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End functionalised copolymers prepared by the addition–fragmentation chain transfer method: styrene/methacrylonitrile system

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Abstract

Copolymers of styrene and methacrylonitrile have been prepared by free radical polymerisation in the presence of the chain transfer agent ethyl α-(*t*-butanethiomethyl)acrylate (**1**). Chain transfer constants vary with co-monomer composition, ranging from 0.42 for methacrylonitrile, through a minimum of 0.23 for co-monomers to 0.90 for styrene. Bulk copolymer composition is independent of the amount of chain transfer.

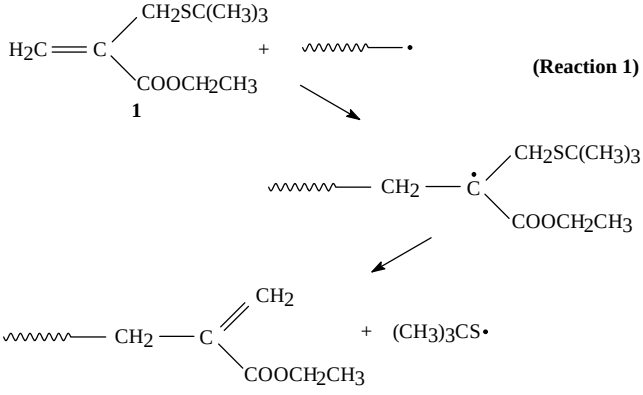
The efficiency of the addition–fragmentation mechanism in producing specifically end-functionalised co-oligomers was investigated by ^{1}H NMR spectroscopy. Spectral peaks are mostly consistent with the expected end groups for all co-monomer feeds. Quantitative measurement of end-group concentrations indicates a consistent deficiency of olefinic end groups of 10–20%.

Keywords: End-functionality; Chain transfer; Addition fragmentation

1. Introduction

The addition–fragmentation chain transfer process has been shown to be a valuable way of utilising free-radical polymerisation for the production of functionalised polymers and oligomers [1]. In this paper, the use of the allylic sulphide, ethyl-α-(*t*-butanethiomethyl)acrylate, structure **1**, as addition–fragmentation chain transfer agent [2,3] (see reaction 1) for the preparation of functionalised polymers of the mixed monomers, styrene (**Sty** in script and subscript **S** in formulae) and methacrylonitrile (**MAN** in script and subscript **N** in formulae) is investigated. These are of interest because of their strong tendency for alternation in the free-radically prepared copolymers (product of reactivity ratios, $r_S r_N = 0.05$ [4]) and because of their potential for property modification in grafted systems.

The main points of focus are the efficiency of the chain transfer agent in controlling the molecular weight (chain transfer constant) and in producing the correct functionality, as determined by NMR spectroscopy. NMR also allows the relative reactivity of the allylic sulphide with the two monomer free-radical end-groups in the growing polymer chain, to be determined.



Previous work on the homo-polymerization of **Sty** has indicated that **1** operates efficiently as a radical addition–fragmentation chain transfer agent with chain transfer constants of 1.0 [2,3]. There has been no previous work with **MAN** in single or co-monomer systems. A paper on the copolymerisation of **Sty** and

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Table 1
Polymerization results of **S** and **MAN** with **1** at 60°C

Monomer feed **S/MAN**	Chain transfer agent **1**			
(mol %)	Concentration (mol/l)	Yield (%)[a]	M_n[d] ($\times 10^3$)	% S in polymer
0/100	0	1.3[b]	12.7	–
	0.016	1.3[b]	11.4	–
	0.032	1.2[b]	10.4	–
	0.064	1.2[b]	8.9	–
	0.424	2.9[c]	4.4[e]	–
7/93	0	9.1	18.7	26
	0.012	8.3	17.2	27
	0.026	9.1	16.8	26
	0.052	9.1	14.5	27
	0.106	9.9	11.4	26
	0.212	7.2	9.4	29
	0.424	3.1	4.7[e]	29
15/85	0	11.1	24.3	39
	0.012	13.5	22.3	38
	0.026	12.9	21.2	38
	0.052	13.0	17.9	38
	0.106	13.3	15.1	38
	0.212	9.7	11.1	38
	0.424	6.7	6.5[e]	39
42/58	0	15.1	36.3	58
	0.012	17.2	32.8	57
	0.026	16.9	28.3	57
	0.052	17.6	23.2	57
	0.106	16.9	18.5	56
	0.212	12.6	13.1	58
	0.424	10.1	6.4[e]	56
74/26	0	20.0	49.4	70
	0.012	18.2	35.8	69
	0.026	20.4	30.1	70
	0.052	19.8	23.1	70
	0.106	20.3	16.2	71
	0.212	13.8	12.0	70
	0.424	10.4	5.4[e]	71
87/13	0	18.1	50.4	78
	0.012	19.3	38.0	78
	0.026	18.1	29.3	77
	0.052	18.6	23.2	78
	0.106	19.7	15.6	77
	0.212	13.6	7.6	82
	0.424	10.2	4.1(i)	82
100/0	0	7.3	144.4	–
	0.010	7.1	52.6	–
	0.024	6.9	28.2	–
	0.042	6.6	20.8	–

[a] Yield after 3 h.
[b] Yield after 2 h.
[c] Yield after 4 h.
[d] M_n values determined by GPC.
[e] These samples fractionated, M_n of fractions (ii) and (iii) determined by VPO, see Table 3.

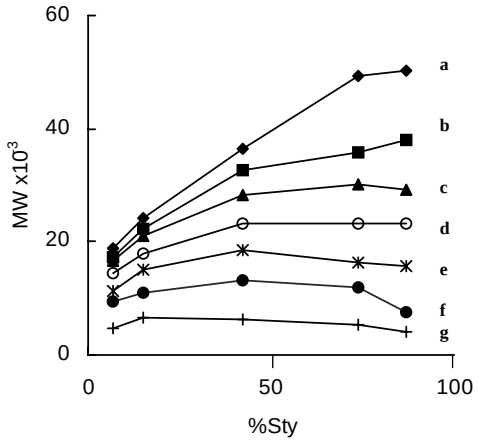


Fig. 1. Number average molecular weights as a function of co-monomer composition for added chain transfer agent **1**, concentration: (a) zero; (b) 0.012 M; (c) 0.026 M; (d) 0.052 M; (e) 0.106 M; (f) 0.212 M; and (g) 0.424 M.

methyl methacrylate in the presence of **1** has recently been published [5].

2. Experimental

2.1. Materials

AIBN initiator was recrystallised twice from ethanol and stored in a refrigerator. Monomers **Sty** and **MAN** were distilled twice under nitrogen at low pressure and stored over calcium hydride at low temperature (<0°C). Chain transfer agent **1** was synthesised by a four step procedure [6] from diethyl malonate or by the reaction of ethyl α-(bromomethyl)acrylate [7,8] with *t*-butanethiol.

2.2. Polymerization procedure

Typically, 20 mg of AIBN, 5 ml of monomer or monomer mixture and the required amount of chain transfer agent were placed in an ampoule, the ampoule was degassed by three freeze–evacuate–thaw cycles at $<10^{-3}$ mm Hg, was 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 concentration of chain transfer agent **1** (0.424 M), the low molecular weight 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 NMR indicated the absence of **1**. 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 a vacuum oven. The remaining solution was allowed to stand for a further 24 h and the next fraction was collected. Up to three fractions were collected in this way.

2.3. Characterisation

Molecular weights were measured by GPC 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 Simopr program compiled by R.W. Garrett. Errors in M_n are estimated to be ±8%.

M_n values of fractionated oligomers ($M_n < 5000$) were determined by vapour pressure osmometry (VPO) with a Hitachi-Perkin–Elmer Molecular Weight Apparatus Model 115. Chloroform was solvent and benzil was calibrant.

Copolymer compositions and end group analyses were determined by ^{1}H NMR spectroscopy with Varian Gemini-200 or Unity-400 instruments. The solvent was $CDCl_3$. Group assignments were aided by 2D COSY proton and heteronuclear multiple quantum coherence (HMQC) ^{1}H–^{13}C correlation experiments. An inverse gated decoupling ^{13}C NMR experiment was also used for one sample.

3. Results and discussion

3.1. Copolymer composition

AIBN initiated polymerisations of single and mixed **Sty** and **MAN** monomers were carried out in the presence of varying amounts of allylic sulphide, **1**. The yields of methanol insoluble polymer/copolymer were generally less than 15%, and none exceeded 21%. Copolymer compositions, determined from ^{1}H NMR spectra by comparing the areas due to phenyl ring protons (~7 ppm) with the area due to the total aliphatic protons of the copolymer, are given in Table 1. The copolymer compositions are only marginally affected by the concentration. Thus, the chain transfer agent has only small or negligible influence on the propagation process involving polymer chain growth.

3.2. Chain transfer constants

M_n values are shown in Table 1. The values consistently decrease with increasing amount of added chain transfer agent within each series of constant co-monomer feed composition. The trend for each copolymer series, at constant concentrations of chain transfer agent, is shown in Fig. 1. Polydispersities were mostly in the expected range for non-reversible [9,10] addition–fragmentation chain transfer polymerisation, i.e. 1.3–2.0. Some low molecular weight copolymers had slightly higher polydispersities and a few copolymers had polydispersities of 1.2. Values lower than 1.5 are probably due to the loss of very low

Table 2
Chain transfer constants determined by the Mayo method and calculated from the Tsuchida equation

Monomer feed **Sty**/**MAN** (mol%)	C_X (**1**)		
	Mayo	Correlation coefficient	Tsuchida
0/100	0.42 ± 0.03	(0.999)	–
7/93	0.31 ± 0.09	(0.986)	0.30
15/85	0.23 ± 0.02	(0.998)	0.26
42/58	0.27 ± 0.01	(0.992)	0.26
74/26	0.35 ± 0.02	(0.991)	0.39
87/13	0.50 ± 0.01	(0.998)	0.53
100/0	0.90 ± 0.05	(0.993)	–

molecular weight material in the methanol precipitation process.

M_n values were converted to number average degrees of polymerisation with the aid of each copolymer composition in order to enable chain transfer constants to be derived from the Mayo equation, see Table 2. The validity of the application of the Mayo equation to copolymers relies on the rate constants of the reaction of the chain transfer agent with each chain-end monomer radical being equal. A more complete analysis of chain transfer with co-monomers, given by Tsuchida [11], links the composite chain transfer constant, $C_X(S,N)$, with copolymerisation reactivity ratios and the chain transfer constants of the pure monomers in Eq. (1), where f_S and f_N are the mole fractions of **Sty** and **MAN** in the feed, respectively, and r_S and r_N are the respective copolymerization reactivity ratios (0.30 and 0.16) [4]. The correlation with experimental values for the

$$C_X(S,N) = \frac{C_x(S)r_S f_S + C_x(N)r_N f_N}{r_S f_S^2 + 2f_S f_N + r_N f_N^2} \quad (1)$$

copolymers prepared in the presence of **1** is shown in Fig. 2.

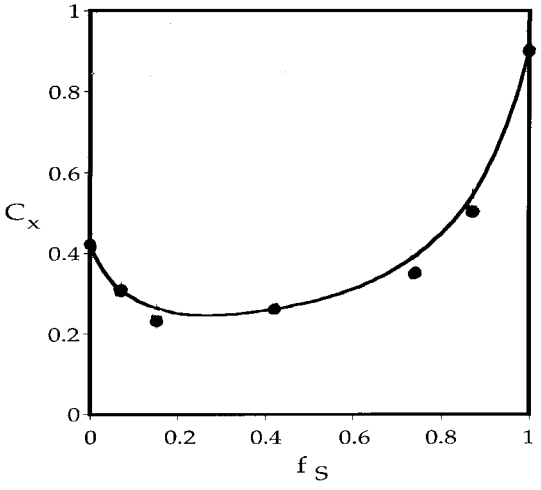


Fig. 2. Chain transfer constants as a function of co-monomer composition, calculated directly from M_ns (solid points) and from the Tsuchida equation (line).

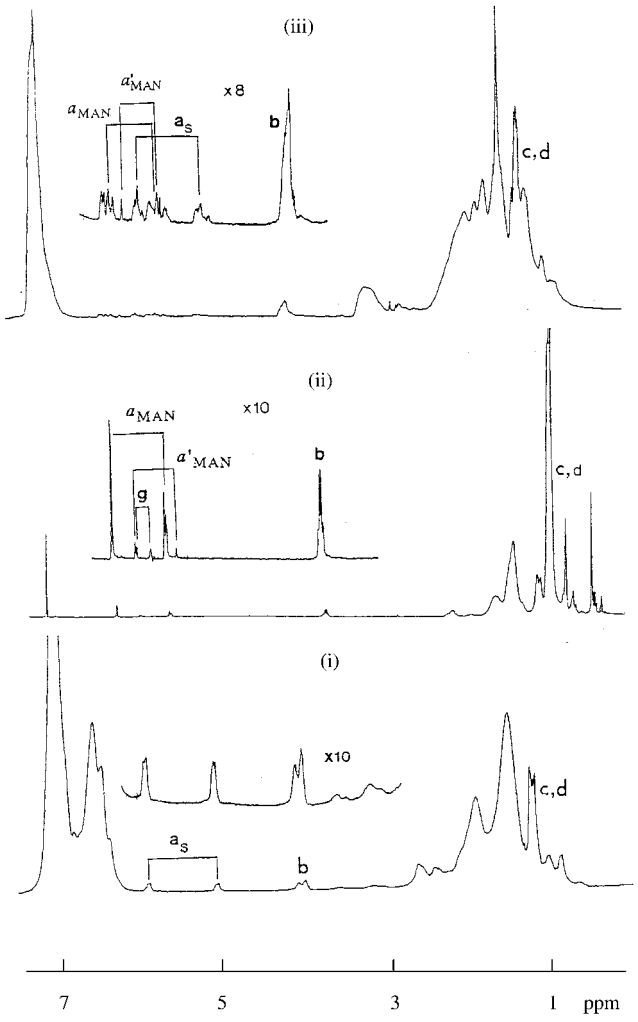
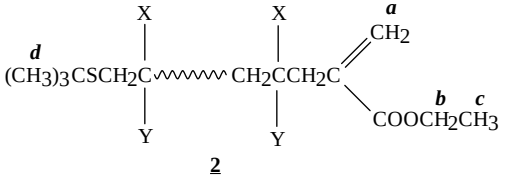


Fig. 3. ^{1}H NMR spectra of: (i) polystyrene, M_n 2800; (ii) polymethacrylonitrile, M_n 4400; (iii) copolymer from feed **Sty**/**MAN** = 15/85, M_n 2500. All made in the presence of 0.424 M chain transfer agent **1**.

3.3. End groups for copolymers prepared with *1*

The ^{1}H NMR spectra of oligomers prepared with relatively high concentrations of the chain transfer agent have been used to obtain quantitative information on oligomer end groups. Typical spectra of poly**Sty** (M_n 2800), poly-**MAN** (M_n 4400), and a copolymer (**Sty**/**MAN** = 15/85 in feed; M_n 2500) are shown in Fig. 3.

Assignments are based on the expected structure **2**.



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Peaks at 5.10–5.24 and 5.92–6.00 ppm in the polySty spectrum confirm the presence of olefinic end groups (**a**)

Table 3
Summary of end groups of **Sty** and **MAN** oligomers prepared with **1** determined from NMR

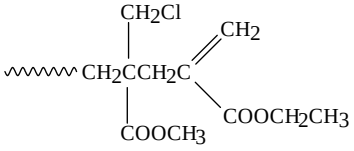
Monomer feed **S/MAN** (mol%)	Concentration of **1** (mol/l)	M_n[a] (kg/mol)	End group concentration (groups/10^3 monomer units)						
			Total Endgroups[b]	**a**	$\mathbf{a_N}/\mathbf{a_S}$	**b**	**d**	**a**/**b**	$\mathbf{a_S}$[N]/$\mathbf{a_N}$[S]
0/100	0.424	4.4(f)	31	19	–	21	20	0.90	
		0.57(f)	235	156	–	200	185	0.78	
7/93	0.212	9.4	16	9	4	12		0.75	3.0
	0.424	4.7	33	8	3.2	10	15(^{13}C)	0.80	5.0
		3.6(f)	43	21	5.1	33		0.64	3.5
		2.6(f)	60	22	3.9	31		0.71	2.3
15/85	0.212	11.1	15	6	1.4	7		0.86	4.3
	0.424	6.5	25	8	1.7	10		0.80	3.8
		2.5(f)	65	23	1.7	27		0.85	3.0
		1.5(f)	77	26	1.7	32		0.81	3.5
42/58	0.212	13.1	13	5	0.5	5		1.00	2.8
	0.424	6.4	27	9	0.55	10		0.90	2.8
		2.6(f)	68	21	0.57	24		0.88	2.4
		2.2(f)	80	31	0.63	33		0.94	2.1
74/26	0.212	12.0	15	6	–	8		0.75	
	0.424	5.4	34	12	0.1	14		0.86	1.8
		4.8(f)	40	30	0.19	35		0.86	1.7
		1.9(f)	98	44	0.18	48		0.92	2.1
87/13	0.212	7.6	26	8	–	10		0.80	
	0.424	4.1	47	15	<0.1	15		1.00	
		3.0(f)	65	41	0.05	43		0.95	3.0
		1.2(f)	162	79	0.07	99		0.80	2.1
100/0	0.424	2.8	75	21		47	46	0.45	

[a] Determined by GPC or VPO (fractionated samples, f).
[b] Based on M_n and copolymer composition.

derived in the fragmentation process immediately following chain transfer by **1**. These peaks have been observed previously by Yamada et al. in poly**Sty** prepared in a similar manner [12]. Peaks at 4.2 and 1.2–1.4 ppm are assigned to the ester methylene (**b**) and a combination of the methyl groups ((**c**) and (**d**)), respectively. The assignments were confirmed by HMQC experiments.

These correlation experiments also indicated that the weak peaks observed at 3.0–3.7 ppm are associated with the ester methylene C atoms (^{13}C chemical shift 60 ppm). These peaks are probably associated with ester groups adjacent to a saturated hydrocarbon environment, suggesting that in Poly**Sty**, some of the functionalised oligomers may have copolymerised, as discussed in our previous paper [5].

The spectrum of poly**MAN** shows a major set of olefinic peaks at 5.7 and 6.5 ppm and two minor sets at 5.6/6.1 and 5.8/6.1 ppm. Correlations were determined by COSY and HMQC experiments. In a spectrum of a lower fraction of poly**MAN** ($M_w < 2000$), the 5.6/6.1 ppm peaks had close to the same intensity as the 5.7/6.5 ppm peaks. Similar peaks have been observed in very low molecular weight poly(methyl methacrylate) prepared in a similar manner [5]. They correlate closely with the assignment of olefinic end-group protons in poly[methyl-α-(chloromethyl)acrylate] (structure **3**) suggested by Yamada et al. [13] at 5.74 and 6.24 ppm. The effect of chlorine on the proton chemical shift at a β carbon (or further) is expected to be comparable to the effect of a sulphur moiety at the same position [14]. Thus, the peaks at 5.6 and 6.1 ppm have been assigned to an oligomer containing only one monomer unit (structure **4**), which is apparently difficult to separate from low molecular weight oligomers.



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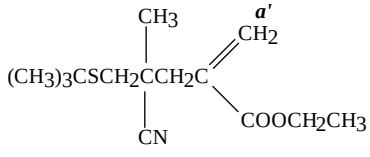

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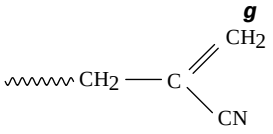
The other minor olefinic peaks are thought to be due to end groups formed by disproportionation, see structure **5**.



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With the perfect addition–fragmentation chain transfer mechanism, all oligomers should have end-groups according to structure **2**. Thus the concentrations **a** (+**a**′), **b** and **d** should be equal and have the same value as half the end-groups calculated from the M_n. Calculations based on the integrations of the proton NMR spectra and the M_n are shown in Table 3. In principle, it is possible to estimate the concentration of **d** end-groups by integration of peaks in the range 1.2–1.4 ppm, due to *t*-butyl end-groups and ester methyl groups, and subtracting 3/2**b**. Unfortunately, the superposition of the small methyl end-group peaks (in the low shift region) on peaks due to strong backbone and other aliphatic peaks led to unacceptable measurement error in most cases. In general, the methyl resonances were of the correct order of magnitude as indicated by the results for poly**MAN** in Table 3, which had a somewhat less complex spectrum. In the case of one copolymer, an inverse-gated decoupling ^{13}C NMR experiment allowed the direct calculation of the concentration of **d** end-groups. The value is in reasonable agreement with the concentration of **b** end-groups in the same copolymer, see Table 3. The ratio of concentrations **a**/**b** in each copolymer is generally within experimental error of unity, but apart from one copolymer fraction, it is always less than unity, see Table 3. This suggests a consistent but small loss of double bonds in the process, possibly by copolymerization or by less than 100% fragmentation. End-group concentrations calculated from the measured M_n and the copolymer composition are mostly close to those determined by NMR.

Analyses of the NMR spectra of copolymers on the basis of the assignments for the homopolymers allowed the peaks due to olefinic end-groups associated with adjacent **Sty** and **MAN** monomer units to be distinguished, as shown by $\mathbf{a}_S$ and $\mathbf{a}_N$ in Table 3. Assuming normal conditions for applying kinetics to free radical polymerisation, the ratio $\mathbf{a}_S/\mathbf{a}_N$ is given by:

$$\mathbf{a}_S/\mathbf{a}_N = (r_S C_S[S])/r_N C_N[N])$$

where r and C are reactivity ratios and chain transfer constants, respectively. Thus, values of $\mathbf{a}_S[N]/\mathbf{a}_N[S]$ should be constant and equal to $r_S C_S/(r_N C_N) = 4.0$, using the chain transfer constants found in this work and the reactivity ratios, $r_S = 0.30$ and $r_N = 0.16$ [4]. The values shown in Table 3 are generally within experimental error of four, however, there is a trend to lower values for co-monomer systems rich in **Sty**. This is probably due to solvent effects, which have been observed to change rate constant ratios in free radical reactions by as much as a factor of 2 [15–17]. The results tell us that the chain transfer agent, **1**, has a clear preference for reaction with **Sty** rather than with **MAN**, except in **Sty** rich mixtures, where the preference is reduced.

4. Conclusions

The chain transfer constants for the copolymerisation of **Sty** and **MAN** with ethyl α-(*t*-butanethiomethyl)acrylate as chain transfer agent lie in the range 0.23–0.90. The bulk copolymer composition is independent of the amount of chain transfer agent used.

The end groups of the co-oligomers in the approximate molecular weight range $1–10 \times 10^3$ prepared from all feed ratios with ethyl α-(*t*-butanethiomethyl)acrylate as chain transfer agent are in reasonable agreement with those expected on the basis of the addition–fragmentation mechanism. However, as with the styrene/methyl methacrylate system [5], there is generally between 10 and 20% deficiency in olefinic end groups at all copolymer feed ratios.

Acknowledgements

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