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Effect of comonomer composition on the controlled free-radical copolymerization of styrene and maleic anhydride by reversible addition–fragmentation chain transfer (RAFT)

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Abstract

Controlled free-radical copolymerization of styrene and maleic anhydride was performed in 1,4-dioxane or tetrahydrofurane solution at 60 °C using the RAFT technique. The effect of monomer feed ratio on copolymerization kinetics and on control over molar mass distribution was examined. It was shown that polymerization was faster and quality of control was poorer when the proportion of maleic anhydride in the monomer feed was larger. These features were assigned to a decrease in the chain transfer constant of the polymeric RAFT agent, most probably due to an increase in the apparent rate constant of propagation with the proportion of maleic anhydride.

Keywords: Controlled free-radical polymerization; Reversible addition–fragmentation chain transfer; Maleic anhydride

1. Introduction

Free-radical polymerization is an extensively used polymerization technique because, besides the easy manipulation, it is applicable to a great variety of monomers [1]. Additionally, with random copolymerization, the range of accessible structures and properties is much broader, covering an unlimited field of possible applications. The types of available structures has recently been extended with the advent of controlled radical polymerization (CRP) [2,3], allowing the simple synthesis of block copolymers and of polymers with more complex architectures [4–6]. A multitude of new macromolecules has been generated, the properties of which are under investigation or still unknown. Besides the exciting possibility of creating new polymers, CRP also offers the chance to better control the structural characteristics of macromolecules that have been known and applied for a long time. This has been the case for most homopolymers (styrene and derivatives, acrylates, methacrylates,…, etc.). Numerous investigations now concern random copolymers. A great advantage of CRP is that these copolymers exhibit not only a homogeneous molar mass distribution, but also a homogeneous composition distribution [5,7]. With the composition drift, a gradient structure can also be observed. In the specific case of copolymerization of an electron-donor monomer and an acceptor one, for example styrene (S) and maleic anhydride (MA), alternate structure is obtained, under selected conditions [8,9]. Composition distribution is necessarily narrow in this case, and the advantage of CRP would be on a better control of the molar mass and molar mass distribution, along with the possible incorporation of such structure in a more complex copolymer architecture. CRP of styrene and maleic anhydride has already been applied, using nitroxides [10,11] and the reversible addition–fragmentation transfer (RAFT) technique [12–18]. When nitroxides were used as mediators, the required polymerization temperature was above 80 °C, which is the upper limit to observe perfect alternance. With an initial proportion of styrene equal to 0.9, a diblock copolymer was obtained in a one step process: the first block was a copolymer with a 2/1 styrene/maleic

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Table 1
Experimental conditions for the copolymerization of styrene and maleic anhydride in 1,4-dioxane or THF solution in the presence of BTB at 60 °C, and effect of initiator concentration and monomer feed ratio on initial conversion rate

Expt.	Solvent	$[S]_0$ (mol l^{-1})	$[MA]_0$ (mol l^{-1})	$f_{S0} = \frac{[S]_0}{[S]_0 + [MA]_0}$	$[AIBN]_0$ (10^{-3} mol l^{-1})	$[BTB]_0$ (10^{-2} mol l^{-1})	Initial conversion rate (10^{-5} s^{-1})
1	Dioxane	3.13	3.13	0.50	1	1	6.4
2	Dioxane	3.13	3.13	0.50	5	1	12.8
3	Dioxane	3.13	3.13	0.50	0	1	0.8
4	Dioxane	3.13	3.13	0.50	0	0	0.8
5	Dioxane	4.43	1.48	0.75	1	1	3.4
6	Dioxane	4.43	1.48	0.75	5	1	5.1
7	Dioxane	5.10	0.55	0.90	1	1	1.2
8	Dioxane	5.10	0.55	0.90	5	1	2.7
9	THF	4.00	1.34	0.75	5	1	

anhydride molar composition, the second block was pure polystyrene [10]. The advantage of the RAFT technique is that it can operate at temperatures lower than 80 °C, like classical radical polymerization. The possibility of forming a diblock copolymer in a one pot recipe also exits, like in nitroxide-mediated polymerization, but the improvement is that the first block exhibits a better alternance, owing to the lower reaction temperature [16]. Whereas S and MA have already been copolymerized in a controlled fashion in the aim of forming well-defined structures and of studying their properties, very little work has actually been performed on the features of the controlled polymerization itself. In this work we studied RAFT copolymerization of styrene and maleic anhydride and focused on the effect of comonomer composition on kinetics and on control over molar mass and molar mass distribution.

2. Experimental part

2.1. Materials

Styrene (Acros, 99% purity) was purified from inhibitor by washing with 10% aqueous solution of NaOH and then with water; after drying over $MgSO_4$, it was filtered and distilled under vacuum. Maleic anhydride (Acros, 99% purity) was purified from maleic acid by sublimation. Azobisisobutyronitrile (AIBN, Aldrich, 99% purity) was recrystallized from ethanol and dried under vacuum. Benzylmercaptan (Aldrich, 99% purity) and S-(thiobenzoyl)thioglycolic acid (Aldrich, 99% purity) were used as received. 1,4-Dioxane (SDS, 99.5% purity) and tetrahydrofurane (THF, Prolabo, 99% purity) were distilled on CaH_2 before use.

3. Synthesis of S-benzyldithiobenzoate (BTB)

S-(Thiobenzoyl)thioglycolic acid (10.6 g, 0.05 mol) was dissolved in dilute alkaline solution containing two equivalents of NaOH (4.0 g, 0.1 mol in 400 ml H_2O). Then, benzylmercaptan (6.82 g, 0.055 mol) was added under stirring, at room temperature. First, the colour changed from orange to light pink, then to deep pink, while dark red drops appeared simultaneously. The mixture was stirred for a period of 15 h. Afterwards, S-benzyldithiobenzoate, which separated out as a heavy dark red oil, was extracted with ether (1 × 600 ml, 1 × 300 ml). The organic extracts were washed with 0.1N aqueous NaOH (3 × 300 ml) and water (3 × 300 ml), then dried over $MgSO_4$, filtered and evaporated. The yield of S-benzyldithiobenzoate (BTB), which remained as a dark red oil after purification, was 94%.

^{1}H-NMR ($CDCl_3$) δ [ppm]: 4.85 (s, CH_2), 7.36–7.44 (m, Ar–H), 8.07–8.11 (d, Ar–H)
^{13}C-NMR($CDCl_3$) δ [ppm]: 227.2 (C=S), 144.4; 132.2–134.7; 126.7–129.1 (Ar), 42.1 (CH_2)

3.1. Polymerization conditions

Maleic anhydride and styrene were first dissolved in the selected solvent, namely 1,4-dioxane or THF. Then AIBN was added, followed by the appropriate amount of BTB. The solutions were poured into ampules (2.5 ml in each) and degassed down to 5×10^{-3} mmHg residual pressure using four freeze-vacuum-thaw cycles. They were immersed, for the required period of time, into an oil bath thermostated at 60 °C. After polymerization, the reaction mixtures were cooled by liquid nitrogen and, when necessary, diluted with acetone. The recovered polymers were precipitated carefully into dry diethyl ether, filtered and dried under vacuum. The experimental conditions are summarized in Table 1.

3.2. Polymerization kinetics

Polymerization kinetics was investigated at the Polymer Department of Moscow State University using a Calvet type differential automatic calorimeter DAK-1-1a. An ampoule containing 0.2 ml of the polymerization medium was put into the working cell. Another ampoule containing the same volume of a previously polymerized reaction medium was put in the reference cell. The amount of released heat was measured in isothermal conditions (60 °C). The conversions were calculated by integration of the calorimetric curves, using the enthalpy of polymerization: for styrene homopolymerization $\Delta H = -69$ kJ mol^{-1} [19] and for styrene–maleic anhydride copolymerization, $\Delta H = -82.5$ kJ mol^{-1} [19]. For experiments **3** and **4** (Table 1) gravimetry was used to investigate the polymerization kinetics. Similarly, for all other experiments, gravimetry was used to measure the overall conversion of the samples selected for molar mass analysis; as maleic anhydride does not evaporate, this was done by weighing the copolymers after precipitation, as described in Section 3.1.

3.3. Analytical techniques

Average molar mass and molar mass distribution of the copolymers recovered after precipitation were measured by size exclusion chromatography (SEC). The analyses were carried out in THF solution at room temperature, with a flow rate of 1 ml min^{-1}. Separation was performed using a GPC Vorsaule PSS SDV 8 × 300 mm, 5μ, linear column. The apparatus is equipped with a refractive index detector (LDC Analytical refractoMonitor® IV), a UV-detector operating at 254 nm (Waters 484), a Viscotek VE 7510 GPC degasser, a Waters 515 pump and a Viscotek VE 5200 autosampler. Chromatograms were recorded using the TriSec Data Acquisition System software from Viscotek. Molar masses were derived from a calibration curve based on polystyrene standards ($300-1.09 \times 10^6$ g mol^{-1}) and calculation was performed using the TriSec 3.0 GPC Software from Viscotek.

Carbon 13 NMR analysis of the copolymers was performed in d6-acetone solution at room temperature, in 10 mm tube. The apparatus is a Bruker ARX250 spectrometer operating at a frequency of 62.9 MHz for carbon 13. Spectra were recorded using an inverse gate sequence, with 19,230 Hz spectral width, 16 K data points, a nutation angle of 30°, and a relaxation time of 5 s.

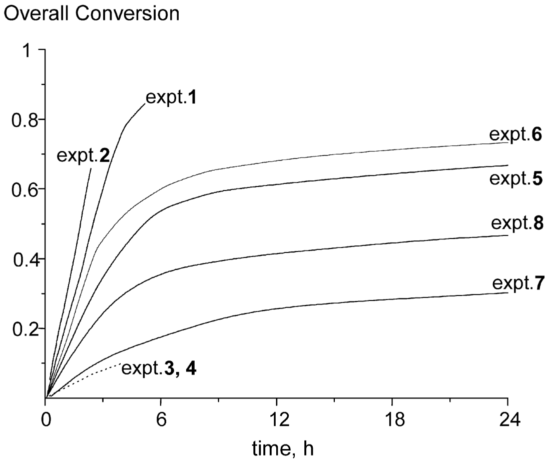


Fig. 1. Kinetics of S–MA copolymerization in 1,4-dioxane at 60 °C at different monomer compositions in the presence of BTB. (See Table 1 for expermental conditions).

4. Results and discussion

We first investigated bulk copolymerization initiated by AIBN in the presence of the RAFT agent, namely BTB. However, owing to the insolubility of the copolymer in the comonomer mixture, solution copolymerization was preferred. 1,4-Dioxane was first selected as a suitable solvent, as reported in previous studies [16,18].

Polymerizations were carried out in 1,4-dioxane at 60 °C in the presence of BTB (Table 1) and the AIBN concentration was varied from 1×10^{-3} to 5×10^{-3} M. Additionally, for two experiments no AIBN was added, one being performed in the presence of BTB (Expt. **3**), the other one in the absence of RAFT agent (Expt. **4**). For the compositions $f_{S0} = 0.50$ and $f_{S0} = 0.90$ (Expts. **1**–**4**, **7** and **8**), the copolymers were soluble in the reaction medium throughout the polymerization. In contrast, the experiments with 75 mol% of styrene (Expts. **5** and **6**) underwent a macrophase separation above 20% conversion; for this reason they were discarded as far as molar mass and molar mass distribution were examined. This phase separation had, however, no significant impact on the copolymerization kinetics as shown below. To account for this phase separation, it should be kept in mind that copolymer composition (more particularly the respective lengths of the copolymer segment and the pure polystyrene one) and S/MA/dioxane ratio changed during the course of the reaction in a different manner for the different systems. This feature might lead to poor solvent conditions under specific initial concentrations and conversions, and would require a more thorough investigation. Interestingly, replacing 1,4-dioxane by tetrahydrofurane (Expt. **9** with $f_{S0} = 0.75$) led to a perfectly homogeneous solution throughout the reaction. For this reason, molar mass and molar mass distribution of the copolymers were examined in comparison with those obtained in 1,4-dioxane.

4.1. Polymerization kinetics

The copolymerization kinetics were investigated by calorimetry for the copolymerizations performed in 1,4-dioxane solution; the results of overall conversion versus time are presented in Fig. 1 and data on initial conversion rate are given in Table 1.

Polymerization proceeded quite rapidly when the initial monomer composition was 50 mol%. However, the increase of styrene proportion in the initial monomer mixture resulted in a dramatic decrease of the polymerization rate. Indeed, to achieve 40% monomer conversion, a reaction time of 1.5 h was sufficient for the 50 mol% initial composition, whereas approximately 9 h were required in the presence of 90 mol% S (for Expts. **2** and **8**, correspondingly). At a given monomer composition, the decrease in AIBN concentration resulted in a lower initial polymerization rate (Table 1), consistent with the classical 0.5th order with respect to the initiator in free-radical polymerization.

To understand the reasons for the change in polymerization rate with the initial proportion of comonomers, it is necessary to take into account two factors. The first one is the previously reported self-initiation of S and MA mixtures [20,21]. The second one is variation of the average propagation rate constant $\langle k_p \rangle$ with comonomer feed ratio. Concerning the composition $f_{S0} = 0.50$ exhibiting the highest polymerization rate, in the absence of added initiator the autopolymerization remained quite insignificant, irrespective of the initial concentration of BTB (Fig. 1 and Table 1). As a consequence, self-initiation alone cannot account for the increase in polymerization rate in the investigated systems. So the effect of monomer composition on the average $\langle k_p \rangle$ seems the most reasonable explanation. Indeed, in classical free-radical copolymerization of S and MA, $\langle k_p \rangle$ was shown to decrease strongly when the initial proportion of styrene was increased [22]. A factor of about 3 was reported for $\langle k_p \rangle$ between copolymerizations with $f_{S0} = 0.50$ and $f_{S0} = 0.90$ molar compositions, which is in correct agreement with our own experimental rate values (Table 1).

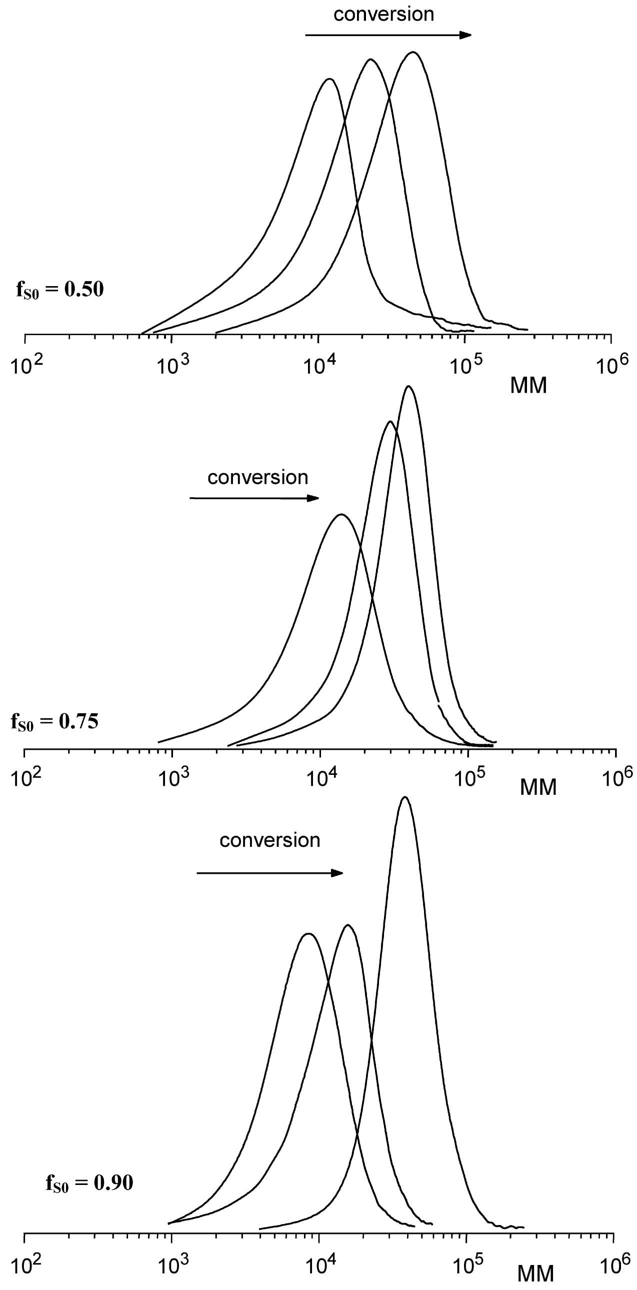


Fig. 2. Size exclusion chromatograms of S–MA copolymers prepared in 1,4-dioxane (expt. **2** with $f_{S0} = 0.50$ and expt. **8** with $f_{S0} = 0.90$) and THF (Expt. **9** with $f_{S0} = 0.75$) at 60 °C with AIBN as an initiator and BTB as a transfer agent. $[\mathrm{AIBN}]_0 = 5 \times 10^{-3}$ mol l^{-1}, $[\mathrm{BTB}]_0 = 10^{-2}$ mol l^{-1}.

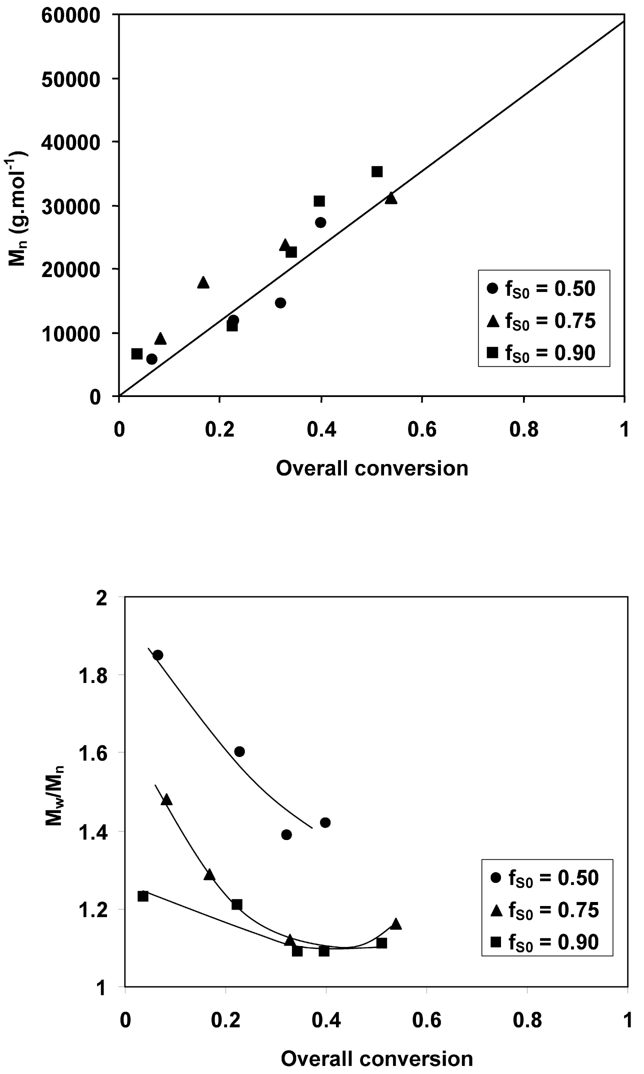
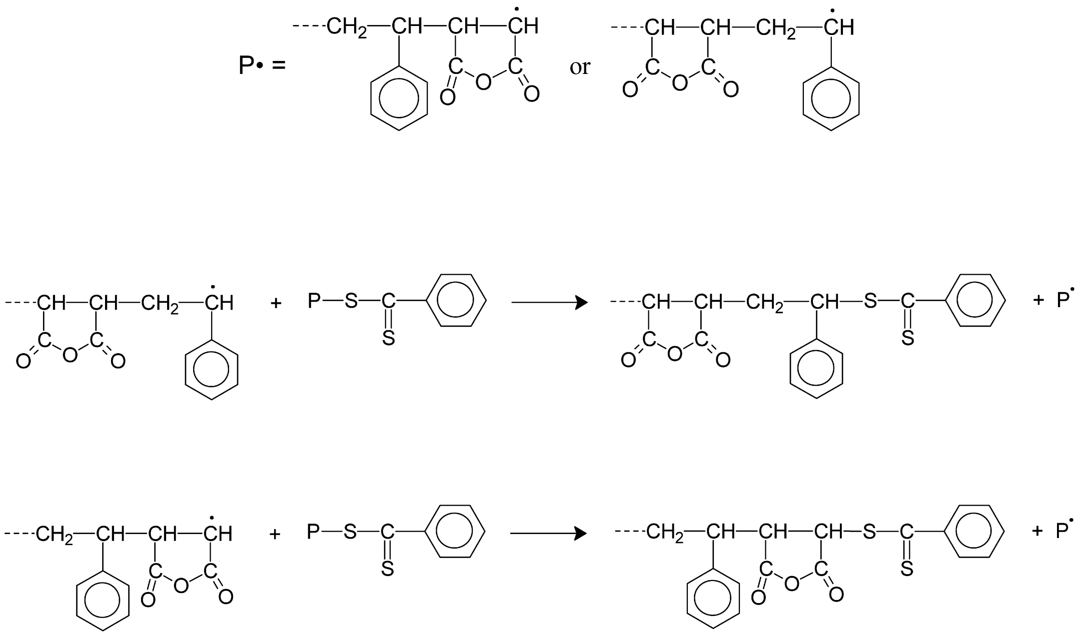


Fig. 3. Molar mass and polydispersity index versus conversion for the S–MA copolymers prepared in in 1,4-dioxane (expt. **2** with $f_{S0} = 0.50$ and expt. **8** with $f_{S0} = 0.90$) and THF (expt. **9** with $f_{S0} = 0.75$) at 60 °C with AIBN as an initiator and BTB as a transfer agent. $[\mathrm{AIBN}]_0 = 5 \times 10^{-3}$ mol l^{-1}, $[\mathrm{BTB}]_0 = 10^{-2}$ mol l^{-1}.



Scheme 1. Possible situations for the exchange reaction in the alternate copolymerization of S and MA.

4.2. Molar mass and molar mass distribution

Molar mass characteristics were investigated for the systems containing 5×10^{-3} M of AIBN and 10^{-2} M of BTB under homogeneous conditions (in 1,4-dioxane for Expts. **2**, **8** and in THF for Expt. **9**). Fig. 2 displays SEC curves at different conversion intervals for the copolymers formed with different monomer feed ratios. For all copolymer compositions, when conversion increased, the SEC peaks shifted towards the region of higher molar masses. This is also illustrated in Fig. 3, which displays the increase in M_n with overall monomer conversion, in a satisfactorily agreement with theory (although data were significantly scattered, which is mainly due to the difficulty of getting accurate conversions by gravimetry for this system—see experimental part), along with the decrease of polydispersity index. For instance, M_w/M_n reached a value of 1.1 for monomer composition $f_{S0} = 0.90$ at 50% conversion. These results fully confirmed that the polymerizations actually proceeded via a controlled mechanism. The quality of control was, however, strongly related to the initial composition of the comonomer mixture. Indeed, for all examined samples, the polydispersity index was significantly larger when the proportion of MA was increased, especially at low conversion (Fig. 3). In addition, the SEC peaks exhibited a tail on the low molar mass side, which was more pronounced when the initial proportion of MA was larger (Fig. 2).

Molar mass characteristics of polymers formed by the RAFT technique are strongly affected by the values of both the chain transfer constant to the low molar mass dithioester ($C_{tr1} = k_{tr1}/k_p$), and the chain transfer constant to the polymeric dithioester ($C_{tr2} = k_{tr2}/k_p$). The former one is related to the consumption rate of BTB [13] and has a direct influence on the variation of M_n with monomer conversion, according to Eq. (1) [23]. C_{tr1} was reported to be 29 for the polymerization of styrene at 110 °C [14], indicating that 77% of BTB is consumed at 5% monomer conversion (in other words, the theoretical over experimental M_n ratio is 0.77). The experimental results of M_n versus conversion in the S and MA copolymerizations (Fig. 3) indicated that C_{tr1} was not much lower for this system, because experimental M_n data followed the theoretical line described by Eq. (2), from early conversions.

$$M_n = \frac{qm_0}{[\mathrm{BTB}]_0(1 - (1 - q)^{C_{tr1}})} \qquad (1)$$

$$M_n = \frac{qm_0}{[\mathrm{BTB}]_0} \qquad (2)$$

In these equations, m_0 is the overall weight concentration of monomers (g l^{-1}) and q is the overall conversion. Providing the transfer to the low molar mass transfer agent is fast enough, the polydispersity index is mainly affected by the chain transfer constant C_{tr2}, which is related to the exchange between active and dormant chains [23,24]. Indeed, it has been shown that M_w/M_n decreases with conversion and, at full conversion $M_w/M_n = 1 + 1/C_{tr2}$ [23]. Consequently, broadening of the molar mass distribution, observed when MA proportion was increased, can be mainly assigned to a variation in the rate of exchange with monomer feed ratio, i.e. a decrease in C_{tr2}. Considering a terminal mode the exchange results from one of the four reactions illustrated in Scheme 1, which depend on the terminal unit of both the incoming macroradical and the dormant polymer chain. All four reactions are described by a specific rate constant of transfer and hence, k_{tr2} is an average value. Therefore, the increase of MA proportion in the initial monomer mixture might result in a decrease of C_{tr2} due to an increase in $\langle kp \rangle$ possibly combined with a decrease of the average rate constant of transfer. Consequently, a better control over molar mass distribution will be obtained by increasing the proportion of S above 0.5 in the comonomer mixture.

4.3. Copolymer structure

The copolymers formed at low conversion were analyzed by ^{13}C-NMR. The purpose was to identify the microstructure according to the previous assignement reported by Nguyen [25]. Expansions in the range 30–60 ppm (carbons of the backbone) and 130–150 ppm (styrene quaternary carbon next to the polymer chain) are shown in Fig. 4. The observed chemical shifts are in perfect agreement with an alternate structure, as reported in Ref. [25]. Indeed, the styrene quaternary carbon exhibits a main peak between 136 and 140 ppm related to the alternating MA–S–MA triad; only a small peak, corresponding to MA–S–S or S–S–S triads appears between 142 and 145 ppm. In the aliphatic carbons region, the three broad peaks between 30 and 60 ppm, also related to the alternating triad, are observed. As a conclusion, the alternate structure, which is usual for conventional radical copolymerization of styrene and maleic anhydride remains preserved, in the presence of a RAFT agent at 60 °C.

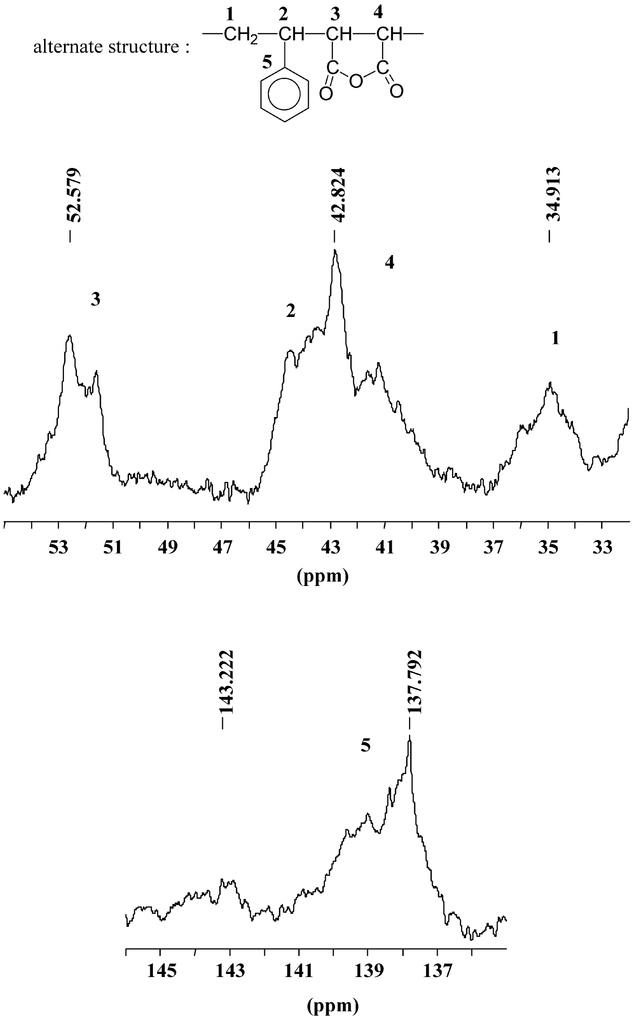


Fig. 4. ^{13}C-NMR spectrum in d6-acetone of the S–MA copolymer from Expt. **6** at 20% conversion. Expansions between 130 and 150 ppm and between 30 and 60 ppm.

5. Conclusions

Styrene and maleic anhydride were copolymerized at 60 °C in the presence of a RAFT agent, S-benzyldithiobenzoate (BTB), in 1,4-dioxane or THF solution depending on the initial composition. The quality of control over molar mass distribution was significantly affected by the initial comonomer composition. It was poorer when the proportion of maleic anhydride was larger. This feature was assigned to a change in the chain transfer constant of the polymeric RAFT agent, mainly due to an increase in the apparent rate constant of propagation with the proportion of maleic anhydride, possibly combined with a decrease of the average rate constant of transfer. In RAFT conditions like in classical free-radical copolymerization, ^{13}C-NMR analysis showed that the expected alternate structure was achieved.

In conclusion, RAFT is a good technique to prepare well-defined poly(styrene-*alt*-maleic anhydride) alternate copolymer that might be further incorporated into more complex architectures, but it is preferable to start the polymerization with an excess of styrene instead of a 50 mol% composition and stop it before (or at) complete MA consumption.

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