MEA}, F_{STY} and f_{MEA}, f_{STY} are the mole fractions of MEA and STY in the copolymer and the comonomer mixture respectively. The average comonomer concentration is denoted by $[M]_{co}$, and ρ_{MEA} and ρ_{STY} are the densities of MEA and STY monomer.

The monomer densities of STY were calculated from Eq. (6) [23]

$$\rho_{STY} = 0.9237 - 8.915 \times 10^{-4} T(°C) \tag{6}$$

The densities of MEA were measured (using a glass density bottle) in the range of 30–80°C and were found to fit the relationship

$$\rho_{MEA} = 0.9454 - 1.0338 \times 10^{-3} T(°C) \tag{7}$$

The low molecular weight inflection point was found to be distinct, especially at high feed ratios of STY where secondary inflection points were also clearly observed, as shown in Fig. 1. However, at high feed ratios of MEA (generally $f_{MEA} \approx 0.5$), the inflection points became less distinct and secondary inflection points became obscured as shown in Fig. 2. The cause of the obfuscation of the 'classical' PLP molecular weight distribution profiles is transfer to monomer at higher concentrations of MEA. As previously, with the AMS–STY copolymerisation system [1], the primary inflection points were used for calculating $\langle k_p \rangle$ provided they gave consistent $\langle k_p \rangle$ values at different pulsing frequencies. The transfer problem became exacerbated at higher temperatures and it was difficult to obtain consistent $\langle k_p \rangle$ values at 60°C even at high pulse frequencies of the laser. The main problem encountered with the experimental design was the difficulty of selecting appropriate reaction conditions. Low laser pulse frequencies yields higher molecular weights but transfer to monomer becomes a significant kinetic process in determining the shape of the molecular weight distribution. However, at higher pulse frequencies, the low propagation rate of MEA coupled with slow termination of 'hindered' MEA radicals also causes problems in interpreting the molecular weight distributions.

The reliability of the PLP method is dictated by imprecision and inaccuracy in the calibration of the GPC system. This is especially a problem in copolymer systems as it is not possible to directly calibrate the GPC using commercial standards. In the present work, the weighted average method, as described by Davis et al. [10] has been used. Whilst this may be a simplification, the overall error associated with the experimental procedure — particularly for monomers such as MEA, is thought to be considerably greater than any calibration error. In addition, it should be noted that the purpose of this work is to determine the trends in propagation behaviour and use these in conjunction with theoretical reasoning to determine the most important factors governing copolymerisation kinetics in this particular reaction. It is also pertinent that in recent work [11], it was shown that even for well-characterised systems like the copolymerisation of MMA with STY it is not feasible to accurately and unambiguously fit kinetic models to propagation rate data when all the errors have been realistically characterised.

The $\langle k_p \rangle$ data obtained at 30–60°C are shown in Tables

Table 2
Results of PLP experiments at 50°C

f_{MEA}	[In] (m mol l^{-1})	t_f (s)	No. of laser flashes	ν_{inf}		$\langle k_p \rangle$ (m mol l^{-1})
				Primary	Overtone	
0.0000	8.83×10^{-3}	0.5	3600	672	1239	231
0.0000	6.22×10^{-3}	0.25	3840	354	680	235
0.1666	5.01×10^{-3}	0.5	3600	976	1877	161
0.1446	7.08×10^{-3}	0.25	3600	497	962	167
0.2156	4.00×10^{-3}	0.5	4200	586	1,128	141
0.2174	8.03×10^{-3}	0.25	4800	214	413	150
0.4336	4.29×10^{-3}	0.5	4200	419	852	105
0.4214	5.93×10^{-3}	0.25	4800	310	583	103
0.5928	4.95×10^{-3}	0.5	5400	312		77
0.6067	5.40×10^{-3}	0.25	8880	160	308	79
0.7322	6.94×10^{-3}	0.25	8880	62		31
0.6639	7.62×10^{-3}	0.5	5400	133		33

(1)–(3). It is clear that at as the concentration of MEA in the feed increases there is a reduction in the $\langle k_p \rangle$ of the copolymerisation reaction.

4. Discussion

As discussed briefly in the Introduction, the physical chemistry defining the kinetics of the STY–MEA copolymerisation is likely to be complex as a number of factors need to be considered. The current state of understanding of copolymerisation kinetics indicates that a substantial enthalpic penultimate unit effect should influence this reaction. The $\langle k_p \rangle$ data at 30°C are plotted in Fig. 3 together with the corresponding $\langle k_p \rangle$ data for the copolymerisation of STY with MMA [12]. It is clear that the two copolymerising systems are behaving differently. At this low temperature, it is not expected that depropagation effects will play an important role and therefore the primary difference between the two systems is the impact of the bulky α-ethyl substituent on the MEA unit, when compared with the less bulky α-methyl group on MMA. The impact of changing the α-substituent on the Arrhenius parameters is shown in Table 4 for both acrylic and styrenic monomer families. It is evident that the low k_p in hindered monomers can be primarily attributed to a low pre-exponential factor rather than significant changes in the activation energy. Therefore in this MEA–STY copolymerisation system, the physical chemistry can be conveniently codified, via the Arrhenius relationship, as an aid to facilitate discussion.

1. First for consideration is the activation energy, E_a, which in turn is governed by the enthalpic contribution to the radical addition process. The basic copolymerisation model adopted since 1944 [26], is founded on the premise that only the terminal radical unit needs to be

Table 3
Results of PLP experiments at 60°C

f_{MEA}	[In] (m mol l^{-1})	t_f (s)	No. of laser flashes	ν_{inf}		$\langle k_p \rangle$ (l mol^{-1} s^{-1})
				Primary	Overtone	
0.0000	8.87×10^{-3}	0.5	4800	1325	2578	317
0.0000	5.91×10^{-3}	0.25	3600	634	1165	303
0.0000	1.24×10^{-2}	0.1	4800	291	545	349
0.0000	1.03×10^{-2}	0.1	2400	289	539	343
0.0994	4.63×10^{-3}	0.5	4800	996		241
0.1140	6.00×10^{-3}	0.25	3600	490	942	237
0.1073	1.16×10^{-2}	0.1	4800	201	399	240
0.1059	1.18×10^{-2}	0.05	4800	104	217	249
1.1867	8.47×10^{-3}	0.25	4800	413	795	200
0.1931	1.40×10^{-2}	0.1	6000	166	180	200
0.1899	1.62×10^{-2}	0.05	6000	87	152	209
0.3940	1.77×10^{-2}	0.1	6000	116		142
0.3741	1.35×10^{-2}	0.05	6000	56	1177	136
0.5837	1.53×10^{-2}	0.1	7200	68		84
0.5759	1.89×10^{-2}	0.05	7200	51		125
0.6753	1.33×10^{-2}	0.1	7200	63		79
0.6698	1.41×10^{-2}	0.05	12 000	51		126

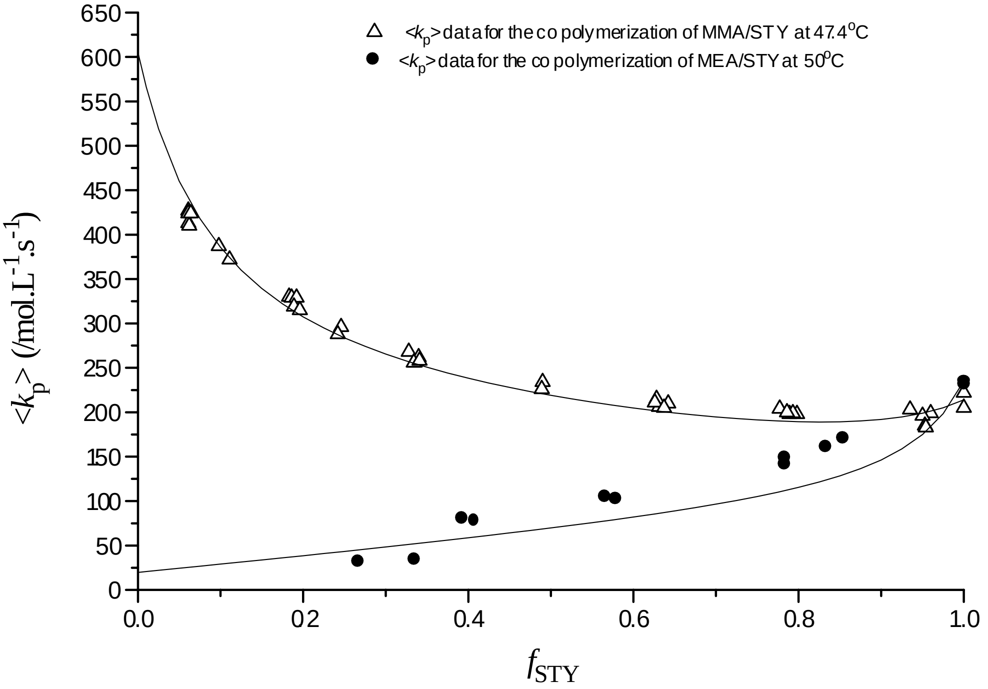


Fig. 3. Comparison of $\langle k_p \rangle$ for the copolymerisation of MMA–STY and MEA–STY. A terminal model fit has been applied to the MEA–STY data whilst an implicit penultimate fit has been made to the MMA–STY data [11].

considered in the estimation of E_a. Fukuda et al. [13] have argued that this assumption is incorrect in most copolymerisation reactions and that the penultimate unit also needs to be considered. In the copolymerisation of STY with MMA the PUE reduces the $\langle k_p \rangle$ by a factor of ~2–3 below the terminal model prediction. As the organic chemistry of MEA and MMA are similar, one would therefore predict a similar enthalpic PUE in the copolymerisation of STY with MEA.

2. The second consideration is the pre-exponential factor — this has been shown to be a dominant factor in determining the k_p of 'hindered' radical polymerisations (as shown in Table 4). Therefore the bulky MEA radical might be expected to play a significant role in the magnitude of $\langle k_p \rangle$ and any difference in the behaviour of the STY–MMA comonomer pair with the STY–MEA monomer pair may originate in the pre-exponential factor. Therefore the results depicted in Fig. 3 should be interpreted in this light. If we compare the k_p of STY with that of AMS, it is clear that bulky α-substitution reduces k_p by at least one order of magnitude.

It therefore seems plausible that the copolymerisation kinetics of this STY–MEA system will be largely governed by the slow propagation of MEA end-groups and that this effect will dominate any enthalpic PUE (this effect will be mediated by the relative fraction of MEA end-groups at any particular feed composition). In what follows, we will define the current models and theories in copolymerisation and critically assess the current MEA–STY experimental data in the light of these ideas.

4.1. The terminal unit model

The simplest copolymerisation model is the terminal unit model, which assumes that radical reactivity in either

Table 4
Activation energies and pre-exponential factors for various vinyl and acrylic monomers

Monomer	Structure $CH_2{=}C^X_Y$	E_A (kJ mol^{-1})	A (l mol^{-1} s − 1)	$\langle k_p \rangle$ at 25°C (l mol$^{-1\ s^{-1}}$)	Reference
Methyl Methacrylate	$X = (C{=}O)OCH_3$ $Y = CH_3$	22.4	$10^{6.43}$	319	[23]
Dimethyl Itaconate	$X = (C{=}O)OCH_3$ $Y = CH_2(C{=}O)OCH_3$	24.9	$10^{5.33}$	9	[24]
Styrene	$X = Ph$ $Y = H$	32.51	$10^{7.630}$	85	[25]
α-Methyl Styrene	$X = Ph$ $Y = CH_3$	36.7	$10^{6.17}$	0.5	[1]

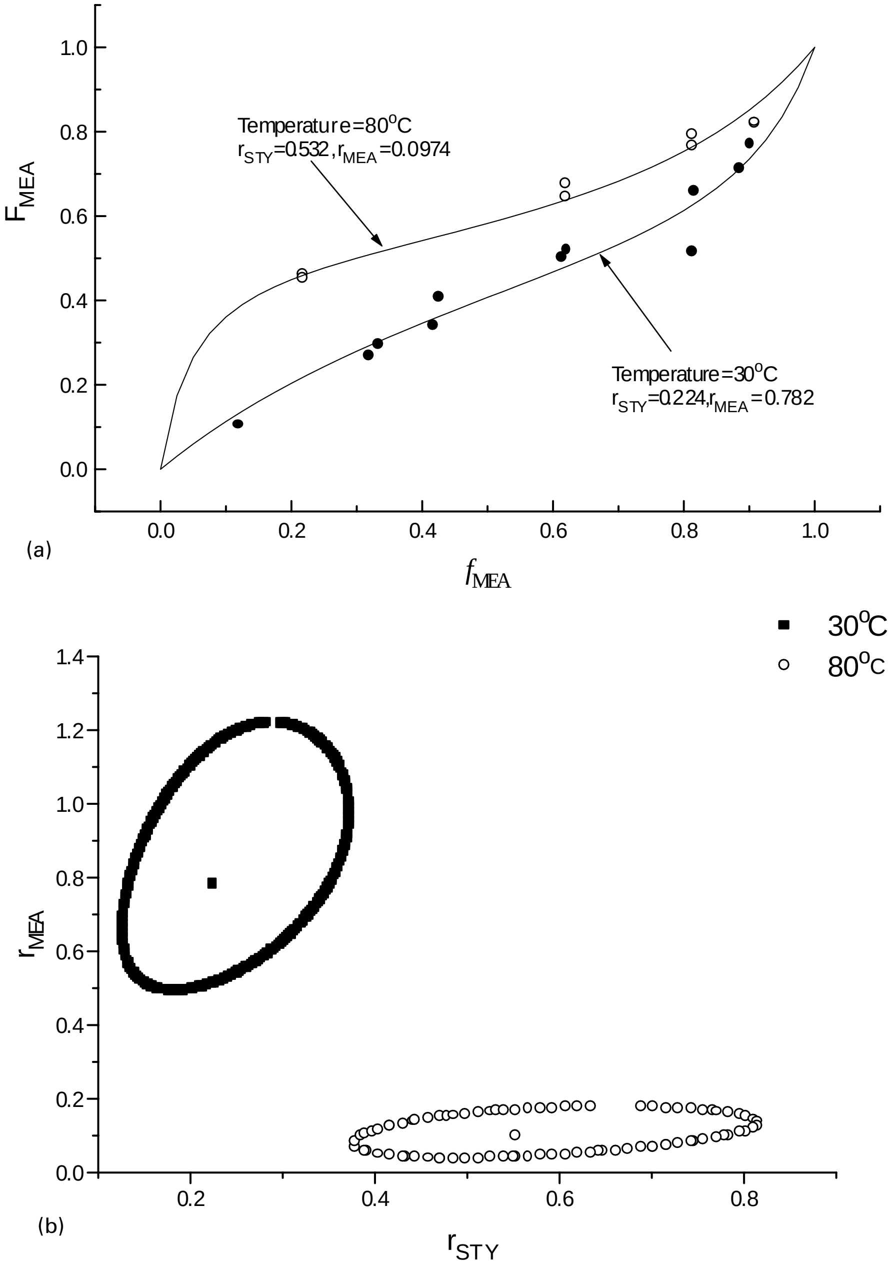


Fig. 4. (a) Plot of f_1 versus F_1 for the copolymerisation of MEA–STY at 30 and 80°C. (b) 95% joint confidence intervals for the reactivity ratios of MEA and STY at 30 and 80°C.

propagation or transfer is only affected by the nature of the terminal unit [26]. As a result, the propagation reaction can be described by four different propagation reactions. Both the copolymer compositions and average propagation rate coefficients can be described by the terminal unit model (at low conversions) by the equations below;

$$\frac{F_1}{F_2} = \frac{f_1}{f_2}\left(\frac{r_1 f_1 + f_2}{r_2 f_2 + f_1}\right)$$

$$\langle k_p \rangle = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{\dfrac{r_1 f_1}{k_{11}} + \dfrac{r_2 f_2}{k_{22}}}$$

where F_1, F_2 and f_1 and f_2 are the molar fractions of monomers in the polymer and in the feed respectively and k_{11} and k_{22} are the homopropagation rate constants. The reactivity ratios, r_1 and r_2 from above are defined as

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

Whilst it has been shown that the terminal unit model describes copolymer composition well for most systems, it has been shown that for most copolymerisation systems, it cannot adequately describe $\langle k_p \rangle$. Coote and Davis [6] have suggested that the use of the terminal model for composition is in fact erroneous (in terms of physical chemistry) for most

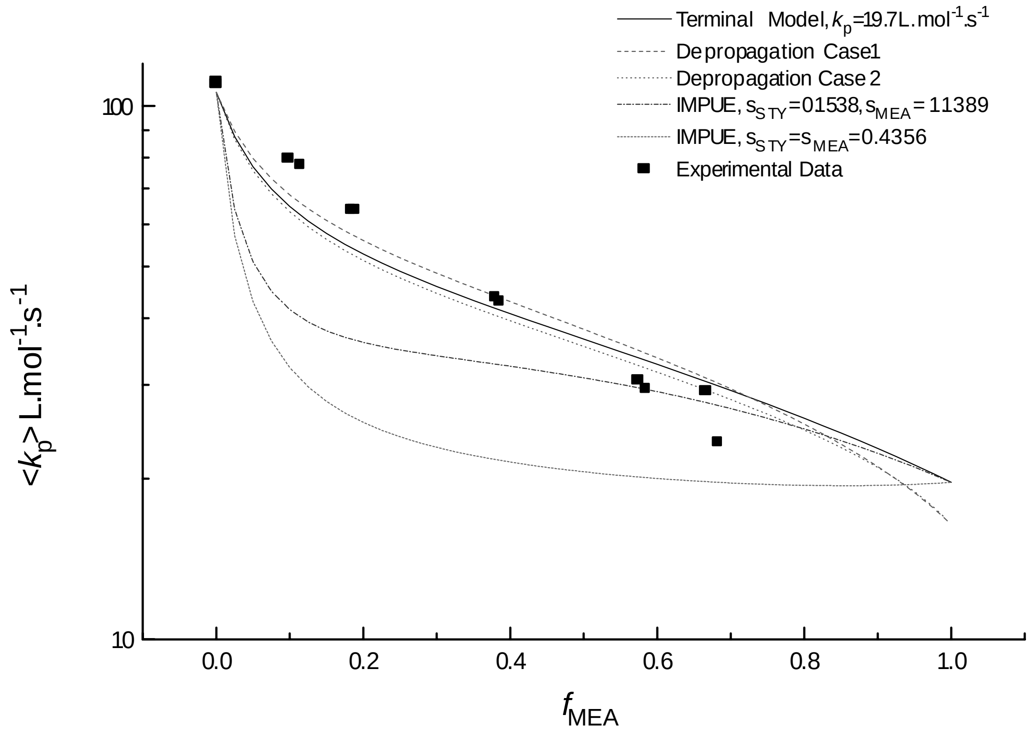


Fig. 5. Experimental and model fitted $\langle k_p \rangle$ data for MEA–STY at 30°C.

systems. However, its use has often been justified by the diktat of simplicity and the knowledge that reactivity ratios are known to be roughly correlated with the expected organic chemistry of the monomers and radicals. In STY–MMA, the terminal model has been used extensively and is successful in predicting copolymer composition from feed composition data using reactivity ratios (this is not too surprising, as this composition data is also the source of the reactivity ratios). In the present system, the hindered MEA terminal radical plays a dominant role in the copolymerisation (as discussed previously) — swamping any enthalpic penultimate unit effect on the MEA radical. Therefore utilisation of the terminal model, seems a valid starting point in the interpretation of the MEA–STY kinetic data.

The main problem encountered in modelling the MEA–STY copolymerisation is the absence of a reliable value for k_p of MEA. A crude attempt at estimating k_p by extrapolating from the copolymerisation $\langle k_p \rangle$ data can be attempted as done previously for AMS [1]. However, this process is inherently flawed as it requires the use of a model to perform the extrapolation undermining the validity of any possible model discrimination. The terminal model can be applied to the copolymerisation data and this leads to a rough value for the k_p of MEA of 20 l mol^{-1} s^{-1} at 30°C. The terminal model does adequately describe both the copolymer composition (see Fig. 4a) and the average propagation rate coefficient (see Fig. 5). In this regard it is similar to previous results obtained for the copolymerisation of STY with AMS [1]. However, some caution should be exercised, in interpreting this result because of the failure to measure an independent value of k_p for MEA. Despite this problem, the extrapolated value for k_p of MEA seems reasonable and even accounting for errors of 100%, the terminal model seems a realistic description of the propagation behaviour in this copolymerisation. This may simply reflect the dominant influence of the terminal MEA unit on the overall measured $\langle k_p \rangle$ values.

Table 5
Critical monomer and feed ratio for MEA at various temperatures

Temperature (°C)	Critical monomer concentration $[M]_c$ (mol l^{-1})	Critical feed ratio, f_{MEA}[a]
30	1.23	0.1444
50	2.66	0.3792
60	3.76	0.4667

[a] Assuming ideal mixing.

4.2. Terminal model reactivity ratios for the copolymerisation of MEA and STY

The reactivity ratios of MEA and STY have been obtained at several temperatures. There is a significant temperature effect on the copolymer composition as illustrated by Fig. 4a which shows plots of f_1 versus F_1 for the two temperature extremes, viz. 30 and 80°C. The corresponding 95% joint confidence intervals are shown in Fig. 4b. A significant temperature effect on the copolymer composition is predictable on the basis of depropagation at the higher temperatures. However, even at lower

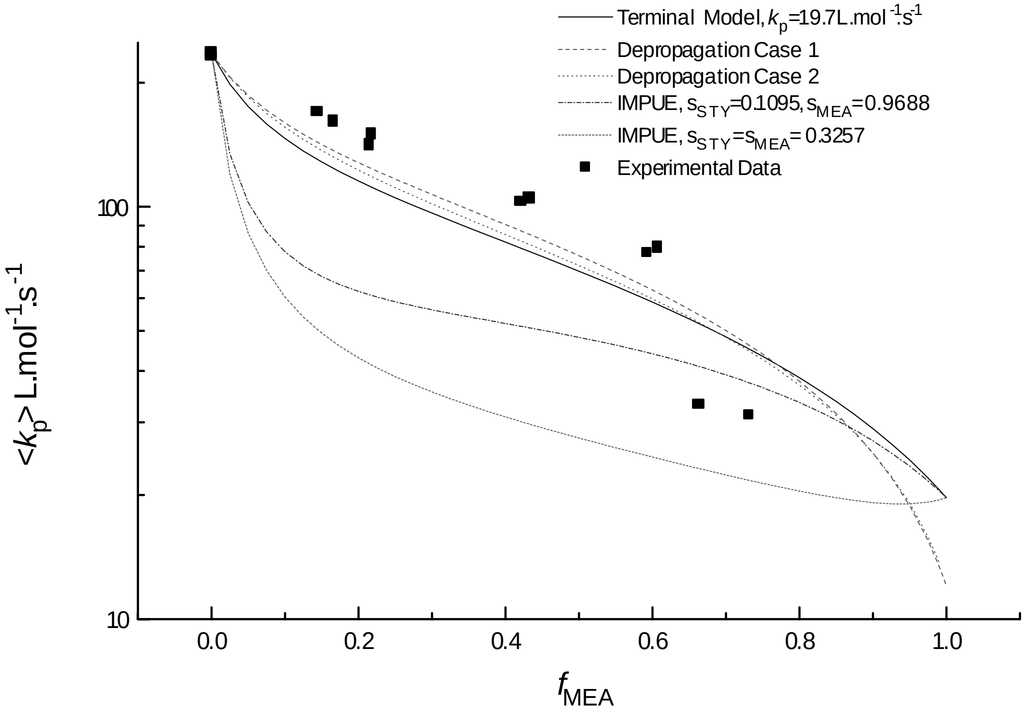


Fig. 6. Experimental and model fitted $\langle k_p \rangle$ data for MEA–STY at 50°C.

temperatures the depropagation reaction has an influence at low concentrations of MEA in the feed, as shown in Table 5. The main point of discussion is that the terminal model can be utilised to model the copolymerisation kinetics of MEA and STY — however, it does not necessarily reflect the elementary mechanisms operating in reaction. The strong influence of temperature on both reactivity ratios is indicative of a general failure of the terminal model. A discussion

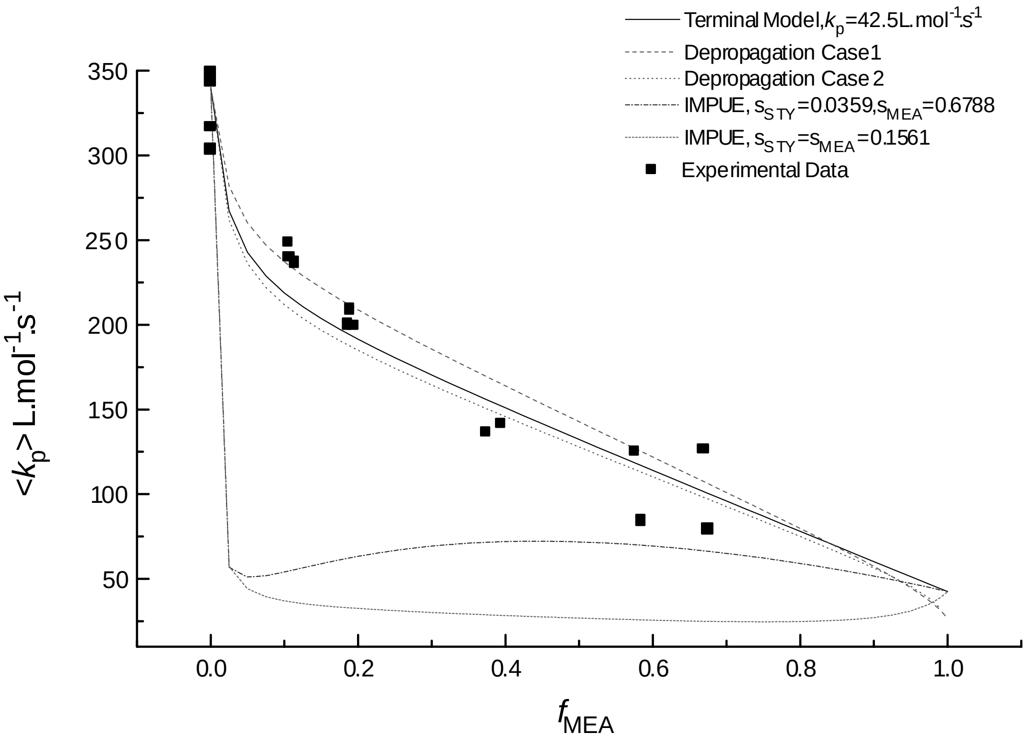
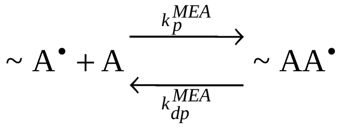
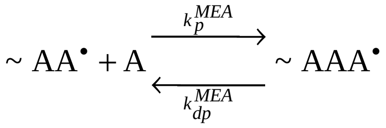


Fig. 7. Experimental and model fitted $\langle k_p \rangle$ data for MEA–STY at 60°C.



$$\sim A^{\bullet} + A \underset{k_{dp}^{MEA}}{\overset{k_p^{MEA}}{\rightleftarrows}} \sim AA^{\bullet}$$

Scheme 1. Depropagation in case II. Only sequences of MEA of two or greater can depropagate.



$$\sim AA^{\bullet} + A \underset{k_{dp}^{MEA}}{\overset{k_p^{MEA}}{\rightleftarrows}} \sim AAA^{\bullet}$$

Scheme 2. Depropagation in case II. Only sequences of MEA of three or greater can depropagate.

of copolymerisation models incorporating depropagation follows later in this paper.

4.3. The implicit penultimate unit model

The terminal model can be extended to include the electronic effects of the penultimate unit on the radical reactivities of the growing chain [7]. The radical reactivities, r_1 and r_2, and the homopropagation rate coefficients, k_{11} and k_{22} are replaced by average values.

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

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

Here, $i \neq j$ and $i, j = 1$ or 2. The monomer reactivity ratios (r_i and r'_i) and the radical reactivities are defined by the following relationship.

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

$$r'_i = \frac{k_{iii}}{k_{jij}}$$

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

where $i \neq j$ and $i, j = 1$ or 2.

In systems where the polymer composition can be described by the terminal unit model, the restriction $r'_i = r_i$ can be made. This restricted penultimate model is known as the "implicit penultimate model" and was originally proposed by Fukuda et al. [13] as a general basis for copolymerisation modelling. In recent work Coote and Davis [6] have provided theoretical and experimental evidence that a 'full' penultimate model, without the restriction $r_1 r_2 = s_1 s_2$, is more generally appropriate. Nonetheless the implicit model can be used to model the copolymerisation of STY with MMA and therefore we applied the model to our current data obtained for STY and MEA.

Figs. 5–7 show a comparison of the implicit penultimate effect model and the terminal model at 30, 50 and 60°C. The terminal model provided a better representation of the data at all temperatures. This is particularly evident at 60°C (Fig. 7) where there is a large deviation between the experimental data and the prediction of the implicit model. In this case the utilisation of reactivity ratios that ignore the phenomenon of depropagation is complicating matters. In the following section we discuss the influence of depropagation on copolymerisation kinetics.

4.4. Depropagation in copolymerisation

In this work, two depropagation models, first proposed by Lowry [27], are investigated. As the terminal model provides the best description of the copolymerisation kinetics — this is used as the basis for the depropagation models — and penultimate unit effects are ignored. The two models are commonly denoted as "depropagation case I" and "depropagation case II" and have been used successfully by Kukulj et al. [1] to describe the copolymerisation of AMS and styrene. In depropagation case I, only MEA sequences two or longer can undergo depropagation (Scheme 1), whilst in depropagation case II, only MEA sequences with three or more units can undergo depropagation (Scheme 2). The derivations for the equations given here were reported by Kukulj et al. [1].

4.4.1. Depropagation case I

The expression for $\langle k_p \rangle$ for depropagation case I, where monomer 2 is the monomer that can undergo depropagation, is given by

$$\langle k_p \rangle = \frac{r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2 - \alpha r_2[M_2]/K}{([M_1] + [M_2])\left(\dfrac{r_1[M_1]}{k_{11}} + \dfrac{r_2[M_2]}{k_{22}}\right)}$$

where K is the equilibrium constant for depropagation ($= k_{22}/k_{dp}^{22}$), $[M_1]$ and $[M_2]$ the monomer concentrations, and α parameter that varies from 0 to 1. The value of α is given by the expression

$$\alpha = \frac{(1 + K[M_2] + K[M_1]/r_1) - \sqrt{(1 + K[M_2] + K[M_1]/r_1)^2 - 4K[M_2]}}{2}$$

The reactivity ratios in these expressions, r_1 and r_2, are fitted to the composition data using the expression

$$F_2 = \frac{[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2 - \alpha r_2[\mathrm{M}_2]/K}{r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2 - \alpha r_2[\mathrm{M}_2]/K}$$

The equilibrium constant for depropagation, K, was calculated from the free energy of polymerisation

$$\Delta G = \Delta H - T\Delta S = -\mathrm{R}T \ln K$$

Values for the enthalpy and entropy of polymerisation (ΔH and ΔS) used in this work were obtained form the work of Penelle et al. [4] By varying the monomer concentration slightly and assuming that the entropy of polymerisation is $-25\ \mathrm{cal\ mol^{-1}\ K^{-1}}$, they found that the enthalpy of polymerisation was $7.4\ \mathrm{kcal\ mol^{-1}}$. However, there was a minor error in their work as the influence of temperature on MEA density was not accounted for. When these values are corrected for density, ΔH, and ΔS are calculated as $-26\ \mathrm{cal\ mol^{-1}\ K^{-1}}$ and $7.6\ \mathrm{kcal\ mol^{-1}}$, respectively. These values are only approximate because they depend on a number of assumptions. However, in the absence of more precise thermodynamic data, these values have been adopted to predict the copolymerisation behaviour expected under the assumptions of terminal model kinetics mediated by depropagation for both depropagation case I and depropagation case II, as shown in Figs. 5–7.

The modification to the terminal model by allowing for depropagation is not large at lower temperatures. However, it does appear that in all cases the depropagation model provides a better representation of the experimental data. This is a significant result because, as stated earlier, this prediction is based on thermodynamic data that were determined in an independent study. As the feed concentration of MEA increases, the data becomes less reliable as the PLP experiment becomes more difficult.

4.4.2. Depropagation case II

The expression for $\langle k_\mathrm{p}\rangle$ for depropagation case II, where monomer 2 is the monomer that can undergo depropagation, is given by

$$\langle k_\mathrm{p}\rangle = \frac{r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2 - \delta r_2[\mathrm{M}_2]/K}{([\mathrm{M}_1] + [\mathrm{M}_2])\left(\dfrac{r_1[\mathrm{M}_1]}{k_{11}} + \dfrac{r_2[\mathrm{M}_2]}{k_{22}}\right)}$$

This expression is identical is mathematical form to that for case I, however, δ has a more complex definition, as shown by the expressions:

$$\beta = \frac{(1 + K[\mathrm{M}_2] + K[\mathrm{M}_1]/r_1) - \sqrt{(1 + K[\mathrm{M}_2] + K[\mathrm{M}_1]/r_1)^2 - 4K[\mathrm{M}_2]}}{2}$$

$$\gamma = \frac{K[\mathrm{M}_1]/r_2 + K[\mathrm{M}_2] - \beta}{K[\mathrm{M}_2]}$$

$$\delta = 1 - (\gamma + 1)\left(\gamma + \frac{1}{1-\beta}\right)^{-1}$$

The reactivity ratios for this depropagation model are fitted to the copolymer compositions in a similar manner to that in depropagation case I.

$$F_2 = \frac{[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2 - \delta r_2[\mathrm{M}_2]/K}{r_1[\mathrm{M}_1]^2 + 2[\mathrm{M}_1][\mathrm{M}_2] + r_2[\mathrm{M}_2]^2 - \alpha r_2[\mathrm{M}_2]/K}$$

When this model was fitted to the data (Figs. 5–7), it was found that there are only minor differences from Case I or terminal kinetics and the current experimental data is not of sufficiently high quality to distinguish among these models.

5. Conclusions

The average propagation rate coefficient, $\langle k_\mathrm{p}\rangle$ in the copolymerisation of MEA and STY is best described by the terminal model. There are strong theoretical grounds for accepting this result as it is possible to argue that the sterically hindered MEA radical dominates the overall copolymerisation kinetics. Whilst it is argued that an enthalpic penultimate unit should be playing a role (by analogy with the STY–MMA system) this smaller enthalpic effect is subsumed within a predominant entropic influence on $\langle k_\mathrm{p}\rangle$ originating from a shielding effect on the terminal radical centre by bulky α-substituents. Further results demonstrate a large temperature effect on the copolymer composition indicating a clear failure of simple terminal model kinetics and a modification to the terminal model allowing for depropagation has been shown to be a more viable physical model for this copolymerisation.

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