Synthesis of Well-Defined Alternating Copolymers by Controlled/Living Radical Polymerization in the Presence of Lewis Acids

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ABSTRACT: Several controlled/living radical polymerization (CRP) techniques (atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), iodide degenerative transfer polymerization (IDTP), and reversible addition−fragmentation transfer polymerization (RAFT)) were studied for the alternating copolymerization of a donor monomer (styrene) and an acceptor monomer (methyl methacrylate or methyl acrylate) complexed with Lewis acid. RAFT polymerization was found to be the most versatile system. The combination of RAFT and Lewis acids complexation techniques allows synthesis of well-defined alternating copolymers poly(styrene-*alt*-methyl methacrylate) with controlled molecular weight (up to $M_n = 70\,000$ g mol^{-1}), low polydispersities ($M_w/M_n < 1.3$), and controlled comonomer sequences (∼90% of alternating triads). These results were obtained in the presence of diethylaluminum chloride and ethylaluminum sesquichloride. Moreover, the alternating copolymers obtained in such copolymerizations retain chain end functionality and were used as macroinitiators for the synthesis of well-defined diblock copolymers poly(methyl methacrylate-*alt*-styrene)-*b*-polystyrene.

Introduction

The target of macromolecular engineering is to design and control several structural parameters of macromolecules (chain length, polydispersity, functionality, composition, microstructure, architecture) in order to precisely adjust their macroscopic properties. In that context, it has been pointed out that controlled comonomer sequence distribution (block, random, alternating, periodic or gradient distributions) may have a significant impact on polymer properties.[1,2] Alternating copolymers belong to a specific class of copolymer in which M_1 and M_2 monomer units alternate in a regular fashion along the chain: ...$M_1M_2M_1M_2M_1M_2$.... Their physical properties have not been fully investigated yet; however, this particular class of polymers may be useful for specific applications.[3]

The ability of a comonomer pair to copolymerize spontaneously in an alternating fashion depends mostly on the polarity of the polymerizable double bonds.[3] For example, electron acceptor monomers with a low electron density double bond will preferentially react with a radical with an electron-donating substituent rather than with their own radical. (It is assumed that the polarization of a radical is similar to its monomer.) This behavior is illustrated by the $Q-e$ classification of monomers,[4] where Q expresses the monomer reactivity and e its polarization (Table 1). Alternation of two monomers is favored when their e values are high and of opposite sign.[3] For example, maleic anhydride ($Q = 0.86$, $e = 3.69$) and styrene ($Q = 1$, $e = -0.8$) copolymerize spontaneously in an alternating fashion. But, for many comonomer pairs, the difference in polarity between electron acceptor and donor monomers is insufficient for an alternating behavior. For example, methyl methacrylate ($Q = 0.78$, $e = 0.40$) and styrene ($Q = 1$, $e = -0.8$) copolymerize only with a small tendency for alternation ($r_S \sim r_M \sim 0.5$). In such case, the tendency toward alternation may be enhanced by a Lewis acid, as first reported by Hirooka et al.[5,6] Subsequently, several studies have shown that Lewis acids such as alkylaluminum chlorides ($EtAlCl_2$, Et_2AlCl, $Et_3Al_2Cl_3$), $ZnCl_2$, $TiCl_4$, BCl_3, or $SnCl_4$ increased the tendency toward alternation for this comonomer pair.[7] The Lewis acid complexes with the polar group of the acceptor monomer and reduces the electron density of the conjugated double bond. This tendency was quantified by Imoto et al., who compared the $Q-e$ values of a $ZnCl_2$−methyl methacrylate complex ($Q = 26.3$, $e = 4.2$) to those of the uncomplexed monomer ($Q = 0.78$, $e = 0.40$).[8]

Table 1. $Q-e$ Parameters for Various Monomers[9]

monomer	Q	e
butyl maleimide	0.88	+3.70
maleic anhydride	0.86	+3.69
phenyl maleimide	2.81	+3.24
methyl acrylate	0.45	+0.64
methyl methacrylate	0.78	+0.40
butyl methacrylate	0.82	+0.28
styrene	1.00	−0.80
isobutene	0.02	−1.20
vinyl isobutyl ether	0.03	−1.27

The mechanism of copolymerization in the presence of Lewis acids has been extensively discussed in the past decades but is still not fully understood. ^{1}H NMR[10] and UV[11] studies showed formation of a ternary complex composed of the donor monomer, the acceptor monomer, and the coordinating Lewis acid (Scheme 1). However, the manner in which this ternary complex participates in the mechanism of an alternating copolymerization was subject to controversy.

Three main mechanisms were proposed (Scheme 2). It was initially proposed that the ternary complex acted as one unit and underwent homopolymerization to an alternating structure (Scheme 2a).[11−13] This mechanism was questioned by several authors, who considered that the concentration of the ternary complex was very low compared to the free monomers and therefore would have to possess an unusual high reactivity to explain

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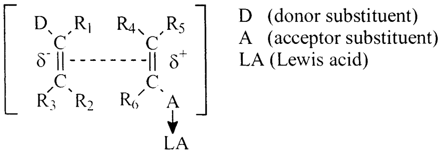
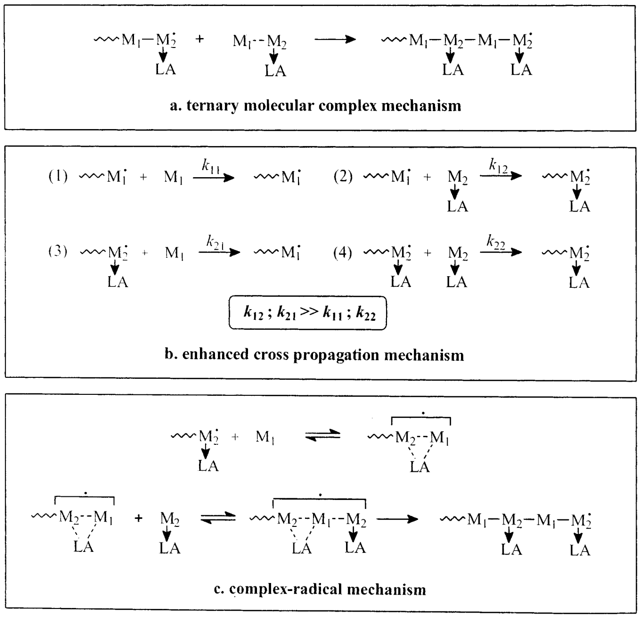
Scheme 1



Scheme 2

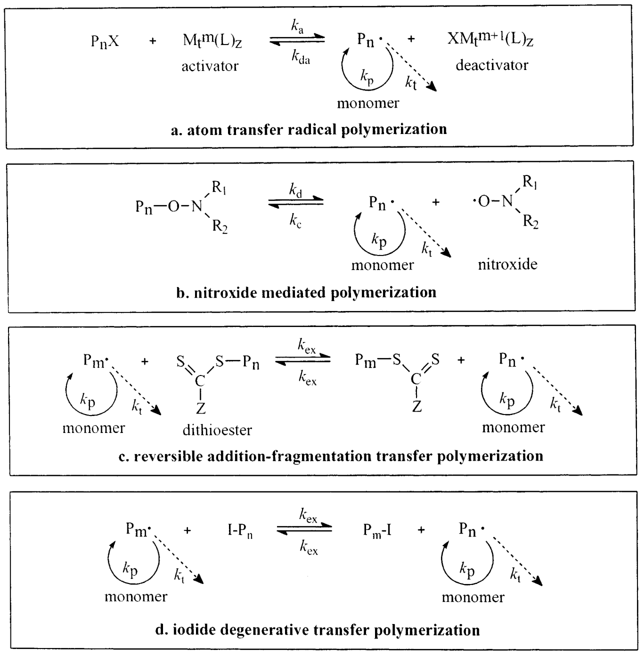


M$_1$: donor monomer ; M$_2$: acceptor monomer ; LA: Lewis acid

the experimental kinetics.[14] Kabanov et al.[15] then advanced a simpler mechanism (Scheme 2b); they postulated that cross-propagation reactions are favored compared to homopropagation, since the addition of a Lewis acid increases the difference in monomer polarity. A third mechanism was proposed by Hirooka et al.,[16] who postulated that the terminal chain acceptor radical formed a ternary complex with the donor monomer and the Lewis acid (Scheme 2c). Most of the recent workers in the field have indicated that the enhanced cross-propagation mechanism is probably the predominant process, regulating alternation (Scheme 2b).[17–22] In particular, Tirrell et al. showed using radical trapping techniques that donor–acceptor complexes do not participate in the mechanism of alternating copolymerizations.[23]

Conventional free radical polymerization conditions have been used in the majority of studies on alternating copolymers.[3] They do not permit control over molecular weight or polydispersity and therefore exhibit a limited potential for macromolecular engineering. Recently, several methods of controlled/living radical polymerization (CRP) have been developed, such as atom transfer radical polymerization (ATRP),[24–26] nitroxide-mediated polymerization (NMP),[27] and degenerative transfer processes with either alkyl iodides via iodide degenerative transfer polymerization (IDTP)[28,29] or dithioesters via reversible addition–fragmentation transfer polymerization (RAFT).[30,31] In these systems, an equilibrium exists between a low concentration of active propagating chains and a large number of dormant chains, which are unable to propagate or self-terminate (Scheme 3).[32] Thus, the probability of bimolecular termination reactions decreases, and the radical polymerization behaves as a controlled/living system.

Scheme 3



CRP allows precise control over macromolecular structures.[1,33–36] However, only a few examples of well-defined alternating copolymers synthesized by CRP have been reported in the literature. The first example was the atom transfer radical copolymerization of acrylates with a large excess of less reactive electron-rich monomers, such as vinyl ethers and isobutene (Table 1).[37,38] Since then, most of the studies have reported copolymers from a combination of comonomers that have a spontaneous tendency for alternation (Table 1): such as a strong electron-accepting monomer (maleic anhydride,[39,40] butyl maleimide,[41] or phenyl maleimide[42–44]) and an electron-donating monomer (styrene). We recently reported, for the first time, the synthesis of a well-defined alternating copolymer, obtained through the combination of CRP and Lewis acids complexation techniques.[45] The RAFT copolymerization of methyl methacrylate and styrene was investigated at 60 °C in the presence of diethylaluminum chloride. This system allows the synthesis of alternating copolymers, which possess controlled chain lengths, polydispersities, and monomer sequence distribution. In the present article, we will discuss in detail the capabilities of several CRP systems for alternating copolymerization of donor/acceptor monomers in the presence of Lewis acids.

Experimental Part

Reagents. Monomers: methyl methacrylate (Aldrich, 99%), methyl acrylate (Aldrich, 99%), and styrene (Aldrich, 99%) were distilled over CaH$_2$ and stored on molecular sieves. Lewis acids: diethylaluminum chloride (97%), ethylaluminum sesquichloride (97%), zinc chloride (beads −10 mesh, 99.999%), and tin(IV) chloride (99%) were purchased from Aldrich and used as received. Initiators: 2,2′-azobis(isobutyronitrile) was recrystallized in ethanol, filtered, and dried. Methyl 2-bromopropionate and ethyl 2-bromoisobutyrate were purchased from Aldrich and used as received. Control reagents: 2,2,6,6-tetramethyl-1-piperidinyloxy (98%), iodoacetonitrile (98%), iodoform (99%), iron(II) bromide (98%), and tetrabutylammonium iodide (98%) were purchased from Aldrich and used as received. *N-tert*-Butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (SG1) (92%) was kindly provided by ATOFINA (CRRA, France). Copper(I) chloride (Acros, 95%) was washed

Table 2. Results of Copolymerization of Styrene with an Acceptor Monomer in the Presence of Et_2AlCl Using Different CRP Techniques

	styrene (mol equiv)	acceptor monomer (mol equiv)	Et_2AlCl (mol equiv)	initiator (mol equiv)	control agent (mol equiv)	temp (°C)	time (min)	$M_{n,exp}$ (g mol^{-1})	M_w/M_n
1	100	100 M[a]	40	1 MBP[b]	1 CuCl/dNbpy[c]	50	0.15		
2	100	100 M	40	1 EBI[d]	1 $FeBr_2$/TBAI[e]	40	13	5 400	2.1
3	150	150 MA[f]	75	0.5 AIBN[g]	1 TEMPO[h]	25	0.01		
4	150	150 MA	75	0.5 AIBN	1 SG1[i]	60	0.01		
5	180	180 MA	72	0.1 AIBN	1 CDB[j]	40	110	15 817	1.32
6	190	190 M	75	0.1 AIBN	1 CDB	60	96	20 000	1.38
7	250	250 M	100	0.3 AIBN	1 iodoacetonitrile	60	30	28 000	1.5
8	250	250 M	100	0.3 AIBN	1 iododoform	60	30	21 600	1.5

[a] Methyl methacrylate. [b] Methyl 2-bromopropionate. [c] Copper chloride/4,4′-di(5-nonyl)-2,2′-bipyridine. [d] Ethyl 2-bromoisobutyrate. [e] Iron bromide/tetrabutylammonium iodide. [f] Methyl acrylate. [g] 2,2′-Azobis(isobutyronitrile). [h] 2,2,6,6-Tetramethyl-1-piperidinyloxy. [i] *N-tert*-Butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide. [j] Cumyl dithiobenzoate.

with glacial acetic acid in order to remove soluble fraction of oxidized species, filtered, washed with ethanol, and dried. 4,4′-Di(5-nonyl)-2,2′-bipyridine (dNbpy)[46] and cumyl dithiobenzoate[47] were synthesized according to published procedures.

Polymerization Conditions in the Presence of Lewis Acid. The dried acrylate monomer and Lewis acid were added to a Schlenk flask in a drybox. The mixture was then stirred for 4 h in order to preform the complex between both reagents. Then, a degassed solution of initiator and a control reagent dissolved in dried styrene was introduced via a degassed syringe. The mixture was heated in a thermostated oil bath, and samples were withdrawn through a degassed syringe at timed intervals.

Synthesis of Diblock Copolymers. The alternating copolymer macroinitiator was dissolved in distilled styrene in a Schlenk flask. The mixture was degassed by flushing with nitrogen for 20 min and then heated to 110 °C.

Analysis. Gel Permeation Chromatography. Molecular weights and polydispersities were measured by gel permeation chromatography (GPC) equipped with a Waters 515 pump and a Waters 2410 differential refractometer using PSS columns (Styrogel 10^5, 10^3, 10^2 Å). GPC was performed using THF as an eluent at the flow rate of 1 mL min^{-1}. Linear poly(methyl methacrylate) standards were used for calibration. Samples were prepared in tetrahydrofuran (HPLC grade). Prior to analysis, a droplet of water was added to the crude samples in order to form a precipitate of hydrated Lewis acid. Then the samples were filtered through 0.2 μm PTFE syringe filters.

600 MHz ^{1}H NMR Spectroscopy. The microstructure of the copolymers was investigated by ^{1}H NMR using a 600 MHz Bruker spectrometer (Avance DRX 600). Spectra were recorded at 28 °C in deuterated chloroform. The crude polymer samples were purified by precipitation by addition to methanol, filtered, and dried under vacuum. The resulting solids were dissolved in tetrahydrofuran and centrifuged at 5000 rpm for 1 h in order to remove a white precipitate of hydrated Lewis acid. The clear solutions were added to methanol for a second time to precipitate the pure polymers, which were then filtered and dried prior to analysis.

Elemental Analysis. The monomer composition of the copolymer was calculated from the results of elemental analysis. Before analysis, samples were purified using the same conditions described above for 600 MHz ^{1}H NMR analysis. The weight fractions of carbon, hydrogen, and oxygen in the samples were measured by Midwest Microlab, LLC (Indianapolis, IN).

Gravimetry. The overall conversion of methyl methacrylate and styrene was determined by gravimetry. (Because of the presence of Lewis acids, the values of conversion measured by a conventional method such as NMR or gas chromatography were inaccurate.) It is important to note that, when exposed to moisture, or solvents containing water, alkylaluminum chlorides react with water, resulting in formation of a white precipitate. It has been shown that several structures of hydrated Lewis acids with different molecular weights may be formed, depending on the conditions.[48,49] Therefore, it is difficult to estimate the contribution of these hydrated forms of the Lewis acid in gravimetry analysis. To overcome this problem, the following procedure was adopted. First, a sample of crude reaction mixture was weighted (typical weight of the samples was around 500 mg). At this stage, the Lewis acid was not hydrated; therefore, its weight contribution to the sample was estimated from the initial weight fraction of the Lewis acid in the reaction mixture. This allowed an estimation of the weight of monomer and polymer in the sample. (The weight contribution of the other reactants was neglected.) Then, the sample was dissolved in a mixture of chloroform (1 mL) and dichloromethane (2 mL). Lewis acid was extracted with 3 mL of water. The organic phase was filtered over a neutral alumina column (80−200 mesh) and then dried under high vacuum (5×10^{-7} Torr) for 10 h. After drying, overall conversion was calculated by comparing the weight of the remaining polymer to the initial weight of monomer and polymer.

Results and Discussion

Comparison of Various CRP Copolymerization Systems in the Presence of Diethylaluminum Chloride. The copolymerization of styrene and an acceptor monomer complexed with a Lewis acid was investigated using various CRP systems (ATRP, NMP, RAFT, and IDTP). For ATRP, RAFT, and IDTP, methyl methacrylate was chosen as the acceptor monomer. In the case of NMP, since nitroxide-mediated polymerization only allows control over methyl methacrylate polymerization in a narrow range of experimental conditions, methyl acrylate was chosen as the acceptor monomer. Diethylaluminum chloride was selected as the Lewis acid, and the ratio of Lewis acid to acceptor monomer (0.4/1) was chosen from the literature data.[7] Table 2 shows the experimental conditions and the most important results for this series of experiments. In the case of ATRP (Table 2, entries 1 and 2), the copolymerization was fast, exothermic, and uncontrolled. After a few seconds of reaction, the polymerization mixture turned black. This behavior is probably due to a side reaction between the basic ligands used for ATRP and the Lewis acid. Another possible side reaction involves diethylaluminum chloride and nitroxyl radicals in the case of NMP (Table 2, entries 3 and 4). Both the TEMPO and SG1 mediated copolymerizations exhibited a violent explosive behavior, even at room temperature. The preparation of well-defined copolymers with controlled molecular weight and narrow molecular weight distribution were only achieved using degenerative transfer systems, such as RAFT and IDTP (Table 2, entries 5−8). In these systems, some side reactions may also occur between the control agent and the Lewis acid; for example, in RAFT polymerizations, the diethylaluminum chloride (Et_2AlCl) may form a complex with the cumyl dithiobenzoate, as evidenced by the formation of an intense orange color (instead of the pink color of the uncomplexed CDB). However, in the presence of Et_2AlCl, the RAFT copolymerization of styrene and an acceptor monomer exhibits controlled/living behavior. IDTP has some limitations due to relatively slow exchange reactions in comparison with propagation. In the presence of Lewis acids, cross-propagation is even faster (vide infra), and copolymers with higher polydispersities were formed.[50] As a result of these preliminary investigations, RAFT was selected as a reference system to determine the capabilities of CRP for materials preparation, since it provided the best control over molecular weight and polydispersity.

Study of RAFT Copolymerization of Styrene and Methyl Methacrylate in the Presence of Diethylaluminum Chloride: A Reference System. The bulk RAFT copolymerization of methyl methacrylate (M) and styrene (S) was conducted at 60 °C in the presence and in the absence of Et_2AlCl. Figure 1a compares the plots of molecular weights M_n and polydispersities M_w/M_n vs conversion for both copolymerizations. In all cases, samples displayed a polydispersity index below 1.5, the molecular weight increases linearly with conversion, and the experimental values are close to the theoretical, assuming quantitative initiation. This behavior shows that the RAFT copolymerization of methyl methacrylate and styrene exhibits controlled/living behavior in both the presence and the absence of Et_2AlCl. These experimental results indicate that the RAFT process, which involves chain transfer with cumyl dithiobenzoate, also takes place in the presence of the Lewis acid. During the 1970s, it was shown that alternating copolymerizations conducted in the presence of Lewis acids were relatively insensitive to the presence of transfer agents such as carbon tetrachloride.[51] Therefore, it was erroneously assumed that the mechanism of such copolymerization was not radical in nature.[52] Our results disagree with this assumption; however, the polydispersity index was found to be higher in the presence of Et_2AlCl than in its absence. This behavior is possibly a consequence of the complexation of cumyl dithiobenzoate end groups with the Lewis acid. This complexation, due to steric and electronic effects, could reduce the rate of the exchange process, which may partially explain the increased polydispersity.[50]

Figure 1b shows the semilogarithmic curves of conversion with time for the RAFT copolymerization of M and S with and without Et_2AlCl. Comparison of the slopes of the conversion curves indicates that the rate of polymerization in the presence of the Lewis acid is about 40 times higher than in the absence of the Lewis acid. This difference may be the consequence of the effect of the Lewis acid on several polymerization parameters. First, the mechanism of initiation with Lewis acid may be more complex. In the absence of Et_2AlCl, the radicals that initiate the RAFT process are generated only by the slow decomposition of AIBN. In the presence of Et_2AlCl, other types of initiation may also take place. It has been shown that some alternating copolymerizations in the presence of Lewis acid may start spontaneously without any added initiator.[14] This behavior may be a consequence of a Redox process involving oxidizable Lewis acids[14] but also could result from possible photolysis of the acceptor monomer−Lewis acid binary complex.[53] However, the difference in the observed rate of polymerization is mainly a result of the increased value of the cross-propagation rate constants in the presence of Et_2AlCl which are much higher than in the absence of Et_2AlCl. This effect is illustrated in Scheme 4 and in Table 3. Scheme 4 shows all the propagation steps which occur in the absence of the Lewis acid (steps 1−4) and in the presence of the Lewis acid (steps 1−8). Table 3 shows the value of the rate constants of propagation associated with all these steps at 20 °C. First, the values confirm the hypothesis of an enhanced cross-propagation mechanism, since k_{S-MC} and k_{MC-S} are significantly higher than the homopropagation rate constants k_{SS}, k_{MM}, k_{MC-M}, k_{MC-MC}, and k_{M-MC}. At 20 °C, the addition rate constant of the methyl methacrylate/Lewis acid complex onto the styryl radical

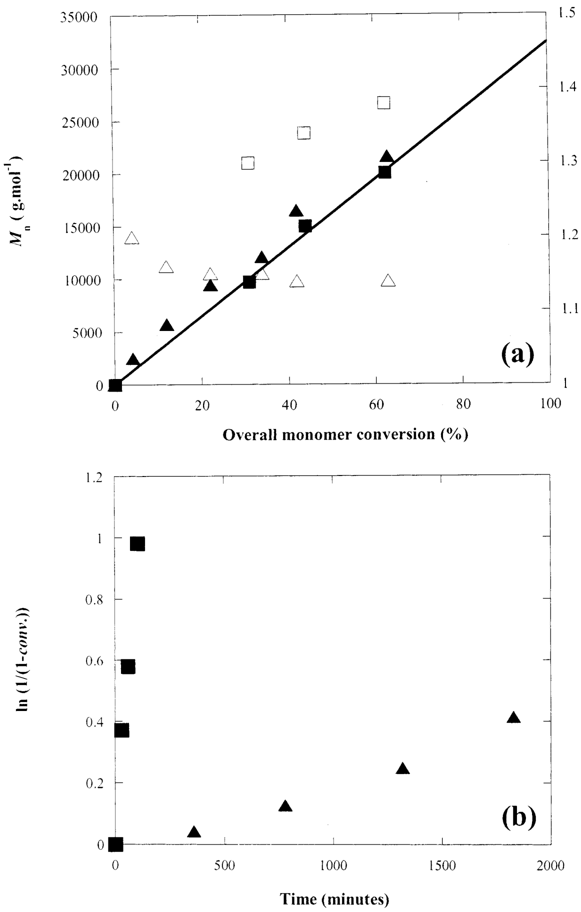
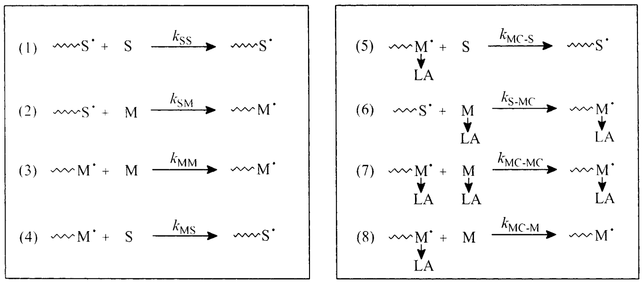


Figure 1. (**a**) Number-average molecular weight M_n (filled symbols) and polydispersity index M_w/M_n (empty symbols) as a function of overall monomer conversion (conv). (**b**) ln(1/(1 − conv)) vs time for the bulk copolymerization of methyl methacrylate and styrene at 60 °C: $[S]_0 = 3.67$ mol L^{-1}; $[M]_0 = 3.67$ mol L^{-1}; $[AIBN]_0 = 1.96 \times 10^{-3}$ mol L^{-1}; $[CDB]_0 = 1.96 \times 10^{-2}$ mol L^{-1}; $[Et_2AlCl]_0 = 0$ mol L^{-1} (▲, △), 1.47 mol L^{-1} (■, □). Theoretical $M_n = ([M]_0 + [S]_0)(conv)(104.15 + 100)/(2(2[AIBN]_0 + [CDB]_0))$.

Scheme 4



S: styrene ; M: methyl methacrylate ; MC: methyl methacrylate/Lewis acid complex ; LA: Lewis acid

Table 3. Rate Constants of Propagation for the Copolymerization of Methyl Methacrylate and Styrene at 20 °C in the Presence of Diethylaluminum Chloride

constant	value ($L\ mol^{-1}\ s^{-1}$)	reference
k_{SS}	70	Buback et al.[55]
k_{SM}	150	calculated from k_{SS} and $r_S = 0.45$[9]
k_{MM}	275	Beuermann et al.[56,57]
k_{MS}	580	calculated from k_{MM} and $r_M = 0.47$[9]
k_{S-MC}	1750	Sigwalt et al.[58]
k_{MC-S}	875	calculated from k_{S-MC} and $k_{MC-S}/k_{S-MC} = 0.5$[22]
k_{MC-MC}/k_{M-MC}	0	Sigwalt et al.[53]
k_{MC-M}	70	calculated from k_{MC-S} and $k_{MC-M}/k_{MC-S} = 0.08$[58]

k_{S-MC} is about 12 times higher than that of an uncomplexed methyl methacrylate k_{S-M}. At the same temperature, the rate constant of addition of styrene to the complexed methacrylic radical k_{MC-S} is nearly 2 times higher than the rate constant of addition of styrene to noncomplexed methacrylic radicals k_{M-S}. These differences suggest a higher rate of polymerization at 20 °C in the presence of Et_2AlCl that in its absence. At 60 °C, this difference in rate of polymerization is expected to be lower but still significant as observed experimentally. Consequently, the ratio of the average rate constant of propagation to that of RAFT exchange is higher in the presence of Et_2AlCl than without, which additionally explain the enhancement of polydispersity observed in the presence of Lewis acids.[50,54]

Figure 2 compares the ^1H NMR spectra of the copolymers P(M-*co*-S) synthesized with and without Et_2AlCl. According to the literature,[59-62] the region from 3.7 to 2.1 ppm is due to the methoxy protons of the poly(methyl methacrylate). This region can be divided into three subregions 3.7−3.2 ppm (*X*), 3.2−2.7 ppm (*Y*), and 2.7−2.1 ppm (*Z*), respectively representative of the M-centered triads with zero, one, and two meso MS diads (Figure 3).[60,61]

The fractions of the various M-centered triads (MMM (homopolymer), MMS + SMM (hetero), SMS (alternating)) may be correlated to the fractions of the areas *X*, *Y*, and *Z* of the methoxy resonance of the copolymer (eq 1−3).[63]

$$F_x = F_{MMM} + 2(1 - \sigma)F_{MMS} + (1 - \sigma)^2 F_{SMS} \quad (1)$$

$$F_y = 2\sigma F_{MMS} + 2\sigma(1 - \sigma)F_{SMS} \quad (2)$$

$$F_z = \sigma^2 F_{SMS} \quad (3)$$

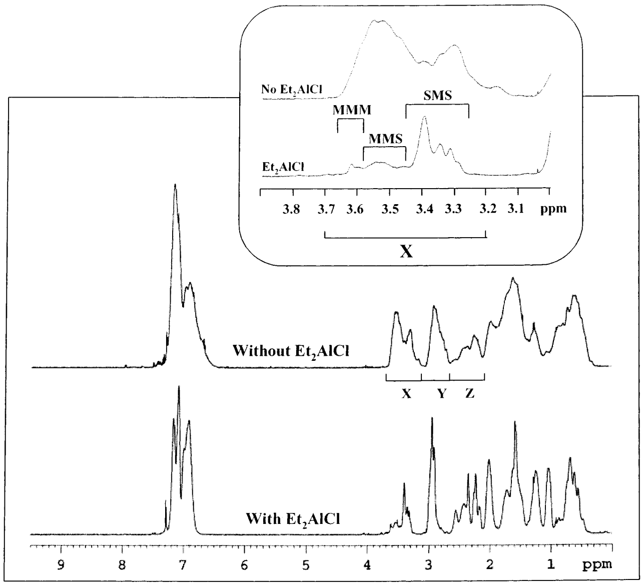
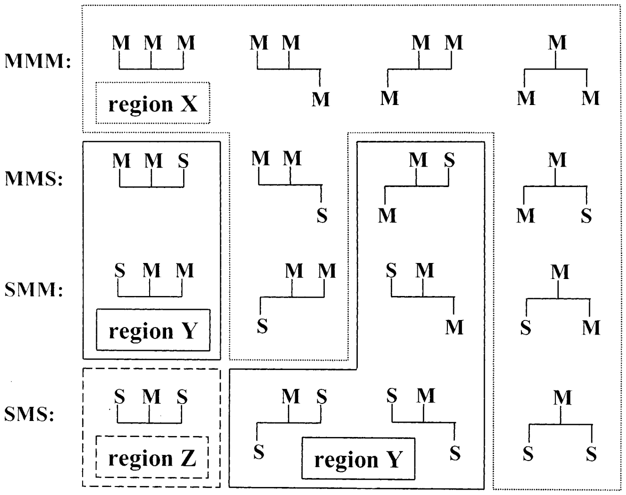


Figure 2. 600 MHz ^1H NMR spectra of copolymers P(M-*co*-S) in $CDCl_3$ at 28 °C. Inset shows the expansion of the region *X* (3.2−3.7 ppm).



X: triads including no meso MS diad ; **Y:** triads including one meso MS diad
Z: triads including two meso MS diads

Figure 3. Possible methyl methacrylate-centered triad configurations for the copolymerization of methyl methacrylate and styrene and their location in ^1H NMR spectra.[60]

Here σ represents the probability of alternating M and S units having the same "coisotactic" configurations, with the assumption that σ is constant regardless of the sequence of addition (i.e., $\sigma = \sigma_{MS} = \sigma_{SM}$). This σ parameter may be calculated from eq 4[63,64]

$$\sigma = (1 - F_x^{1/2})(1 + r_M f_M/f_S) = (1 + r_M f_M/f_S)/(1 + 2F_x/F_y) \quad (4)$$

where r_M is the reactivity ratio of the methacrylic radical, f_M is the mole fraction of methyl methacrylate in the monomer feed, and f_S is the mole fraction of styrene in the monomer feed.

Table 4 shows the value of F_x, F_y, F_z, f_M/f_S, r_M, and σ for copolymerization systems both with and without added Lewis acid. The areas *X* and *Y* can be determined by direct integration of the NMR spectra with measurement errors less than 1%. Because of overlap with the methine region, area *Z* cannot be measured by integra-

Table 4. Microstructure Parameters for Styrene and Methyl Methacrylate Copolymerization with and without Lewis Acid

	without Et_2AlCl	with Et_2AlCl
F_x[a]	0.499	0.259
F_y[a]	0.404	0.497
F_z[a]	0.096	0.244
f_M/f_S	1	1
r_M	0.47[9]	0.08[58]
σ[b]	0.43	0.53
F_{SMS}[c] (%)	52	87
$2F_{MMS}$[c] (%)	34	12
F_{MMM}[c] (%)	14	1

[a] Measured by ^1H NMR. [b] Calculated from eq 4. [c] Calculated from eqs 1−3.

tion; however, O'Driscoll et al.[65] have shown that the area Z can be analyzed by using eq 5.

$$\text{area } Z = (3/8)(F_M)(\text{total area of the spectra}) - \text{area } X - \text{area } Y \quad (5)$$

It has been reported that Lewis acids may influence the stereocontrol of radical polymerization of methacrylic monomers.[66] Indeed, the value of σ calculated for the Et_2AlCl complexed copolymerization of M and S (Table 4) is higher than the value calculated for the copolymerization without Lewis acid. However, as already reported,[67] this difference is not significant enough to suggest stereocontrol in the presence of Et_2AlCl.

The values of F_x, F_y, F_z, and σ were used to calculate the fractions of the M-centered triads (Table 4) from eqs 1−3. Without the addition of Et_2AlCl, the proportion of hetero triads MMS + SMM ($2F_{MMS}$) is equal to 34%. This indicates that, in the absence of Lewis acid, the resulting copolymer has a low tendency toward alternation. On the other hand, the predominant structure in the presence of Et_2AlCl is the alternating triad SMS, with a content of 87%. The copolymers synthesized in the presence of Et_2AlCl are therefore predominantly alternating P(M-*alt*-S). This microstructure of the copolymer can also be qualitatively evaluated from the expanded region X.[61] Within this region (inset, Figure 2), it is possible to distinguish three signals: a signal from 3.25 to 3.44 ppm due to the alternating triad SMS, a signal from 3.44 to 3.58 ppm due to the hetero triad MMS, and a signal from 3.58 to 3.65 ppm due to the homopolymer triad MMM. The signals inside region X are broad when no Lewis acid was used. This behavior indicates that, in the absence of an added Lewis acid, the copolymer contains all possible triads. On the other hand, when Et_2AlCl was added, while it is possible to distinguish all three previously described peaks inside the range 3.7−3.2 ppm, the most intense peaks are due to the alternating triad, SMS. In conclusion, RAFT copolymerization conducted in the presence of a Lewis acid allows the synthesis of well-defined alternating copolymers, which possess controlled chain lengths, polydispersities, and sequence distribution whereas RAFT copolymerization alone only controls the chain length and polydispersity. Figure 4 compares the kinetics of Lewis acid complexed copolymerization of M and S in bulk and in toluene solution. As expected, a slower rate of polymerization was observed for the diluted system. However, in both cases a similar control over molecular weight, polydispersity, and comonomer sequences was observed. Slightly higher alternating control was observed in toluene solution.

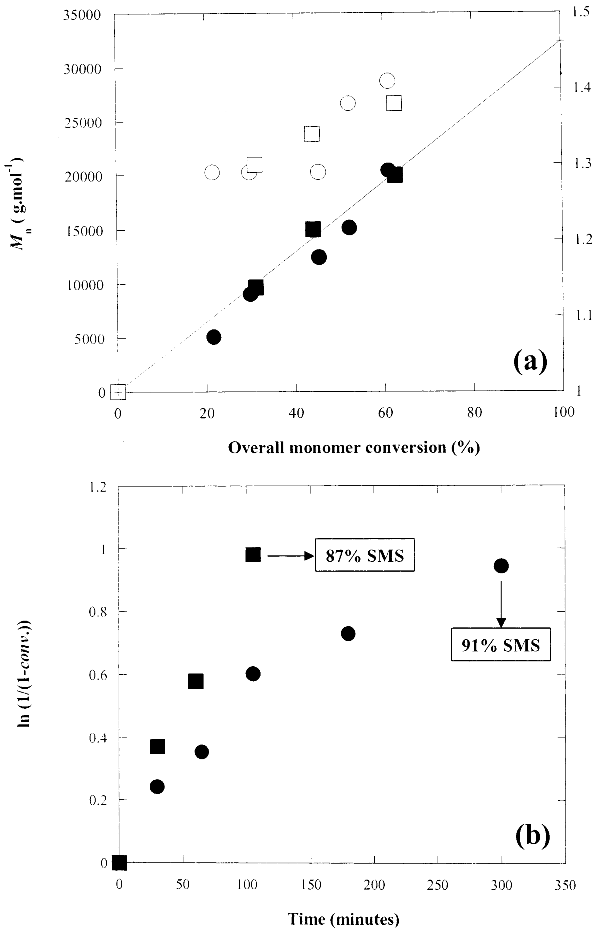


Figure 4. (**a**) Number-average molecular weight M_n (filled symbols) and polydispersity index M_w/M_n (empty symbols) as a function of overall monomer conversion (conv). (**b**) ln(1/(1 − conv)) vs time for the copolymerization of methyl methacrylate and styrene at 60 °C in bulk (■, □) ($[S]_0 = 3.67$ mol L^{-1}; $[M]_0 = 3.67$ mol L^{-1}; $[AIBN]_0 = 1.96 \times 10^{-3}$ mol L^{-1}; $[CDB]_0 = 1.96 \times 10^{-2}$ mol L^{-1}; $[Et_2AlCl]_0 = 1.47$ mol L^{-1}) or in toluene solution (●, ○) ($[S]_0 = 1.85$ mol L^{-1}; $[M]_0 = 1.85$ mol L^{-1}; $[AIBN]_0 = 9.86 \times 10^{-4}$ mol L^{-1}; $[CDB]_0 = 9.86 \times 10^{-3}$ mol L^{-1}; $[Et_2AlCl] = 0.74$ mol L^{-1}). Theoretical $M_n = ([M]_0 + [S]_0)(\text{conv})(104.15 + 100)/(2(2[AIBN]_0 + [CDB]_0))$.

The influence of the initial monomer composition on the copolymerization behavior was also investigated. A series of copolymers of M and S were prepared starting with various initial monomer mole fractions (Table 5). In all experiments, the ratio $[Et_2AlCl]_0/[M]_0$ and the targeted degree of polymerization for complete overall conversion were the same. The copolymers synthesized in this series of experiments were initially investigated by ^1H NMR. The ratio of the signals in regions X, Y, Z depends on the initial monomer feed. Equation 4 may be rearranged to eq 6 to express the monomer feed dependence of F_x.

$$1/(1 - F_x^{1/2}) = 1/\sigma + (r_M/\sigma)(f_M/f_S) \quad (6)$$

Figure 5 shows the plot of $1/(1 - F_x^{1/2})$ vs f_M/f_S for this series of experiments. As expected, a linear dependency of $1/(1 - F_x^{1/2})$ with f_M/f_S was observed. The value of the y-axis intercept allows one to calculate an average value of the coisotactic parameter σ for the RAFT copolymerization of M and S in the presence of Et_2AlCl. This measured value $\sigma = 0.56$ is similar to the result previously calculated for the conventional radical po-

Table 5. Effect of Monomer Feed on the Alternating Copolymerization[a]

	f_M[b] (%)	f_S[b] (%)	F_M[c] (%)	F_S[c] (%)	time (min)	$M_{n,exp}$ (g mol^{-1})	M_w/M_n	F_X	F_{SMS} (%)
1	90	10	78	22	330	7 815	1.14		
2	80	20	64	35	165	5 900	2.27	0.426	65 ± 5
3	70	30	65	35	95	11 200	1.40	0.411	65 ± 5
4	60	40	58	42	75	21 700	1.39	0.303	85 ± 5
5	50	50	50	50	100	20 200	1.38	0.259	80 ± 5
6	40	60	54	46	72	22 300	1.36	0.233	95 ± 5
7	30	70	49	51	115	20 700	1.27	0.234	95 ± 5
8	20	80	51	48	240	13 800	1.31	0.202	100 ± 5
9	10	90	47	52	330	9 800	1.25	0.187	100 ± 5

[a] Experimental conditions: bulk, 60 °C, $([M]_0 + [S]_0)/(2[AIBN]_0 + [CDB]_0) = 315$; $[Et_2AlCl]_0/[M]_0 = 0.4$; $[CDB]_0/[AIBN]_0 = 10$. [b] Initial monomer mole fractions. [c] Mole fraction of each comonomer in the final copolymer, determined by elemental analysis.

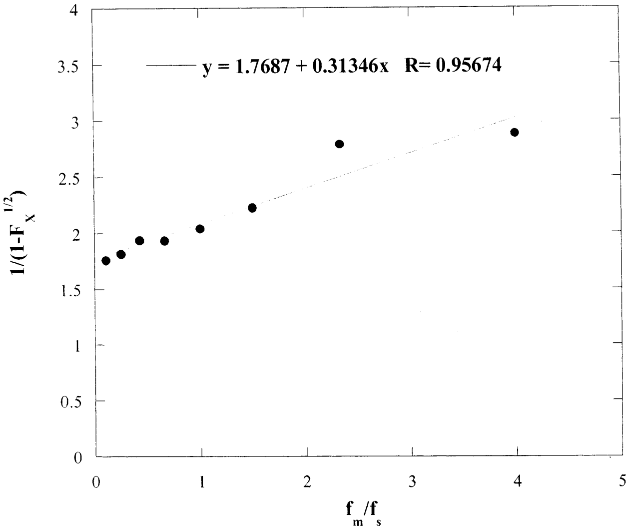


Figure 5. Plots of $1/(1 - F_X^{1/2})$ vs f_M/f_S for the RAFT copolymerization of methyl methacrylate and styrene at 60 °C in bulk and in the presence of Et_2AlCl. $([M]_0 + [S]_0)/(2[AIBN]_0 + [CDB]_0) = 315$; $[Et_2AlCl]_0/[M]_0 = 0.4$; $[CDB]_0/[AIBN]_0 = 10$.

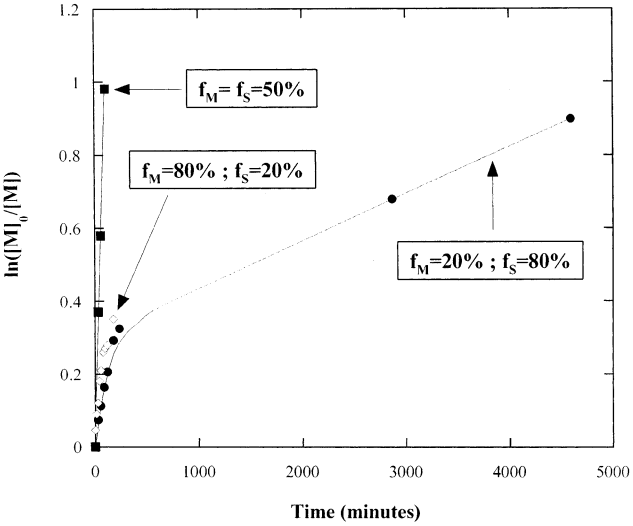


Figure 6. ln(1/(1 − conv)) vs time for the copolymerization of methyl methacrylate and styrene at 60 °C in bulk: $([M]_0 + [S]_0)/(2[AIBN]_0 + [CDB]_0) = 315$; $[Et_2AlCl]_0/[M]_0 = 0.4$; $[CDB]_0/[AIBN]_0 = 10$; $[M]_0/[S]_0 = 80/20$ (◇), 50/50 (■), 20/80 (●).

lymerization of M and S in the presence of Et_2AlCl.[67] The slope of Figure 5 also permits determination of a value for the reactivity ratio, $r_M = 0.17$, which is 2 times higher than the one previously reported.[58] Using these newly calculated values of σ and r_M, the proportion of alternating triads F_{SMS} was determined for this series of experiments (Table 5). For S-rich monomer feed, a very strong alternating tendency is observed. For M-rich systems, alternation tendency is reduced. This is in agreement with values of cross-propagation reported from Table 3, since S radical reacts very fast with even a small amount of the complexed monomer, but the opposite scenario is less selective.

At high M feed ratios ($f_M > 70\%$), poorly defined copolymers with broad molecular weight distribution were obtained (Table 5, entries 1−3). The loss of control over molecular weight and polydispersity in these experiments is probably a consequence of a slow decomposition of the dithioester chain end due to a side reaction with the Lewis acid. Since in this series of experiments $[Et_2AlCl]_0/[CDB]_0$ increases with f_M, the decomposition of the chain ends probably becomes a more significant process. For $f_M < 60\%$, well-defined alternating copolymers, with controlled chain lengths, polydispersities, and sequences, were obtained (Table 5, entries 4−9). At low M feed ratios ($f_M < 40\%$), the reaction kinetics may be divided into two steps: a fast copolymerization regime is initially observed, and then the rate of polymerization abruptly becomes slower (Figure 6). The microstructure of the copolymer prepared at the end of the first regime was analyzed (Table 5, entries 7−9). At that stage, the fraction of methyl methacrylate units in the final copolymer F_M was found to be close to 50%, and the fraction of alternating triad F_{SMS} was close to 100% in all cases. This result indicates that the first regime corresponds to a fast alternating copolymerization of the Lewis acid-complexed methyl methacrylate with styrene. The second regime is due to a slow RAFT homopolymerization of styrene. In this second stage, the Lewis acid does not participate in the polymerization mechanism, and the rate of polymerization is comparable to that seen for RAFT homopolymerization of styrene in the absence of Lewis acid.[68]

A series of copolymerizations of M and S with various targeted molecular weights (from 10 000 up to 100 000 g mol^{-1}) were undertaken at 60 °C in the presence of diethylaluminum chloride (Figure 7). For the series of experiments with targeted molecular weight below 50 000 g mol^{-1}, polymers with predominantly alternating microstructures, low polydispersities, and good agreement between experimental and theoretical M_n were obtained. However, in the experiment with the highest targeted molecular weight, the polymers isolated from the reaction beyond 40% of conversion displayed higher polydispersities, and the experimental M_n were found to be lower than theoretical values. Since the ratio $[Et_2AlCl]_0/[CDB]_0$ increases with the targeted molecular weight, when high molecular weight polymers are targeted, the probability that the dithioester chain

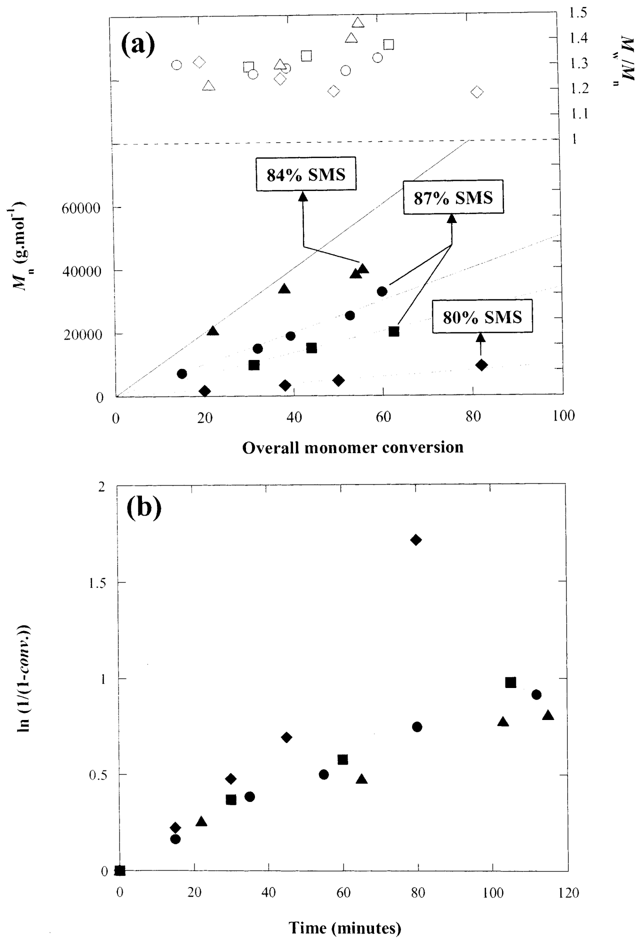


Figure 7. (a) Number-average molecular weight M_n (filled symbols) and polydispersity index M_w/M_n (empty symbols) as a function of overall monomer conversion (conv). (b) ln(1/(1 − conv)) vs time for the copolymerization of methyl methacrylate and styrene at 60 °C in bulk: $[S]_0 = 3.67$ mol L^{-1}; $[M]_0 = 3.67$ mol L^{-1}; $[Et_2AlCl]_0 = 1.47$ mol L^{-1}; $[CDB]_0 = 6.28 \times 10^{-2}$ mol L^{-1} (◆, ◇), 1.96×10^{-2} mol L^{-1} (■, □), 1.25×10^{-2} mol L^{-1} (●, ○), 5.95×10^{-3} mol L^{-1} (▲, △), $[CDB]_0/[AIBN]_0 = 10$. Theoretical $M_n = ([M]_0 + [S]_0)(\text{conv})(104.15 + 100)/(2(2[AIBN]_0 + [CDB]_0))$.

ends may be decomposed by the Lewis acid significantly increases. Further evidence for this possible decomposition of the chain ends with Et_2AlCl was seen in the limited ability for chain extension of the synthesized alternating copolymers. Attempts were made to synthesize a diblock copolymer P(M-*alt*-S)-*b*-PS from alternating copolymer macroinitiators; however, whatever was their initial molecular weight, the macroinitiators prepared in the presence of Et_2AlCl exhibited a low efficiency of initiation (below 50%).

Comparison of Different Lewis Acids. RAFT copolymerization of methyl methacrylate and styrene was studied in the presence of various Lewis acids: tin(IV) chloride ($SnCl_4$), zinc chloride ($ZnCl_2$), ethylaluminum sesquichloride (EASC), and diethylaluminum chloride. The order of Lewis acidity is

$$SnCl_4 > ZnCl_2 > EASC > Et_2AlCl$$

Table 6 shows the final values of M_n and M_w/M_n of the polymers obtained in this series of experiments. In all experiments, the targeted degree of polymerization for complete conversion was the same, DP = 315.

Table 6. Effect of Lewis Acid on Alternating Copolymerization of Styrene and Methyl Methacrylate in the Presence of Cumyl Dithiobenzoate[a]

	Lewis acid	temp (°C)	time (min)	$M_{n,exp}$ (g mol^{-1})	M_w/M_n
1	Et_2AlCl	60	100	20 200	1.38
2	EASC	60	9	31 500	1.45
3	EASC	40	80	24 500	1.22
4	$ZnCl_2$	60	15	7 600	3.74
5	$ZnCl_2$	40	125	10 800	1.80
6	$SnCl_4$	40	120	2 800	2.50

[a] Experimental conditions: bulk, $[S]_0/[CDB]_0 = [M]_0/[CDB]_0 = 190$; $[\text{Lewis acid}]_0/[M]_0 = 0.4$; $[CDB]_0/[AIBN]_0 = 10$.

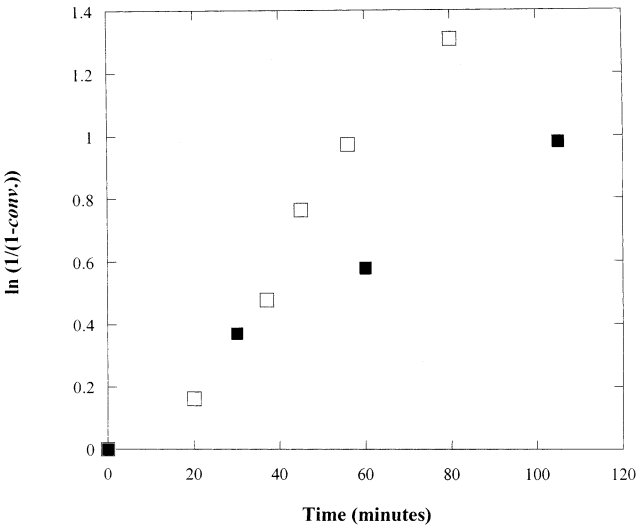


Figure 8. Semilogarithmic plots for the bulk copolymerization of methyl methacrylate and styrene at 60 °C in the presence of Et_2AlCl (■) and at 40 °C in the presence of EASC (□). $[S]_0/[CDB]_0 = [M]_0/[CDB]_0 = 190$; $[\text{Lewis acid}]_0/[M]_0 = 0.4$; $[CDB]_0/[AIBN]_0 = 10$.

At 60 °C, the only copolymerization that was controlled was the one conducted in the presence of Et_2AlCl. With stronger Lewis acids, fast, uncontrolled polymerizations were observed (Table 6, entries 2 and 4). Therefore, copolymerization in the presence of $SnCl_4$, $ZnCl_2$, and EASC were investigated at a lower temperature (40 °C) (Table 6, entries 3, 5, and 6). There was still poor control of the copolymerization in the presence of the strongest Lewis acids ($SnCl_4$ and $ZnCl_2$) at 40 °C ($M_w/M_n > 2$). As already mentioned, the Lewis acids may form a complex with the cumyl dithiobenzoate transfer agent (indicated by a orange color), but additional side reactions may participate in decomposing this control agent. With $SnCl_4$ and $ZnCl_2$, the reaction mixtures were found to be yellow and heterogeneous, which may be the consequence of a significant decomposition of CDB. On the other hand, in the presence of EASC, the copolymerization of M and S exhibited a controlled/living behavior. The rate of copolymerization in the presence of EASC was faster at 40 °C than at 60 °C in the presence of Et_2AlCl (Figure 8). However, lower polydispersity indexes were obtained in the presence of EASC ($M_w/M_n < 1.3$).

To investigate the capabilities of EASC, a series of copolymerizations of M and S with various targeted molecular weights (from 10 000 up to 100 000 g mol^{-1}) were conducted at 40 °C in the presence of this Lewis acid (Figure 9). In these experiments, copolymers with low polydispersities ($M_w/M_n < 1.3$) and good agreement

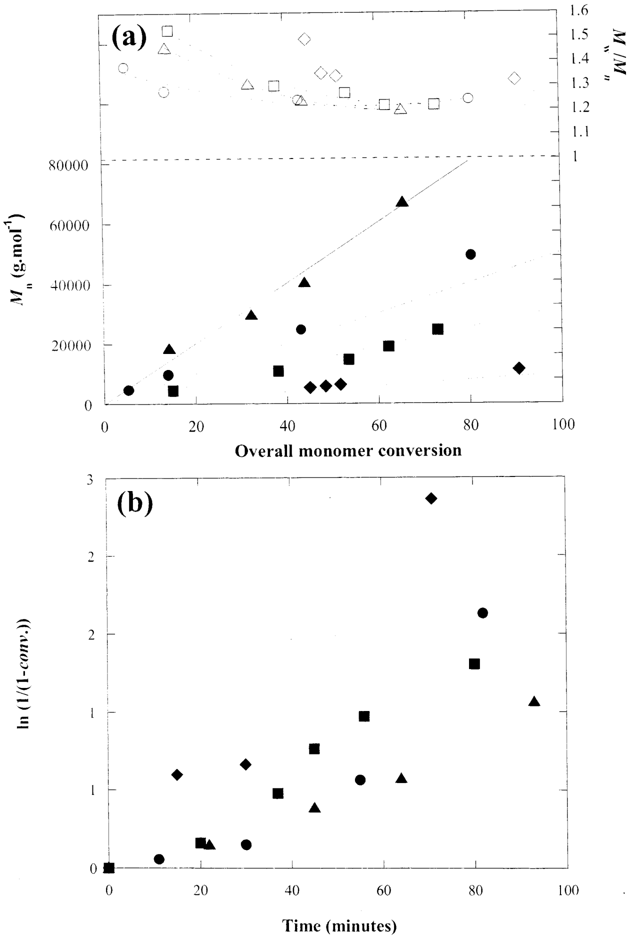


Figure 9. (**a**) Number-average molecular weight M_n (filled symbols) and polydispersity index M_w/M_n (empty symbols) as a function of overall monomer conversion (conv). (**b**) ln(1/(1 − conv)) vs time for the copolymerization of methyl methacrylate and styrene at 40 °C in bulk: $[S]_0 = 3.2$ mol L^{-1}; $[M]_0 = 3.2$ mol L^{-1}; $[EASC]_0 = 1.28$ mol L^{-1}; $[CDB]_0 = 5.32 \times 10^{-2}$ mol L^{-1} (◆, ◇), 1.69×10^{-2} mol L^{-1} (■, □), 1.06×10^{-2} mol L^{-1} (●, ○), 5.3×10^{-3} mol L^{-1} (▲, △), $[CDB]_0/[AIBN]_0 = 10$. Theoretical $M_n = ([M]_0 + [S]_0)(conv)(104.15 + 100)/(2(2[AIBN]_0 + [CDB]_0))$.

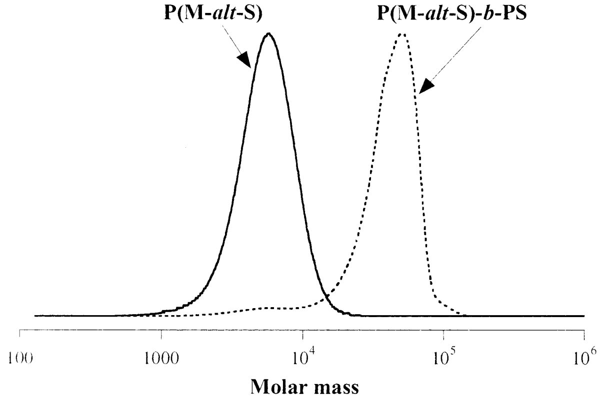


Figure 10. GPC plots for the synthesis of a P(M-*alt*-S)-*b*-PS diblock copolymer initiated by a P(M-*alt*-S) RAFT macroinitiator ($M_n = 5200$ g mol^{-1}, $M_w/M_n = 1.2$). 110 °C; $[S]_0 = 8.72$ mol L^{-1}; $[\text{macroinitiator}]_0 = 1.86 \times 10^{-2}$ mol L^{-1}.

between experimental and theoretical M_n (up to 70 000 g mol^{-1}) were obtained. In all cases, good control over comonomer sequence distribution (~90% of SMS) was observed by ^{1}H NMR.

The alternating copolymers synthesized by RAFT polymerization in the presence of EASC were also used as macroinitiators for the synthesis of block copolymers. Figure 10 shows the GPC plots obtained in the synthesis of a diblock copolymer P(M-*alt*-S)-*b*-PS. Complete conversion of styrene was observed after 30 h at 110 °C. The polymerization proceeded in a controlled/living fashion, as evidenced by a clear shift of the molecular weight and a low final polydispersity index ($M_w/M_n = 1.22$). A small signal attributed to the macroinitiator remained in the GPC plot indicating that the macroinitiator had limited functionality. However, these chain extension results indicate that the alternating copolymers synthesized in the presence of EASC possess much higher dithioester chain-end functionality than the copolymers obtained with Et_2AlCl as the Lewis acid.

Conclusions

We studied the ability of several CRP systems (RAFT, ATRP, NMP, and IDTP) to control an alternating copolymerization of a Lewis acid-complexed methyl methacrylate with styrene. Among the CRP methods evaluated, RAFT polymerization was chosen for further examination since the dithioester control agent interacted less with Lewis acids than ATRP catalysts or nitroxide stable radicals. When diethylaluminum chloride was used as the Lewis acid in a RAFT copolymerization at 60 °C well-defined alternating copolymers poly(methyl methacrylate-*alt*-styrene) were synthesized possessing controlled molecular weight, low polydispersities ($M_w/M_n < 1.4$), and controlled comonomer sequences (~90% of alternating triads). However, some limitations were observed for this system. The dithioester chain ends were partially decomposed by side reactions with the Et_2AlCl. As a consequence, it was not possible to synthesize well-defined copolymers with molecular weights above 40 000 g mol^{-1}, and it was not possible to chain extend the alternating copolymers in a living fashion. The RAFT copolymerization of methyl methacrylate and styrene was then studied in the presence of other Lewis acids: $SnCl_4$, $ZnCl_2$, and ethylaluminum sesquichloride. In the presence of strong Lewis acids such as $SnCl_4$ or $ZnCl_2$, no control of the radical copolymerization was observed. On the other hand, at 40 °C in the presence of ethylaluminum sesquichloride, it was possible to prepare polymers with controlled molecular weight (up to $M_n = 70\,000$ g mol^{-1}), low polydispersities ($M_w/M_n < 1.3$), and controlled comonomer sequences (around 90% of alternating triads). The alternating copolymers obtained in these copolymerizations retain chain-end functionality and were used as macroinitiators for the synthesis of well-defined diblock copolymers. This study demonstrates that control of molecular parameters attainable in CRP methods can be enhanced by using concepts from conventional radical polymerization. For example, complexation with Lewis acids may affect monomer reactivity and stereoselectivity in radical processes, opening the possibility to control microstructure in the sense of sequence distribution and tacticity, which is currently investigated.

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