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End-functionalised copolymers prepared by the addition–fragmentation chain transfer method

Styrene/methyl methacrylate system

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Abstract

Co-oligomers and copolymers of styrene and methyl methacrylate have been prepared by free radical polymerisation in the presence of the chain transfer agent ethyl-α-(*t*-butanethiomethyl)acrylate. Chain transfer constants are not significantly influenced by the co-monomer composition and lie in the range 0.47–0.90. Bulk copolymer composition is independent of the amount of chain transfer agent in the higher MW range ($>$ 20 000). In contrast, the styrene content of lower MW oligomers extracted by fractional precipitation decreases with decreasing MW below about 1000. The efficiency of the addition–fragmentation mechanism in producing specifically end-functionalised co-oligomers (MW $<$ 5000) was investigated by ^{1}H n.m.r. spectroscopy. Spectral peaks are mostly consistent with the expected end groups for all co-monomer feed systems. Quantitative consistency of end group concentrations is also good for co-oligomers with MW $>$ 1500. At lower MWs, there is an increasing deficiency in olefinic end groups and a high ester group concentration relative to that expected from the MW. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: End functionality; Chain transfer; Addition fragmentation

1. Introduction

There is widespread current interest in functional oligomers for use in reactive processing. They can be synthesised by many methods ranging from the more established methods of condensation, ionic and free radical, to the more recently developed methods of phase transfer catalysis, group transfer and ring-opening polymerisation and 'constructive degradation' of high-molecular weight polymers. Of these, condensation methods and, to a lesser extent, ionic methods have led to industrial application. Free radical polymerisation in which functionalisation is achieved by the use of efficient chain transfer agent or functional initiators is probably the most versatile method, in that it provides a method for a wide range of monomers or mixed monomers for property variations. The potential for the use of free radical methods has been greatly enhanced by the recent discovery of several types of chain transfer agents which operate with a high degree of efficiency by an addition–fragmentation mechanism [1–12]. For example, allylic sulfides produce a high degree of functionality by the mechanism shown in Scheme 1.

End group functionality can be designed by varying the groups R and R′. A wide range of other types of chain transfer agent which undergo similar addition–fragmentation mechanisms are now known including allylic bromides, sulfones, peroxides and phosphonates, vinyl ethers, ketene acetals and thiono and hydroxamic esters.

In this paper we describe a detailed investigation of the copolymerisation of styrene and methyl methacrylate (MMA) in the presence of the allylic sulfide, ethyl-α-(*t*-butanethiomethyl)acrylate (EBTMA, where in Scheme 1, R is $C(CH_3)_3$ and R′ is Et). In particular, chain transfer constants and the nature and concentration of end groups of the resultant copolymers for a range of co-monomer mixtures have been the focus of attention. This is the first reported investigation of functionalised copolymers produced by the addition–fragmentation chain transfer method.

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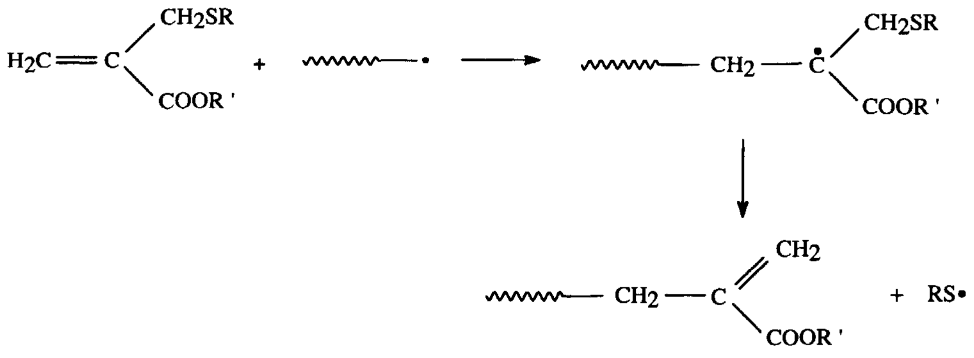


Scheme 1.

In previous work EBTMA has been observed to act as an efficient chain transfer agent with both styrene and methyl methacrylate in single monomer systems [1,12].

2. Experimental

2.1. Materials

AIBN initiator was recrystallised twice from ethanol and stored in a refrigerator. Monomers styrene and methyl methacrylate were distilled twice under nitrogen at low pressure and stored over calcium hydride at low temperature (< 0°C). Chain transfer agent EBTMA was synthesised from diethyl malonate in four steps [13–15].

2.2. Polymerisation procedure

Typically 20 mg AIBN, 5 ml of monomer or monomer mixture, and the required amount of EBTMA, were placed in an ampoule, degassed by three freeze–evacuate–thaw cycles at $< 10^{-3}$ mmHg, the ampoule sealed and placed in a 60°C thermostat bath. Trial experiments with a dilatomer were carried out to determine appropriate times required for conversions in the range 5–15%. Polymer was precipitated in methanol and purified by three reprecipitations before drying in a vacuum oven at 40°C.

For polymerisations with high chain transfer agent concentration (0.424 M) the low-MW methanol-soluble fractions were collected by applying high vacuum at ambient temperature to remove excess monomers. The dried oligomers were redissolved in methanol and the drying process repeated until proton n.m.r. indicated the absence of EBTMA. The methanol-soluble oligomers were then further fractionated by redissolving and allowing the solvent to evaporate at ambient temperature for 24 h. The precipitated oligomer was collected and dried in the vacuum oven. The remaining solution was allowed to stand for a further 24 h and the next fraction was collected. Up to six fractions were collected in this way.

2.3. Characterisation

MWs were measured by g.p.c. with a Millipore-Waters instrument model 501 using ultrastyragel linear columns, differential refractomer as detector and THF as solvent. Narrow MWD polystyrene standards were used for calibration and the data analysis was by the Simopr program compiled by R.W. Garrett. Errors in $\bar{M}_N$ are estimated to be ± 8%.

MWs of oligomers (MW < 5000) were determined by vapour pressure osmometry (VPO) with a Hitachi–Perkin-Elmer Molecular Weight Apparatus Model 115. Chloroform was solvent and benzil was calibrant. A check on the credibility of benzil calibration for polymers was made by measuring $\bar{M}_N$ for some polystyrene g.p.c. standards. VPO gives reasonable results for MWs in the low thousands but way out results for a MW of 10 000 (i.e., values measured by VPO: 714, 1923, 5326; cf. actual values: 760, 2100, 10 300, respectively)

Copolymer composition and end group analysis were determined by ^{1}H n.m.r. spectroscopy with Varian Gemini-200 or Unity-400 instruments. The solvent was $CDCl_3$. Group assignment was aided by 2-D COSY proton correlation and HMQC ^{1}H ^{13}C correlation experiments. An inverse gated decoupling ^{13}C n.m.r. experiment was also used for one sample to confirm quantitative data from a ^{1}H n.m.r. experiment.

3. Results and discussion

3.1. Chain transfer constants

Polymerisations of single and mixed styrene and MMA monomers were carried out with varying amounts of EBTMA under identical conditions of initiator concentration and temperature (60°C). The yields were generally low (mostly < 10%) and the MWs of polymers and copolymers, insoluble in methanol and measured by g.p.c., decrease consistently with increased concentration of chain transfer agent EBTMA in the polymerisation mixture (see Table 1).

Table 1
Molecular weights of polymers and copolymers of styrene and methyl methacrylate prepared in the presence of EBTMA

Monomer feed STY/ MMA (mol.%)	EBTMA (mol/l)	Polymerisation time (h)	% yield	M_n^a (g.p.c.)	M_w/M_n
0/100	0.000	1	14.7	432 300	2.0
	0.012	1	10.1	77 800	1.6
	0.024	1	8.8	52 500	1.5
	0.048	1	8.6	35 900	1.6
19/81	0.000	2	6.7	129 600	1.4
	0.016	2	6.2	60 500	1.4
	0.032	2	5.3	44 100	1.5
	0.064	2	5.7	24 700	1.9
48/52	0.000	2	7.1	126 400	1.3
	0.016	2	8.9	52 600	1.6
	0.032	2	9.0	48 300	1.4
	0.064	2	8.1	32 200	1.6
79/21	0.000	2	5.6	100 200	1.3
	0.016	2	6.1	50 400	1.5
	0.032	2	5.9	28 500	1.8
	0.064	2	5.8	19 100	1.8
100/0	0.000	3	7.3	144 400	1.4
	0.010	3	7.1	52 600	1.9
	0.024	3	6.9	28 200	1.9
	0.042	3	6.6	20 800	2.05

[a] MWs are polystyrene equivalent

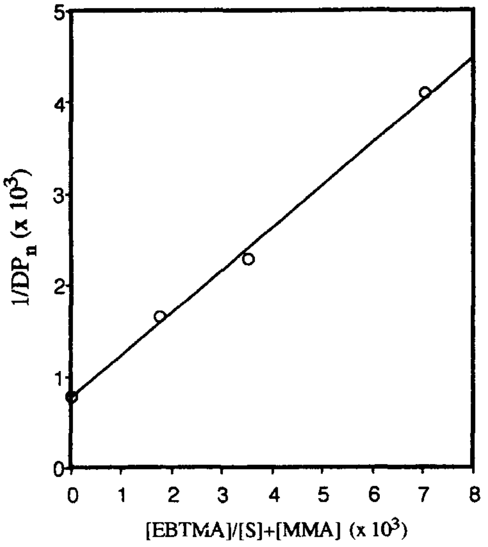


Fig. 1. Typical Mayo plot for copolymers made with feed composition 19% S, 81% MMA.

Table 2
Chain transfer constants determined by the Mayo method compared with those calculated from the Tsuchida equation [17]

Monomer feed styrene/MMA (mol %)	C_x	
	Mayo (corr. coeff.)	Tsuchida
0/100	0.53 ± 0.14 (0.984)	—
19/81	0.48 ± 0.08 (0.998)	0.46
48/52	0.47 ± 0.06 (0.979)	0.47
79/21	0.60 ± 0.04 (0.994)	0.62
100/0	0.90 ± 0.05 (0.993)	—

The fact that the yields of any one series of polymers or copolymers after a fixed polymerisation time were not suppressed appreciably by the presence of EBTMA indicates the efficiency of the fragmentation/re-initiation process in the chain transfer process. The relative narrowness of the MW distributions (< 2.2) is also consistent with efficient re-initiation.

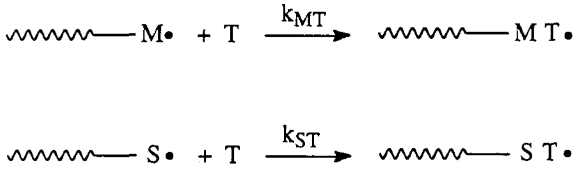
Chain transfer constants, C_x, were determined by Mayo plots of data for each polymer or copolymer, for which the MW was measured in a comparable manner, over the chain transfer agent concentration range: [EBTMA] = 0–0.064 M. For copolymers, the number average degree of polymerisation was obtained by dividing the observed MW by the weighted average molecular weight of monomer, M_F:

$$M_F = 104x_S + 100(1 - x_S) \tag{1}$$

where x_S is the mole fraction of styrene in the copolymer (determined by n.m.r., see later). A typical Mayo plot is shown in Fig. 1 and C_x values are given in Table 2.

The C_x values obtained for pure styrene (0.90) and pure MMA (0.53) are in reasonable agreement with the results obtained by Rizzardo and co-workers [1,12], i.e. 0.95 and 0.74, respectively. The propagation rate constants for styrene and MMA at 60°C are 279 and 759 l mol^{-1} s^{-1}, respectively[16], thus the values of k_{ST} and k_{MT} (251 and 402 l mol^{-1} s^{-1}, respectively) indicate that EBTMA reacts 1.8

times slower with styrene-propagating radicals than with MMA-propagating radicals.



The Mayo equation is not strictly appropriate for application to copolymers, since its use infers the assumption $k_{ST} = k_{MT}$.

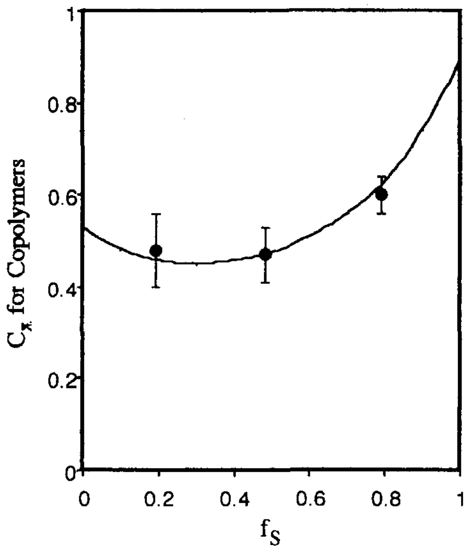


Fig. 2. Chain transfer constants for copolymers as a function of feed composition. Full line, Tsuchida equation; points, experimental.

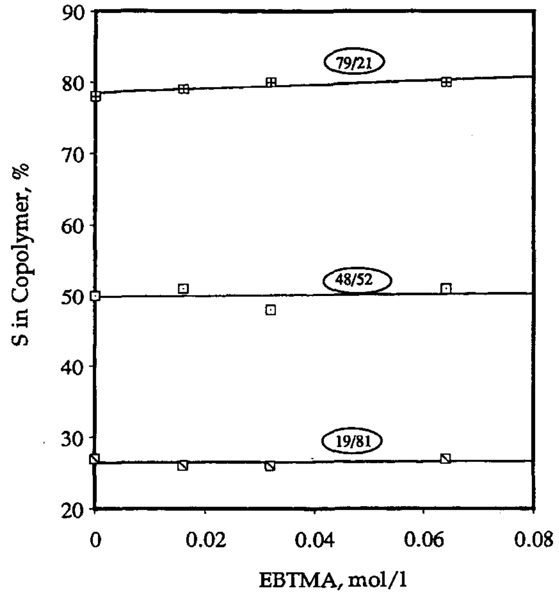


Fig. 3. Composition of copolymers prepared from constant feed mixes as a function of EBTMA concentration. Mol.% feed ratio, S/MMA, recorded on each line. S = styrene.

Tsuchida et al. derived an equation relating the C_x value for copolymers based on the Mayo equation, with the C_x values for the separate homopolymers, the feed composition and the reactivity ratios for the copolymer system [17]. The analysis is based on the terminal model of copolymerisation. The equation is:

$$C_x(\mathrm{S,M}) = \frac{C_x(\mathrm{S}) r_\mathrm{S} f_\mathrm{S} + C_x(\mathrm{M}) r_\mathrm{M} f_\mathrm{M}}{r_\mathrm{S} f_\mathrm{S}^2 + 2 f_\mathrm{S} f_\mathrm{M} + r_\mathrm{M} f_\mathrm{M}^2} \qquad (2)$$

where f_S and f_M are the mole fractions of styrene and methyl methacrylate, respectively, in the feed. The variation of C_x(S,M) for the copolymers with feed composition, using Eq. (2) and reactivity ratios [18], $r_S = 0.52$, $r_M = 0.46$, is shown along with the experimental points in Fig. 2. The results are in reasonable agreement.

3.2. Copolymer composition

The styrene content of the copolymers, determined from the proton n.m.r. spectra by comparing the integral for the phenyl ring protons at 7 ppm to that for the methoxyl protons at 2.7–3.8 ppm, is shown as a function of EBTMA concentration in the feed (decreasing MW) in Fig. 3. The copolymer composition is independent of the amount of chain transfer agent used for this MW range (> 20 000).

In contrast, the styrene content of low-MW oligomers extracted by fractional precipitation from samples made at high EBTMA concentration (0.424 M), for MWs see Table 3, decreases markedly at low MW, see Fig. 4. There may be two contributing factors. The drift may be due to a preference of the initiating thiyl radicals for reaction with MMA rather than styrene. With only a few monomer units in the polymer chains, such a preference in a single step would influence the composition. The preference for reaction with MMA by thiyl radicals has also been observed by Heiland et al. [19]. The drift may also be caused by the relative sorption of monomers in the growing polymer chains being MW dependent, resulting in decreased styrene content in the lower MW copolymers. This was the explanation presented for similar composition variations in low-MW copolymers found in styrene/MMA and other copolymer systems [20].

3.3. End group identification

Polymerisations of single and mixed styrene and MMA were carried out with a large amount (0.424 M) of EBTMA in order to obtain low-MW samples for end group determination by n.m.r. Except for polystyrene, all resultant polymers were fractionally precipitated using methanol as solvent to allow separation of oligomers of different MW ranges. M_N values measured by vapour pressure osmometry are recorded in Table 3. The pure polystyrene product was investigated without fractionation.

The proton n.m.r. spectra of the styrene oligomer (MW 2780), a methyl methacrylate oligomer (MW 1150) and a typical co-oligomer (feed styrene:MMA (79:21), MW 930)

Table 3
End groups of oligomers and co-oligomers of styrene and methyl methacrylate determined by n.m.r.

Monomer feed[a] styrene/MMA (mol.%)	% yield[b] (time/h)	MW[c] (g/mol)	End group concentration (groups/10^3 monomer units)						End group ratio	
			Total[e] end groups	a_S	a_M	a_M'	b	d	a/b	a/d
0/100	8.8 (1.5)	4580	44		12		13	14	0.92	0.86
		3130	64		20		20	18	1.0	1.11
		2370	84		32	1	34	35	0.97	0.94
		1150[d]	211		79	29	129	114	0.84	0.95
					81	28	142	113	0.73	0.92
19/81	7.2 (3.0)	3950	51	10	13		22	24	1.05	0.97
		3470	58	14	16		31	30	0.97	0.94
		2150	94	20	23		53	53	0.81	0.81
		1350	176	28	50	1	117	87	0.68	0.91
		930	277	37	75	12	335	192	0.37	0.64
		510	658	36	129	36	379	270	0.53	0.74
48/52	8.5 (3.0)	2770	74	25	6		35	34	0.89	0.92
		2220	92	27	14		42	42	0.98	0.98
		1660	123	50	22	4	79	81	0.96	0.94
		780	353	66	32	30	293	237	0.44	0.55
		590	526	56	82	163	762	674	0.40	0.45
79/21	7.4 (3.0)	2600	79	25			31	60	0.81	0.42
		2100	98	44	4		50	36	0.96	1.33
		930	282	95	14	3	236	188	0.47	0.59
		650	460	114	15	23	617	367	0.25	0.41
100/0	5.1 (3.0)	2780	75	21			47	46	0.45	0.46

[a] Polymers prepared in the presence of 0.424 M EBTMA, [initiator] = 0.025 M
[b] Total yield before fractionation
[c] MWs determined by VPO
[d] MW by g.p.c. = 1400
[e] Values based on MW and copolymer composition

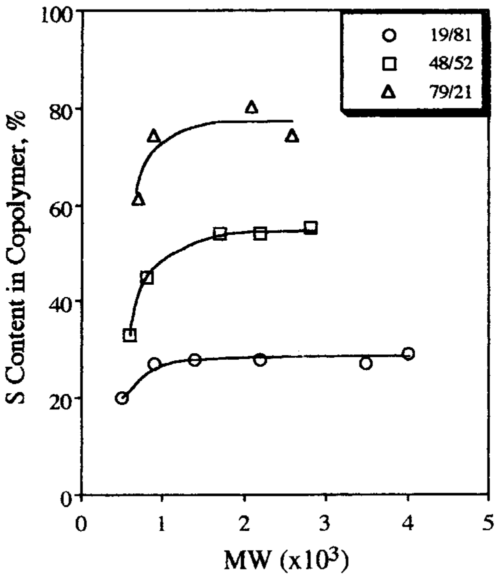
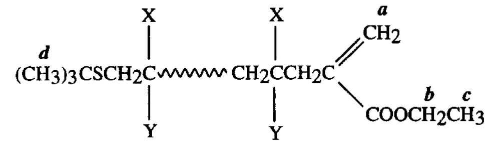


Fig. 4. Composition of co-oligomer fractions as a function of their MW. Caption is mol.% feed ratio, S/MMA. S = styrene.

are shown in Fig. 5. Signals due to end groups of the expected oligomer structure (Structure I) based on the addition–fragmentation chain transfer mechanism (Scheme 1) can be assigned as follows. Olefinic protons, *a*, are most useful as the chemical shift is sensitive to the nature of the adjacent monomer unit. With styrene as the adjacent monomer, the signals appear at 5.17 and 5.96 ppm, and with MMA they appear at 5.37 and 6.16 ppm.



$$(CH_3)_3CSCH_2C(X)(Y)\sim\sim\sim CH_2C(X)(Y)CH_2C(=CH_2)COOCH_2CH_3$$

Structure I

where for methyl methacrylate, X = CH_3, Y = $COOCH_3$, and for styrene, X = H, Y = C_6H_5.

Correlations were confirmed with 2D-COSY experiments. The signals due to the methylene protons of the ester moiety of EBTMA, *b*, were insensitive to the nearby monomer unit but were well separated from other signals.

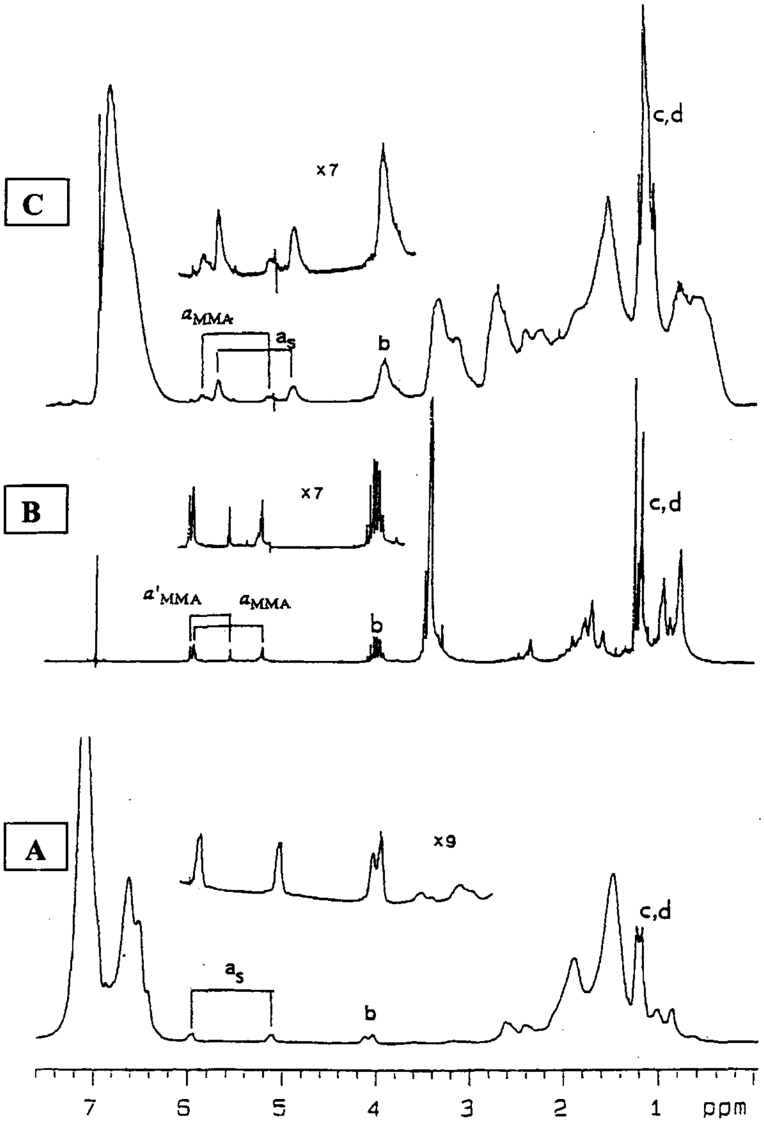
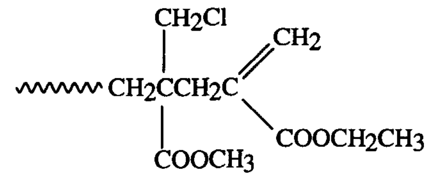


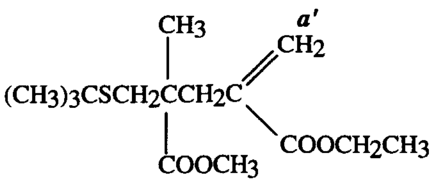
Fig. 5. ^{1}H n.m.r. spectra of (A) polystyrene, MW 2780, (B) polymethyl methacrylate, MW 1150 and (C) S/MMA copolymer fraction, MW 930 prepared with EBTMA, concentration 0.424 M.

They occur at 4.2 ppm. Signals due to methyl protons *c* and *d* occur at 1.2–1.4 ppm. This assignment was confirmed by a HMQC experiment which resolved the signals into two distinct peaks with ^{13}C resonances at 13 and 31 ppm. These assignments are consistent with those of Meijs et al. [3] for a polymethyl methacrylate sample polymerised in the presence of EBTMA.

Signals due to olefinic peaks at 5.79 and 6.24 ppm were also observed in very low-MW polymers and copolymers of MW $<$ 1000. These chemical shifts are very close to those for end groups of polymethyl 2-(chloromethyl) acrylate (Structure II) assigned by Yamada et al. [5] (5.74 and 6.27 ppm). Since the effect of a Cl atom attached to the C atom γ to the olefin unit is expected to be similar to that of a sulfur moiety, we have assigned these signals to the olefinic protons of Structure III, a'_M.

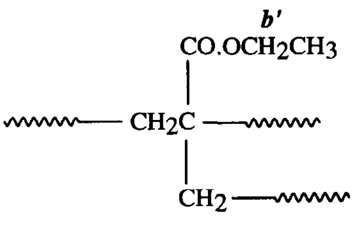


Structure II



Structure III

In the proton spectrum of polystyrene, weak broad signals at about 3.1 and 3.7 ppm were found to correlate with a ^{13}C chemical shift of 60 ppm by a HMQC experiment. This suggests that the signals are due to the methylene group of the ester moiety from EBTMA, b', connected to a saturated nearby group, Structure IV.



Structure IV

This may arise from the occasional copolymerisation of EBTMA terminated oligomer into growing polymer. Corresponding signals could not be observed in polymers or copolymers of MMA due to the presence of other strong signals in this spectral region.

3.4. End group distribution

The amount of each chain transfer-derived moiety was calculated from peak areas of the ^{1}H n.m.r. spectra. A check on the accuracy was made by running an inverse gated decoupling ^{13}C experiment on one PMMA sample (MW = 1150). The results from the two experiments are in close agreement. A quantitative summary of the endgroups is given in Table 3. Endgroup d was obtained by subtracting the integral of c, equal to $3/2b$, from the total integral of the signal at 1.2–1.4 ppm. If the chain transfer addition/fragmentation mechanism operates efficiently, then integrals total a should be equal to b and also to d. The ratios a/b and a/d are generally fairly close to unity for copolymers and polymethylmethacrylate with MW > 1500 (see Table 3) indicating an efficient mechanism. The ratios fall off for lower polymers indicating loss of olefinic groups. Also, with polystyrene (a single unfractionated sample) there is a significant shortage of olefinic protons to satisfy an efficient mechanism. This sample, of course, contains the low MW fraction, and end groups from the low MW fraction will dominate the count. It is possible that some of the olefinic groups may be lost by copolymerisation as indicated by the observed weak signals due to ester methylene groups in a saturated environment in the polystyrene sample (see above). If this is so it is not clear why the imbalance should only occur in the low MW oligomers.

Another anomaly for low-MW oligomers is the apparently high concentration of ester end groups in comparison with the total end group concentration based on the measured MW. The observation of the specific compound (III) in low-MW oligomers and copolymers containing MMA has already been mentioned, the amounts are given in Table 3. Clearly the chemistry associated with the formation of the very low-MW oligomers differs in some respects from that of the higher oligomers, for which the end group types and concentration are consistent with the expected mechanism. Further investigation of the low-MW oligomers is required.

Table 4
Values of $(a_S[M])/(a_M[S])$ calculated from the ratio of olefinic end groups adjacent to styrene and MMA units determined by n.m.r. analysis

Monomer feed styrene/ MMA (mol %)	MW	$(a_S[M])/(a_M[S])$
19/81	3950	3.3
	3470	3.8
	2150	3.7
	1350	2.4
	930	2.1
48/52	2770	4.6
	2220	2.1
	1660	2.5
	780	2.3
79/21	2600	—
	2100	2.9
	930	1.8

The chain transfer agent EBTMA has a choice of reaction with styrene or MMA terminal free radicals. A comparison of a_S with a_M for all three copolymers shows there is a clear preponderance of olefinic groups attached to styrene over those attached to MMA in relation to the monomer feed ratio. Assuming the normal conditions for applying kinetics to free radical polymerisation, the ratios of the yields of these two end groups is given by:

$$\frac{a_S}{a_M}=\frac{R_{ST}}{R_{MT}}=\frac{k_{ST}[\sim\sim S\cdot]}{k_{MT}[\sim\sim M\cdot]}=\frac{k_{ST}k_{MS}[S]}{k_{MT}k_{SM}[M]}=\frac{r_S C_S[S]}{r_M C_M[M]} \qquad (3)$$

where R is the rate of production of terminal olefinic groups. Thus, values of $(a_S[M])/(a_M[S])$ should be constant and equal to $(r_S C_S)/(r_M C_M) = 1.9$ from reactivity ratios [18], $r_S = 0.52$, $r_M = 0.46$ and the chain transfer constants derived in this work, $c_S = 0.90$, $c_M = 0.53$. Experimental values of $(a_S[M])/(a_M\,[S])$ from the n.m.r. analysis of copolymers with relatively constant overall composition (see Fig. 4) are shown in Table 4. There is a reasonable degree of consistency but the average value (2.9) is somewhat high compared with the value of $(r_S C_S)/(r_M C_M)$.

4. Conclusions

The chain transfer constants for the copolymerisation of styrene and MMA with EBTMA as chain transfer agent lie in the range 0.47–0.90. The bulk copolymer composition is independent of the amount of chain transfer agent used for copolymers with MW > 2×10^4 and for fractionated co-oligomers with MW in the range $1\text{–}5 \times 10^3$. However, the styrene content decreased significantly in co-oligomers with MW < 10^3. This is possibly due to a combination of the preferential reaction of fragmented thiyl radicals with MMA becoming significant when there are only a few monomer units in the chain and the MW dependence of the relative sorption of monomers in the growing polymer chains.

The nature and concentration of end groups of the co-oligomers in the MW range 1.5–5.0 × 10^3 prepared from all feed ratios with EBTMA as chain transfer agent are in agreement with those expected on the basis of the addition–fragmentation mechanism. At lower MWs, there is an increasing deficiency in olefinic end groups and a high ester group concentration relative to that expected from the MW.

Acknowledgements

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