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Effect of ethyl aluminium sesquichloride on the relative reactivity of methyl methacrylate and buta-1,3-dienes towards initiator radicals

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Abstract

The end-group method of Bevington et al. was applied to the investigation of methyl methacrylate (MMA) copolymerisation with a series of buta-1,3-dienes (butadiene, 2,3-dimethylbutadiene, isoprene, and 2,3-diphenylbutadiene) in the presence of relatively low concentrations of the Lewis acid ethylaluminium sesquichloride (EASC). The reactivity of the radical species produced by decomposition of azo-bis-methylisobutyrate methyl-^{13}C (AIBMe), azo-bis-isobutyronitrile methyl-^{13}C (AIBN) and azo-bis-1-phenylethane methyl-^{13}C (APE) were investigated. The relative reactivity of the radical derived from AIBMe was consistent with the reactivity of the poly(MMA) radical in these systems, and showed a consistent behaviour in addition to all donor monomers that could be fit adequately in terms of the *Q*–*e* scheme using $Q = 24$–28 and $e = 2.1$. Little change was seen in the reactivity of the radical derived from AIBN, in contrast to the copolymerisation of MMA and styrene (S) in the presence of EASC, where the selectivity of this radical is comparable to that derived from AIBMe. This could not be interpreted in terms of the *Q*–*e* scheme and indicates an interaction with styrene giving anomalously high selectivity, which will be the topic of future investigation. The radical derived from APE showed an extremely high selectivity towards MMA, as expected, and the magnitude of 1-phenylethyl radical addition to styrene was consistent with previous work on the MMA–S–EASC system. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Lewis acid catalysts have been widely reported to induce alternating copolymerisation between a wide range of electron donor and electron acceptor monomers [1–9]. This alternation is most pronounced in the case of alkyl aluminium chlorides and alkyl boron chlorides, and is frequently accompanied by spontaneous initiation. There has been no clear consensus as to the mechanism of the propagation reaction responsible for alternation in these systems. The two most frequently postulated mechanisms are: concerted addition of a ternary complex formed from the Lewis acid, the electron acceptor monomer, and the electron donor monomer; or enhanced cross-propagation reaction so that a complexed-acceptor monomer adds predominantly to donor radicals and a donor monomer adds predominantly to complexed acceptor radicals.

One class of donor monomers in which this phenomenon is observed are the dienes, butadiene (B), 2,3-dimethylbutadiene (DMB), isoprene (IP), and 2,3-diphenylbutadiene (DPB). The formation of alternating poly(B-co-MMA) was first reported by Gaylord and Takahishi in 1969 [10], and in the presence of a variety of Lewis acids ($SnCl_4$, $ZnCl_2$, ethyl aluminium dichloride (EADC)) butadiene has been observed to produce alternating copolymers and Diels–Alder cycloadducts with acrylonitrile, methacrylonitrile, methyl vinyl ketone, methyl methacrylate (MMA), and methyl acrylate

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[11–15]. The rate of copolymerisation reaches a maximum at moderate acid strength, with cyclodimerisation predominating at high acid strengths – $AlBr_3$ and $TiCl_4$ are reported to catalyse formation of the cycloadduct exclusively [14]. In the presence of EADC, spontaneous copolymerisation occurs in high yield at a 1:1 EADC:Acceptor ratio; at a 1:10 ratio only acrylonitrile copolymerises to any great extent [16]. Alternating copolymers of DMB, IP, and DPB with MMA and acrylonitrile have also been reported under Lewis acid catalysis [7,8]. The investigation of these alternating copolymers has rarely been considered except in combination with the formation of diene/acceptor Diels–Alder cycloadducts, a subject that has generated considerable interest [7,17–24]. This research on Lewis-acid-induced alternation has concentrated on elucidating the mechanism of spontaneous initiation that occurs at relatively high Lewis acid concentrations, and relatively little attention has been paid to the propagation step in these reactions. In copolymerisations of methyl acrylate with butadiene and IP in the presence of EASC, it has been reported that an enhanced cross-propagation mechanism can adequately explain all phenomena observed [8,25].

We have previously investigated the effect of ethyl aluminium chloride species on the copolymerisation of MMA and styrene (S) [26,27] a system which has been extensively studied by a number of groups [1–6,28–31]. Building on the previous work of Krstina et al. [32], we used the end-group method first described by Bevington et al. [33] to show that the presence of ethyl aluminium sesquichloride (EASC) has a marked effect on the relative reactivity of styrene and MMA towards the 1-methyl-1-(methoxycarbonyl)ethyl (R_{MMA}), 1-cyano-1-methylethyl (R_{MAn}) and 1-phenylethyl (R_S) radicals. These species, which are structurally similar to the poly(MMA), poly(methacrylonitrile), and poly(styrene) radicals respectively, have been shown to be good models for the polymer radicals in terms of their relative reactivity to a wide range of monomers [34–39]. They were generated by the photolysis of azo-bis-methylisobutyrate methyl-^{13}C (AIBMe), azo-bis-isobutyronitrile methyl-^{13}C (AIBN) and azo-bis-1-phenylethane methyl-^{13}C (APE) respectively and used to initiate copolymerisation. The ^{13}C-NMR spectra of the copolymers obtained showed distinct peaks which could be attributed to R_{MMA} and R_S end groups, allowing the reactivities of the monomers towards radical R to be compared through the relationship

$$\frac{A_{MMA\sim}}{A_{S\sim}} = \frac{k_{MMA}}{k_S}\frac{[MMA]}{[S]} \tag{1}$$

where A_{MMA} and A_S are the areas of the NMR peaks corresponding to the R_{MMA} and R_S end-group peaks respectively, k_{MMA} and k_S are the respective rate constants for addition of R to MMA and styrene, and [MMA] and [S] are the concentrations of monomer in the feed. The spectrum is acquired under conditions such that the end-group peak areas are directly proportional to the relative numbers of end groups in the copolymer, and the reaction must be constrained to low conversion in order to maintain constant [MMA] and [S]. The results of these studies indicated that it is unnecessary to postulate the participation of a ternary complex in the copolymerisation of styrene and MMA; the composition and end-group data obtained were consistent with an enhanced cross-propagation mechanism where, in the presence of relatively low concentrations of EASC, k_{MMA}/k_S for R_{MMA} is 0.06 ± 0.03 and k_S/k_{MMA} for R_S is <0.003. There is some evidence to suggest that both k_{MMA}/k_S and k_S/k_{MMA} are dependent on the concentration of EASC, as might be expected. k_{MMA}/k_S to R_{MMA} was found to be 0.07 by Lyons at 0.055 M EASC [40] and 0.088 by Fellows at 0.036 M EASC [41], while the corresponding reactivity of the poly(MMA) radical was determined by Polton et al. to be 0.08 at 0.5 M EASC [28] and 0.045 at 1.0 M EASC [29]. At 1.0 M EASC, Polton et al. found addition to the poly(styrene) radical was considerably less selective than addition to R_S, giving k_S/k_{MMA} of approximately 0.03 [29].

The present paper reports on the application of the end-group method to determine the effect of EASC on the relative reactivities of MMA and the donor monomers butadiene (B), DMB, IP, and DPB towards the radicals R_{MMA}, R_{MAn} and R_S. The relative reactivity of these monomers towards these radical species has previously been reported, providing a good benchmark to gauge the effect of Lewis acid addition. These are given in Table 1, together with the reported Alfrey–Price Q–e values for the copolymerisation.

It will be recalled that the Q–e scheme is an empirical means of correlating reactivity ratios across the range of possible copolymerisations, where the reactivity ratios r_1 and r_2 are given by the expressions

$$r_1 = \frac{Q_1}{Q_2}e^{-e_1(e_1-e_2)} \quad \text{and} \quad r_2 = \frac{Q_2}{Q_1}e^{-e_2(e_2-e_1)} \tag{2}$$

Rogers et al. [42] have shown that the number e_n can be correlated with the electronegativity of the monomer n (the higher the e value, the greater the electronegativity) while Q_n can be related to the free energy of propagation E_Y in the reaction

$$CH_3^{\bullet} + CH_2{=}CXY \rightarrow CH_3CH_2{-}CXY^{\bullet} \tag{3}$$

where $CH_2{=}CXY$ is the monomer n. The two parameters are related by an expression of the form $\ln Q = aE_Y + b$. Davis et al. have disclaimed any predictive value for this correlation between E_Y and Q, but it will be used in this report to discuss the physical

Table 1
Literature values for 2,3-butadiene reactivity ratios [60] expressed as the relative reactivity of various radical species towards MMA and 2,3-butadienes

	MMA	B	DMB	IP	DPB[a]
Q	0.78	1.70	1.42	1.99	0.6 (0.5)
e	0.4	−0.50	−0.43	−0.55	−1.13 (−0.7)
^{13}C-AIBN	1.0	6.3 ± 0.5	3.3 ± 0.4	6.5 ± 0.5	1.4
Poly(MAn)	1.0	4.0	3.3	4.8	2.2
^{13}C-AIBMe	1.0	1.3 ± 0.1	0.7 ± 0.1	1.2 ± 0.1	0.7
Poly(MMA)	1.0	1.1	0.9	1.2	0.2
^{13}C-APE	1.0	3.0 ± 0.4	1.9 ± 0.2	4.2 ± 0.4	1.1 ± 0.1
Poly(S)	1.0	3.1	2.6	3.7	1.4

[a] First value [49]; second value [39].

phenomena underlying the Q values determined in a semi-qualitative manner.

2. Experimental procedures

The ^{13}C-methyl initiators AIBMe [35], AIBN [43] and APE [44] were prepared as previously described. EASC (0.91 M solution in toluene, Aldrich) was used as supplied. Butadiene (Aldrich) was degassed by repeated freeze–thaw cycles on a high vacuum line and distilled into a glass vessel of known volume in line with a mercury manometer. This allowed a quantity of butadiene corresponding to a known pressure to be distilled into the reaction vessel. DMB (Aldrich) was washed with 10% aqueous NaOH to remove hydroquinone inhibitor until both layers remained clear. It was then washed with distilled water and dried, first over anhydrous sodium sulphate and then over calcium hydride, before fractional distillation under N_2. DPB (Fluka) was used as supplied. IP (Aldrich) and MMA (BDH Ltd.) were both washed multiple times with 5–10% aqueous NaOH to remove *t*-butylcatechol or quinol inhibitor. They were then washed with distilled water and dried over anhydrous sodium sulphate, then distilled from calcium hydride under N_2 at reduced pressure. MMA and diene monomer were combined with initiator and dry toluene in a dilatometer provided with a tap and degassed by three freeze–thaw cycles. After detachment from the vacuum line the dilatometer was transferred to a glove bag and the EASC solution added under dry nitrogen to give a final monomer concentration of 20% (v/v). After further degassing, the resulting solutions were polymerised to low conversion (<10% of total monomer) using UV light of 365 nm to photolyse the azo initiators at a temperature of 30°C. Copolymers were recovered by precipitation in methanol to which a few drops of HCl had been added, purified by reprecipitation from toluene or benzene into methanol, and dried under vacuum at room temperature. The spin–lattice relaxation times of the ^{13}C-methyl carbon atoms of the end groups have previously been determined for these species [39], and accordingly the ^{13}C-NMR spectra were recorded with delay times of at least 3.0 s. In the not infrequent cases where the end-group peaks were found to overlap peaks derived from the polymer backbone, copolymers were prepared both with and without ^{13}C-labelled initiator and the difference of the two ^{13}C-NMR spectra was taken.

3. Results

3.1. Copolymer composition

In preliminary work, it was verified that EASC could indeed induce a strong tendency towards alternating copolymerisation of MMA with each of the four dienes. Copolymerisation of MMA with the dienes in the presence of 0.15–0.59 M EASC gave copolymers with ^{1}H- and ^{13}C-NMR spectra indicative of a highly alternating structure. In Fig. 1, ^{13}C-NMR spectra of poly(B-alt-MMA), poly(DMB-alt-MMA), poly(IP-alt-MMA) and poly(DPB-alt-MMA) are shown together with peak assignments. The diene units in the copolymers are incorporated almost exclusively in the *cis* position, an assignment made by comparison with previously obtained spectra of copolymers prepared in the absence of EASC [40]. The only exception to this trend is poly(DPB-alt-MMA), where both *cis* and *trans* addition is seen. It is unnecessary to expand on the high degree of order exhibited by these spectra.

It has been reported [45] that the spontaneous polymerisation of MMA and B in the presence of EASC yields only poly(MMA). No poly(MMA) was isolated from the copolymerisations reported on in this work, and it must be assumed that the far higher radical flux and lower concentrations of Lewis acid in this work effectively marginalised the cyclodimerisation or anionic polymerisation predominating in the reported system.

In Fig. 2, the ^{1}H-NMR spectra of the same alternating polymers are displayed. In each case, clearly separated regions of the ^{1}H-NMR spectrum can be seen,

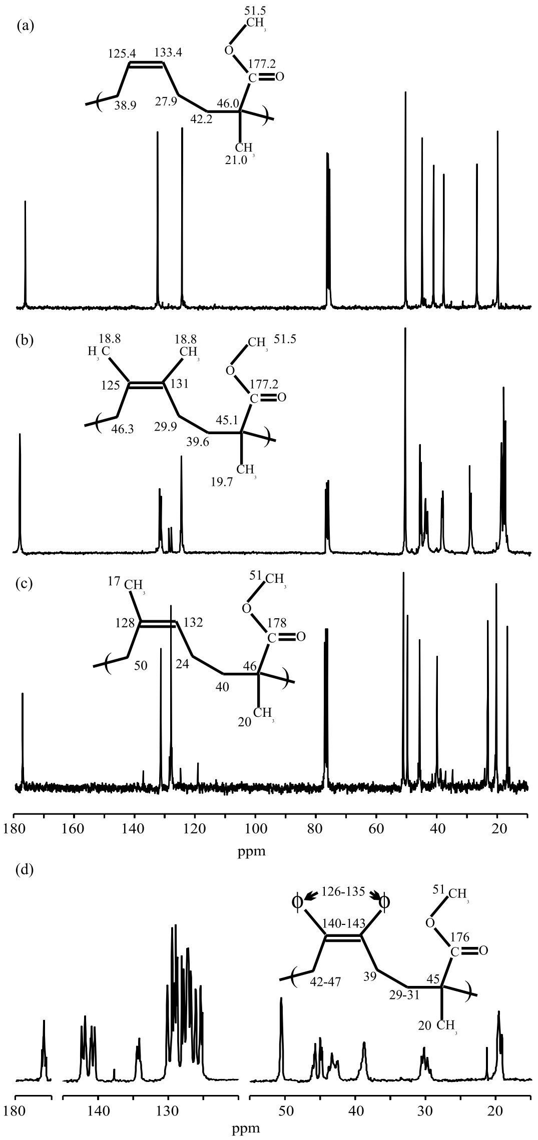

Fig. 1. ^{13}C-NMR spectra of alternating copolymers of MMA with (a) butadiene, [EASC] = 0.55 M, (b) DMB, [EASC] = 0.15 M, (c) IP, [EASC] = 0.59 M, (d) DPB, [EASC] = 0.55 M.

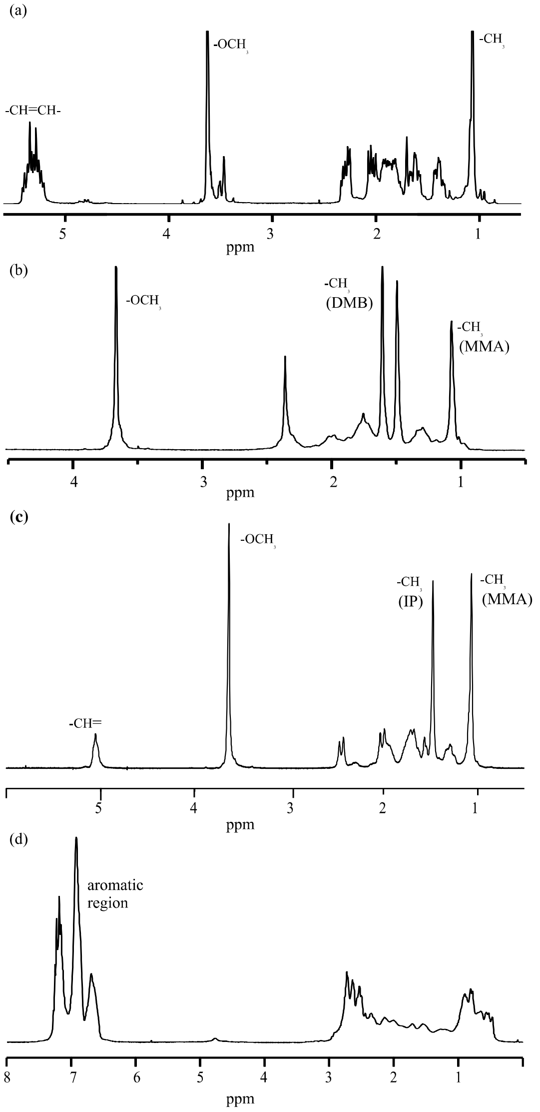

Fig. 2. ^{1}H-NMR spectra of alternating copolymers of MMA with (a) B, [EASC] = 0.55 M, (b) DMB, [EASC] = 0.15 M, (c) IP, [EASC] = 0.59 M, (d) DPB, [EASC] = 0.55 M.

allowing the near equimolar composition to be verified by integration. Corresponding spectra prepared at more extreme feed compositions and lower EASC concentrations showed a lesser tendency towards alternation. Appropriate areas of these spectra were integrated in order to provide estimates of copolymer composition.

Alfrey–Price *Q–e* values from the chemical literature were used to estimate curves of copolymer composition as a function of feed composition in the absence of EASC assuming a terminal model for propagation [46]. These compositions are given in Fig. 3, together with the copolymer compositions determined by integration in the presence of EASC and a least-squares curve fitting those data points to a terminal model. Although the feed ratios used in this work were selected in order to display quantifiable end-group peaks over as wide a composition range as possible, not to provide optimal information for determination of reactivity ratios [47], the reactivity ratios estimated from the available data may be of use in comparing the reactivity of polymer radicals with their small radical models.

The values obtained for the reactivity ratios used to fit the composition data are given in Table 2 with their associated errors (the range over which the sum of least squares values was within 20% of the minimum value).

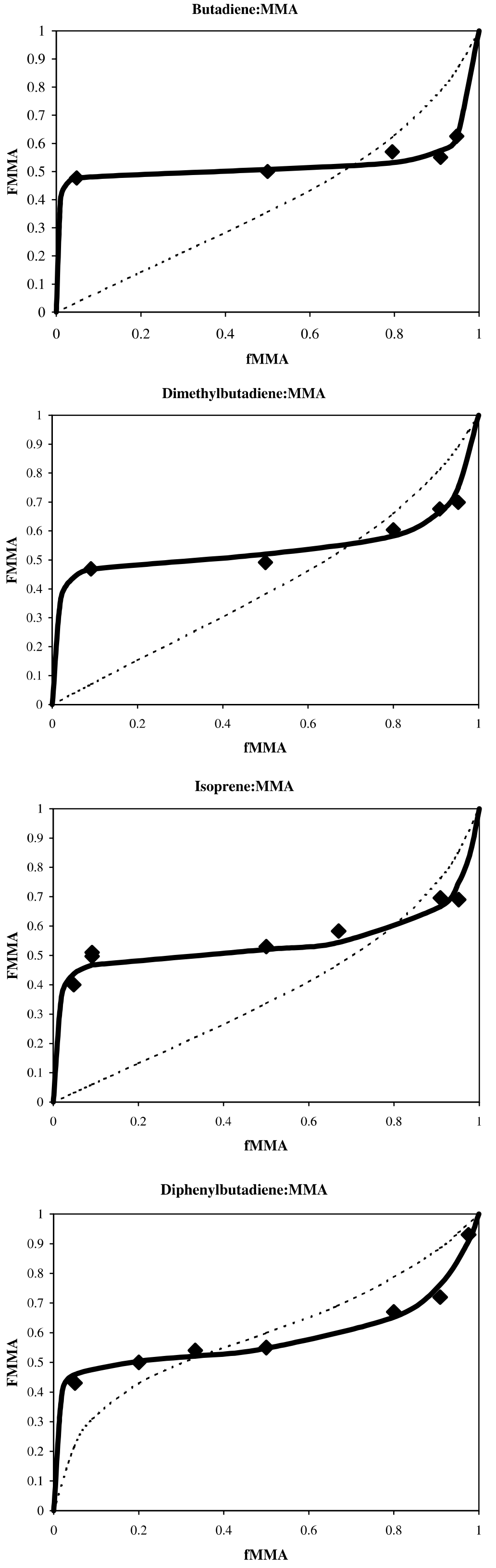

Fig. 3. Composition of copolymers prepared in the presence of 0.036 M EASC. Diamonds are data points, solid line is the terminal model fit to the data, and broken line the calculated composition in the absence of EASC from literature *Q* and *e* values [39,60].

3.2. The 1-methyl-1-(methoxycarbonyl)ethyl radical

Copolymers of MMA and butadiene prepared at feed ratios rich in MMA initiated with ^{13}C-methyl–AIBMe in the presence of 0.036 M EASC showed a prominent R_{MMA} B end-group signal and a small R_{MMA} MMA end-group signals at locations consistent with results previously reported in the absence of EASC [39]. Comparison of the areas of the R_{MMA} B and R_{MMA} MMA signals allowed a value for k_B/k_{MMA} of ~20 to be calculated, considerably higher than the value reported in the absence of EASC, 3.0 ± 0.4 [39]. This value is also considerably higher than the reactivity ratio reported for poly(MMA) in the absence of EASC, $R_{MMA} = 5.9$ [39]. Fig. 4 shows a typical ^{13}C-NMR difference spectrum of the end-group region of poly(B-co-MMA).

Similarly, R_{MMA} DMB end-group signals were found at a chemical shift consistent with previous work. A k_{DMB}/k_{MMA} value of 7.4 ± 3.9 was obtained, in comparison to previously reported values in the absence of a Lewis acid catalyst of 1.9 ± 0.2 for R_{MMA} and 2.9 for the poly(MMA) radical (Fig. 5) [39].

The general appearance of the end-group spectra of poly(IP-co-MMA) was similar in the presence and absence of EASC, as may be seen in Fig. 6. The increased complexity of these spectra in comparison to the spectra obtained in copolymerisation of butadiene and DMB is related to greater number of possible isomers formed in addition of an asymmetric diene. The R_{MMA} IP end-group peaks may be assigned as follows [8]: 1,4 addition at 25.5 ppm, 4,1 addition at 24.8 ppm (apparently all *cis*) and 1,2 addition at 27.0 and 24.5 ppm, split because of the chiral centre this introduces into the backbone. It is worth noting that the relative probabilities of 1,4, 4,1, and 1,2 addition appear to be unchanged upon addition of EASC [39,40]. A value for k_{IP}/k_{MMA} of 20 ± 3 was obtained, considerably higher than the value reported in the absence of EASC for R_{MMA}, 4.2 ± 0.4 [40] and the poly(MMA) radical, 3.7 [48].

Some difference spectra of poly(DPB-co-MMA) are shown in Fig. 7. It can be seen that the selectivity of R_{MMA} is strongly enhanced in the presence of EASC. A value of $k_{DPB}/k_{MMA} = 3.2 \pm 0.2$ was obtained for R_{MMA}, which may be compared with the value of 1.1 ± 0.1 reported for R_{MMA} and 1.4 for the poly(MMA) radical in the absence of EASC [39,49]. A further effect of EASC addition can be seen if the small peaks between 27 and 28 ppm are considered; these can clearly be seen in spectrum (a) of Fig. 7, but not in spectrum (b), and were

Table 2
Estimated Q and e values for MMA–EASC. r_{diene} and r_{MMA} optimised for best fit to diene data $Q = 28$, $e = 2.1$ and for best fit to styrene data $Q = 24$, $e = 2.0$

	r_{diene}			r_{MMA}			
	(Copolymer)	($Q = 28$)	($Q = 24$)	(Copolymer)	(AIBMe)	($Q = 28$)	($Q = 24$)
B	0.005 ± 0.002	0.017	0.020	0.035 ± 0.005	~0.05	0.070	0.095
DMB	0.015 ± 0.005	0.017	0.021	0.10 ± 0.01	0.14 ± 0.05	0.097	0.131
IP	0.017 ± 0.002	0.017	0.020	0.11 ± 0.01	0.05 ± 0.02	0.054	0.074
DPB	small	0.003	0.003	0.22 ± 0.03	0.32 ± 0.03	0.241	0.217

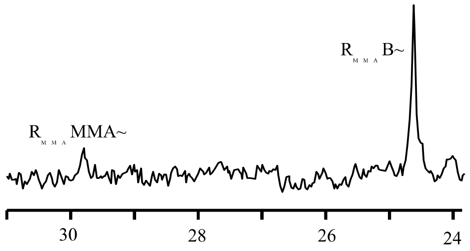

Fig. 4. ^{13}C-NMR difference spectrum of the end groups of poly(B-co-MMA) prepared from a 10:1 MMA:B feed composition in the presence of 0.036 M EASC using ^{13}C-methyl–AIBMe initiator.

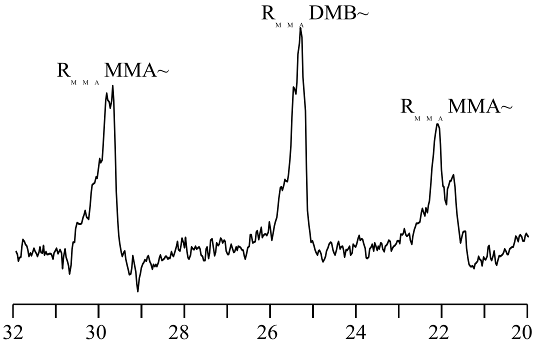

Fig. 5. ^{13}C-NMR spectrum of the end groups of poly(DMB-co-MMA) prepared from a feed composition of 10:1 MMA:DMB using ^{13}C-methyl–AIBMe initiator in the presence of 0.036 M EASC.

not seen in any of the copolymers prepared with EASC. These two peaks were previously assigned to $R_{\text{MMA}}\,DPB_{1,2}$ end groups, suggesting strongly that EASC is altering the probability of 1,2 addition to the R_{MMA} radical. This is in contrast to the situation with IP, where no obvious change in the ratio of 1,2 to 1,4 addition was observed.

3.3. The 1-phenylethyl radical

Copolymers of MMA and butadiene initiated with ^{13}C-α-APE in the presence of 0.036 M EASC showed a prominent R_SMMA end-group signal in their ^{13}C-NMR spectra. No sign of any R_SB end-group signal was apparent at B:MMA feed ratios below 10:1. This result is not unexpected, as previous work [27] has shown a very high reactivity of the R_S radical towards MMA complexed with EASC. As the reactivity of the poly(styrene) radical towards butadiene is not significantly different from its reactivity towards styrene ($r_S = 0.46$) [40], it is reasonable to assume a similar degree of selectivity for the addition to MMA will be seen in both cases.

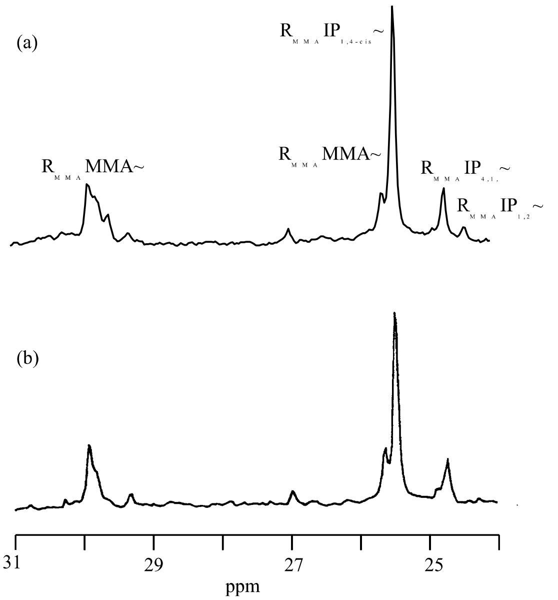

Fig. 6. ^{13}C-NMR spectrum of the end groups of poly(IP-co-MMA) prepared using ^{13}C-methyl–AIBMe initiator from a feed composition of (a) 20:1 MMA:IP in the presence of 0.032 M EASC, (b) 3:1 MMA:IP in the absence of EASC [40].

At B:MMA ratios of 10:1 and greater (see Fig. 8), small R_SB-peaks were observed. The areas of these peaks can be used to determine the relative reactivity of MMA and butadiene towards R_S as $k_{\text{MMA}}/k_B \sim 150$. This value may be extrapolated using the proven similarity in reactivities of the poly(styrene) and R_S radicals [39] to give an estimate of $k_{\text{MMA}}/k_S \sim 310$. It has not been possible to quantify this value through direct observation of R_S reactivity in the copolymerisation of

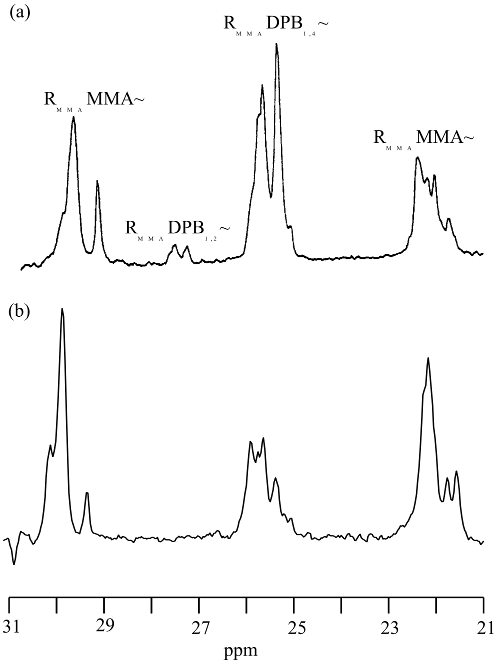

Fig. 7. ^{13}C-NMR spectrum of the end groups of poly(DPB-co-MMA) prepared using ^{13}C-methyl–AIBMe initiator from a feed composition of (a) 1.0:1 MMA:DPB [40], (b) 10:1 MMA:DPB in the presence of 0.032 M EASC.

styrene and MMA in the presence of the same [EASC] [27], the ^{13}C-NMR spectra obtained allowed only the limit $k_{MMA}/k_S > 100$ to be set for the R_S radical.

No R_SDMB end-group peaks could be seen in copolymers of DMB and MMA prepared in the presence of 0.036 M EASC for feed ratios up and including 10:1 DMB:MMA. The reactivity ratio in DMB:S copolymerisation, $r_S = 0.52$ [39], suggests that the expected proportion of R_SDMB end groups will be similar to the proportion of R_SB end groups seen in the copolymerisation of butadiene. It can be seen in Fig. 9 that the noise in the baseline is sufficient to obscure a signal of the expected magnitude.

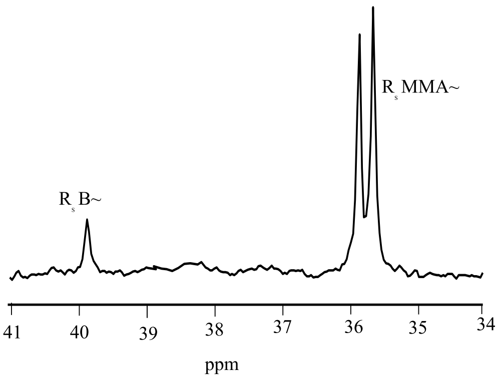

Fig. 8. ^{13}C-NMR difference spectrum of the end groups of poly(B-co-MMA) prepared from a 20:1 B:MMA feed composition in the presence of 0.036 M EASC using ^{13}C-α-APE initiator.

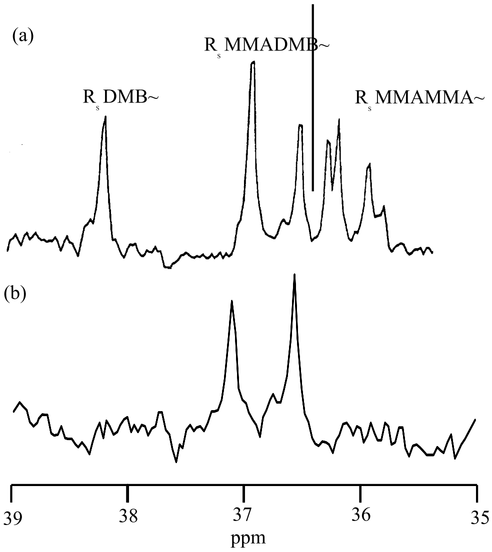

Fig. 9. ^{13}C-NMR spectrum of the end groups of poly(DMB-co-MMA) prepared using ^{13}C-α-APE initiator (a) from a 1:1 feed composition in the absence of EASC [40], (b) from a 10:1 DMB:MMA feed composition in the presence of 0.032 M EASC.

In copolymerisations of IP and MMA prepared with ^{13}C-α-APE in the presence of 0.036 M EASC, large R_S MMA IP end groups were observed. These were virtually identical in appearance to the R_S MMA B and R_S MMA DMB signals obtained. An end-group spectrum of a copolymer prepared with a high IP:MMA ratio is shown in Fig. 10, along with an equivalent spectrum prepared in the absence of EASC. The small peaks observed at ~37.8 ppm in Fig. 10(a) coincide with the most prominent R_S IP end-group peak of the poly(MMA-co-IP) prepared in the absence of EASC. This same peak is clearly seen in the spectrum of copolymer prepared at higher IP:MMA ratios. Assignment of the ~37.8 ppm peak to R_S IP allows the relative reactivity of MMA and IP towards R_S to be estimated as $k_{MMA}/k_{IP} \sim 100$. This value may be extrapolated using the relative reactivity of the poly(styrene) radical toward styrene and IP to give an estimate of $k_{MMA}/k_S \sim 250$, consistent with the estimate of ~310 obtained in the butadiene copolymerisation. These two values have previously been reported by Fellows and Senogles [27] in connection with a discussion of the alternating copolymerisation of styrene and MMA in the presence of EASC.

No R_SDPB end-group peaks were observed in the copolymerisation of MMA and DPB in the presence of

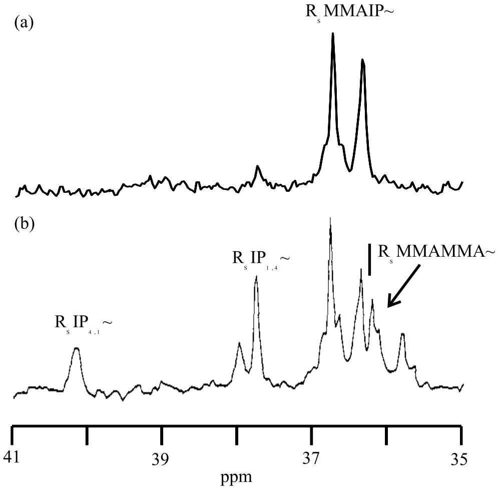

Fig. 10. ^{13}C-NMR spectra of the end groups of poly(IP-co-MMA) prepared using ^{13}C-α-APE initiator, prepared from a IP:MMA feed composition of (a) 10:1 in the presence of 0.032 M EASC, (b) 1:3 in the absence of EASC [40].

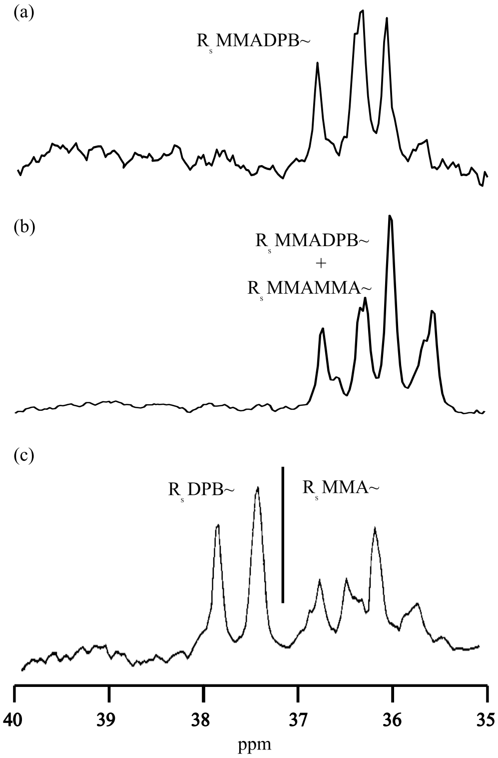

Fig. 11. ^{13}C-NMR spectrum of the end groups of poly(DPB-co-MMA) prepared using ^{13}C-α-APE initiator from a feed composition of (a) 10:1 DPB:MMA, [EASC] = 0.036, (b) 1:10 DPB:MMA, [EASC] = 0.036, (c) 1:1 DPB:MMA in the absence of EASC.

0.036 M EASC. The R_S MMA DPB end-group peaks illustrated in Fig. 11 are substantially the same at feed compositions ranging from 1:1 to 10:1 DPB:MMA. At feed ratios with a higher proportion of MMA, R_S MMA MMA end groups are also seen in the region 37.0–35.5 ppm. Due to overlap, it is impossible to quantify the selectivity of the R_SMMA$^\bullet$ radical, but qualitatively it appears to be of the same order as seen in the copolymerisation of styrene and MMA under the same conditions.

It is interesting to note that the signal for the R_S MMA DPB end group is noticeably different from that of the R_S MMA B, R_S MMA DMB and R_S MMA IP end groups, which were almost identical, though differing slightly in position. It appears to be a combination of two sets of doublets, where each of the other three gave only a single doublet. α-^{13}C–R_S MMA S end-group signals show an intermediate case, with poorly resolved doublets [50]. This may be related to the stereospecificity of addition to the R_S MMA$^\bullet$ radical; in the copolymer, B, DMB and IP have been seen to add predominantly in the *trans* position, while DPB apparently does not favour *cis* over *trans* addition; in the presence of EASC, styrene is expected to add to the MMA radical cosyndiotactically and coisotactically with equal facility.

3.4. The 1-methyl-1-cyanoethyl radical

In contrast to the marked effects on relative reactivity seen towards the R_S and R_{MMA} radicals, EASC was found to have only a limited effect on the selectivity of the R_{MAn} radical derived from AIBN. No significant differences were seen between the end-group spectra of poly(butadiene-co-MMA) obtained with ^{13}C-methyl–AIBN initiator in the presence and absence of EASC. A typical end-group spectrum for these polymers is shown in Fig. 12.

The values obtained for k_B/k_{MMA} towards the R_{MAn} radical were 4 at [EASC] = 0.036 and 10 at [EASC] = 0.15, which may be compared with 6.3 ± 0.5 obtained in the absence of EASC [39]. The fact that a relatively low reactivity is seen even at the higher EASC concentration, where the NMR spectra of the polymer backbone show no observable deviations from alternation, is strong evidence that the lack of change in selectivity is not an artefact due to oxidation of the EASC by an impurity in the AIBN. No significant difference was found between the end-group spectra of the other copolymers prepared with AIBN in the presence and absence of EASC. For the copolymerisation of MMA with DMB in the presence of 0.036 M EASC k_{DMB}/k_{MMA} was found to be 3.1 ± 0.9, which can be compared to a value of 3.3 ± 0.4 determined in the absence of Lewis acid [39]. Similar results were obtained for IP ($k_{IP}/k_{MMA} = 10.7 \pm 2.7$ cf. 6.5 ± 0.5 [39]), and for DPB ($k_{DMB}/k_{MMA} = 2.0 \pm 0.2$ cf. 1.4 [39]). The small increase in the apparent selectivity of

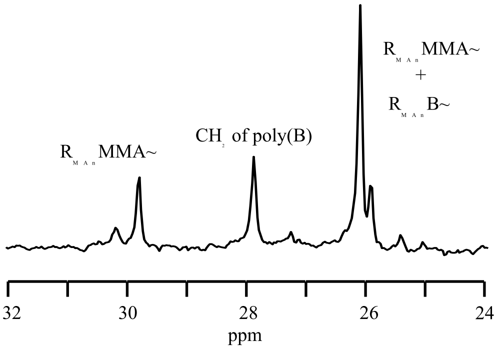

Fig. 12. ^{13}C-NMR spectrum of the end groups of poly(B-co-MMA) prepared using ^{13}C-methyl–AIBN initiator with a 4:1 MMA:B feed composition.

the R_{MAn} radical towards IP may be a real enhancement in its reactivity, but it is not significant in comparison to the large changes seen with the R_{MMA} radical. The ratio of 4,1 to 1,4 addition found by integration of the appropriate end-group peaks (see Fig. 13) is comparable with that reported previously in the absence of EASC [39]. The limited sensitivity of the R_{MAn} radical to the presence of EASC in MMA:Diene copolymerisations is in marked contrast to the strong influence of EASC seen in MMA:Styrene copolymerisation, where the selectivity of R_{MAn} is comparable to that of R_{MMA} [26].

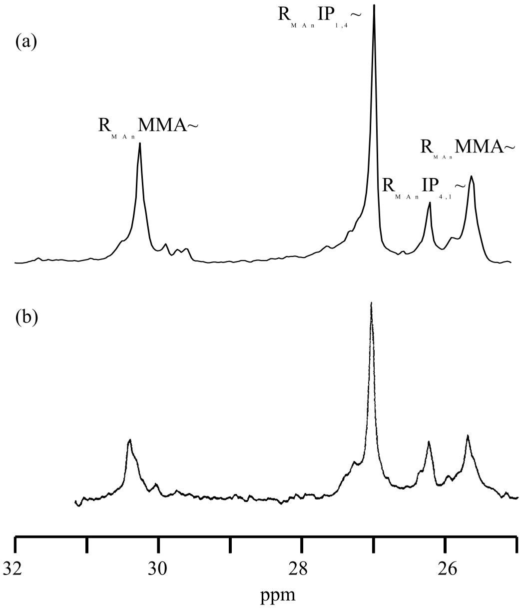

Fig. 13. ^{13}C-NMR spectrum of the end groups of poly(IP-co-MMA) prepared using ^{13}C-methyl–AIBN initiator at a feed composition of (a) 20:1 MMA:IP in the presence of 0.032 M EASC, (b) 4.2:1 MMA:IP [39].

4. Discussion

4.1. The 1-phenylethyl radical

The results obtained for the relative reactivity of the R_S radical in the presence of EASC are in good agreement with previous work showing a very strong selectivity for the MMA–EASC complexed species. Due to the inordinately high selectivity observed, it is not possible to estimate the reactivity ratios k_{diene}/k_{MMA} with a high degree of precision. Making the physically reasonable assumption that reactivity ratios are commutative (i.e. $k_A/k_C = k_A/k_B \times k_B/k_C$), k_S/k_{MMA} can be estimated to be approximately 0.003 [27]. This figure should be compared with the value of 0.03 found by Polton et al. [29] for the relative reactivity of the poly(styrene) radical in the presence of EASC at a concentration comparable to that of the monomers. Two possible explanations for this discrepancy can be immediately formulated.

(a) A penultimate unit effect, where the presence of a penultimate acceptor monomer unit, whether complexed with EASC or not, reduces the selectivity of the growing radical. Previous work has suggested that such an effect may be operating to reduce the selectivity of the poly(styrene) radical in the alternating copolymerisation of styrene and maleic anhydride [51]. Thus, an initiating donor radical (with no penultimate group) will always be more selective than a polymer donor radical with a penultimate acceptor unit.

(b) Incorporation of a large proportion of the styrene available as EASC–MMA–S complex at higher concentrations of EASC. Previous work of Ghesquiere et al. [52] strongly suggests that addition of donor–acceptor complexes to a radical centre will be favoured only if a large gain in stability can be achieved in going to the product radical. It is unlikely that this would be the case in addition of EASC–MMA–S to R_S. Addition of ternary complex to any appreciable extent to the R_S radical in the copolymerisation of styrene and MMA at the concentrations of EASC and monomers used was previously ruled out by the observation that significant amounts of R_S MMA MMA end groups were observed, with an R_S MMA MMA/R_S MMAS ratio identical to that observed for the poly(MMA) radical in these systems, while no R_S S end groups were seen even at feed ratios highly enriched in styrene [27] (i.e. addition to R_S is much more selective than apparent addition to the R_S MMA radical). Therefore, it appears that the rate of addition to the ternary complex would be slow and it is more probable that a penultimate unit effect is responsible for the lower selectivity of the poly(styrene) radical.

The absolute value for the rate coefficient of addition to the R_S radical (k_{EASC}) will be considered, first assuming the absence of ternary complex. The overall rate constant for addition of MMA to R_S in the presence of

EASC may be estimated as $k_{p1}/(k_S/k_{MMA})$, where k_{p1} is the rate constant for the addition of the R_S radical to styrene homopolymerisation. There is a great deal of uncertainty in this value [61], though theoretical considerations suggest that it should be approximately four times the long-chain propagation rate coefficient [62] (i.e. 400 $dm^3\,mol^{-1}\,s^{-1}$ at 30°C [53]). This suggests a value of greater than 3×10^4 $dm^3\,mol^{-1}\,s^{-1}$ for the rate constant of addition of MMA to R_S. However, it must be remembered that this value incorporates the rate of addition of both complexed and uncomplexed MMA, and a more reasonable estimate of k_{EASC} can be made by assuming the relation:

$$k_S/k_{MMA} = k_S/(k_{EASC}[\text{MMA–EASC}]/[\text{MMA}_{total}] + k_{MMA}[\text{MMA}]/[\text{MMA}_{total}]) \qquad (4)$$

Assuming all EASC is incorporated into MMA–EASC complex and taking typical values of $[\text{MMA}_{total}]$ and $k_{MMA} = 2800$ $dm^3\,mol^{-1}\,s^{-1}$ (k_{p1} in MMA homopolymerisation divided by the S/MMA reactivity ratio [53,54]), this expression gives $k_{EASC} \sim 3 \times 10^5$ $dm^3\,mol^{-1}\,s^{-1}$ based on the B results and $\sim 5 \times 10^5$ $dm^3\,mol^{-1}\,s^{-1}$ based on the IP results. Assuming k_{p1} is approximately $4k_p$ [62], this gives a k_p of the order 1×10^5 $dm^3\,mol^{-1}\,s^{-1}$ for the addition of EASC–MMA to the poly(styrene) radical. This value is not physically unreasonable, comparable to values recently obtained in the pulsed-initiation polymerisation of acrylic acid [63], but is an extremely high rate constant for a propagation reaction.

4.2. The 1-methyl-1-methoxycarbonyl(ethyl) radical

In the presence of 0.036 M EASC, the reactivity ratios for addition of dienes (and S) to R_{MMA} were found to be in good agreement with reactivity ratios for the poly(MMA) radical determined from copolymer composition. These values are tabulated in Table 2. In all cases, the correlation between the selectivity of the monomeric and polymeric radicals is strong.

In toluene, it has been demonstrated that the complex between MMA and EASC is monomeric, involving four-coordinate aluminium from the diethyl end of the EASC [29]; this is consistent with results showing identical reactivity of the R_S radical toward MMA–EASC and MMA–diethylaluminium chloride [27]. It is therefore suggested that the structure of the R_{MMA}–EASC complex is a complex of the R_{MMA} radical with a monomeric diethylaluminium chloride.

From the reactivity ratios obtained for R_{MMA} and for the poly(MMA) radical, it is possible to obtain estimates for Q and e in the complexed system. In order for these values to have any physical significance, it is necessary to assume that the R_{MMA}–EASC complexed radical and MMA–EASC complex are overwhelmingly dominant in reaction with styrene and the poly(styrene) radical, respectively, despite the low overall concentration of EASC. The Q–e values were estimated by mapping the sum of the square of the difference between the calculated and experimental reactivity ratios to a coarse grid and testing the response of this map to removal of each monomer in turn. Table 2, indicates the reactivity ratios obtained and Q–e values estimated (a) by optimising for best fit to the values obtained at the same [EASC] for experimental reactivity ratios from the well characterised S/MMA/EASC system; (b) by optimising for best fit to the full set of diene data.

It is reasonable to assume that these values have real significance for the complexed poly(MMA)–EASC radical, since almost no addition to uncomplexed poly(MMA) radicals is expected to occur in this system [55]. The participation of a ternary complex is likely to be low at the small EASC concentrations employed, and the similarity between the reactivity ratios found for R_{MMA} and the poly(MMA) radical suggests that penultimate unit effects are of little importance. From the data presented in Table 2, it appears evident that the e value for MMA–EASC is in the range 2.0–2.1 and that the Q value lies between 20 and 30. This e value is quite high and is comparable to that of monomers that spontaneously form alternating polymers with styrene in the absence of a catalyst (e.g. diethyl fumarate, fumaronitrile, maleimide [56]). The Q value is very much higher than any normal monomer (cf. vinylidene cyanide, $Q = 14$ [56]), indicating that its overall tendency to propagate is extremely high, and that this factor is largely responsible for bringing about the high degree of alternation observed. The data set used to obtain this very high Q value is extremely small, but the consistency is such that it may well be physically significant. Q and e values have been reported for MMA–$ZnCl_2$ in copolymerisation with styrene ($Q = 13.5$, $e = 1.74$) and with vinyl dichloride ($Q = 26.3$, $e = 4.2$) [57] lying in this extreme range.

The empirical relation found by Davis et al. suggests that E_Y for addition of CH_3 to the MMA–EASC complex should be in the range –184 to –187 kJ mol^{-1} [42]; this would obviously be amenable to testing by computational chemical methods.

The disappearance of the R_{MMA} 1,2-DPB signal in the presence of EASC may be explained by a relatively modest difference in the electron donating capacity of DPB in the conformations that lead to 1,2 and 1,4 addition. When no EASC is present, $r_{1,2} = Q_1/Q_2 e^{-e_1(e_1-e_2)}$ and $r_{1,4} = Q_1/Q_4 e^{-e_1(e_1-e_4)}$ and the 1,2:1,4 ratio is given by $Q_4/Q_2 e^{-e_1(e_1-e_2)+e_1(e_1-e_4)}$, where Q_2 and e_2 are the Q–e values for 1,2 addition of the diene, Q_4 and e_4 are the Q–e values for 1,4 addition, and Q_1 and e_2 are the Q–e values for uncomplexed MMA. In the presence of EASC, the 1,2:1,4 ratio will change to $Q_4/Q_2 e^{-e_c(e_c-e_2)+e_c(e_c-e_4)}$, where e_c is the e value for complexed MMA. A 5- to 10-fold decrease in 1,2 addition can be obtained by postulating $e_2 \sim -1.7$ to -2.0, reasonable values for a 1-allyl-1-phenyl substituted radical species, (cf. $e_4 \sim -0.7$ from this work).

4.3. The 1-cyano-1-methylethyl radical

In comparison to the marked enhancement in reactivity seen by R_{MMA} towards donor monomers and by R_{MAn} towards styrene, no significant enhancement in reactivity of R_{MAn} towards the diene species was observed in the presence of 0.036 M EASC. The reactivity ratios k_{MMA}/k_{Donor} determined are shown in Table 3.

The complexed R_{MAn} radical is much less reactive towards the dienes than towards the vinyl monomer styrene, although the Q and e values of styrene falls within the range covered by the diene species used. This makes it impossible to make any estimate of the Q and e values of the complexed R_{MAn} radical and strongly suggests that a peculiarity of styrene is responsible for the high reactivity of the R_{MAn}–EASC complex toward that species. This effect may be explicable in terms of the geometry of the complexed radical species; in toluene solution, it is likely that the complex of R_{MAn} and EASC will be monomeric, involving only half of the EASC. As a planar configuration of the radical centre is expected, the nitrile of R_{MAn} will hold the aluminium centre in the plane of the orbital where the unpaired electron is localised, giving the possibility of steric or electronic interactions with substituents of the double bond in the transition state of the propagation reaction. The phenyl ring of styrene may then be able to participate in π orbital donation back to aluminium, providing additional stability in the transition state; this possibility is absent in the case of addition to butadiene, dimethylbutadiene, and IP, as the monomer will be physically unable to approach the aluminium centre while in a position to interact with the radical centre; the increased bulk of diphenylbutadiene may work against any π donation from its phenyl substituents to the aluminium centre. At the moment this is purely a hypothesis based on the estimate distances between the radical and aluminium centres, although ab initio self-consistent field calculations are planned in order to put it on a firmer basis.

Table 3
Reactivity ratios for R_{MAn} obtained in the presence and absence of EASC

	Without EASC	0.036 M EASC
S	0.56	0.10 ± 0.01
B	0.16 ± 0.01	~0.25
DMB	0.30 ± 0.04	0.32 ± 0.13
IP	0.16 ± 0.01	0.09 ± 0.03
DPB	0.71	0.50 ± 0.06

Little information appears to be available on the alternating polymerisation of methacrylonitrile with dienes in the presence of organoaluminium catalysts [58], so the acquisition of copolymer composition data comparable to that obtained for MMA in this work would be advisable.

5. Conclusions

Reactivity ratios have been determined for the R_{MAn}, R_{MMA} and R_S radicals for addition to MMA and a series of dienes in the presence of 0.036 M EASC (Table 4).

From the reactivity ratios determined towards the R_S radical, $k_S/k_{MMA\text{–}EASC}$ was determined to be 0.003–0.004 at [EASC] = 0.036. This result is in good agreement with the composition of poly(S–co–MMA) prepared under these conditions and is consistent with the results of end-group studies on the S–MMA–EASC system [27]. The k_p for the first addition step in this reaction was estimated to be $4 \pm 1 \times 10^5$ dm^3 mol^{-1} s^{-1}, suggesting a k_p of approximately 1×10^5 dm^3 mol^{-1} s^{-1} for the addition of MMA–EASC to the poly(styrene) radical.

R_{MMA} radical showed a strongly modified reactivity, with much more selective addition to the diene monomers. A similar strong modification of the poly(MMA) radical was evident from the composition of the copolymers obtained. Q and e values were calculated for the 'MMA–EASC' monomer giving results broadly in accordance with previously measured values in other polymerisation systems involving relatively weak Lewis acids [59]. The e value obtained for MMA–EASC, 2.0, is large, but well below reported values for many monomers that spontaneously form alternating copolymers with donor monomers [56]. The Q value found of 20–30, however, is well above that of any common uncomplexed monomer [56], suggesting that complexation of the acceptor species vastly increases the possibility for delocalisation of the unpaired electron density in the radical, and hence the reactivity of the monomer. Application of the empirical correlation found by Davis et al. [42] suggests that E_Y for the addition of a methyl radical to the EASC–MMA complex is of the order -185 kJ mol^{-1}; ab initio calculations are planned to test this prediction.

The selectivity of the 2-cyanopropyl radical was not greatly modified by the presence of EASC in any of the

Table 4
Reactivity ratios, k_{diene}/k_{MMA}, obtained in the presence of 0.036 M EASC

	DPB	BD	DMB	IP
R_{MAn}	2.0 ± 0.2	4.1 ± 0.5	2.1 ± 0.3	10.7 ± 0.7
R_{MMA}	3.2 ± 0.2	~20	7.4 ± 0.9	20 ± 3
R_S	Large	120 ± 30	Large	100 ± 20

systems, in contrast to results obtained in copolymerisations with styrene. Ab initio quantum calculations are planned in order to relate this observation to the conformations of the complexed R_{MMA} and R_{MAn} radicals and the possible interactions of these radicals with the phenyl substituent of styrene.

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