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CHAIN TRANSFER BY ADDITION–FRAGMENTATION MECHANISM—9. ACCESS TO DIENE-FUNCTIONAL MACROMONOMERS USING 5-(SUBSTITUTED)-1,3-PENTADIENE-TYPE ADDITION–FRAGMENTATION CHAIN-TRANSFER AGENTS IN RADICAL POLYMERIZATION

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Abstract—Radical polymerizations of methyl methacrylate (MMA) and styrene (St) in bulk at low conversion were carried out in the presence of pentadienic chain transfer agents (CTA), 5-bromo-1,3-pentadiene (**1**), 5-benzenesulphonyl-1,3-pentadiene (**2**) and methyl 2-bromomethyl-4-methyl-2,4-pentadienoate (**3**), to produce conjugated diene-end capped macromonomers by a addition–fragmentation mechanism. The chain-transfer constants (C_{tr}) of **1**, **2** and **3** for MMA polymerization were obtained from the Mayo equation, respectively. Correction to zero conversion afforded an accurate value of the chain transfer constant for **1**. The chain transfer was found to be degradative. The pentadienyl group formed by fragmentation of the macroradical abduct is quantitatively introduced at the ω-end of the polymer.

INTRODUCTION

Radical chain transfer appears as one of the most convenient and hence widely employed method for the synthesis of macromonomers. In order to prepare macromonomers with a good control of the degree of functionalization and both molar mass and molar-mass distribution, it is necessary to have a previous knowledge of the kinetics and mechanism of polymerization. Therefore, the goal of the present work is to report the radical polymerization of MMA and St in the presence of new addition–fragmentation CTA.

The addition–fragmentation process involved an intramolecular evolution [1]. The intermediate radical formed by the addition of the propagating radical on the chain-transfer agent undergoes fragmentation, generating another radical entering into the polymerization cycle. The concomitant incorporation of a terminal functional group following fragmentation is an attractive feature of this technique. When the functional groups are polymerizable, this method appears to be a viable route for the single step synthesis of macromonomers.

In previous works, the unsaturation produced at polymer terminal by addition–fragmentation reactions on 2(-*substituted*)methyl(acrylic or styrenic) derivatives are heavily α-substituted acrylates and styrenics, whose polymerizability is known to be very poor [2–9]. In these cases, the reactivity of the macromonomer was found to be very poor and propagation is completed by the fragmentation of the polymer radical leading to premature chain termination [10, 11].

Recently, some 5-substituted-1,3-pentadiene such as 5-*tert*-butylthio-1,3-pentadiene [12a] and 5-bromo-1,3-pentadiene [12b] have been drawn attention as efficient chain-transfer agents through the addition–fragmentation mechanism in radical polymerization. Thus, the introduction of *tert*-butylthio or a bromo fragment and pentadiene end-groups were shown to be quantitatively introduced at the α- and ω-terminuses of PMMA and PS prepared by radical polymerization. These functional polymers are to be considered as macromonomers because of the pentadiene fragment, whose polymerizability has been recently studied [13].

The significance of macromonomers in the design of tailor-made graft polymers is well established [11, 14]. Their conventional syntheses link the functional group to the polymer chain by a relatively fragile ester or isocyanate bond and the general synthesis route cannot be applied to all polymer systems. On the other hand, the macromonomer formed by the addition–fragmentation link the function to the chain by a C—C bond. Furthermore,

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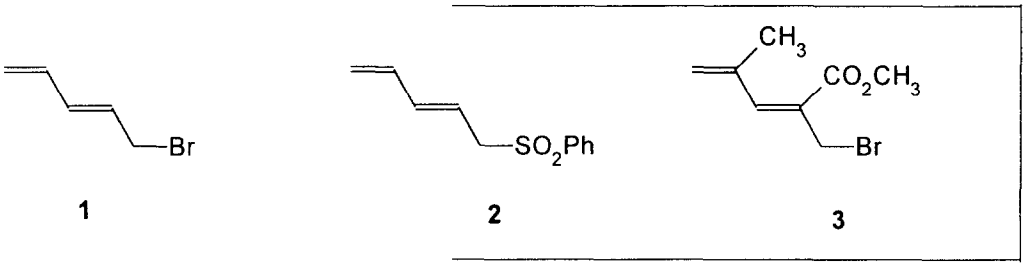
their synthesis is accomplished in a single-step reaction.

This paper deals with the comparison of chain-transfer properties of compounds **1**, **2** and **3** in the syntheses of pentadiene-functional macromonomers of MMA and styrene. This study was undertaken as part of a search for new examples of the addition–fragmentation type chain-transfer reaction [15]. The kinetics of the associated retarded polymerization was studied and the characterization of the macromonomers described.



1 **2** **3**

EXPERIMENTAL

Materials

Methyl methacrylate (MMA) was *vacuum*-distilled from finely powdered CaH_2 *prior* to use. Styrene (St) was stored for a few hours over sodium wire, then *vacuum*-distilled. 2,2′-Azobis(*iso*butyronitrile) (AIBN) was purified by recrystallization from methanol. Monomers and initiator were stored at − 10°C. Solvents (i.e. diethyl ether, pentane, heptane, methanol, acetone) were reagent grade and used without further purification. Tetrahydrofuran (THF) was dried with CaH_2 and distilled under argon. 3-Hydroxy-1,4-pentadiene, tribromophosphine, sodium benzenesulfinate and poly(ethylene oxide) (POE 400, $M_w = 400$) were purchased from Aldrich and used as received unless otherwise specified.

Instruments

Monomer conversion was determined by gravimetry as described below. Number-average molar mass (M_n) of the polymers were determined by size-exclusion chromatography (SEC), using a Waters Instrument (Waters WISP710b automatic injector, Schimadzu LC6a pump), coupled with Waters R401 refractometer, Beckmann 167 dual-UV detector and Chromatix CMX100 LS detector. The flow rate of tetrahydrofuran (THF) used as eluent through a set of 4 PL-Gel packed columns was 1 mL/ min. ^{1}H NMR and ^{13}C NMR spectra were performed on $CHCl_3$ solutions and recorded on a Bruker AC-200 spectrometer and are reported in ppm downfield from tetramethylsilane (TMS). Evaporative distillation refers to bulb-to-bulb distillation under reduced pressure using a Büchi Kugelrohr oven. Flash column chromatographic purifications were carried out on Merck silica gel 60 (60–200 mesh) and monitored by TLC using Merck precoated silica gel 60 F_{254} (0.25 mm thickness) aluminium-backed plates. The plates were visualized under UV or iodine vapor. Mixtures of Et_2O and heptane were used as eluant. Elemental analyses were done by ICS-Microanalytical Services (Strasbourg) and are reported for new compounds. Analyses of the compounds gave satisfactory agreements between calculated and found values with gaps lower than 0.5% for carbon, hydrogen and oxygen.

Test of the transfer ability of 5-substituted-1,3-pentadiene

2,2′-Azobis(*iso*butyronitrile) (St and MMA: 40 mg, 2.44×10^{-4} mol) was dissolved in distilled monomer (40 mL). Aliquots (5.0 mL) were removed and added to cleaned and dried Pyrex test tubes (18 × 200 mm). A solution of CTA (5×10^{-4} mol) in a monomer (10 mL) was also prepared and used to add the required amounts of the chain-transfer agent to the ampoules. The tubes were evacuated by three freeze/pump/thaw cycles and sealed under *vacuum* (while frozen). Next, the tubes were placed in a thermostated oil bath for a defined period of time (60 C; St and MMA, 1 hr; conversions were kept below 3% for styrene and 10% for MMA), after which the tubes were rapidly frozen with dry ice/2-propanol bath and opened. 15 mL of 0.1% solution of hydroquinone in THF was added to each tube and the polymers were precipitated by addition of the solution to 300 mL of heptane or methanol. The polymers were filtered off in weighted sinter glass funnels, dried in a *vacuum* oven at 60 C for 12 hr and weighed. The monomer conversion was calculated from the mass of the polymer and the initial amount of the monomer.

Synthesis of 5-bromo-1,3-pentadiene (**1**)

We have followed the procedure described by Viehe *et al.* [16].

Synthesis of 5-benzenesulphonyl-1,3-pentadiene (**2**)

The sulfonated derivative **2** was prepared according to the method previously described by Colombani *et al.* [17]. To a solution of 5-bromo-1,3-pentadiene **1** (2.96 g, 0.02 mol), poly(ethylene oxide) (POE, $M_w = 400$, 1.0 g and THF (10 mL) was added finely ground benzenesulfinate (3.6 g, 0.022 mol). The mixture was stirred and reflux for 1 hr. The reaction was monitored by ^{1}H NMR, examining the disappearence of CH_2Br signals. After evaporation of the solvent under *vacuum*, the product was extracted with diethyl ether (2 × 10 mL). The combined organic layers were washed with water (2 × 10 mL), dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Purification by column chromatography on silica gel (60 g) using a mixture Et_2O/heptane (50/50; $R_f = 0.47$) as eluant yield neat sulfone (2.9 g, 70%). The NMR analysis showed that the product is a mixture of the *cis* and *trans* isomers with 93% *trans* content. ^{1}H NMR ($CDCl_3$): δ 7.7–7.5 (m, 5H, C_6H_5), 6.4–6.0 (m, 2H, CH=CH), 5.7–5.5 (m, 1H, CH_2=CH), 5.3–5.1 (m, 2H, CH_2=CH), 4.1–3.6 (d, 2H, CH_2SO_2). ^{13}C NMR ($CDCl_3$): δ 139.8 [C^2]; 138.4 [C^6]; 135.3 [$C^{9'}$]; 135.3 [C^{9}]; 133.7 [C^3]; 129.0 [$C^{8,8'}$]; 128.4 [$C^{7,7'}$]; 119.7 [C^4]; 118.6 [C^1]; 60.1 [C^5]. Found: C, 63.67; H, 6.02; O, 15.19. $C_{11}H_{12}O_2S$ required: C, 63.44; H, 5.81; O, 15.36%.

Synthesis of methyl 2-bromomethyl-4-methyl-2,4-pentadienoate [*18*] (**3**)

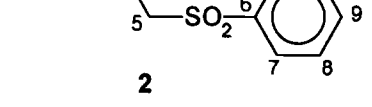
A mixture of methyl acrylate (13.0 g, 0.15 mol), methacrolein (7.0 g, 0.10 mol) and DABCO (1.6 g, 0.015 mol) was stirred at room temperature for 21 days. Volatile unreacted starting materials were evaporated under reduced pressure. The residue was then dissolved in diethyl ether (50 mL) and washed successively with dilute hydrochloric acid aqueous solution (10% w/w, 100 mL) and water (2 × 100 mL). The organic layer was dried over $MgSO_4$ and the solvent was eliminated under reduced pressure to give methyl 3-hydroxy-4-methyl-2-methylene-4-pentenoate (10.1 g, 65%).

Table 1. Number-average degrees[a] of polymerization (Dp_n), chain-transfer constant (C_{tr}) and conversions[b] of isolated polymers obtained by the use **1** at 60 C in the bulk polymerization of MMA

Polymerization conditions	[1] × 10³ (mol/L)	DP_n	[1]/[MMA] × 10⁴	C_{tr}	Conversion[b] (%)
t:15 min	0	5440	0		2.1
(M_w/M_n:	5	300	5.61	5.20	1.8
1.8–2.2)	10	160	11.2		1.6
	20	85	22.4		1.5
t:30 min	0	5440	0		3.8
(M_w/M_n:	5	330	5.61	4.73	3.3
1.8–2.2)	10	160	11.2		2.9
	20	90	22.4		2.5
t:60 min	0	5660	0		6.9
(M_w/M_n:	5	305	5.61	4.43	5.9
2.0–2.03)	10	200	11.2		5.8
	20	100	22.4		5.2

[a][AIBN] = 3.05 × 10⁻³ mol/L.
[b]Determined from the weight of the isolated polymer.

A solution of PBr_3 (39.0 g, 0.144 mol) in diethyl ether (100 mL) was added dropwise to a cooled (− 10°C) mixture of methyl 3-hydroxy-4-methyl-2-methylene-4-pentenoate (45.0 g, 0.288 mol) taken in dry diethyl ether (200 mL). The system was then kept agitated at room temperature for 12 hr. It was then cooled to − 20°C and distilled water (200 mL) was added carefully. The crude product was extracted with diethyl ether (three times) and the organic layers were dried over $MgSO_4$. The solvent was evaporated and the residue (52.5 g, 83%) distilled under reduced pressure ($b.p._{0.01}$ = 74°C) to give pure methyl 2-bromomethyl-4-methyl-2,4-pentadienoate (19.7 g, 32%). ^1H NMR ($CDCl_3$): δ 7.25 (m, 1H, CH), 5.42–5.36 (m, 2H, CH_2=C), 4.40 (s, 2H, CH_2Br), 3.83 (s, 3H, CO_2CH_3), 2.01 (s, 3H, CH_3). Found: C, 43.98; H, 4.93; O, 14.73. $C_8H_{11}O_2Br$ required: C, 43.86; H, 5.06; O, 14.61%.



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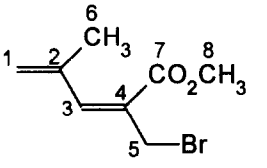

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Procedure for polymerizations

The polymerization of MMA and St in the absence and presence of small amounts of **1**, **2** or **3** proceeded at almost the same initial rate and a considerable decrease in M_n was induced by coexistence of CTA as shown in Tables 1–3. For the determination of the chain-transfer constants, the polymerizations were carried out in sealed evacuated pyrex glass tubes. The tube, containing the weighed quantities of monomer, initiator (AIBN) and CTA were deaerated by at least three cycles of freezing, evacuating and thawing. It was then sealed under vacuum and polymerized at the required temperature in a thermostated oil bath. The contents were precipitated into large excess of heptane (for PMMA) or methanol (for PS) and the polymer isolated by filtration, dried and weighed. The rate determining step of the addition–fragmentation chain transfer is considered to be the addition to CTA when no CTA units is incorporated in the polymer, involving efficiency of the intramolecular process. Whereas polymerizations and copolymerizations of 5-*tert*-butylthio-1,3-pentadiene yielded the polymers and copolymers bearing the pentadienyl end-group, the faster fragmentation of poly(M)-**1** radical seems to compete efficiently with propagation.

Table 2. Number-average degrees[a] of polymerization (DP_n), ratio of the rate of polymerization with and without CTA (R_p/RR_{p0}) and chain-transfer constants (C_{tr}) of CTAs in the polymerization of MMA at 60°C, extrapolated to zero conversion

Monomer	[1] × 10³ (mol/L)	DP_n[a]	[1]/[M] × 10⁴	C_{tr}	(R_p/R_{p0})
MMA	0	5450	0		(1.00)
T = 60°C	5	295	5.61	5.42	(0.91)
	10	160	11.2		(0.70)
	20	82	22.4		(0.71)

[a][AIBN] = 3.05 × 10⁻³ mol/L.

Table 3. Polymerization[a] of MMA with AIBN for 1 hr at 60 C in bulk in the presence of **2**

10³ × [2] (mol/L)	Conversion[b] (%)	M_n × 10³
0	9.5	419
0.5	9.1	216
2.5	8.6	86.3
5	8.5	48.5
10	7.7	28.0
20	7.2	11.5

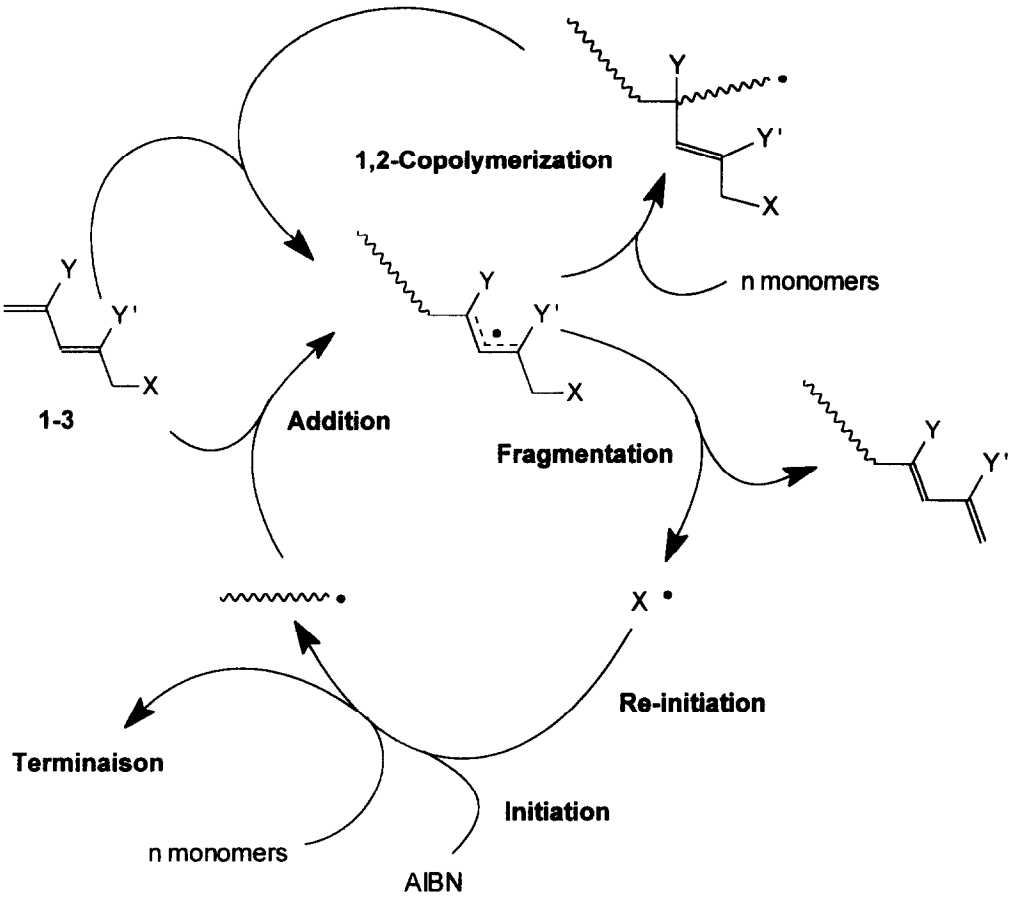
[a][AIBN] = 3.05 × 10⁻³ mol/L.
[b]Determined from the weight of isolated polymers.

RESULTS AND DISCUSSION

Free radical addition–fragmentation processes were recently reported as new methods for chain-length control [19]. They have been identified as an effective means for generating macromonomers, but the double bonds of the allylic or α-substituted acrylic or styrenic type exhibit generally poor polymerizability. In this work, a polymerizable conjugated diene function was introduced at chain terminal by using **1** and **2** as addition–fragmentation agents. The mechanism suggested for the formation of the diene-macromonomer is the addition of the propagating radical to the CTA, to generate an intermediate radical, which undergoes immediate fragmentation affording a diene function at chain terminal (Scheme 1).

Evidence for the above mechanism comes from the fact that the molar mass of the formed polymers are significantly lowered without significant retardation of the polymerization rate. The driving force for the fragmentation seems to be the formation of a conjugated diene. It can be expected that the rate-determining step is the addition of the radical to the CTA, since the fragmentation seems very fast.

During the course of the polymerization, the pentadienyl end-group on macromonomers is not

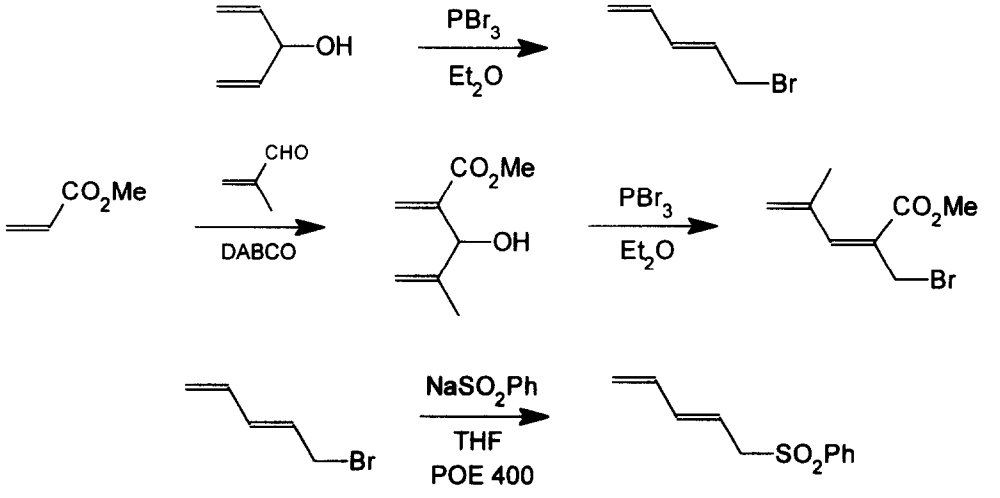


Scheme 1. General mechanism of the chain-transfer process.

inactive toward PMMA radical and copolymerization of the dienyl end-fragment with the propagating radical giving rise to branched structures occured to enhance M_n and M_w/M_n with conversion. In order to avoid such a phenomenon, which will be developed in a further paper, results were obtained exclusively in low-conversion polymerization. Hence, it is imperative to limit the conversion in order to have narrow molar mass distributed macromonomers.

Synthesis of the chain-transfer agents

5-Bromo-1,3-pentadiene (**1**) and methyl 2-bromomethyl-4-methyl-2,4-pentadienoate (**3**) were prepared easily by reaction of phosphorus tribromide on 3-hydroxy-1,4-pentadiene, proceeding with clean



Scheme 2. Synthesis of the chain-transfer agents.

rearrangement [20] (Scheme 2). This rearrangement was regioselective, but not totally stereoselective, giving a mixture of *E* and *Z* isomers **1** in a 92/8 ratio.

The phenylsulfonylation of **1** produces 5-benzenesulphonyl-1,3-pentadiene (**2**) corresponding to a direct substitution of the bromine atom [17]. Nevertheless, it was shown in the case of others allylic bromocompounds that total inversion was taken place step by an addition–elimination process of the sulfinate anion.

Chain-transfer activity

Chain-transfer efficiency and retardation in radical polymerization were the two criteria in the assessment of these new CTAs. The chain transfer constants of these dienic compounds **1–3** were determined at 60°C in the polymerization of MMA and styrene in the presence of AIBN as the initiator. The retardation effect was also estimated by the decrease in the conversion or by the ratio of the propagation rates in the presence (R_p) or in the absence (R_{p0}) of CTA (Tables 1–3). These polymerizations were carried out at constant AIBN concentration, while the transfer agent/monomer ratio was progressively increased. The activity of radical transfer from styryl and (meth)acrylyl macroradicals to these dienes was calculated according to the Mayo's equation [21].

The polymerization were typically carried out in glass ampoules at 60°C for 1 hr and for five concentrations of a given chain-transfer agent in a monomer and the chain transfer constants were obtained from the gradients of graphs of $1/DP_n$ vs the relative concentrations of the chain transfer agents and monomers, using the simplified Mayo equation: $1/DP_n = 1/DP_{n0} + C_{tr} \times [CTA]/[M]$, where DP_{n0} and DP_n are the number-average degrees of polymerization of the polymer obtained at low conversion in the absence or presence of the chain-transfer agent respectively. Concentrations of the transfer agent and the monomer were assumed to be constant at low conversions. To control the molar mass and end-groups simultaneously with the chain transfer agents over a wide conversion range. C_{tr} should be close to unity otherwise concentration ratio of monomer to CTA would change with conversion [22].

The polymerization conditions, monomer conversion and the number-average molar mass of the polymer obtained at various concentration of CTA are summarized in Table 1. The chain-transfer constant (C_{tr}), calculated with the Mayo equation, varied from 5.20 to 4.43, with the polymerization time in the range 15–60 min, respectively (Table 1).

When the concentration of the CTA change considerably with the conversion, the ratio [CTA]/[M] varies with the conversion and, therefore, feed values of [CTA]/[M] cannot be utilized in the Mayo equation. The average molar mass and hence the transfer constant might be affected by a large error. In this way, cases were described in the literature. In order to avoid this fact, determination of the chain-transfer constant was realized to zero conversion (Figs 1 and 2) and calculated to be close to 5.4 (Table 2), which compares with that of *n*-butanethiol (C_{tr} = 0.66–0.68) [23].

The efficiency of CTAs in radical polymerization depends on many factors that function in concert: (1) the affinity of the double bond towards the propagating radicals; (2) the stabilization of the radical adduct; (3) the nature of the intramolecular evolution; (4) the activity of the expelled radicals.

The first criterion, i.e. the affinity of the double bend towards the propagating radical, may be analysed in terms of comonomer reactivity ratio, following the same general picture as in a classical free radical copolymerization. Thus, MMA being quoted as M_1, the chain-transfer constant of **1** is consistent with the copolymerization parameters of

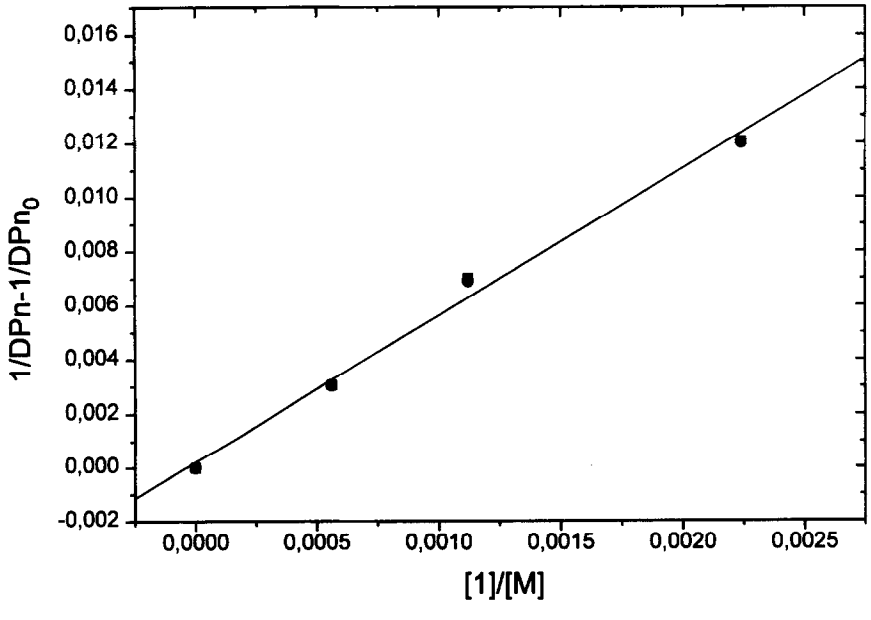


Fig. 1. Determination of the chain-transfer constant, at zero conversion.

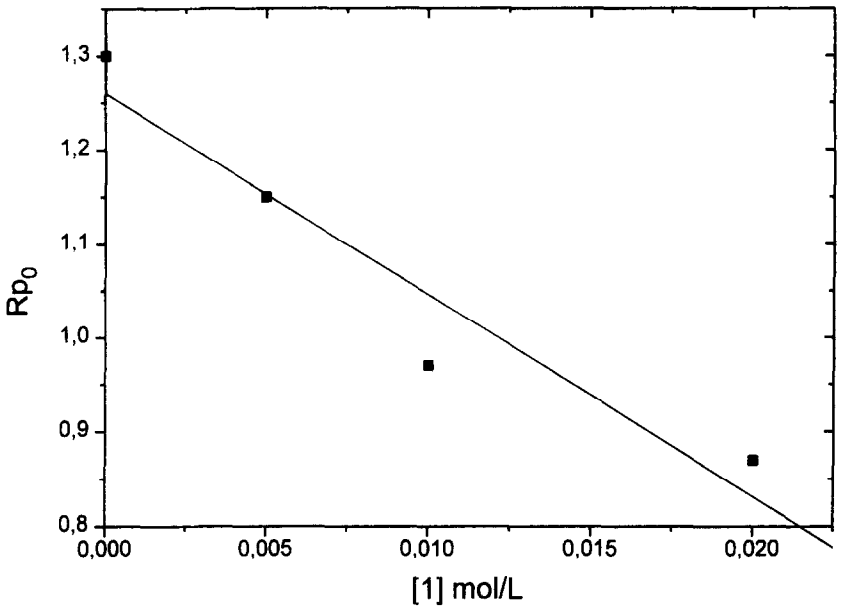


Fig. 2. Initial rate of polymerization of MMA vs the concentration of **1**, determined at zero conversion.

the corresponding comonomers M_2, butadiene ($r_1 = 0.25$ at 60°C) [24] and 1,3-pentadiene ($r_1 = 0.40$ at 50°C) [25], assuming that $r_1 = k_{11}/k_{12} = k_p/k_{tr} = 1/C_{tr}$.

Although there was a decrease in the yields of the precipitated polymers as the concentration of **1** or **2** increased (see Tables 1 and 3, % conversion column), it is clear that the lowering of molar mass is predominantly by true chain transfer, rather than by termination of growing polymer chains without re-initiation (i.e. retardation or degradative chain transfer).

The 5-benzenesuphonyl-1,3-pentadiene (2) showed also some chain-transfer activity in MMA polymerization (Table 3); this was consistent with the fact that carbon–sulfur bond are relatively weak.

As mentioned above, when **2** act as chain-transfer reagent in the addition–fragmentation regulation of a radical polymerization, a benzene sulfonyl fragment and a pentadienyl fragment are expected to

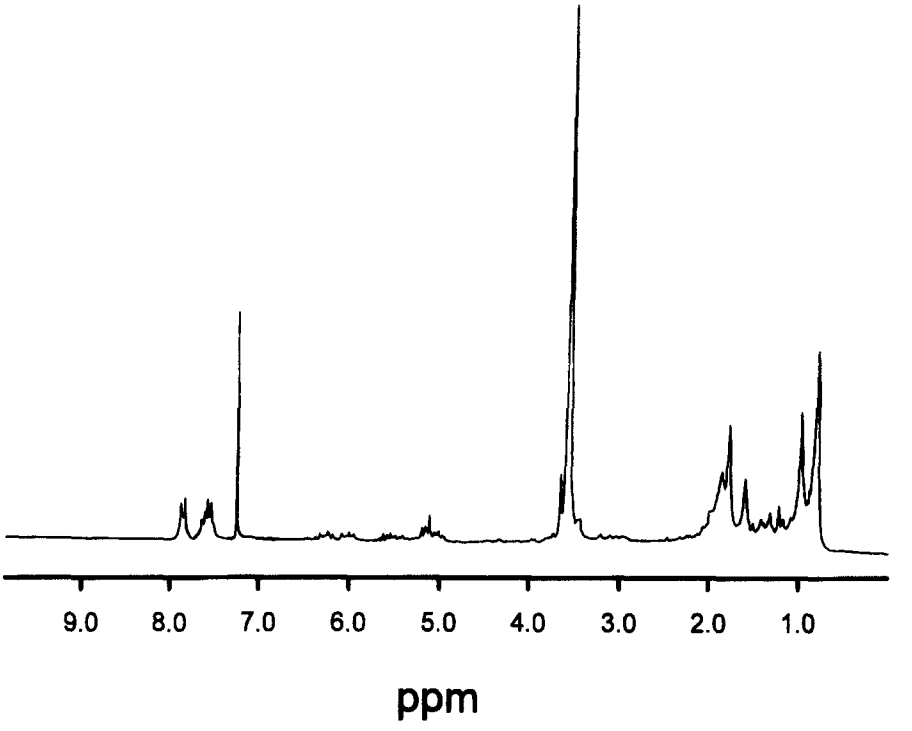


Fig. 3. ^{1}H NMR spectrum of poly(MMA) formed in the bulk polymerization of MMA in the presence of **2**. [AIBN] = 3.05×10^{-3} mol/L and [**2**] = 0.7 mol/L.

Table 4. Number-average degrees[a] of polymerization (DP_n) and conversions[b] of isolated polymers obtained by the use **3** at 60 C in the bulk polymerization of MMA and St

Polymerization conditions	[3] × 10³ (mol/L)	DP_n	[3]/[M] × 10⁴	C_{tr}	C_{tr}[b] (R_p/R_{p0})
MMA	0	2863	0		12.9 (1.00)
t:60 min	0.5	2008	0.59		12.3 (0.95)
(M_w/M_n:	2.5	700	2.80	7.4	7.3 (0.57)
2.3–1.7)	5	205	5.59		4.7 (0.36)
	10	80	11.2		2.7 (0.21)
	20	46	28.0		1.5 (0.12)
St	0	920	0		4.1 (1.00)
t:60 min	0.5	634	0.59		4.0 (0.97)
(M_w/M_n:	2.5	233	2.81	8.1	3.5 (0.85)
2.2–1.7)	5	129	5.61		2.8 (0.66)
	10	96	11.2		2.5 (0.60)

[a][AIBN] = 3.05 × 10⁻³ mol/L in MMA and St.
[b]The conversion is the ratio of the mass of recovered polymer to the initial mass of monomer.
[c](R_p/R_{p0}): ratio of the rates of polymerization with and without CTA, determined from SEC data.

be attached at both terminal-end of the resulting polymers. In order to try to identify accurately both ends of the telomers, a ^1H NMR spectrum of poly(MMA) prepared using **2** at higher concentration ([**2**] = 7.02 × 10⁻¹ mol/L); DP_n = 27 is represented in Fig. 3. Absorptions at 6.4–4.9 ppm are ascribable to dienic protons and those at 8.0–7.5 ppm to aromatic protons of the benzene sulfonyl group.

Introduction of an ester group on the diene fragment results in lowering the LUMO energy of the unsaturation. As anticipated, a great enhancement of reactivity is observed for **3**. Thus, examination of chain-transfer properties of such a compound in methyl methacrylate and in styrene (Table 4) revealed an important decrease in molar mass of the polymer prepared in the presence of increasing amounts of that compound. Compound **3** showed some chain-transfer activity in styrene and MMA polymerization (Table 4).

The rate of addition of the styryl or (meth)acrylyl macroradicals on **3** increases and the radicals adducts are also stabilized. The radical formed by addition of the propagating macroradical to **3**, therefore, was anticipated to fragment readily. However, strong retardation occurred during the polymerization reactions; the process cannot be seen as a true chain transfer. In the case of MMA, the chain transfer appeared to be mainly degradative. For example, when sufficient of the chain-transfer agent was added to lower the molar mass of PMMA by 62 times (2 × 10⁻² mol/L; [**3**]/[monomer] = 28.0 × 10⁻⁴, the conversion decreased to roughly 12% of that of the unregulated polymerization. Such a phenomenon appeared less important in the case of styrene. The reason for the inhibition phenomenon is not clear although it is often encountered in the polymerization of vinylic monomers involving allylic CTA derivatives. It might be attributed to the decrease of the rate of polymerization due to the addition step on the CTA, and not to primary radical termination, as usually claimed. A thorough investigation of the addition–fragmentation reactions leading to high inhibition will be presented in a forthcoming paper. In such cases, as mentioned above, the number quoted from Mayo equation is the "*apparent*" chain-transfer constant. In styrene and MMA, apparent C_{tr} for **3** was estimated to be 8.1 and 7.4, respectively. Nevertheless, chain-transfer agents with such high activities are of little practical utility, because they need constant replenishment throughout the polymerization if a reasonable narrow distribution of molar mass is to be obtained at any but the smallest conversions. Accordingly, we did not

Table 5. Chain-transfer constants (C_{tr}) and retardation[a] (R_p/R_{p0}) for $CH_2{=}CR^1(CH{=}CR^2)_nCH_2X$ at 60°C in the radical polymerization of MMA, St and MA

Entry	R^1	R^2	X	*n*	C_{tr}[a] MMA	St	MA	Ref.
1	CO_2Me	/	Br	0	0.93	2.34	2.93	[8]
2	CO_2Et	/	Br	0	1.45	/	2.33	[6]
3	CO_2Et	/	SBu,	0	0.74 (0.8)[b]	0.95 (0.9)[c]	/	[3]
4	CO_2Et	/	SO_2Ph	0	1.14	5.75	/	[6]
5	CO_2Me	/	OOBu,	0	0.63	1.64	/	[4]
6[d]	CO_2Et	/	C(SMe)CN	0	0.33 (0.1)	1.98 (0.4)	/	[16]
7	Ph	/	Br	0	2.27	2.93	5.25	[6]
8	Ph	/	SBu,	0	1.24 (0.8)[b]	0.80 (0.9)[c]	/	[3]
9	Ph	/	OOBu,	0	0.83	0.89	/	[4]
10	Ph	/	$OOCMe_2Ph$	0	0.80	/	/	[4]
11	H	H	Br	1	3.4[e] (0.87)[f]	/	/	[g]
12[d]	H	H	SBu,	1	0.92 (0.06)	0.34 (0.9)		[16]
13					1.1 (0.7)[f,h]			[i]
14	H	H	SO_2Ph	1	3.0 (0.77)[g]	/	/	[g]
15[d]	H	H	C(SMe)CN	1	0.66 (0.1)	1.7 (<0.1)	/	[16]
16[f]	CH_3	CO_2Me	Br	1	7.4 (0.12)	8.1 (0.60)		[g]
17[d]	CH_3	CO_2Me	SBu,	1	0.33 (0.1)	1.51 (0.1)		[16]

[a]The ratio R_p/R_{p0} is mentioned in parentheses, and determined from the rate of polymerization with and without added CTA.
[b]MMA, bulk, 1 hr, 60°C, [AIBN] = 12.1 × 10⁻³ mol/L.
[c]St, bulk, 3 hr, 60°C, [AIBN] = 8.37 × 10⁻³ mol/L.
[d]Polymerization conditions: bulk, 60°C, under N_2, conversion <5%, [AIBN]/[M] = 10⁻³, [CTA]/[M] = 5 × 10⁻³.
[e]C_{tr} extrapolated to conv. = 0% is 5.4.
[f][CTA] = 10⁻² mol/L, [AIBN] = 3.05 × 10⁻³ mol/L.
[g]Present work.
[h]Ratio copolymerization/fragmentation = 1.5.
[i]Unpublished results.

Table 6. Proportion of unsaturation in macromonomers prepared at low conversion

Reaction time (hr)	Conversion (%)	M_w $\times 10^{-3}$	Number of unsaturations	Number of Br units
30	9	10	4	3
9	9.6	15	3.9	2.5

investigate the polymerizations of methyl and butyl acrylates with CPP further.

The transfer reaction of growing polymer chain on **1–3** is very influenced by the polarity of the involved macroradicals and the electron density of the unsaturation of the CTA. The increased chain-transfer constant observed in MMA was expected from the increased electrophilicity of associated macroradicals, respectively, Such phenomenon have already been observed on similar dienic chain transfer agents (Table 5).

The above method appears as a simple means to prepare a diene-macromonomer by a single step reaction. The functionality of the macromonomer so formed depends upon the efficiency of the addition–fragmentation reaction (which can be considered as a chain-transfer reaction) and hence on the chain-transfer constant. It was found that addition of the chain-transfer agent caused substantial retardation in polymerization rate.

The proportion of double bonds in the macromonomers prepared at low conversion was estimated by their unsaturation content using both the bromination method and the titration method (using the mercuric acetate/tetrabutylammonium hydroxide system following the Johnson–Fletcher method [26]). Macromonomers were characterized by SEC and the results are given in Table 6. The unsaturation content of the macromonomers appeared always greater than those theoretically expected (i.e. only a single conjugated doubled bonds at the end of the polymer chain) and the disparity increased as the molar mass increased.

The unsaturations on the backbone of the polymer are supposed to result from the copolymerization of either the CTA or the formed macromonomer with the monomer. Since significant unsaturation was noticed even for low molar mass macromonomers prepared at a high concentration of CTA and at very low monomer conversion (where there is little chance for copolymerization with macromonomer), it is to be concluded that the residual unsaturation in these cases results essentially from the copolymerization of the CTA with the monomer.

CONCLUSIONS

Although the detailed mechanism for the activity of molar-mass control of the pentadienyl CTAs is not clear, the free radical addition–fragmentation reaction using **1** and **2** appears an elegant single-step method for the preparation of pentadiene-capped macromonomers. Copolymerization competes with the addition–fragmentation which, however, does not impair the functionality nor the utility of the resultant polymers as macromonomers. The macromonomers need to be synthesized in low conversion in order to obtain narrow molar mass distribution. Comparing the activity of **1** and **3** in which the same leaving group (the bromo radical) is involved but the diene substituents vary, indicates the important role of the diene polarity in the addition–fragmentation process.

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