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Radical copolymerization of maleic anhydride and substituted styrenes by reversible addition-fragmentation chain transfer (RAFT) polymerization

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Abstract

Reversible addition fragmentation transfer (RAFT) copolymerization with benzyl dithiobenzoate (BDTB) as chain transfer agent was used to copolymerize maleic anhydride (MA) with styrene (St) and with the substituted styrenes *p*-chlorostyrene (*p*ClSt), *p*-methoxystyrene (*p*MeOSt) and *p*-methylstyrene (*p*MeSt). Kinetic studies indicated that radical copolymerizations proceeded with apparent 'living' character, deduced from experiments demonstrating an increase in molar mass with monomer conversion, narrow molar mass distribution and chain extension to form block copolymer. All copolymers were alternating in chain structure as confirmed by determinations of monomer reactivity ratios. The degree of control in the RAFT mechanism and the establishment of the fragmentation equilibrium incorporating MA are discussed for styrene and for *p*-substituted styrenes, in relation to experimental copolymerizations producing molar masses somewhat higher than expected. For copolymerizations of MA with α-methylstyrene (αMeSt), conventional rather than controlled behaviour was observed, suggesting that the fragmentation equilibrium could be shifted towards the αMeSt propagating radical.

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Keywords: Radical copolymerization; Maleic anhydride; Substituted styrenes

1. Introduction

Alternating copolymerization permits the formation of a wide range of regulated chain structures. Significant effort has been directed to conventional radical chain copolymerizations involving maleic anhydride (MA), which does not homopolymerize readily. (The term conventional defines a classical mechanism consisting of initiation, propagation, and termination). MA is a strongly electron accepting monomer. Generally, strong electron donation in the comonomer will increase the tendency towards alternation, and Trivedi and Culbertson [1] have collated information on donor molecules in an excellent survey of the copolymerization of MA. Mechanistic interpretations of a strong alternating tendency in conventional radical copolymerizations have been subjected to detailed investigations [2].

In the past decade, syntheses of well-defined polymers by controlled radical polymerization (CRP) have been developed [3–6]. CRP is particularly appealing as it not only delivers polymers having a narrow molar mass distribution (MMD) with pre-determined average molar mass but also can be performed using normal radical procedures without the stringent experimental conditions required in living ionic polymerization. Several systems have been applied to control molar mass and end group functionality, and these methods include nitroxide mediated polymerisation (NMP) [7], atom transfer radical polymerization (ATRP) [8,9], other transition metal systems using cobalt [10] and nickel [11], and reversible addition fragmentation chain transfer polymerization (RAFT) [12–15].

The use of nitroxide mediated polymerization for the copolymerization of MA and styrene (St) appears problematic, since the products were not alternating copolymers due to the high temperature (~120 °C) required to operate

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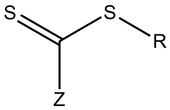
the nitroxide method [16,17]. Control within NMP and ATRP systems is governed by two principles. First, initiation should be fast in order to rapidly provide a constant concentration of growing polymer chains. Second, the majority of the growing chains are dormant species, which still have the ability of further growth due to a dynamic equilibrium that is established between the dormant species and the growing radicals. By keeping the concentration of active species low throughout the polymerization, bimolecular radical–radical termination is suppressed. ATRP fulfils these principles by use of a transition metal catalyst (usually copper halide) in combination with a suitable ligand. The catalyst complex establishes the reversible equilibrium that can be altered by adjustment of the ligand. Though ATRP has become a useful CRP method, which is tolerant to a number of functionalities, acidic monomers are very difficult to polymerise directly. This is due to interactions of carboxylic acid functionality with the catalyst. It was postulated that carboxylic acids react with Cu(II) species by displacing the halogen atom, resulting in the formation of metal carboxylates which inhibit polymerization [6]. MA also poses problems with regard to polymerization and copolymerization with an ATRP system. Attempts in the literature [18] and in our own laboratory have failed to produce MA containing copolymers by ATRP due to poisoning of the Cu catalyst. MA functionality is similar to carboxylic acids, and if hydrolysed a dicarboxylic acid is produced. Protecting group chemistry is not helpful as MA would need to be ring-opened, and then the ester or acid groups protected. This increases the steric hindrance on the double bond lowering the reactivity of the monomer and making copolymerization difficult.

Chiefari and co-workers [12] developed RAFT polymerization in 1998 and have reviewed the understanding of the mechanism [19,20]. RAFT polymerization involves the use of a highly efficient chain transfer agent (CTA) of the general structure (**1**), known collectively as RAFT reagents.



(1)

The mechanism of RAFT polymerization involves a reversible addition-fragmentation sequence of transfer of the S=C(Z)S– moiety between active and dormant chain ends. Provided that the exchange reaction is fast compared to propagation and that each chain contains one end group derived from the RAFT reagent, then the theoretical molar mass at any conversion can be calculated.

A distinguishing feature of RAFT polymerization is its applicability to a wide range of monomers, containing for example acid groups, acid salts, hydroxyl groups or tertiary amino groups [12], which have proved to be difficult with other CRP methods. The process is similarly tolerant of the functionality in the RAFT reagent and the initiator, which allows the synthesis of a wide range of polymers with end group or side chain functionality in one step without the need for protecting group chemistry. Davis and Matyjaszewski observed that little was published on statistical copolymers by methods involving RAFT [21].

The work reported here was directed to the copolymerization of MA by RAFT with various styrene comonomers. The effect of differing functional groups substituted on the styrene ring and the use of the sterically hindered monomer α-methyl styrene (αMeSt) allowed the application of the RAFT method to be evaluated. The CTA was benzyl dithiobenzoate (BDTB) having the following groups in (**1**)

$$\mathbf{R = CH_2P}h \quad \mathbf{Z = P}h$$

Klumperman et al. reported initial studies of copolymerizations of StMA in the presence of a RAFT reagent [18]. Whilst the final product had a narrow MMD and the final molar mass was close to the expected theoretical value, results for molar masses as a function of polymerization conversion were not reported. Zhu et al. also studied RAFT copolymerization to prepare StMA [22], but again from the limited number of experiments it was not possible to discern consistent behaviour dependent on conversion. Here, we investigate a comparison of experimental molar mass with theoretical molar mass throughout monomer conversion during copolymerization not only for StMA but also for other substituted styrene monomers with MA, namely *p*-chlorostyrene (*p*ClSt), *p*-methoxystyrene (*p*MeOSt) and *p*-methylstyrene (*p*MeSt), which was directed in part towards assessing the effectiveness of the RAFT reagent in the early stages of copolymerization. For all these copolymerizations of MA, it was important to demonstrate the degree of CRP from relevant experimental studies of the time dependence of monomer conversion, the dependence of molar mass on conversion, the dependence of polydispersity on conversion, and sequential monomer addition. An overall objective was the production of a range of alternating copolymers of MA having well-defined molar mass and structure with narrow MMD.

2. Experimental

2.1. Materials

High purity chemicals and solvents were purchased from Aldrich Chemical Company. Fisher Chemicals, Acros Organics, Cambridge Isotope Laboratories and Carless Solvents, and were used as received unless otherwise stated. 2,2′-Azobisisobutyronitrile (AIBN) (98% from Fluka) was recrystallized from methanol. Maleic anhydride (99%) was recrystallized from toluene. Styrene and styrene-based monomers were passed through a glass column containing inhibitor remover. Monomer was vacuum distilled over dry magnesium sulfate prior to use.

2.2. Synthesis of benzyl dithiobenzoate (BDTB)

The title compound was prepared according to the facile synthetic method of Chiefari et al. [12] Dry tetrahydrofuran (THF) (30 mL) and carbon disulfide (3.44 g, 0.045 mol) were mixed at 25 °C. Phenyl magnesium bromide (14 mL, 3 M ether solution) was added dropwise over 30 min. The dark red solution was heated to 40 °C and benzyl bromide (7.69 g, 0.04 mol) was added dropwise over 30 min. The solution was heated at 50 °C for 12 h. Ice water (100 mL) was added and the organic products extracted with Et_2O (200 mL). The aqueous phase was re-extracted with ether, and the combined ethereal phases washed with distilled water and dried over $MgSO_4$. The solvent was removed by rotary evaporation to furnish the title compound as a red oil (9.76 g) which was purified by column chromatography (ethyl acetate). The purity was ~99%. Characterization was by ^{1}H NMR: ($CDCl_3$) (ppm): 4.61 (s, 2H); 7.23–7.43 (m, 8H) and 8.02 (m, 2H).

2.3. Copolymerization procedure

All copolymers were prepared in glass schlenk tubes equipped with taps and magnetic stirrer bars. Solutions were degassed by repeated freeze pump thaw cycles. For kinetic experiments equimolar concentrations of monomers (M_1:M_2 = 50:50) were studied. A stock solution was prepared and divided equally such that each tube contained MA (0.015 mol), a styrene comonomer (0.015 mol), AIBN (0.0832 mmol), BDTB (0.167 mmol) and dioxane (10 mL). The tubes were immersed in a pre-heated oil bath at 60 °C and allowed to react for a designated time. For experiments directed towards determinations of monomer reactivity ratios, a series of MA concentrations (5–25 mmol) (total monomer 30 mmol) was prepared under the same conditions as above, but reaction times were restricted to low conversions of comonomers. The reactions were terminated by rapid cooling and the products isolated by precipitation into cold methanol. Since the isolation procedure may result in formation of half esters in copolymers, reconversion to succinic anhydride units was accomplished by drying at > 80 °C under vacuum for 24 h to remove water and confirmed by FTIR. Conversions were determined gravimetrically, and spectroscopic and chromatographic instrumentations were employed for product characterization. Kinetic plots were constructed from the monomer concentrations at zero time and reaction time t, $[M]_0$ and $[M]_t$, respectively.

2.4. Block copolymerization

MA (7.5 mmol), St (7.5 mmol), AIBN (0.04 mmol), BDTB (0.08 mmol) and dioxane (10 mL) were added to 2 schlenk tubes containing magnetic stirrer bars and equipped with glass taps and rubber septums. The tubes were evacuated by freezing the contents and pumping to constant pressure. The freeze, pump, thaw cycle was repeated twice before the tubes were immersed in an oil bath held at 60 °C for 15 h. The first tube was terminated by freezing the contents and opening the tap to air. A separate solution containing *p*MeSt (15 mmol) in dioxane (10 mL) was added to the second tube by degassed syringe, and the contents were maintained at 60 °C for a further 15 h. The contents of both tubes were precipitated into MeOH and the solid collected by suction filtration. The products were dried under vacuum at 80 °C for 24 h to yield pale pink powders and then subjected to spectroscopic and chromatographic characterization. The methyl group in the B block of pMeSt was identified by ^{1}H NMR spectroscopy.

2.5. Instrumentation

Size exclusion chromatography (SEC) was performed with an instrument (PL-GPC 110) equipped with a refractive index detector supplied by Polymer Laboratories [23]. A set of 2 columns (PLgel 5 (m MIXED-D 300× 7.5 mm) supplied by Polymer Laboratories was used. The eluent was a mixed system (v/v) of THF (90%) and acetic acid (10%) and was used at a flow rate of 1.0 mL min^{-1}. The analysis was carried out at 40 °C. Copolymers for analysis were prepared by dissolving the samples (2 mg mL^{-1}) in the mobile phase and allowing complete dissolution by standing for > 2 h. After filtering and adding dry toluene (10 (L) as internal reference, the solutions were injected onto the columns. Calibration was carried out using 10 different polystyrene (PS) standards with narrow distributions and molar masses ranging from 580 to 325,000 g mol^{-1} (supplied by Polymer Laboratories). The data was processed using a RM 575 computer operating Caliber GPC software from Polymer laboratories. Experimental values of molar masses, number average M_n (SEC) and weight average M_w, were computed, and the ratio M_w/M_n (SEC) represented the polydispersity (PDI) of the MMD.

Dual detection SEC was carried out using a Knauer HPLC pump 64 with a six port injection valve coupled to a Knauer refractive index detector and a Pye-Unicam GC-UV, UV detector. The same column type as stated above was used with THF as the eluent at a flow rate of 1.0 mL min^{-1} at 20 °C. The inter-detector delay was assessed with standards. The outputs from the detectors were transferred via a data capture unit to the computer above, in order to plot chromatograms.

Fourier transform infrared (FTIR) spectroscopy was performed on a Nicolet 20 DXC-FTIR spectrometer. Samples were prepared in a mixed system (v/v) of chloroform (50%) and dimethyl sulfoxide (DMSO) (50%). The number of scans was typically 50 over a wavenumber range of 650–4000 cm^{-1}. Spectra were processed using an IBM compatible computer operating Omnic software. Determination of carbonyl concentration in a copolymer involved a calibration procedure. With succinic anhydride as the calibrant for carbonyl concentration, a calibration curve was derived by accurately preparing solutions of the succinic anhydride calibrant in concentrations from 0.005 to 0.03 mol dm^{-3} and measuring the carbonyl absorbance between 1667 and 1897 cm^{-1}. A linear calibration plot of absorbance versus carbonyl concentration was constructed with $r^2=0.99$. Copolymer samples were accurately weighted and made up to known concentration with the solvent. From measurements of carbonyl absorbance for copolymer the molar concentration of succinic anhydride groups per copolymer was calculated from the calibration plot, permitting determination of the molar composition of the copolymer (mol fraction MA) since the copolymer concentration in solution was known. With knowledge of the copolymer composition (experimental error $<10\%$) across a range of comonomer feed ratios, the monomer reactivity ratios were estimated first by the method of Fineman–Ross [24] and then determined more accurately by the linear method Kelen–Tudos [25] which effectively weights all experimental results for which we chose the parameter α set at 1.0. Our preference for this approach, rather than non-linear methods of treatment of results [26, 27], was because we wished to compare our reactivity ratios for RAFT coplymerizations with data for conventional radical copolymerizations tabulated in Polymer Handbook [28] which contains data obtained by the linear method of Kelen–Tudos [25].

Spectroscopic characterization by ^{1}H NMR was performed with a Brucker 400 MHz instrument. Samples were dissolved in $CDCl_3$ (20 mg mL^{-1}) or d_6 DMSO. All NMR solvents had TMS already added as an internal reference. Samples for ^{1}H NMR determination were typically scanned 64 times between δ values of 0–10 ppm. ^{1}H NMR was used both qualitatively and quantitatively for structural analysis.

3. Results and discussion

The definition of a CRP may be compared and contrasted with the polymerization criteria summarised for living polymerization by Quirk and Lee [29]. In living ionic chain polymerization, the classical polymerization conditions are fast quantitative initiation and slow propagation, ensuring a fixed concentration of propagating centres, presuming that transfer and termination reactions are absent.

In Scheme 1, the mechanism of a RAFT mediator involves reversible addition-fragmentation sequences in which transfer of the (S=C(Z)S) moiety between active and dormant chain ends ensures that living character is maintained throughout the polymerization. Chain formation from initiator derived radicals $I^{\bullet}$ is presumed to be absent. In Scheme 1, the species $P_{n^{\cdot}}$ and $P_{m^{\cdot}}$ are chain radicals and $R^{\bullet}$ will be the benzyl radical for the involvement of BDTB. It is clear that chains resulting from transfer and equilibration reactions have the S=C(Z)S– moiety as one end group, and formation of the RAFT intermediates and identification of this end group have been confirmed by spectroscopic methods [19]. Therefore, as a first experimental test of the behaviour of a RAFT reagent it is necessary to investigate the course of a polymerization, with emphasis on molar mass and MMD as a function of monomer conversion, kinetics and block copolymerization. From these characteristics, the degree of control during our copolymerizations may be assessed.

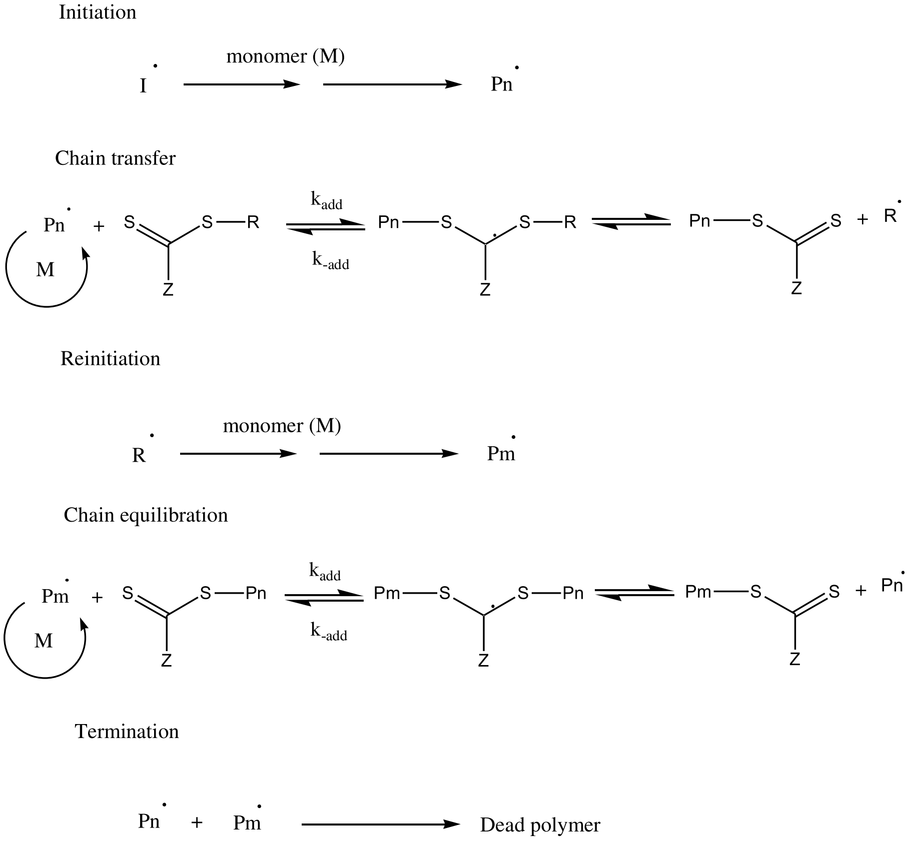
3.1. Monomer conversion

St monomers were copolymerized with MA using BDTB [0.024 mol% with respect to MA] as the RAFT mediator and with AIBN [0.012 mol% wrt MA] as the radical initiator. For each St comonomer a series of copolymerizations (equimolar ratio of monomers M_1 and M_2) was performed in parallel for different periods of time in order to achieve differing conversions. SEC chromatograms for copolymer samples StMA, *p*MeStMA, *p*ClStMA and *p*MeOStMA are shown in Figs. 1 and 2, clearly demonstrating an increase in chain size as a function of reaction time during copolymerization. The molar ratio of AIBN:BDTB of 1:2 investigated here followed the initial communication of Zhu et al. [22] who reported a sample of StMA with polydispersity (PDI) ~1.2 corresponding to our results in Fig. 3(a). Chernikova et al. [30] also investigated a 1:2 ratio, but in copolymerizations of St and MA in equimolar concentrations their PDI results were higher exceeding 1.4 at low and intermediate conversions. Results for molar mass and PDI for our 4 types of copolymers are displayed in Figs. 3 and 4, respectively. Values of the theoretical number average molar mass M_n (calc) for a CRP according to Scheme 1 were calculated with the equation

$$M_n(\text{calc}) = xM_o\frac{[\text{M}]}{[\text{RAFT}]} \tag{1}$$

where [M] is the total monomer concentration, [RAFT] is the concentration of the RAFT reagent, x is the fractional conversion and M_o is the average molar mass of the comonomers (e.g. $M_o=101$ g/mol for the monomer units in StMA).

The criterion that molar mass increases linearly with conversion has been used extensively for CRP systems to suggest that there might be living character. Number average molar mass M_n (SEC) determined from SEC chromatograms was found to increase with increasing conversion for StMA, *p*MeStMA, *p*ClStMA and *p*MeOStMA copolymers. Linear regression of these experimental data for M_n (SEC) for the conversion range $x>0.05$ results in straight lines in Figs. 3 and 4 and therefore may indicate a degree of living character brought about by mediation with BDTB. However, further examination of the plots of molar mass against conversion, and comparison with the theoretical molar masses calculated by Eq. (1),



Scheme 1. Raft polymerization mechanism.

reveals that for all the systems studied the molar masses measured by SEC are higher than those predicted for the total consumption of BDTB.

A reason for the differences in M_n (SEC) and M_n (calc) may include error in molar mass measurement by SEC due to differences in hydrodynamic volume between PS and the copolymers subjected to characterization. Errors in molar mass measurement can be evaluated by considering StMA copolymers. The Mark–Houwink (MH) constants for both PS and StMA in THF have been reported [31]. This allows the SEC calibration for PS to be adjusted to a calibration valid for StMA, presuming that samples are separating by size exclusion so that the universal calibration approach based on hydrodynamic volume is valid. The universal calibration equation and the MH equations can be rearranged to obtain

$$\mathrm{Log}\,M(\mathrm{StMA}) = \frac{1+a(\mathrm{PS})}{1+a(\mathrm{StMA})}\mathrm{Log}\,M(\mathrm{PS}) + \frac{1}{1+a(\mathrm{StMA})}\mathrm{Log}\frac{K(\mathrm{PS})}{K(\mathrm{StMA})} \quad (2)$$

where M is molar mass, K and a are Mark–Houwink constants. Calibrations for PS and StMA are presented in Fig. 5 in which the difference in slope is due to the a value in the MH equation. Molar mass data determined from chromatograms with both these calibrations are compared in Table 1. For sample MCD236 there is a reduction in M_n (SEC) when the StMA calibration is employed. The calibration plots in Fig. 5 converge at a molar mass of 20,000 g/mol, and so M_n (SEC) is not dependent on which calibration is used. The reduction in molar mass for low molar mass samples brought about by using the StMA calibration is not significant enough to account for the differences between the experimental and calculated molar masses of StMA produced by RAFT copolymerization. It should be borne in mind that the above analysis used MH constants for PS and StMA copolymers dissolved in THF. The SEC analysis was carried out in THF/acetic acid (90:10 v/v); however, previous analysis for MA copolymers indicated that use of THF/acetic acid for PS only had a small effect on the MH constants $K=1.16\times10^{-4}$ dL g^{-1} (THF), $K=1.52\times10^{-4}$ dL g^{-1} (THF/acetic acid), $a=0.72$ (THF), $a=0.71$(THF/acetic acid) [23]. From our extensive experience with SEC techniques [23] we estimate that the accuracy of molar masses for StMA copolymers is about 5% for $M_n \sim 10{,}000$ g/mol with a somewhat higher error for the other 3 types of St copolymers. An alternative experimental procedure instead of universal calibration would have been to consider molar mass detection for SEC [30]. However, it is questionable whether light scattering (poor sensitivity to short chains) or MALDI mass spectroscopy (accuracy for

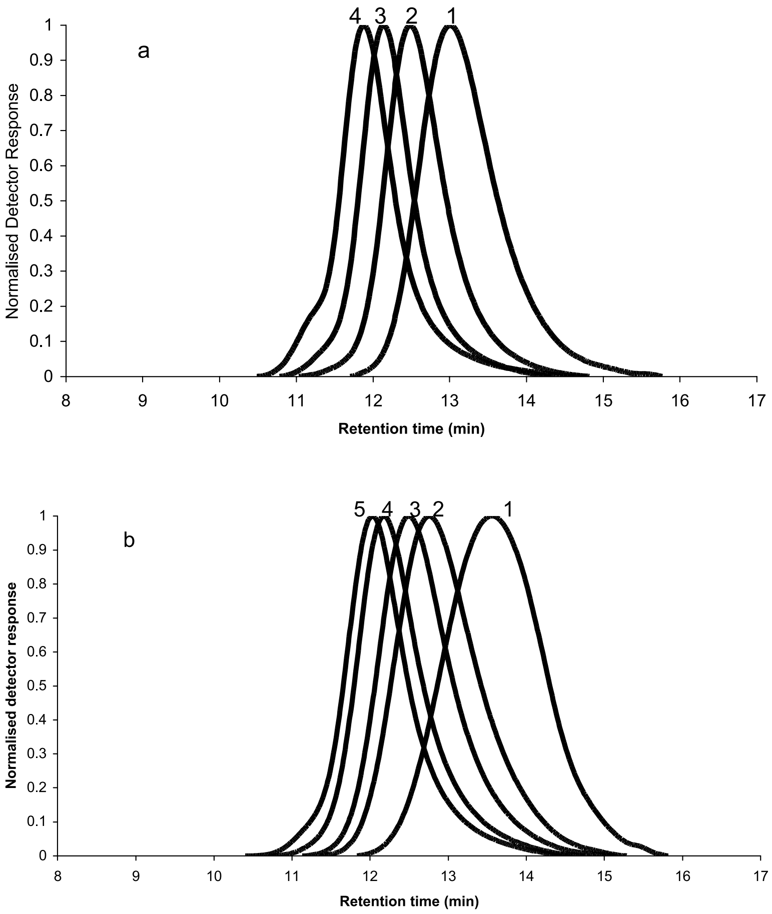


Fig. 1. SEC chromatograms for products of RAFT copolymerizations in dioxane at 60 °C (M_1:M_2 = 50:50). (a) StMA conversions; (1) 22% 60 min; (2) 44% 120 min; (3) 70% 240 min; (4) 97% 1040 min. (b) *p*MeStMA conversions; (1) 7% 60 min; (2) 32% 120 min; (3) 49% 180 min; (4) 80% 439 min; (5) 91% 1218 min.

polydisperse samples?) would represent a significant improvement for the title copolymers. The use therefore of MH constants based on THF rather than THF/acetic acid was not considered to invalidate the above conclusion that hydrodynamic volume differences do not account for the observed differences in molar masses M_n (SEC) and M_n (calc) in Figs. 3 and 4.

Plots of molar mass against conversion for StMA, *p*MeStMA, *p*ClStMA and *p*MeOStMA copolymers in Figs. 3 and 4 do not include experimental results at the start of the polymerization ($x = 0$–0.05). The molar mass produced during the initial monomer conversion was assessed from the positive intercepts on the molar mass axis after linear extrapolation of experimental data for M_n (SEC) to zero conversion. For copolymer *p*MeStMA an intercept of approximately 5000 g/mol is exhibited, provided the SEC characterization is reliable. Subtraction of this intercept of molar mass from the experimental M_n (SEC) results in values which are close to data for M_n (calc), indicating that M_n is a linear function of monomer conversion at intermediate conversions. Similar observations can be made for StMA, *p*ClStMA and *p*MeOStMA copolymers, as shown in Figs. 3 and 4. From this qualitative analysis, it is possible to postulate that prediction of M_n (calc) with Eq. (1) is not correct at the start of copolymerization. Whilst adventitious peroxide at the start of polymerization might be invoked, this is slight due to careful experiments to exclude oxygen, namely high purity chemicals (Section 2.1), liquids were blanketed with nitrogen and solutions for polymerization were prepared by high vacuum conditions (Sections 2.3 and 2.4). Scheme 1 requires the RAFT reagent to be fully effective throughout

Table 1
Molar mass data for StMA

Sample	M_n (SEC) g mol^{-1} PS calibration	M_n (SEC) g mol^{-1} StMA calibration	M_n (Calc) g mol^{-1}
MCD236	11,100	10,600	4000
MCD237	19,300	19,300	8100

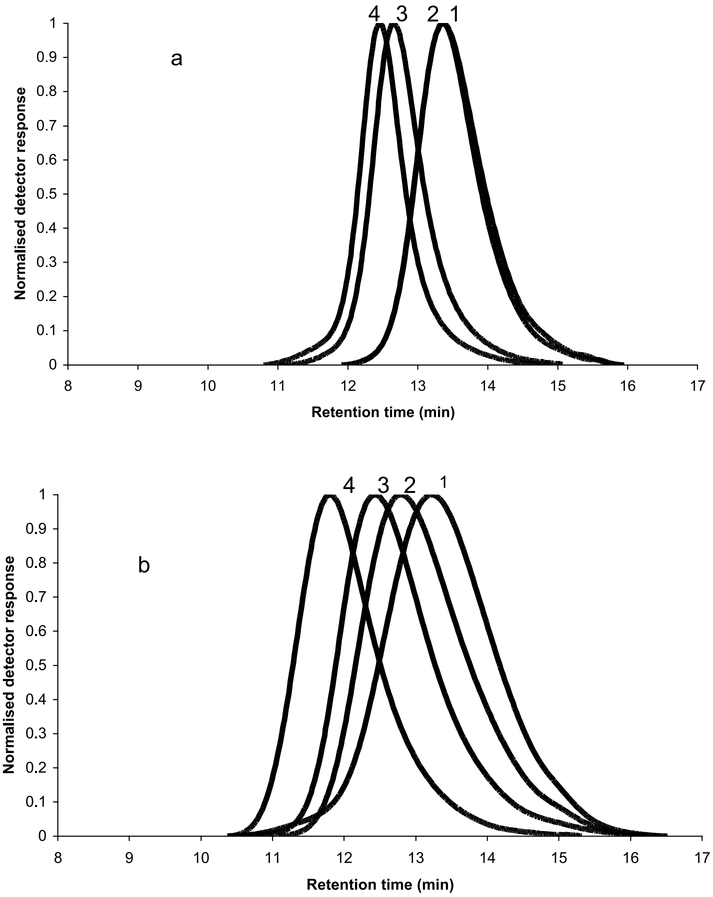


Fig. 2. SEC chromatograms for products of RAFT copolymerizations in dioxane at 60 °C (M_1:M_2=50:50). (a) *p*ClStMA conversions; (1) 21% 300 min; (2) 27% 279 min; (3) 45% 621 min; (4) 74% 1110 min. (b) *p*MeOStMA conversions; (1) 19% 60 min; (2) 44% 90 min; (3) 40% 120 min; (4) 59% 180 min.

monomer conversion. Therefore, for $x=0$–0.05 in these copolymerizations the value of [RAFT] in Eq. (1) could be lower than BDTB = 0.167 mmol introduced at the start of the experimental copolymerizations, and so molar masses at low conversions of monomers for all 4 copolymer systems are substantially above values predicted on the basis of complete involvement of BDTB. It appears that these observations might be considered to be a hybrid living/conventional behaviour which can be induced by low values of the rate constant k_{add} in Scheme 1, and studies have indicated the feasibility of such hybrid radical polymerizations [32,33].

It can be concluded that experimental conditions can be chosen to achieve close to complete conversion of monomer, e.g. the quantitative copolymerizations of StMA and *p*MeStMA in Fig. 3. Data for M_n appear to be close to a linear dependence on monomer conversion, though establishing control is not instantaneous at the start of copolymerization. Thus, molar mass can be controlled by reactant concentrations with dependence on the RAFT reagent demonstrated. Therefore, it might be argued that these copolymerizations have apparent living character.

3.2. Molar mass distribution

The essential requirements for the formation of a polymer or copolymer with a Poisson distribution are that monomers add exclusively to active centres, all the active centres are equally susceptible to reaction with monomer and initiation is very fast. If all these conditions are met, then a near monodisperse MMD of $M_w/M_n < 1.1$ will be achieved and the system must behave as a living one as exemplified by anionic chain polymerisation [34]. For RAFT to be an effective CRP technique for MA the rate constant, k_{add}, in Scheme 1 should be high relative to the propagation rate constant. The consequences of this condition not being fulfilled are hybrid living/conventional behaviour and the raising of polydispersity. However, a low radical concentration is desirable to optimise control in the mechanism [35,36].

SEC chromatograms for StMA copolymers in Fig. 1(a) indicate relatively narrow MMDs as illustrated by values of polydispersity (PDI) in the range 1.19–1.30, i.e. below results for PDI in a conventional radical polymerization. The sample with PDI = 1.3 at $x=0.22$ in Fig. 3 has the highest PDI, which may indicate slow consumption of

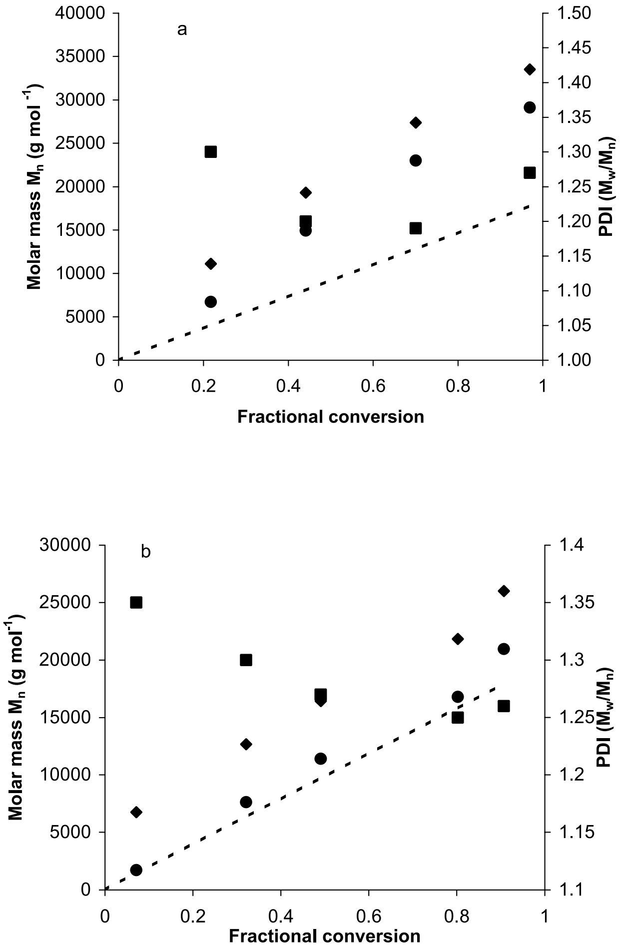


Fig. 3. Molar mass and PDI data. (a) StMA (M_1:M_2 =50:50). (b) *p*MeStMA (M_1:M_2=50:50), (◆ M_n (SEC), ■ PDI, - - - M_n(Calc), ● M_n(SEC)-M_n(SEC intercept)).

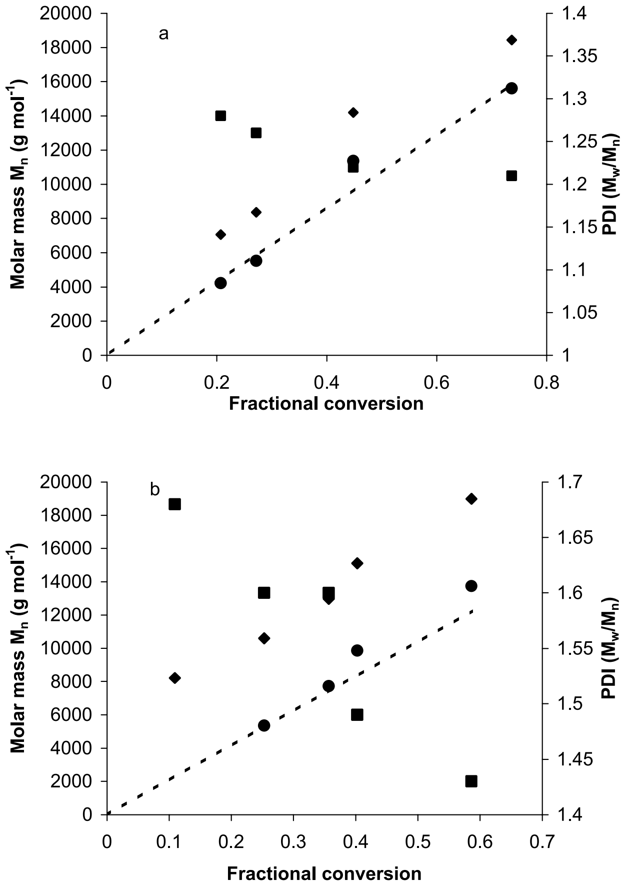


Fig. 4. Molar mass and PDI data. (a) *p*ClStMA (M_1:M_2=50:50). (b) *p*MeOStMA (M_1:M_2=50:50). (◆ M_n(SEC), ■ PDI, - - - M_n(Calc), ● M_n(SEC)-M_n(SEC intercept)).

BDTB and sluggish establishment of the RAFT equilibrium early on in the copolymerization. Results for PDI for *p*MeStMA copolymers are in the range 1.27–1.38 in Fig. 3, corresponding to copolymerizations of St and *p*MeSt monomers in which quantitative conversions were achieved. The MMD narrowed with increasing conversion, a common characteristic of a living polymerization, or in the case of a RAFT polymerization this trend in part may be due to the slow establishment of the addition-fragmentation equilibrium. Somewhat narrower MMDs (polydispersities in the range 1.17–1.26) were obtained for *p*ClStMA copolymers compared to StMA and *p*MeStMA, as displayed in Fig. 4, but *p*MeOStMA copolymers exhibited broader MMDs (polydispersities in the range 1.48–1.60) indicating reduced control during RAFT copolymerization. Values of $M_w/M_n < 1.15$ were not produced with any of the copolymer systems investigated. Polymerization conditions and choice of RAFT reagent for achieving $M_w/M_n < 1.2$ for PS homopolymers have been considered [37].

3.3. Kinetics of copolymerization and copolymer composition

Kinetic plots for StMA, *p*MeStMA, *p*ClStMA and *p*MeOStMA (equimolar ratios of monomers) are essentially linear in the semi-logarithmic format in Figs. 6 and 7, in which $[M]_0$ and $[M]_t$ are monomer concentrations at reaction times zero and t, respectively. The kinetic plot for StMA results in a linear regression that has an intercept close to the origin. Examination of conversion data and

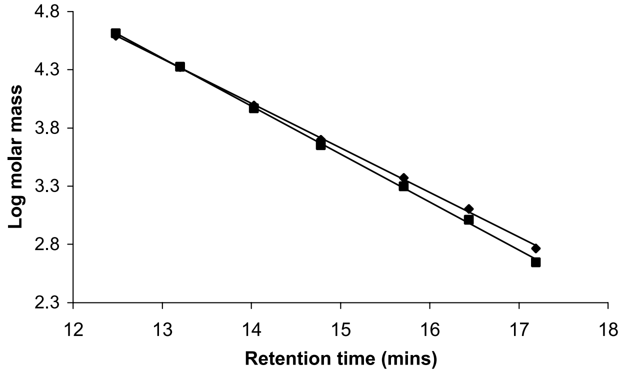


Fig. 5. SEC calibrations for PS (◆) and StMA (■) in THF.

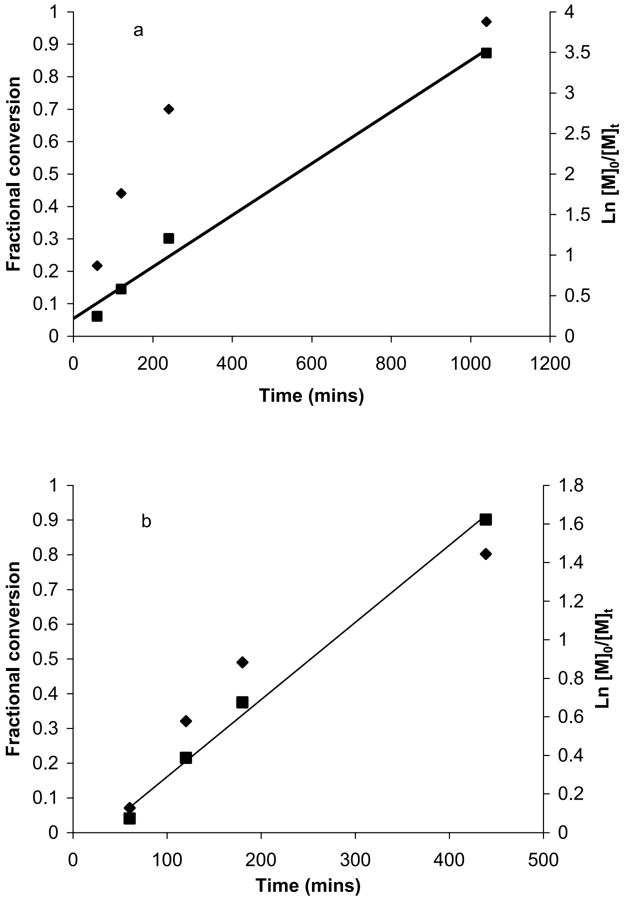


Fig. 6. RAFT copolymerization kinetics. (a) StMA in dioxane at 60 °C (M_1:M_2 = 50:50). (b) *p*MeStMA in dioxane at 60 °C (M_1:M_2 = 50:50). (Fractional conversion ◆, Ln$[M]_0/[M]_t$ ■).

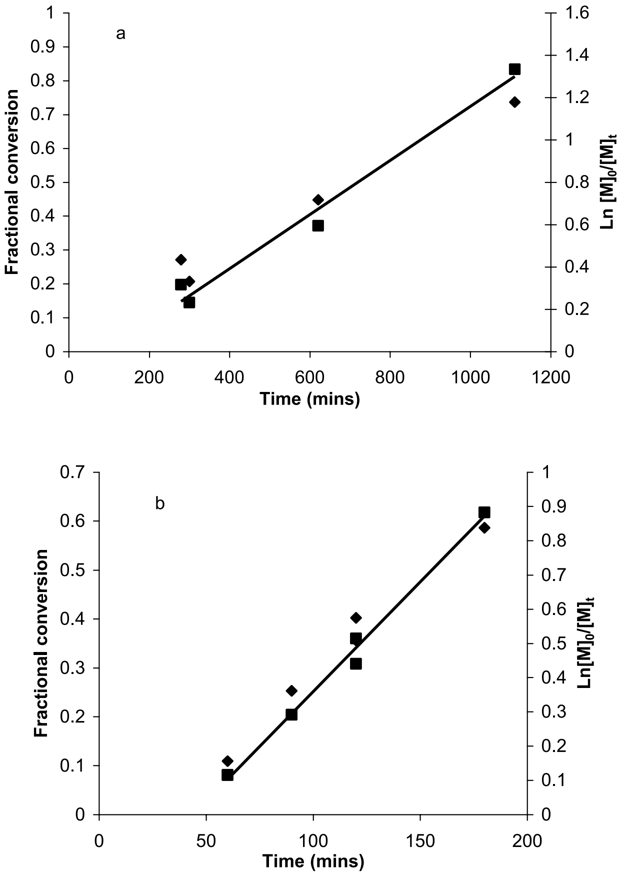


Fig. 7. RAFT copolymerization kinetics. (a) *p*ClStMA in dioxane at 60 °C (M_1:M_2 = 50:50). (b) *p*MeOStMA in dioxane at 60 °C (M_1:M_2 = 50:50). (Fractional conversion ◆, Ln$[M]_0/[M]_t$ ■).

copolymerization kinetics for *p*MeStMA and *p*MeOStMA reveals that the onset of steady state behaviour may be delayed. The possible existence of retardation in rate for styrene in particular, but also for other monomers, has been discussed for polymerizations with RAFT reagents. However, there are different views on the mechanisms involved which have been debated in the current literature [37–41]. A possible interpretation of CRP with reversible transfer is the accumulation of the intermediate species in Scheme 1. In contrast for CRP with reversible deactivation in NMP and ATRP systems, a slow decrease in rate is connected to a build-up of nitroxide and Cu(II), respectively.

The initial rate of copolymerization R_p for each system was calculated by converting fractional conversion to values for concentration of copolymer produced and then taking the slope of a limiting tangent to the data points at low conversion. Values of R_p increased in the order *p*ClStMA > *p*MeStMA > StMA > *p*MeOStMA. Differences in rate may be considered qualitatively by considering the polarity factor *e* in the *Q*-*e* scheme for interpreting copolymerization behaviour [28]. The apparent rate constant for cross-propagation (k_{12}) is dependent upon the differences in polarity of the comonomers, described by the *e* value. The greater the difference in the value of *e* the higher the rate of cross-propagation. It follows that provided the MA copolymers here are strictly alternating then the rate of cross-propagation approximates to the rate of copolymerization. Differences in *e* value between MA and comonomer increase in the order *p*MeSt ~ *p*ClSt > St > *p*MeOSt [28], and this analysis suggests there is a partial correlation between our trends in R_p assessed from experimental data for initial rates and the electronic character of the comonomers. However, these observation have to treated cautiously because of different propagation and termination rate constants in a copolymerizaation system in which retardation effects operate [39,40].

Experimental results for copolymer compositions and monomer feed ratios for copolymers of StMA, *p*MeStMA, *p*ClStMA and *p*MeOStMA are plotted in Figs. 8 and 9, demonstrating that copolymer composition is equimolar (within the experimental error for MA composition) over the range of mol fraction investigated. From these composition results monomer reactivity ratios were determined by the methods outlined in Section 2 and were found to approach zero within experimental error. It is concluded that alternating copolymers are formed in line with expectation for conventional radical copolymerizations.

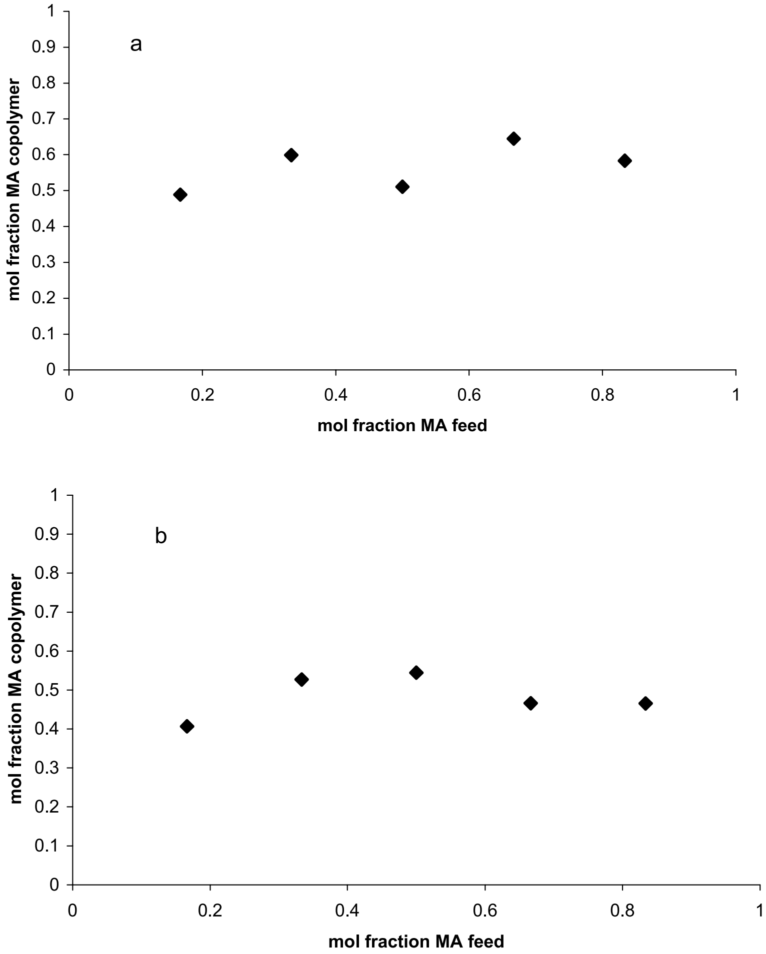


Fig. 8. Copolymer composition and monomer feed plot for RAFT copolymerization in dioxane at 60 °C. (a) StMA. (b) *p*MeStMA.

3.4. Block copolymerization

An important criterion of living ionic polymerization is the capacity to add further monomer, either to extend the kinetic chain length of a homopolymer or to add a different monomer to form a block copolymer [34,42]. In order to assess whether chains of alternating StMA produced in the presence of a RAFT reagent would undergo chain extension, the synthesis of an AB block copolymer of StMA-*b*-*p*MeSt was performed by RAFT polymerisation.

In the preparation of StMA-*b*-*p*MeSt after formation of the A block, no further initiator or RAFT mediator was introduced on addition of *p*MeSt. The overall concentrations of AIBN and BDTB are therefore different with regard to total monomer concentration for the initial StMA copolymer and StMA-*b*-*p*MeSt copolymer. This procedure optimises the attachment of the second B block. Approaches examined by others [13] include the isolation of the A block before reinitiation with further addition of initiator, the A block acting as a macromolecular RAFT reagent. RAFT alternating copolymerization of StMA was allowed to proceed to high conversion (83%) before the addition of the B block with a conversion of 29% for *p*MeSt. SEC chromatograms comparing the A block comprising StMA with StMA-*b*-*p*MeSt are presented in Fig. 10(a). Molar mass data calculated from these chromatograms were $M_n=$ 20,900 g/mol and PDI = 1.23 for StMA copolymer, and values of 24,400 g/mol and 1.38, respectively, for StMA-*b*-*p*MeSt. These results signify the attachment of the B block. Consideration of MH parameters in the Polymer Handbook [43] indicates that a para substituent on styrene does not change solution properties of polymer chains markedly. We estimate that a value of M_n estimated for this block copolymer from an SEC chromatogram is about 10%, i.e. somewhat higher than the molar mass error cited for the universal calibration method with MH parameters in Section 3.1. Broadening of the SEC chromatogram for StMA-*b*-*p*MeSt in Fig. 10(a) and the increase in PDI arise from small shoulders at high and low molar mass. The low molar mass shoulder at retention time 14 min corresponds to the peak retention time of the StMA precursor and may indicate that a small number of chains have failed to initiate the second monomer.

The presence of *p*MeSt in the StMA-*b*-*p*MeSt product was confirmed by ^{1}H NMR spectroscopy by the appearance of a broad peak at ~1.0 ppm indicative of the methyl group

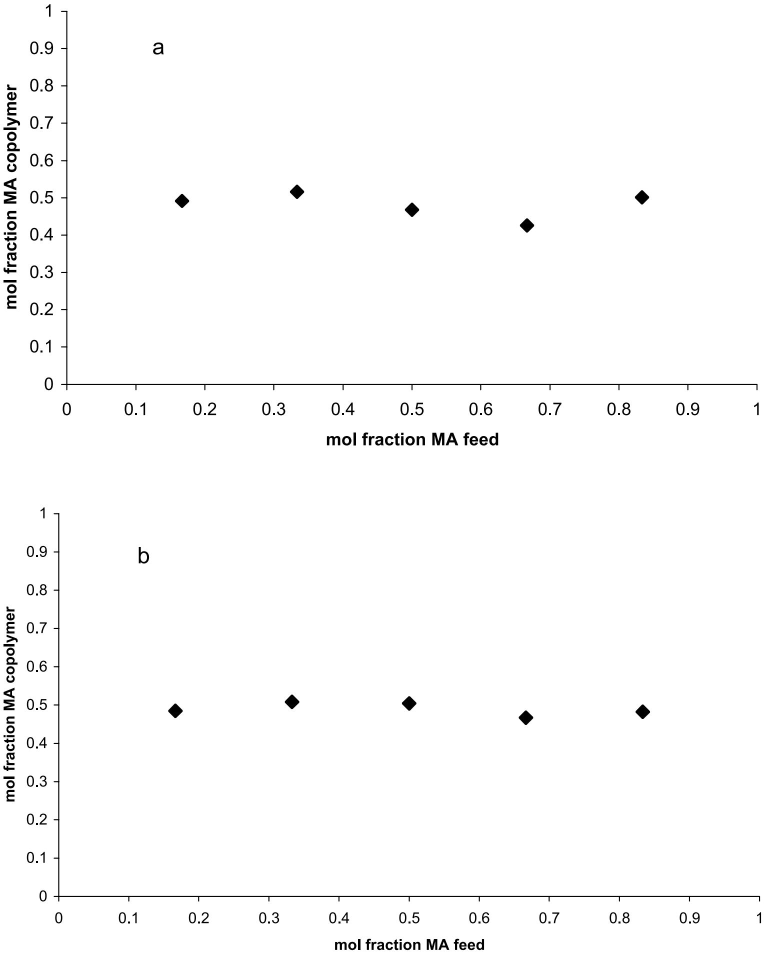


Fig. 9. Copolymer composition and monomer feed plot for RAFT copolymerization in dioxane at 60 °C. (a) *p*ClStMA. 9b) *p*MeOStMA.

associated with *p*MeSt. However, an important test of block copolymer formation is to characterize spectroscopically on-line with SEC. Therefore, StMA-*b*-*p*MeSt was characterized by dual detector SEC, and chromatograms from RI and UV detectors are displayed in Fig. 10(b). Additionally, a UV chromatogram for the StMA precursor is shown. The UV detector at 330 nm is specific to the thiocarbonyl-ended chains, and so the peak height maxima from the two detectors both positioned at a retention time of 13 mins (accounting for the inter-detector delay) is strong evidence for the product being a block copolymer. In passing, it should be noted that RI and UV responses detect masses and numbers of chains, respectively, and so the chromatograms for the two detectors depict mass and number distributions, respectively. Calculations for narrow distributions (e.g. polydispersity ~ 1.2) demonstrate that it is expected that the positions of peak height maxima on the retention time axis will coincide for mass and number distributions [44]. However, in order to facilitate the comparison in Fig. 10(b), the UV chromatograms displayed are mass distributions computed by multiplying the UV response by molar mass from the calibration method according to Eq. (2), as a function of retention time. Therefore, it is observed that BDTB mediation operates during the polymerization in the formation of the B block, contributing to an increase in M_n.

3.5. Observations on RAFT copolymerization of StMA

It is of interest for the participation of the RAFT reagent in a copolymerization to consider that the intermediate radical in chain equilibration in Scheme 1 may have one or both neighbouring MA monomer units indeed, based on observations of RAFT polymerizations at 0 °C by electron spin resonance (esr) spectroscopy Fu-Sheng Du et al. concluded that the intermediate radical for a StMA copolymerization is derived from a MA-ended propagating radical, and they also inferred that their observations aligned with a copolymerization mechanism based on the charge-transfer complex (CTC) model [45]. The question is whether these conclusions from esr measurements are relevant to our copolymerizations at 60 °C. Fu-Sheng Du et al. [45] commented that the relevant esr signal for StMA at 0 °C could not observed at 70 °C, and it is to be expected that CTC formation will be temperature dependent. We

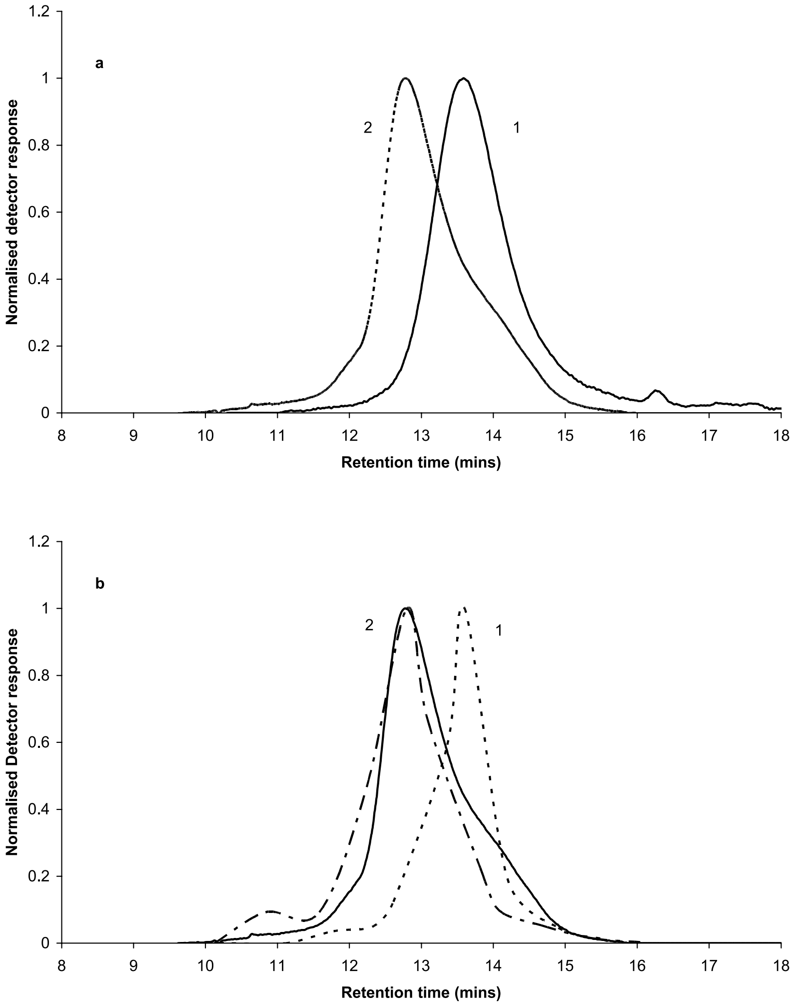


Fig. 10. SEC chromatograms for block copolymer. (a) StMA (solid curve 1); StMA-*b*-*p*MeSt (broken curve 2) (both curves RI detection); (b) Dual detection for StMA-*b*-*p*MeSt (solid curve RI detection, broken curve 2 UV detection at 330 nm), and for comparison StMA (broken curve 2 UV detection at 330 nm). (UV chromatograms converted to mass distributions by multiplying the UV response by molar mass).

attempted both ^{1}H NMR and UV spectroscopy experiments in order to establish the existence of a CTC for MA copolymerized with St and with *p*MeOSty monomers. However, scanning UV spectroscopy did not reveal a unique absorbance that could be assigned to a CTC. Whilst a shift in the peak due to MA in ^{1}H NMR experiments was observed, the results were not reproducible and so a reliable result for a CTC equilibrium constant was not obtained. Even if a CTC is present, it does not have to participate in copolymerization. In relation to the kinetics of copolymerization above, reference has been made to the polarity factor *e* in the *Q*-*e* scheme for correlating an alternating tendency. Whilst CTC formation might contribute to the copolymerization, the lack of sound spectroscopic evidence leads to the conclusion that a model based on polar contributions brought about by differences in donor strength of the electron donor monomers influences the mechanism. Indeed, general observations suggest that discrimination amongst copolymerization models is not straightforward [46], but Sanayei et al. [47] reported evidence that StMA obeys the penultimate model with the majority of propagating radicals carrying a terminal St unit.

3.6. Copolymerization of α-methylstyrene with maleic anhydride

Copolymers of αMeSty and MA were prepared with BDTB [0.024 mol% wrt MA] and AIBN [0.012 mol% wrt MA], and compositions were found to be constant near equimolar across the [MA] range from 0.005 to 0.025 mol. From the composition data monomer reactivity ratios were determined by the methods outlined in Section 2 and were found to approach zero within experimental error. Results for molar mass are collected in Table 2. It is observed that molar mass does not vary with conversion and that copolymer of high molar mass is formed early in the reaction, which are both typical of conventional radical polymerizations. Therefore, it is presumed that initiation,

Table 2

RAFT Copolymerization results for (MeStMA in dioxane at 60 °C (M_1:M_2=50:50)

Sample	Time (mins)	Yield (g)	Fractional conversion	M_n (SEC) (g mol^{-1})	PDI (M_w/M_n (SEC))	M_n (Calc) (g mol^{-1})	$[M]_0$ (mol dm^{-3})	$[M]_f$ (mol dm^{-3})	Ln ($[M]_0/[M]_f$)
MCD249	60	0.24	0.07	17,400	1.77	1400	3.0	2.78	0.08
MCD250	128	0.37	0.11	14,000	1.86	2200	3.0	2.66	0.12
MCD251	249	0.46	0.14	13,000	1.84	2700	3.0	2.58	0.15
MCD252	491	0.62	0.19	18,700	1.71	3700	3.0	2.44	0.21
MCD253	1303	1.49	0.45	16,800	1.76	8900	3.0	1.64	0.60
MCD254	5565	3.06	0.93	16,300	1.88	18,200	3.0	0.21	2.64

propagation and termination are rapid with dead copolymer chains being formed early in the reaction. Longer reaction times serve only to increase conversion to polymer and have no effect on molar mass. Values of polydispersity in the range $M_w/M_n=1.7$–1.9 indicate an expected MMD for a conventional radical polymerization.

Comparison of the conversion data in Table 2 with results in Fig. 6 indicates that the rate of copolymerization for αMeStMA is significantly lower than StMA. This effect appears to be due to steric hindrance of the α-methyl group, as αMeSt is a stronger donor monomer than St. The isolated products were white rather than the pink colour observed with previous successful RAFT copolymerizations of StMA, *p*MeStMA, *p*ClStMA and *p*MeOStMA. This observation along with the data for the dependence of molar mass on conversion suggests that RAFT mediation by BDTB was ineffective in the copolymerization of αMeStMA. Dual detector SEC with a UV detector set at 330 nm in series with a RI detector was used to examine the presence of thiocarbonyl-ended chains. SEC chromatograms for a PS standard, StMA copolymer prepared by RAFT copolymerization and αMeStMA copolymer also prepared by RAFT copolymerization are presented in Fig. 11. Examination of the chromatogram for PS reveals a strong peak due to the RI detector and only a very weak peak from the UV detector set at 330 nm. UV detectors for SEC are more sensitive than RI detectors as is illustrated by the difference in peak intensities for StMA. The S=C–S chromophore absorbs at 330 nm and a lack of absorbance for PS, produced by anionic polymerization, confirms that the UV detector is selective for chains ended with a thiocarbonyl fragment. Equal concentrations of StMA and αMeStMA copolymers of similar molar mass were analysed. The key observation in Fig. 11 is the ratio of the peak heights for the UV and RI detectors respectively. It is evident that a significantly higher UV absorbance relative to the RI response is detected for StMA copolymer compared to αMeStMA copolymer. End group detection at 330 nm provides confirmation that there is a significant reduction in concentration of thiocarbonyl ended chains when RAFT copolymerization is used to prepare αMeStMA copolymers compared to StMA copolymers.

It is of interest to consider the conclusion of Fu-Sheng Du et al. [45] that the intermediate radical in Scheme 1 for a StMA copolymerization is derived from a MA-ended propagating radical. This appears not to be a unique explanation of the results reported here, since we observe different levels of control in RAFT copolymerizations for substituted styrene monomers when MA monomer is held constant, compare *p*MeOStMA in Fig. 4 with StMA in Fig. 3, and in particular there is a lack of control for αMeStMA with BDTB. Scheme 1 is a presentation of the addition-fragmentation mechanism in which *R* is defined by CH_2Ph for BDTB, in which the intermediate radical fragments in favour of the radical leaving group by cleaving the S–CH_2 bond. Alternatively, it may be presumed that in the case of

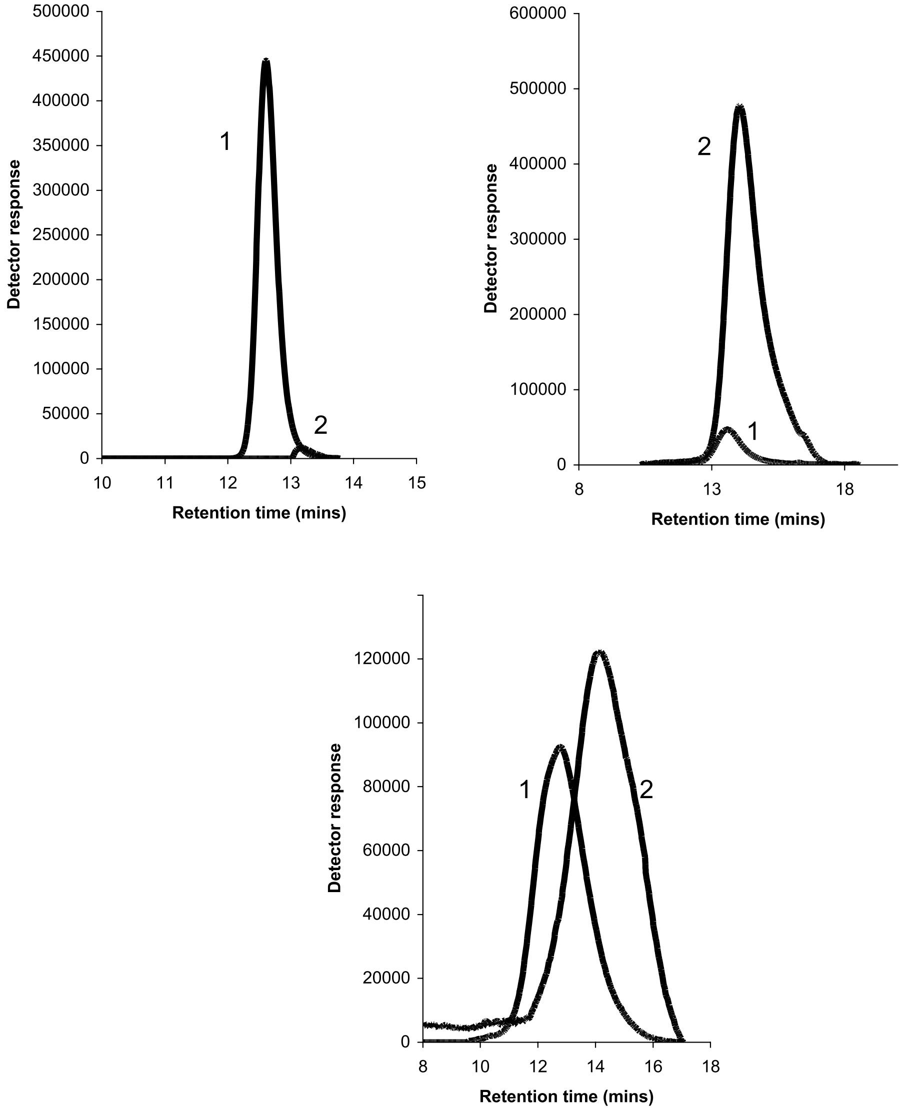


Fig. 11. Dual detection SEC for PS Standard (upper left), StMA (upper right) and αMeStMA (below) ((1) RI detector; (2) UV detector at 330 nm).

αMeStMA fragmentation might result in a chain with an αMeSt ended radical. Therefore, when the αMeSt propagating centre and the RAFT reagent are reformed, a new chain cannot be initiated and further monomer is added to the active chain. This will tend to generate characteristics of conventional radical polymerization and a reduced concentration of thiocarbonyl ended chains. Similar observations have been reported for poly(methyl methacrylate) (PMMA), which also contains a tertiary radical propagating centre [48]. In this study, the RAFT reagent contained a leaving group which yielded a primary radical, and fragmentation to reform the PMMA radical was favoured resulting in uncontrolled polymerization. Chong et al. [37] indicated that lack of control in MMA polymerizations was due to the relatively low chain transfer constant of BDTB, and presumably this could be true for αMeSt. Undoubtedly, characteristic features of αMeSt such as steric hindrance of the monomer caused by the α-methyl substituent, enhanced cross propagation with MA due to the increased electron donating capacity of αMeSt monomer, and formation of stabilized tertiary radicals are likely to influence the participation of BDTB whose involvement may not always release the benzyl radical as the leaving group according to Scheme 1.

4. Conclusions

RAFT polymerization using BDTB as mediator has been used to copolymerize MA with St and with three para-substituted St monomers. All copolymers had an alternating chain structure. Whilst these copolymerizations display features such as an increase in molar mass with monomer conversion, narrow MMD and end group functionality for formation of block copolymer, which are also observed in living ionic polymerization, the experimental molar masses for all copolymers were higher than those expected based on the quantitative participation of the RAFT mediator. The resulting tendency towards high molar mass copolymer broadens the MMD. It is concluded that these copolymerizations exhibit apparent living character, and polymerizations incorporating mediation by RAFT deliver well defined copolymers. In the case of copolymerizations of αMeSt with MA in the presence of BDTB, results for molar mass and polydispersity are consistent with behaviour in a conventional radical polymerization. For αMeStMA copolymerizations, the fragmentation equilibrium could be shifted towards the propagating chain radical rather than the leaving group.

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