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THE REACTIVITY OF MALEIC ANHYDRIDE TOWARD THE 1-PHENYLETHYL RADICAL

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Abstract—The behaviour of the 1-phenylethyl radical as an initiating species was investigated using the end group method of Bevington *et al.* for a number of copolymerisations of methyl methacrylate with maleic anhydride and similar species. A strong selectivity for addition of the 1,2 disubstituted monomer was found in each case. The reactivity ratios obtained for addition of the 1-phenylethyl radical to styrene and maleic anhydride, when compared with published equivalents for the poly(styrene) radical, showed addition to the 1-phenylethyl radical to be more selective by a factor of approximately two. Similar results were found for each of the other species examined and it is suggested a penultimate effect of steric origin is responsible for the decreased selectivity of the poly(styrene) radical. No significant solvent effect was found on the reactivity of the 1-phenylethyl radical in the copolymerisation of methyl methacrylate and maleic anhydride. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

One approach to investigating aspects of the kinetics of free radical polymerisation is the use of small radical species as models for polymer radicals [1]. The polymer end group method developed by Bevington *et al.* [2] uses radicals structurally similar to polymer radicals to initiate free radical copolymerisation. Radicals isotopically enriched with ^{13}C are used, making it possible to observe signals from the end groups of the copolymers by ^{13}C-NMR spectroscopy.

Most applications of this method have used azo-initiators (R–N=N–R) as radical sources, as the decomposition of these compounds provides carbon centred radicals exclusively. Thermal or photochemical dissociation of an azo-initiator gives the following scheme for initiation of binary copolymerisation:

$$\begin{aligned} R\text{—N}{=}\text{N—}R &\longrightarrow 2R^{\bullet} + \text{N}_2 \\ R^{\bullet} + M_1 &\longrightarrow RM_1^{\bullet} \\ R^{\bullet} + M_2 &\longrightarrow RM_2^{\bullet} \end{aligned} \qquad (1)$$

Where R is the initiating radical and M_1 and M_2 are comonomers. If copolymerisation is carried out to low conversion, so that the ratio M_1/M_2 does not vary significantly, the following relationship will hold:

$$\frac{RM_1\sim}{RM_2\sim} = \frac{k_1[M_1]}{k_2[M_2]} \qquad (2)$$

Use of the ^{13}C-labelled form of the initiator allows the observation of ^{13}C-NMR signals corresponding to $RM_1\sim$and $RM_2\sim$. If the spectrum is obtained such that the enriched carbon atoms are fully relaxed, the ratio $[RM_1\sim]/[RM_2\sim]$ will be the same as the ratio of the corresponding peak areas. This ratio is plotted as a function of the feed composition $[M_1]/[M_2]$, and the relative reactivity of the comonomers toward R, k_1/k_2, is determined from the slope of this graph.

It has been found that a number of small radicals derived from azo-initiators have relative reactivities toward certain comonomers comparable to the reactivities of structurally similar polymer radicals [2–4]. In recent years the 1-phenylethyl radical derived from the decomposition of 1,1′-azobis(phenylethane) (APE) has been shown to give relative reactivity data in excellent agreement with that obtained for the poly(styrene) radical [4, 5]. In the case of styrene (S) and acrylonitrile (An), the 1-phenylethyl radical was found to give a value of k_S/k_{An} similar to that of a poly(styrene) radical with a penultimate S unit, but significantly different to that of a poly(styrene) radical with a penultimate acrylonitrile unit [6].

In this work, the polymer end group method was used to investigate the reactivity of maleic anhydride toward the 1-phenylethyl radical. Styrene and maleic anhydride (MA) copolymerise readily to give a product with a strong tendency toward a 1:1 alternating composition. This reaction is not explicable by the Mayo–Lewis terminal model of copolymerisation [7]. A large body of data has been accumulated in an effort to explain this alternating tendency, which has been reviewed by Ebdon *et al.* [8]. One of two mechanisms is most likely to be responsible for the alternating tendency of S:MA copolymerisation:

(1) A model involving participation of a S:MA charge-transfer complex. The existence of such a charge-transfer complex is well attested. It has been observed both by NMR and UV/vis spectroscopy

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and has an equilibrium constant of formation of ca. 0.3 $\mathrm{dm^3\,mol^{-1}}$ at room temperature [9, 10]. At one time it was thought that the alternating copolymerisation might proceed through the concerted addition of this S:MA complex to the growing chain end, to the exclusion of the free comonomers. This is now known not to be the case [8], but the possible participation of the complex in the copolymerisation has not been ruled out.

Fitting reactivity ratios to the composition data of Ebdon *et al.*, O'Donnell *et al.* determined that the complex would be slightly more reactive than the free MA monomer in only one propagation reaction; addition to the S radical [11]. The complex participation model was found to be very insensitive to the numerical values used, giving equally good fit to the composition data for a large number of postulated reactivity ratios. Unlike the vinyl acetate (VAc):MA system, where the addition of VAc:MA complex to the polymer radical is favoured by the much higher stability of the poly(MA) radicals (Q values 0.86 MA cf. 0.026 VAc) [12], there appears to be no theoretical basis for the postulated enhanced reactivity of the S:MA complex.

(2) An enhanced cross-propagation mechanism, where styrene has a very high selectivity for the polymer radical with a terminal maleic anhydride unit (a strong acceptor radical) and maleic anhydride has a very high selectivity for the polymer radical with a terminal styrene unit (a donor radical). The deviations from Mayo–Lewis kinetics in the copolymerisation can then be explained by invoking a penultimate unit effect on the selectivity of the polymer radicals [13]. Recent work using pulse laser polymerisation to determine mean k_p values at varying S:MA feed compositions has given data that fits well to a penultimate unit effect model, but cannot be fitted to a complex participation model [14].

As yet, there has been no definitive discrimination between the two models. Although the bulk of the evidence appears to favour a cross-propagation mechanism, the competing mechanism is still commonly cited [15, 16].

Most models of the S:MA. system have assumed, based on the reluctance of MA to homopolymerise, that there is no homopropagation reaction of MA in the copolymerisation [8]. If the MA radical is very reluctant to add MA under normal experimental conditions, it is therefore the reactivity of the radical with the terminal S unit that is of primary importance in establishing the mechanism.

There are pronounced solvent effects on S:MA copolymerisation, which have not been satisfactorily explained within the framework of either mechanism.

The aim of this work is to investigate the reactivity of the 1-phenylethyl radical toward MA. We examine the effect of solvent on the relative reactivity of maleic anhydride and methyl methacrylate (MMA) toward the 1-phenylethyl radical. Five solvents were investigated: benzene, which forms a weak complex with maleic anhydride and has been commonly employed for the copolymerisation; n-hexane, which forms no complex with S or MA; dimethylformamide (DMF); tetrahydrofuran (THF); and dimethylsulfoxide (DMSO), which has a high equilibrium constant for complex formation with MA [13, 17–19]. Reactivity ratios previously determined using the end group method for S:MMA copolymerisation [3] were then used to determine the relative reactivity of MA and S toward the 1-phenylethyl radical, according to the relation:

$$\frac{k_\mathrm{MA}}{k_\mathrm{S}} = \frac{k_\mathrm{MA}}{k_\mathrm{MMA}}\frac{k_\mathrm{MMA}}{k_\mathrm{S}} \tag{3}$$

(This relation assumes there is no appreciable solvent effect in S:MMA copolymerisation with the solvents of interest [20].)

This procedure was followed since the high selectivity of the 1-phenylethyl radical for MA, predicted by all models, requires a low mole fraction of MA in the feed to obtain end groups other than RMMA$\sim$. Therefore, it is advisable to use a comonomer with a low reactivity toward MA, as the consumption of MA will otherwise rapidly skew the feed ratio — even after 5% conversion, a 20:1 feed of S:MA will be converted to a 40:1 feed.

A number of compounds structurally similar to MA display a similar tendency toward alternation in reaction with S. These include maleimide (Mal) [21], *N*-phenyl maleimide (NPM) [22, 23], and citraconic anhydride (CA) [24]. A further aim of this work was to compare the reactivity of these species with that of MA.

EXPERIMENTAL

Materials

1,1′-azobis(1-phenylethane) (APE) enriched with ^{13}C in the α-carbon was prepared from acetophenone with a ^{13}C enriched carbonyl group (Cambridge Isotope Laboratories) according to the method of Cywar and Tirrell [6]. MMA was purified by standard techniques and stored at −10°C over molecular sieves. MA was purified by sublimation under vacuum. *N*-phenyl maleimide (Sigma) was recrystallised from benzene. Citraconic anhydride (Sigma) was distilled prior to use and maleimide (Sigma) was used as supplied. Benzene and n-hexane were dried over sodium wire and used without further purification. DMSO was distilled from calcium hydride under nitrogen onto molecular sieves and stored at room temperature. DMF was distilled and stored over molecular sieves at room temperature. THF was refluxed over sodium wire in the presence of benzophenone, then distilled and used immediately.

Copolymerisation procedure

Polymerisations were carried out in sealed degassed dilatometers either photochemically (maximum emission of lamp 360 nm) at 27°C or thermally at 100°C. Each preparation contained 20% total monomer by volume with one of five solvents — benzene, n-hexane, DMSO, DMF, or THF. All preparations were made up with 36 $\mathrm{mmol\,dm^{-3}}$ APE. Conversions were monitored dilatometrically and limited to less than 10%. The resulting MA:MMA polymers were recovered by precipitation in petroleum ether or methanol, then purified by repeated reprecipitation from benzene before drying under vacuum at room temperature. ^{13}C-NMR spectra were recorded for filtered 2–10% w/v polymer solutions in $\mathrm{CDCl_3}$ using a

Bruker AM300 spectrometer operating at 75.468 MHz. A pulse repetition rate of 2.5 s was used, which was verified to be more than five times the spin-lattice relaxation time (T_1) of either ^{13}C enriched site.

RESULTS

Copolymers of MMA and MA prepared photochemically showed only trace incorporation of MA. Peaks in the ^{13}C-NMR spectra corresponding to MA in the backbone of the copolymer could be observed only at low MMA:MA feed ratios. The degree of MA incorporation was estimated using ^{13}C-NMR spectroscopy and standard reactivity ratios [25] and it was found that for a 10.0 MMA:MA feed ratio, all solvents except n-hexane gave copolymers containing less than 2% MA. In n-hexane, copolymers obtained at a 10:1 MMA:MA feed ratio contained an estimated 10% MA. The degree of conversion was monitored in each copolymerisation and the effect of composition drift taken into account by taking the average of the initial feed composition and the calculated final feed composition as the plotted value $[M_1]/[M_2]$.

Figure 1 shows end group spectra for copolymers prepared photochemically in benzene from MMA:MA feed ratios of 60 and 10.0. The peaks between 41.5 and 39.5 ppm are attributed to *R*MA∼ end groups, while the peaks between 36.8 and 35.5 ppm are attributed to *R*MMA∼ end groups. These latter signals are identical to the *R*MMA∼ end groups found in poly(methyl methacrylate) [26]; their relative simplicity in comparison to the *R*MA∼ signals may be explained on stereochemical grounds, since the *R*MA∼ end group contains three chiral centres in succession while in the *R*MMA∼ end-group two chiral centres are separated by an achiral carbon. It is apparent from Fig. 1 that MA has a much greater affinity for the 1-phenylethyl radical than does MMA. From the areas of the end group signals shown and others, the relative reactivity of MA and MMA toward the 1-phenylethyl radical in benzene was determined to be 84 ± 7 (Fig. 2).

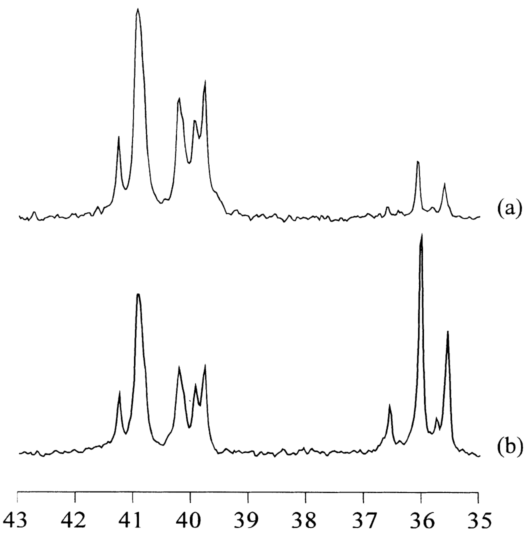

Fig. 1. ^{13}C-NMR spectra of the end-group region of poly(MMA-co-MA) prepared from a MMA/MA feed ratio of (a) 10:1 and (b) 60:1.

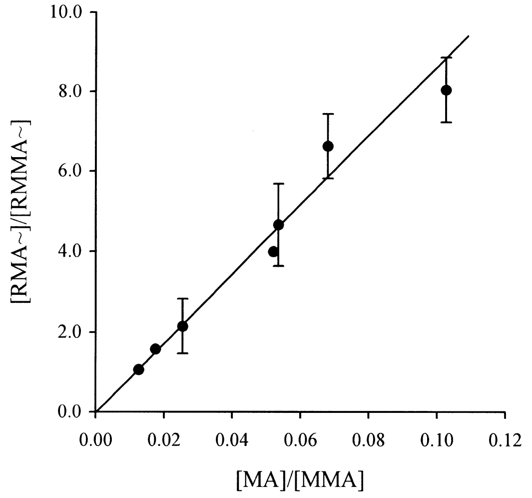

Fig. 2. End-group composition of poly(MMA-co-MA) as a function of feed composition for copolymerisation in benzene.

From previous work with APE [3], $k_{\mathrm{MMA}}/k_{\mathrm{S}} = 2.1 \pm 0.2$, and therefore $k_{\mathrm{MA}}/k_{\mathrm{S}}$ ($1/r_{\mathrm{S}}$) can be estimated as 180 ± 20. This value is larger, by a factor of approximately two, than comparable values of $1/r_{\mathrm{S}}$ for the poly(styrene) radical derived from composition analyses [13, 27, 28, 25].

Table 1 shows the reactivity ratios obtained in the five solvents studied. It can be seen that the observed solvent effects are small, and that there is no clear correlation with solvent polarity. In every case the selectivity is greater than values determined from copolymer composition for the poly(styrene) radical. The best defined end groups were obtained for the non-polar solvents benzene and n-hexane, with DMSO and DMF giving particularly small end-group signals suggesting copolymers of larger molecular weight. The rate of copolymerisation in these solvents also appeared to be somewhat reduced, which suggests a reduced rate of initiation due to the UV absorbance of these solvents.

In copolymerisation of MMA with the three MA analogue species in benzene, an enhancement in selectivity very similar to that seen with MA was observed. These copolymers all showed negligible incorporation of the MA analogue species. Typical end-group spectra for the three different copolymers are shown in Fig. 3. *R*MMA∼ end group peaks can in each case be seen between 35.5 and 36.8 ppm,

Table 1. Calculated reactivity ratios ($k_{\mathrm{MA}}/k_{\mathrm{S}}$) for the 1-phenylethyl radical

Solvent	$1/r_{\mathrm{S}}$	95% conf. interval
n-Hexane	130	20
Benzene	180	20
DMSO	155	30
DMF	165	15
THF	130	40

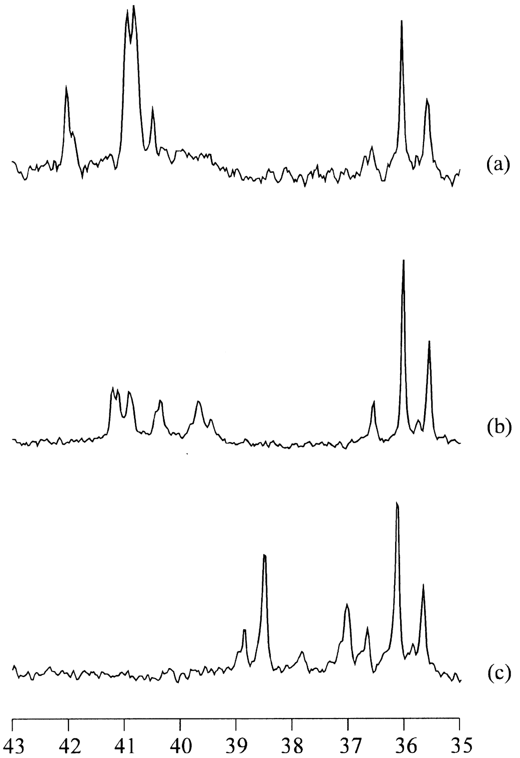

Fig. 3. ^{13}C-NMR spectra of the end-group region of (a) poly(MMA-co-NPM) prepared from a MMA/NPM feed ratio of 40:1, (b) poly(MMA-co-Mal) prepared from a MMA/Mal feed ratio of 20:1, and (c) poly(MMA-co-CA) prepared from a MMA/CA ratio of 10:1.

essentially identical with each other and with end group signals in poly(methyl methacrylate). The *R*NPM∼ and *R*Mal∼ end group signals occupy the same region (39.5 to 42.0 ppm) as the *R*MA∼ end group signals, but the *R*CA∼ end group signals are shifted slightly upfield by the shielding effect of the methyl group on CA (36.8 to 39.2 ppm). Figure 4 summarises the results obtained for the three systems at 27°C.

The reactivity ratios found in these experiments are shown in Table 2, together with corresponding values for the poly(styrene) radical derived from the terminal model in a number of composition studies [21, 23, 24]. These have been adjusted to 27 or 100°C as appropriate using the temperature dependence formula of O'Driscoll [29]. It can be seen that in every case we have found a greater selectivity for addition of the 1-phenylethyl radical toward the monomer than previously reported for the poly(styrene) radical.

DISCUSSION

Enhanced selectivity of addition to the 1-phenylethyl radical

The very high selectivity of the 1-phenylethyl radical for MA and a number of analogous species over styrene supports an enhanced cross-propagation mechanism for the alternating copolymerisation of S and MA. As no S is present in the systems investigated, the high selectivity we have noted cannot be due to the participation of a S:MA complex or analogous species. The complexation of MA and MMA has been reported, $K = 0.43\ \mathrm{dm^3\ mol^{-1}}$ [30], and it is possible that this complex has a different reactivity than free MA monomer. The greater incorporation of MA into the copolymer when hexane is the solvent, where the concentration of the MMA:MA complex should be a maximum, suggests that the participation of this complex cannot be discounted entirely.

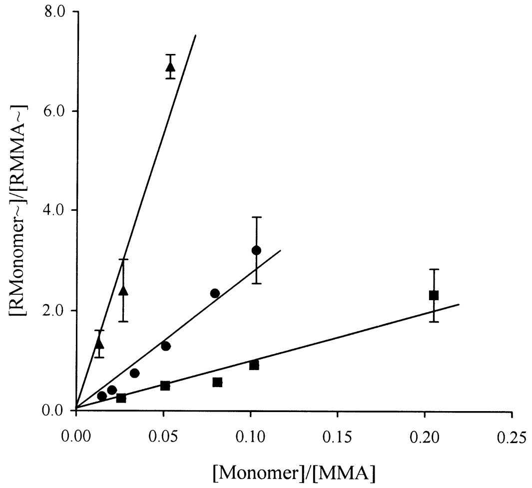

Fig. 4. End-group composition of poly(MMA-co-NPM) (s), poly(MMA-co-Mal) (l), and poly(MMA-co-CA) (n) as a function of feed composition for copolymerisation in benzene.

According to the recent pulse laser polymerisation work of O'Driscoll *et al.* [14] interpreting the copolymerisation by a penultimate model, $1/r_{SS} = 50$ and $1/r_{MAS} = 19$ at 30°C in butanone. In earlier work Klumperman and Vonk [28] obtained $1/r_{SS}$ values between 41 and 53 and $1/r_{MAS}$ between 16 and 23 for a number of solvents at 60°C, using copolymer composition data. Hill *et al.* [27], using the same methods on the bulk copolymerisation at 60°C, found $1/r_{SS} = 56$ and $1/r_{MAS} = 35$. Dodgson and Ebdon [8] calculated a value of $1/r_S = 31$ using the Alfrey–Price equation [31]. In work in which composition data was fitted to a complex participation model, the greatest value considered for $1/r_S$ by Hill *et al.* was 100 [27].

Table 2. Calculated reactivity ratios for the 1-phenylethyl radical and reported reactivity ratios for the poly(styrene) radical

Monomer		1-Phenylethyl	Poly(S) (lit.)
27°C	MA	180	53
	CA	23	7.7
	Mal	60	27
	NPM	220	71
100°C	CA	14	5.4
	Mal	35	14
	NPM	140	29

Table 3. Reactivity ratios for the 1-phenylethyl radical and poly(S) radicals

Radical	r_S
~MAS	0.053
~SS	0.020
1-Phenylethyl	0.007

In comparison, this work has obtained values for $1/r_S$ based on reactivity toward the 1-phenylethyl radical of between 130 and 180. This is considerably greater than the most reliable determinations of $1/r_{SS}$, and rather greater than the most extreme numbers previously put forward for $1/r_S$. A number of explanations may be considered to account for this enhancement in selectivity:

(1) Participation in S:MA copolymerisation of a complex which can add to the S radical from either its S or MA end, and is therefore less selective in its addition than the free MA monomer. Such behaviour has been predicted in certain formulations of the complex participation model — O'Donnell *et al.* obtained such a result from curve fitting [11], while Dodgson, Ebdon and Towns have calculated that if the polar properties of the complex are an average of those of the free monomers, the selectivity of addition for a poly(styrene) radical to the MA side of the complex would be considerably less than toward MA [8]. In such a case the degree of selective addition to a styrene —like radical observed in a system where both S and MA are present should be less than in a system where S is absent, such as in this work. On the other hand, if such a complex was of importance, a greater tendency toward alternation should be noted at lower total concentrations of monomer. This has not been reported.

(2) Poorly chosen experimental conditions, such that the assumed relationship (3) does not hold. This would be the case if the MMA:MA complex were more reactive toward the 1-phenylethyl radical than free MA, as discussed above. This is highly unlikely both from theoretical consideration of the reactivity of such a complex and from the persistence of the same selectivity in solvents, such as DMSO, that complex MA far more strongly than MMA does.

(3) A bootstrap effect, where S and MA are partitioned differently between the bulk solvent and the immediate environment of growing polymer chains, so that the comonomer ratio near the polymer radicals is significantly different from the global comonomer ratio [32, 33]. In order to explain the results, S would be required to solvate preferentially to the growing poly(S-co-MA) chain, giving a local enrichment of S close to the radical centre. Since the selectivity we have observed persists both in aromatic solvents similar to styrene and in highly polar solvents, this explanation postulates highly unusual solvation behaviour for the S:MA system.

(4) The simplest and most plausible explanation for the variance is that in the S:MA system the 1-phenylethyl radical is no longer a good model for the poly(styrene) radical. In previous work, this relation has failed to hold true only in systems in which there is good evidence to suggest a penultimate unit effect is operating — for example, the styrene:acrylonitrile system, where the reactivity of the 1-phenylethyl radical was similar to that of the S radical with a penultimate S unit, but quite different from that of the S radical with a penultimate An unit [6].

No previous work has suggested a penultimate unit effect of S on the poly(S) radical, but that appears to be the most likely explanation for our observations. This must be in some way connected with the very high reactivity of styrene-like radicals for MA and similar species.

Recent theoretical work has suggested that penultimate unit effects have their origin in the hindrance of internal rotations in the transition state affecting the frequency factor for propagation [34]. In copolymerisations, this effect should be evident only when the penultimate units differ greatly in size and/or shape. It appears likely that the absence of any penultimate group strongly favours the addition of MA over S; i.e., congestion about the radical centre retards the addition of MA more than the addition of S.

Sterically, it will be relatively easier for a vinyl group such as that borne by styrene to find its way to a congested radical centre than for the inflexible double bond of the maleic anhydride ring. Table 3 shows a comparison of the "r_S" value determined in this work with r_{SS} and r_{MS} values obtained in the work of O'Driscoll *et al.* [14]. The decreased selectivity toward MA for a S radical with a penultimate MA unit in comparison to a penultimate S unit suggests that MA is the monomer more sensitive to steric hindrance, as we have found in the case of the 1-phenylethyl radical.

Examination of molecular models for these three cases shows increased congestion around the radical centre as the selectivity for MA decreases. This congestion hinders rotation about the forming bond, which is one of the major contributing motions to the frequency factor in radical copolymerisation [34]. Rotation of the terminal C–C bond in the radical species, another major contributing motion, also appears increasingly hindered as H is replaced with a S unit and then with a MA unit. It would obviously be of great value to carry out self-consistent field calculations to investigate the penultimate effect in this system, but the size of the system is such that calculations at a physically meaningful level of theory would be unworkable at the present time.

In an alternative formulation of the penultimate unit effect, substituents to the 1-phenylethyl radical could act to reduce its electron-donating power, which would also tend to reduce its reactivity in the same order as observed. Recent work has shown that electronic penultimate unit effects of this nature are of minor importance in comparison with steric effects [34, 35].

The three MA analogues studied displayed a similar enhancement of rate under all conditions, suggesting a similar effect may be responsible in each case. All four species have the same five-membered planar ring structure, and in the asymmetrical case (CA) addition of the 1-phenylethyl radical occurs to the less hindered end of the double bond.

The degree of enhancement of selectivity does not vary greatly, despite variations in the electronic character of the monomers that greatly influence the reactivity ratio in S:acceptor copolymerisation. Indeed, within the uncertainties of the data there is no real difference in the degree of enhancement in the four cases. This is as would be expected for a steric effect dependent only on the shape of the MA moiety.

Klumperman and O'Driscoll [33] have suggested that a solvent effect they observed on the composition of S-co-MA may be due to a bootstrap effect. This was investigated by Klumperman and Vonk [28], who determined $1/r_{SS}$ values in toluene at 60°C. Our results show no definitive evidence for any solvent effect on the addition of MMA and MA to the 1-phenylethyl radical; the general trend of our results (see Table 1) shows only a very slight correlation with polarity and all variations can be contained within calculated experimental error. Clearly, any solvent effects observed in this work cannot be due to a bootstrap mechanism, as there can be no effect of preferential solvation to the 1-phenylethyl radical. The reactivity ratios determined in this work for benzene ($k_{MA}/k_S = 180$) and DMF ($k_{MA}/k_S = 170$) may be compared to those observed by Klumperman and Vonk in toluene ($1/r_{SS} = 43$) and DMF ($1/r_{SS} = 53$). It can be seen that the solvent effect trends are in opposite directions. This finding is indirect evidence in support of the suggestion that the solvent effect observed by these workers is due to a bootstrap mechanism.

CONCLUSIONS

In summary, this work has found an enhanced selectivity for addition to the 1-phenylethyl radical as compared with the poly(styrene) radical for MA and a number of analogous species. It appears likely that this increased selectivity is due to a penultimate effect on the poly(styrene) radical retarding the addition of MA in S:MA copolymerisation, and of analogous compounds in similar copolymerisations.

The high selectivity of the 1-phenylethyl radical for MA and similar electron-accepting monomers makes it superfluous to postulate an enhanced reactivity for the S:acceptor complex as a source of the alternating tendency observed in these systems.

No solvent effects can be reported with confidence from this work, which supports the hypothesis that certain solvent effects observed in S:MA copolymerisation are best explained by a bootstrap effect.

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