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Chain Transfer by the Addition-Fragmentation Mechanism. 6.[1] Radical Polymerization toward the Synthesis of End-Functional Telomers, Macroinitiators, and Block Copolymers

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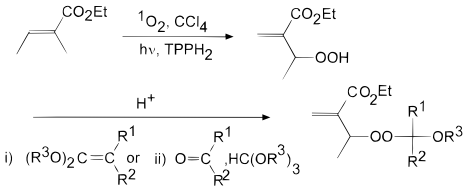
ABSTRACT: Acetal- or peroxyketal-terminated oligomers were prepared *via* a powerful process and characterized. Methanolysis of alkoxy(oxiranyl)-terminated or peralkoxy(oxiranyl)-terminated precursors were used to obtain the desired structures through an addition-substitution evolution on new chain transfer agents, 3-(cumylperoxy)-3-OY-2-phenyl-1-propene (see Chart 1) with Y = Me (CPMPP), Y = Et (CPEPP), and Y = $OCMe_2Ph$ (dCPPP). The free radical polymerization of methyl methacrylate (MMA), styrene (St), and methyl acrylate (MA) in the presence of such peroxyketals and precipitation of the polymer in methanol afforded directly the end-functional polymers. Chain transfer constants (C_{tr}) for these compounds in the monomer polymerization at 60 °C were determined from measurements of degrees of polymerization. C_{tr} values for CPMPP were determined to be 0.49, 0.92, and 1.94 in MMA, St, and MA, respectively. CPMPP behaves as an ideal transfer agent for styrene at temperatures close to 60 °C. The chain transfer activation energies, $E_{a,tr}$, for the reactions of PS and PMMA radicals with CPMPP were estimated to be 46.0 and 12.4 $kJ\cdot mol^{-1}$, respectively. The thermolysis activation energies of these peroxyketals, $E_{a,th}$ = 134.7 and 127.7 $kJ\cdot mol^{-1}$, respectively, to CPMPP and dCPPP were calculated from the Arrhenius plot of the homolytic decomposition rate constants, k_{th}, at various temperatures. dCPPP was used to design a monofunctional macroinitiator, a precursor of diblock copolymers.

Introduction

End-functional polymers can be obtained by means of chain transfer agents (CTA) in free radical polymerization. Apart from classical thio derivatives, many studies have been done dealing with addition-fragmentation agents.[2−12] The addition-fragmentation process occurs in free radical polymerization when a growing polymer chain reacts with a compound carrying both an activated unsaturation and a weak bond. The intermediate radical formed by the addition of the propagating radical on the transfer agent undergoes fragmentation of the weak bond, generating another radical entering into the polymerization cycle. Such a process occurs with formation of a functional group in the backbone of the polymer, or at the end of the polymer chain. A number of chain transfer agents able to generate an additon-fragmentation process have been developed so far, and Colombani and Chaumont submitted recently a review dealing with the wide area of addition-fragmentation processes in the free radical polymerization.[13] However, the industrial valorization is still limited because of problems related mostly to the synthetic availability of these compounds at a reasonable cost. Such materials could be conveniently used for the preparation of building blocks for large structures, including block and graft copolymers, by condensation reactions. Indeed, the properties of these large structures are often sensitive to the molar masses and polymolecularity of the telomers involved. The chain transfer agents which follow the addition-fragmentation mechanism are of particular interest in organic and polymer chemistry. We have recently reported new classes of CTA that act *via* a two-step radical addition-substitution process: (1) *tert*-alkyl permethacrylates, which involve the formation of *ω*-(2,3-epoxy-2-methyl-3-oxopropyl) oligomers,[11] and (2) ethyl 2-subtituted-cinnamates as new precursors of macromonomers.[1]

Scheme 1. Synthesis of Peroxyketals by Photooxygenation of Ethyl Tiglate and Transacetalization of the Corresponding Hydroperoxide



Ethyl 2-(1-hydroperoxyethyl)propenoate-derived peroxyketals[10,14] are useful transfer agents in the polymerization of methyl methacrylate (MMA), styrene (St), and alkyl acrylates. However, the method of preparation of the hydroperoxy precursor by photooxygenation of commercial ethyl tiglate[15] (Scheme 1) could not be envisaged for large scale production.

We now report preliminary experiments which demonstrate that functionalized oligomers are easily available through the use of appropriately substituted unsaturated peroxyketals (Chart 1) as wonderful chain transfer agents in free radical polymerization (Scheme 2).

Experimental Section

Instruments. NMR spectra were recorded on a Bruker AC 200 spectrometer, using $CDCl_3$ as solvent. The molar masses of the polymers were estimated by size exclusion chromatography (SEC) using a Waters instrument (Waters WISP710b automatic injector, Schimadzu LC6a pump) connected to four PL-Gel columns coupled with a refractometer (Waters R401) and a dual-UV detector (Beckmann 167). Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 $mL\cdot min^{-1}$, and the system was calibrated using narrow molar mass distribu-

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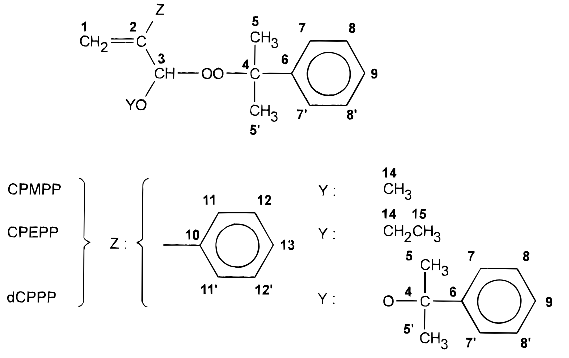
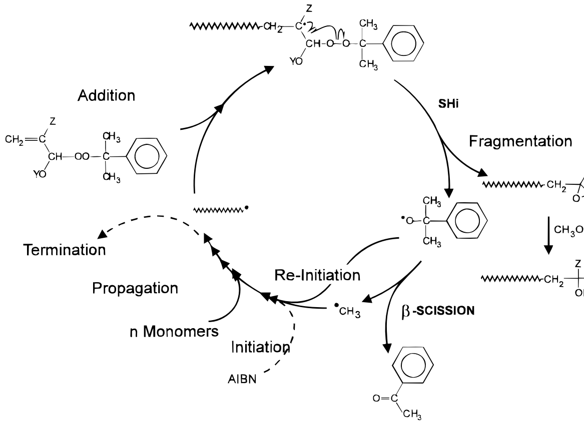


Chart 1. 3-Cumylperoxy-3-OY-2-phenyl-1-propene with Carbon Naming for NMR Analysis



Scheme 2. Radical Mechanism of Polymerization in the Presence of a Transfer Agent

tion PMMA and PS standards (Waters). Thermal stability studies were performed using differential scanning calorimetry (DSC) (Perkin-Elmer DSC 4 instrument). Flash column chromatographic purifications were carried out on Merck silica gel 60 (60−200 mesh) and monitored by thin layer chromatography (TLC) using Merck precoated silica gel 60 F-250 (0.25 mm thickness) aluminum-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 experimental values with gaps lower than 0.5% for carbon, hydrogen, and oxygen.

Materials. Methyl methacrylate (MMA), styrene (St), and methyl acrylate (MA), available from CdS Chimie, were purified by vacuum distillation over Na or CaH_2 before use and stored at −10 °C. Styrene, trimethyl orthoformate, formic acid (40% w/w in water), and *p*-toluenesulfonic acid monohydrate (PTSA) were used as received from Aldrich. Cumyl hydroperoxide, commercially available as an 87% w/w solution in cumene, was stirred and heated to 40 °C and then concentrated by evaporation of the solvent under reduced pressure (10^{-2} mmHg). Cumyl hydroperoxide was obtained with good purity, which was then accurately determined by iodometric titration[16] before use. The solvents (THF, $HCCl_3$, EtOH, Et_2O, methanol, heptane, etc.) were reagent grade and used without further purification. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich) was repeatedly crystallized from methanol.

3-(Cumylperoxy)-3-methoxy-2-phenyl-1-propene (CPMPP). It was prepared easily from atropaldehyde.[17] The latter one was obtained in three steps from styrene (52 g, 0.50 mol) as white crystals (24 g, 36%). ^{1}H NMR ($CDCl_3$): δ 9.83 (s, 1H, CHO), 7.50−7.39 (m, 5H, C_6H_5), 6.64 and 6.20 (2s, 2H, CH_2=C). Cumyl hydroperoxide (99%, 3.22 g, 21 mmol) was added very slowly at room temperature to the ketal formed by the reaction of atropaldehyde (2.64 g, 20 mmol) with trimethyl orthoformate (2.23 g, 21 mmol) in the presence of PTSA (15 mg, 0.15 mmol). The methanol formed was eliminated stepwise under reduced pressure (10 mmHg). The crude product was then purified by chromatography on a column of silica gel (60 g) to give CPMPP as a colorless liquid (3.5 g, 59%); R_f = 0.42, heptane/Et_2O = 88/12 (for spectroscopic analysis, see Chart 1). ^{1}H NMR ($CDCl_3$): δ 7.50−7.20 (m, 10H, C_6H_5), 5.6−5.3 (m, 3H, CH_2=C and CH), 3.53 (s, 3H, OCH_3), 1.60 and 1.58 (2s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 145.2 [C^6], 143.2 [C^2], 138.1 [C^{10}], 128.2−124.4 (9 peaks) [$C^{11,11'}$, $C^{12,12'}$, C^{13}, $C^{7,7'}$, $C^{8,8'}$, C^9], 117.0 [C^1], 106.7 [C^3], 83.4 [C^4], 56.2 [C^{14}], 27.5−26.2 [$C^{5,5'}$]. Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43; O, 16.09. Found: C, 76.75; H, 7.21; O, 15.98.

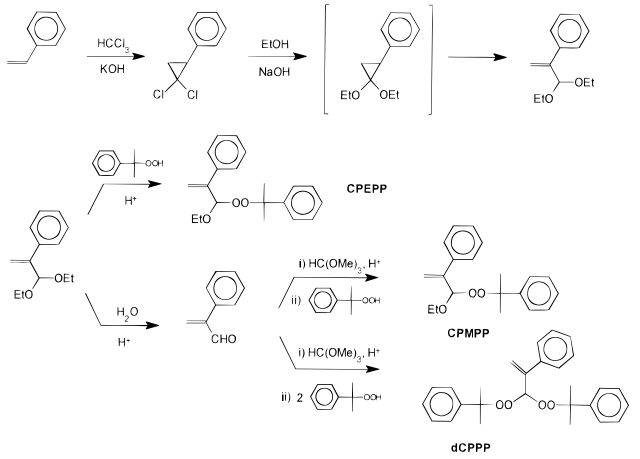
3-(Cumylperoxy)-3-ethoxy-2-phenyl-1-propene (CPEPP). To a mixture of 3,3′-diethoxy-2-phenyl-1-propene[17] (6.18 g, 30 mmol) and PTSA (10 mg, 0.06 mmol) was added dropwise, at room temperature, cumyl hydroperoxide (87%, 5.59 g, 32 mmol). The ethanol formed was continuously eliminated under reduced pressure (5−10 mmHg), and the residue was purified by column chromatography on silica gel (90 g) to yield pure CPEPP (7.2 g, 77%); R_f = 0.45, heptane/Et_2O = 90/10. ^{1}H NMR ($CDCl_3$): δ 7.50−7.20 (m, 10H, C_6H_5), 5.6−5.4 (m, 3H, CH_2=C and CH), 4.0−3.6 (m, 2H, OCH_2), 1.60 and 1.58 (2s, 6H, $C(CH_3)_2$), 1.25 (t, J = 7.1 Hz, 3H, OCH_2-CH_3). Anal. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74; O, 15.37. Found: C, 76.78; H, 7.80; O, 15.45.

3,3-Bis(Cumylperoxy)-2-phenyl-1-propene (dCPPP). A mixture of cumyl hydroperoxide (99.5%, 6.10 g, 40 mmol), atropaldehyde[17] (2.64 g, 20 mmol), trimethyl orthoformate (2.33 g, 22 mmol), and PTSA (12 mg, 0.07 mmol) was stirred at room temperature for 1 h. The methanol formed was eliminated under vacuum. The pure diperoxyketal was isolated from column chromatography on silica gel (80 g) as a viscous colorless liquid (6.5 g, 78%); R_f = 0.37, heptane/Et_2O = 88/12) (for spectroscopic analysis, see Chart 1). ^{1}H NMR ($CDCl_3$): δ 7.52−7.23 (m, 15H, C_6H_5), 5.55−5.44 (m, 3H, CH_2=C and CH), 1.63 and 1.61 (2s, 12H $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$): δ 145.2 [C^6]; 143.2 [C^2]; 138.0 [C^3]; 128.2−125.6 (several peaks), 124.3 [$C^{11,11'}$, $C^{12,12'}$, C^{13}, $C^{7,7'}$, $C^{8,8'}$, C^9]; 116.9 [C^1]; 106.6 [C^3]; 83.4 [C^4]; 27.1 26.2 [$C^{5,5'}$]. Anal. Calcd for $C_{27}H_{30}O_4$: C, 77.48; H, 7.23; O, 15.29. Found: C, 77.63; H, 7.32; O, 15.08.

Macroinitiators (MI_1 and MI_2). The preparation of the macroinitiators MI_1 and MI_2 was performed in styrene under the typical polymerization procedure presented below using [AIBN] = 3.05×10^{-3} mol·L^{-1} and [dCPPP] = 0.1 (for MI_1) and 0.5 mol·L^{-1} (for MI_2). The reaction mixture was heated at 60 °C for 2 h. Molar masses of the corresponding macroinitiators MI_1 and MI_2 were determined by SEC: M_n = 8000 and 2500 g·mol^{-1}, respectively. The macroinitiators were separated from dCPPP by successive precipitations in methanol and dried at 25 °C under vacuum.

Typical Polymerization Procedure. 2,2′-Azobis(isobutyronitrile) (in St and MMA, 40 mg, 2.44×10^{-4} mol; in MA, 8 mg, 4.88×10^{-5} 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 monomer (10 mL) was also prepared and used to add the required amounts of the chain transfer agent to the ampules. The tubes were evacuated by three freeze/pump/thaw cycles and sealed under vacuum (while frozen). Then, the tubes were placed in a thermostated oil bath for a defined period of time (60 °C; St and MMA, 1 h; MA, 10 min; conversions were kept below 3% for styrene and 10% for MMA and MA), after which the tubes were rapidly frozen with a dry ice/2-propanol bath and opened. A 15 mL aliquot of a 0.1% solution of hydroquinone in THF was added to each tube, and the polymers were precipitated by addition of the solution to 350 mL of heptane or methanol. The polymers were filtered off in weighed sintered glass funnels, dried in a vacuum oven at 60 °C for 12 h, and weighed. The monomer conversion was calculated from the weight of the polymer and the initial amount of the monomer. The molar masses of poly(methyl acrylate) were estimated from polystyrene calibration (without consideration of the differences in hydrodynamic volumes).

Scheme 3. Synthetic Strategy for the Preparation of the Peroxyketals and the Diperoxyketal



Polymerization of MMA Initiated by MI$_1$. Two cleaned and dried Pyrex tubes were used to investigate the activity of dCPPP-functionalized polymer as macroinitiator. In both, MMA (1.5 g, 15 mmol) and triphenylmethane (1.65 g, 6,8 mmol) were dissolved in toluene (1.84 g, 20 mmol) as a solvent. In the first tube, MI$_1$ (M_n = 2500 g·mol^{-1}, 25 mg, 10^{-5} mol) was added. The tubes were evacuated by three freeze/pump/thaw cycles and sealed while frozen under vacuum. Then, the tubes were placed in a thermostated oil bath (120 °C) for 2 h, after which the tubes were rapidly frozen and opened. The reaction media were immediately injected into the SEC apparatus, without precipitation, in order to determine the molar mass distribution and the relative conversion.

Results and Discussion

This paper describes the synthesis of end-functional telomers of methyl methacrylate, styrene, and methyl acrylate by the means of new and easily available CTA involving the addition-fragmentation process.

Synthesis of the Vinylic Peroxyketals. In previous work,[10,14] a method of preparation of vinylic peroxyketals was reported and based on the transacetalization of ethyl 2-(1-hydroperoxyethyl)propenoate-derived unsaturated hydroperoxide on various acetals. However, the method of preparation of the hydroperoxy precursor by photooxygenation of ethyl tiglate[15] could not be envisaged for large scale production. The synthesis of atropaldehyde-type peroxyketals and diperoxyketal developed in this paper is based on the transacetalization of a commercial hydroperoxide on atropaldehyde diethyl and dimethyl acetals[17] (Scheme 3). Indeed, the latter products are available in large scale, avoiding the use of uneasily available starting material, especially under industrial constraints. Attempts to prepare 2-(ethoxycarbonyl)propenal by chromic oxidation[18] of ethyl 2-(hydroxymethyl)propenoate failed, and formation of polymer materials was observed. The high polymerizability of the expected 2-(ethoxycarbonyl)propenal could explain such a result.

The synthesis of macroinitiators MI$_1$ and MI$_2$ was performed by the radical polymerization of styrene in the presence of dCPPP as chain transfer agent. The chain transfer constant of dCPPP was estimated to be *ca.* 0.9, which is similar to that obtained for CPMPP. Such a result is in accordance with the similar steric hindrance of the cumylperoxy group and of methoxy groups located far away from the unsaturation. The chain transfer mechanism applied to dCPPP yielded the structure of the macroinitiator described in Scheme 4. Taking into account the reactivity of the alkoxyoxirane ring with hydroxylated substances,[19] precipitation of macroinitiators in methanol was expected to yield an ω-terminated polymer bearing an α-hydroxyperoxyacetal function (Scheme 4).

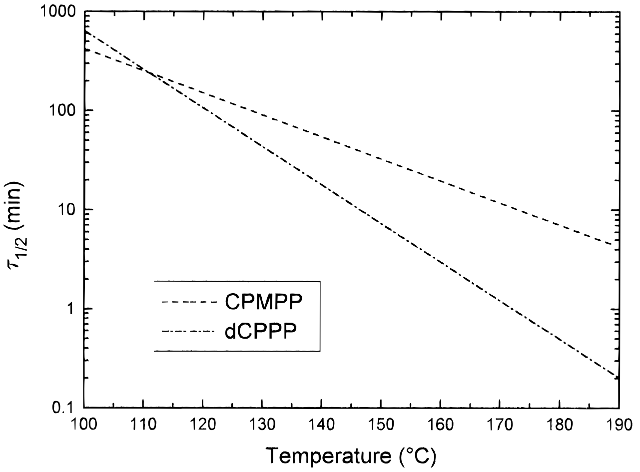
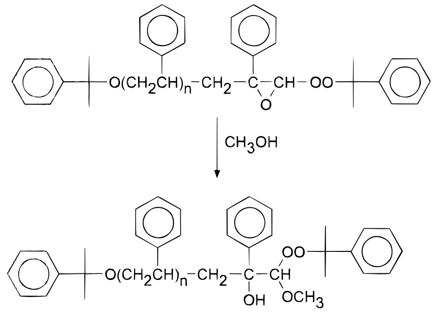


Figure 1. Half-life times of CPMPP and dCPPP as functions of the reciprocal thermolysis temperature.

Scheme 4. Methanolysis of ω-Peralkoxyoxiranyl Oligomers



Thermal Stability of the Peroxyketals. The study of the thermal stability of the peroxyketals CPMPP and dCPPP was realized according to the procedure previously developed.[20] DSC study of the thermolysis was performed in a diphenylmethane–triphenylmethane solution to inhibit side reactions of induced homolytic decomposition of the unsaturated peroxyketals by addition-substitution reactions. In such a case, the thermolysis was studied as a true first-order reaction to give homolytic dissociation rate constants, k_{th}, activation energies, $E_{a,th}$ = 134.7 and 127.7 kJ·mol^{-1}, respectively, and frequency factors, $A_{th} \times 10^{13}$ = 7.9 and 0.79 s^{-1}, respectively. The half-lives of the peroxyketals *versus* temperature are reported in Figure 1. Allylic peroxyketals appeared to be as thermally stable as those reported before.[10] As mentioned previously, the reaction conditions of the polymerization have to be controlled to minimize the thermolysis of the peroxyketal.[1,10] This latter phenomenon remains a minor side reaction whatever the conditions used, and such compounds could be considered as "stable" in the conditions of the polymerization.

Chain Transfer Constants. When samples of MMA or St containing various concentrations of CPMPP (Table 1) were polymerized for 1 h at 60 °C with AIBN as initiator, the resultant polymers were of markedly lower molar mass as compared to those prepared in the absence of CPMPP. The chain transfer constant (C_{tr}), reflecting the relative rate constants for chain transfer *versus* propagation and calculated by using the Mayo

Table 1. Number-Average Degrees[a] of Polymerization (DP_n) and Conversions[b] of Isolated Polymers Obtained by the Use of CTAs (Chain Transfer Agents) at 60 °C in the Polymerization of MMA, St, and MA

entry	monomer	CTA	DP_n[a]	[CTA]/ [M] × 10^4	conv,[b] % (R_p/R_{p0})[c]	C_{tr}
1	MMA	CPMPP	5407	0	6.1 (1.00)	
2	MMA	CPMPP	4278	0.56	5.5 (0.95)	
3	MMA	CPMPP	2734	2.80	5.6(0.91)	0.49
4	MMA	CPMPP	2038	5.59	5.1 (0.83)	
5	MMA	CPMPP	1161	11.2	4.7 (0.71)	
6	MMA	CPMPP	635	28.0	3.7 (0.53)	
7	St	CPMPP	1910	0	1.5 (1.00)	
8	St	CPMPP	1833	0.56	(0.95)	
9	St	CPMPP	1333	2.81	(0.92)	0.92
10	St	CPMPP	1131	5.61	(0.83)	
11	St	CPMPP	697	11.2	(0.81)	
12	St	CPMPP	377	28.1	(0.78)	
13	MA	CPMPP	7297	0	(1.00)	
14	MA	CPMPP	5822	0.59	(0.93)	
15	MA	CPMPP	1763	2.96	(0.86)	1.94
16	MA	CPMPP	977	5.92	(0.40)	
17	MA	CPMPP	456	11.8	(0.27)	
18	MA	CPMPP	172	29.6	n.d.[c]	
19	St	dCPPP	1500	0	6.0	
20	St	dCPPP	77	112.2	10.2	0.9

[a] [AIBN] = 3.05×10^{-3} mol·L^{-1} in MMA and St and [AIBN] = 6.1×10^{-4} mol·L^{-1} in MA. [b] Ratio of the weight of recovered polymer to the initial weight of monomer, in %. [c] n.d. = not determined. (R_p/R_{p0}) = ratio of the rates of polymerization with and without CTA, determined from SEC data.

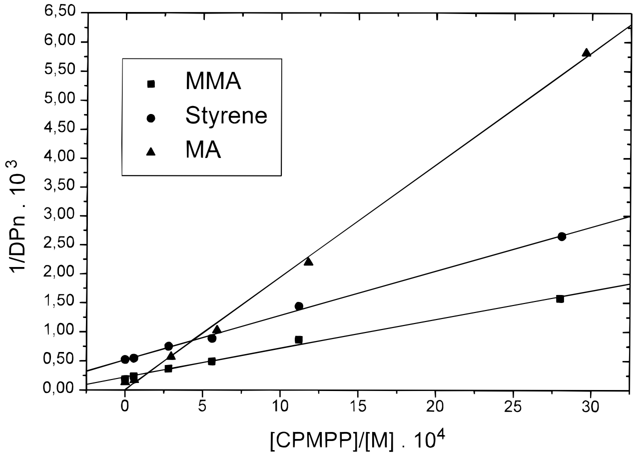


Figure 2. Reciprocal degrees of polymerization (DP_n) of a monomer (M) as a function of the molar ratio of CPMPP to M. Values of DP_n were determined by SEC. The lines are least-squares fits to the data represented by the corresponding filled symbols.

Table 2. Number-Average Degrees[a] of Polymerization (DP_n), Conversions,[b] and Chain Transfer Constants (C_{tr}) of CPMPP in the Polymerization of MMA and St at Various Temperatures

polymerization conditions	monomer	DP_n[a]	[CPMPP]/ [M] × 10^4	conv,[b] % (R_p/R_{p0})[e]	$C_{tr} \times 10^2$
	MMA	6950	0	3.3 (1.00)	
	MMA	5390	0.55	3.7 (1.07)	
	MMA	3245	2.77	3.6 (1.10)	0.52
	MMA	2140	5.55	3.9 (0.98)	
temp = 50 °C	MMA	1325	11.1	3.8 (1.06)	
t = 90 min	MMA	630	27.7	3.9 (1.19)	
[MMA][c] = 9.01 mol·L^{-1}	St	2495	0	0.9 (1.00)	
[St][c] = 8.45 mol·L^{-1}	St	2143	0.55	1.0 (1.00)	
	St	1805	2.77	1.1 (1.22)	0.77
	St	1172	5.55	1.2 (1.02)	
	St	855	11.1	1.3 (1.6)	
	St	n.d.[d]	27.7	1.4 (1.10)	
	MMA	4790	0	5.9 (1.00)	
	MMA	3780	0.57	6.0 (1.01)	
	MMA	2825	2.85	6.3 (1.01)	0.46
	MMA	2025	5.69	6.2 (1.04)	
temp = 70 °C	MMA	1345	11.4	6.5 (1.05)	
t = 30 min	MMA	665	28.5	7.6 (1.20)	
[MMA][c] = 8.78 mol·L^{-1}	St	1404	0	2.1 (1.00)	
[St][c] = 8.78 mol·L^{-1}	St	1313	0.57	1.9 (0.99)	
	St	1128	2.85	2.1 (0.99)	1.03
	St	962	5.69	2.2 (1.03)	
	St	668	11.4	2.2 (1.06)	
	St	383	28.5	2.0 (1.24)	
	MMA	2760	0	6.5 (1.00)	
	MMA	2505	0.58	6.8 (1.02)	
	MMA	2015	2.89	6.2 (0.98)	0.42
	MMA	1600	5.77	7.0 (1.03)	
temp = 80 °C	MMA	1170	11.5	7.2 (1.09)	
t = 15 min	MMA	645	28.9	8.1 (1.13)	
[MMA][c] = 8.66 mol·L^{-1}	St	951	0	1.9 (1.00)	
[St][c] = 8.66 mol·L^{-1}	St	884	0.58	2.0 (0.95)	
	St	789	2.89	2.1 (0.96)	n.d.[d]
	St	666	5.77	2.3 (1.01)	
	St	530	11.5	2.5 (1.09)	
	St	300	28.9	2.6 (1.22)	

[a] Determined from SEC data. [b] Based on isolated polymer from the starting material. [c] d (MMA) = $(0.968-1.225) \times 10^{-3}$. T and d (St) = $(0.9224-8.69) \times 10^{-4} T$ (T in °C). [d] n.d. = not determined. [e] (R_p/R_{p0}) = ratio of the rates of polymerization with and without CPMPP, determined from SEC data.

equation,[21] was 0.49 (Figure 2). The compound therefore has the same order of magnitude as the thiols commonly used for reducing molar mass (*e.g.* *n*-butanethiol,[22] C_{tr} = 0.67).

The chain transfer constants observed with CPMPP in MMA were lower than those obtained with 3-(*tert*-butylperoxy)-2-phenyl-1-propene[8] (C_{tr} = 0.83). As observed previously,[10] it can be explained by a steric hindrance occurring in the addition step of the transfer reaction between the growing PMMA radical (α-methyl fragment) and CPMPP (α-(cumylperoxy)methoxymethyl group). This phenomenon was less important in MA polymerization (Z = H) and the electronic effects are more favorable, which can explain the satisfactory chain transfer constant obtained in this latter case (C_{tr} = 1.94).

The peroxyketal CPMPP was also efficient in lowering the molar mass in styrene polymerization (Table 1). The chain transfer constant (60 °C) in this case was 0.92, which is close to the ideal[23] value of 1.0 and contrasts with that of a typical thiol (*e.g.* 1-dodecanethiol,[22] C_{tr} = 15−19). This transfer constant was slightly higher than those obtained for 3-[(cumylperoxy)methyl]-2-phenyl-1-propene[8] (C_{tr} = 0.80). Such a result could be explained by the electron-withdrawing effect of the supplementary methoxy group α to the unsaturation which could decrease the electron density on the double bond, favoring the addition of a nucleophilic polystyryl macroradical on the chain transfer agent and stabilizing the intermediate adduct radical. Such an electronic effect was recently observed by Yamada *et al.*[24,25] As mentioned previously for methacrylic-type transfer agents, the steric hindrance of the chain transfer agent seems to be of low importance in the case of styrene polymerization.

Thermodynamics of the Transfer Reaction. In order to calculate the thermodynamic parameters (especially $E_{a,tr}$), C_{tr} values were determined at various temperatures (Table 2). Considering the fact that the addition reaction is the limiting step of the transfer process, the rate constants, k_{tr}, are a good approximation of the addition rate constants, k_{add}, of the growing polymer radicals to the double bond of CPMPP. The

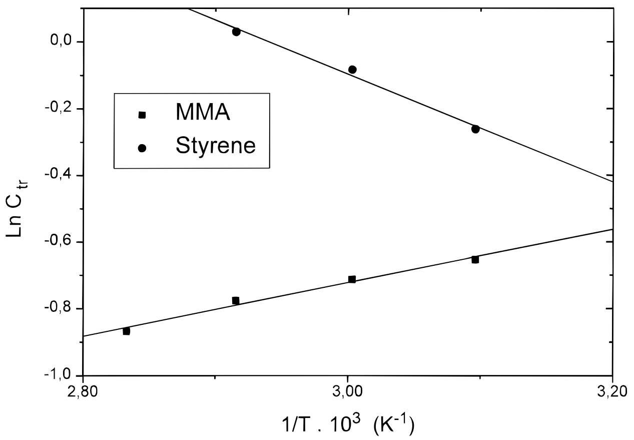


Figure 3. Chain transfer constant Neperien logarithm of PMMA and PS macroradicals on CPMPP as a function of the reciprocal reaction temperature. The line is a least-squares fit to the data represented by the filled symbols.

Table 3. Absolute Rate Constants (k_{tr}) of the Growing Polymer Radical with CPMPP at Various Temperatures

		polymerization temp (°C)			
monomer	kinetics	50	60	70	80
MMA	C_{tr}	0.52	0.49	0.46	0.42
	k_p (L·mol^{-1}·s^{-1})	560	705	866	1050
	k_{tr} (L·mol^{-1}·s^{-1})	291	345	398	441
St	C_{tr}	0.77	0.92	1.03	
	k_p (L·mol^{-1}·s^{-1})	122	176	247	342
	k_{tr} (L·mol^{-1}·s^{-1})	94	162	255	

literature values of k_p are also reported in Table 3 with the calculated k_{tr} values.

$$\text{For MMA:}^{26}\quad k_p = 0.087 \times 10^7 \exp\left(-\frac{19700}{RT}\right) \quad (\text{L·mol}^{-1}\text{·s}^{-1})$$

$$\text{For styrene:}^{27}\quad k_p = 2.16 \times 10^7 \exp\left(-\frac{32600}{RT}\right) \quad (\text{L·mol}^{-1}\text{·s}^{-1})$$

$$\text{with } R = 8.314 \text{ J·mol}^{-1}\text{·K}^{-1} \text{ and } T \text{ in K}$$

The Arrhenius equation for the chain transfer constant C_{tr} is

$$C_{tr} = \frac{k_{tr}}{k_p} = \frac{A_{tr}}{A_p} \exp\left(\frac{E_{a,p} - E_{a,tr}}{RT}\right)$$

The experimental activation energies, $E_{a,p} - E_{a,tr}$, and the frequency factors, A_{tr}/A_p, were calculated from the plot of the Neperien logarithm of the chain transfer constants of PMMA and PS macroradicals on CPMPP *versus* the reciprocal reaction temperature (Figure 3).

The absolute activation energies, $E_{a,tr}$, and the frequency factors, A_{tr}, were determined from the experimental estimation of $E_{a,p} - E_{a,tr}$) and (A_{tr}/A_p), respectively, using the literature values of $E_{a,p}$ and A_p (Table 4). The absolute activation energy, $E_{a,tr}$, for the termination of PMMA radicals by transfer on CPMPP is slightly higher than the activation energy, $E_{a,p}$, for the propagation step of the monomer polymerization.

Spectroscopic Characterization of the Functionalized Polystyrene. The mechanism shown in Scheme 2 leads to an expectation that the low-molar-mass polymer chains prepared with the peroxyketals studied would be terminated by an α-hydroxyacetal fragment. To test this hypothesis, a low-molar-mass PS (MI_2, M_n = 2500 g·mol^{-1}) was prepared using dCPPP and was purified by repeated precipitations to remove all traces of the unreacted chain transfer agent. The ^{1}H NMR spectrum shows signals at δ 4.2−4.0 ppm and signals at 3.52 and 3.49 ppm, confirming the presence of the acetal hydrogen and the methoxy group (2 diastereoisomers), respectively. Signals centered at δ 3.2−2.9 ppm and δ 1.62 and 1.59 ppm, indicative of cumyl O*CH₂* fragments and methyl groups from cumyl fragments, respectively (Figure 5), were also observed. The presence of the alcohol function was shown around 3.4 ppm. Moreover, evidence for acetal formation was obtained from the ^{13}C NMR spectra which display signals at δ 105 and 87 ppm (see Figure 4) for each of the chiral carbons.

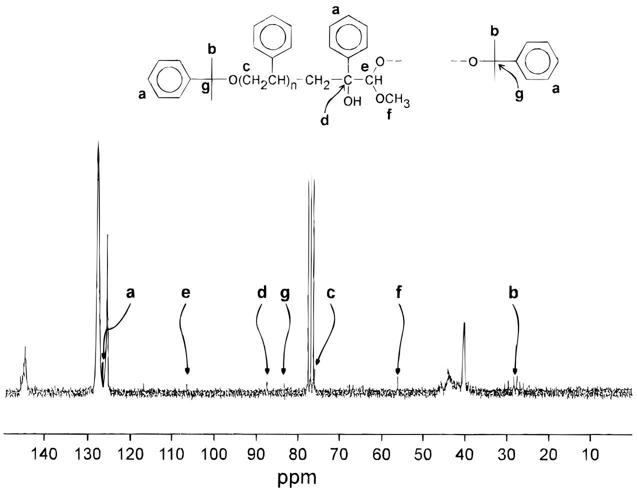


Figure 4. ^{13}C NMR (63 MHz) spectrum of polystyrene (M_n = 2500) prepared using CPMPP as a chain transfer agent.

Table 4. Thermodynamic Parameters of the Transfer Reaction of CPMPP with PS and PMMA Radicals

monomer	$E_{a,p} - E_{a,tr}$[a] (kJ·mol^{-1})	$E_{a,tr}$[b] (kJ·mol^{-1})	A_{tr}/A_p[c] (mol·L^{-1})	A_{tr}[d] × 10^{-7} (L·mol^{-1}·s^{-1})
St	−13.4	46.0	165	387
MMA	7.3	12.4	0.035	0.163

[a] Experimental activation energy. [b] Activation energy for transfer. [c] Relative frequency factor. [d] Frequency factor for transfer reaction.

Table 5. Polymerization of Styrene in the Presence of 3,3-(Dicumylperoxy)-2-phenyl-1-propene (dCPPP) at 60 °C for 2 h

	blank	MI₁	MI₂
[dCPPP] (mol·L^{-1})	0	0.1	0.5
M_n	100 000	8000	2500
M_w	163 700	15 500	5600
conv (%)	6	10	12

Polymerization Initiated by Macroinitiator MI₂. MI₂ was used to initiate the free radical polymerization of MMA (Scheme 5). In order to determine the reactivity of MI₂ as a free radical initiator, two experiments were performed, both of them using the same quantity of MMA as monomer and of triphenylmethane to control the molar mass of the polymer formed. In the first experiment, MI₂ was added. The results are shown in Table 6. The SEC diagrams obtained (using both a differential refractometer and a UV detector operated at 254 nm) from analysis of pure MI₂ and from the reaction media involving MI₂ as initiator are compared in Figure 6. The following points can be outlined: (a)

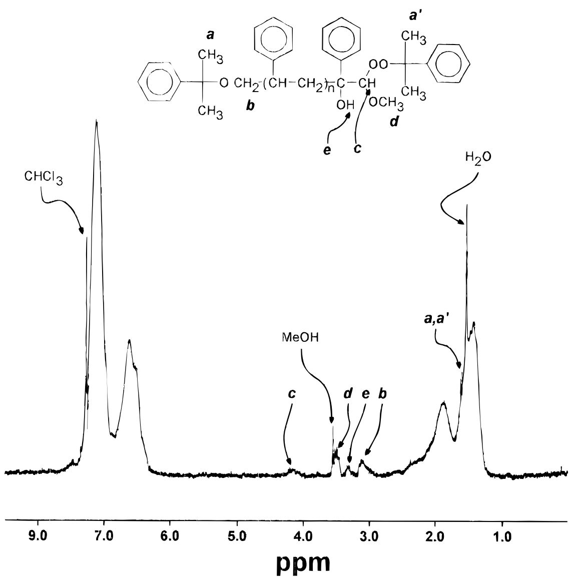


Figure 5. ^{1}H NMR (200 MHz) spectrum of polystyrene (M_n = 2500) prepared in the presence of CPMPP as a chain transfer agent.

Scheme 5. Synthesis of Block Copolymers from a macroinitiator

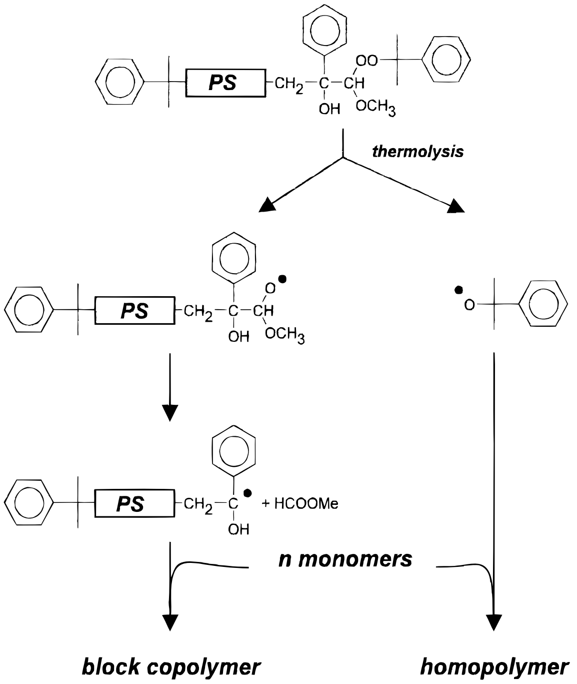


Table 6. Copolymerization of MMA in the Presence of a Styrene Macroinitiator MI$_2$ at 120 °C for 2 h

	(0)	(1)
[MI$_2$] (mol·L^{-1})	0	0.01
M_n	171 000	7500
M_w	333 150	77 700
conv (%)	5	37

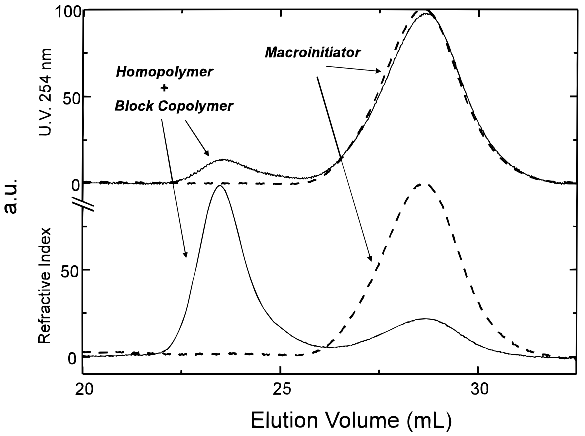


Figure 6. SEC chromatograms for copolymerization.

The SEC refractometer diagrams of the PMMA sample prepared in the absence of MI$_2$ show a simple peak located at 23 mL, whereas the UV (254 nm) signal is negligible. After refractometer calibration using PMMA standards, the MMA conversion for this experiment was determined to be 5% (attributed to "thermal" initiation). (b) The MI$_2$ SEC diagrams exhibit a simple molar mass distribution at 28 mL (see Figure 6). The differential refractometer and UV (254 nm) normalized signals are exactly the same. (c) The SEC diagrams corresponding to the polymerization of MMA in the presence of MI$_2$ exhibit two peaks (see Figure 4), the first one located within the same elution volume range as the "thermal" PMMA (23 mL) and the other one located at the elution volume corresponding to MI$_2$ (28 mL). In the latter case, the refractometer and the UV signals are quite different: (a) The peak located at 28 mL is attributed to MI$_2$ (either unreacted or dead polymer). (b) According to Scheme 5, the peak located at 23 mL (higher molar mass range) is attributed to PMMA homopolymer, initiated either by a "thermal" process or by the small alkoxy radicals expelled into the medium through MI thermolysis, and/or to block copolymer initiated by the MI$_2$ macroradical (also expelled through thermolysis of MI$_2$). The presence of this latter species is confirmed by the UV-absorption peak of the polystyrene aromatic rings in the same elution volume domain. After calibration of both detectors (refractometer and UV spectrometer) by means of PMMA and PS standards, the MMA conversion was calculated to be 37%. The fact that this value is much higher than the conversion obtained in the absence of MI$_2$ is a consequence of the activity of MI as initiator. The problem is to evaluate the fraction of macroradicals effectively giving rise to block copolymer. This can be done by determination of UV-peak areas: all the macroradical species expelled by thermolysis giving rise to block copolymer are shifted from 28 to 23 mL in the UV–SEC diagrams. The temperature of the reaction media being 120 °C, the rate constant of thermolysis of the peroxide group carried on MI$_2$ is calculated (from the activation energy and the frequency factor) to be *ca.* 8×10^{-5} s^{-1}. Therefore, after 2 h of reaction, the conversion of MI$_2$ is about 0.4. If one supposes that the efficiency factor of macroradicals is equal to 1, the ratio of UV peaks located at 23 and 28 mL, respectively, should be equal to 0.67 (*i.e.* 0.4/0.6). In fact, in the case of MI$_2$, the ratio is 0.08 (0.07/0.93). Letting f be the efficiency factor, one can write

$$\frac{0.4f}{0.4(1-f)+0.6} = \frac{0.07}{0.93}$$

Thus, the efficiency factor f of the macroradicals is roughly equal to 0.2. Such a value can be compared to those of micromolecular peroxide initiators like lauryl peroxide[28] (f = 0.65). The lower efficiency of MI$_2$ is a classical behavior of peroxide-type macroinitiators[29] compared to similar micromolecular compounds, because radical pairs formed after scission of macroinitiator scissile bonds tend to recombine or disproportionate due to slow diffusion out of the cage. In the case of classical macroinitiators, bearing multiple peroxide bonds in the main chain, this lower efficiency of scissile bonds can be covered by another scissile point in the same chain, resulting in improving the practical block efficiency. In our case, the lack of efficiency gives rise to 80% dead polymer. This study is, as far as we know, the first attempt to determine the efficiency factor of a macroinitiator by means of SEC multiple detector analysis.

Conclusion

The free radical addition-substitution reaction using vinylic-ketal-derived peroxyketals appears to be a useful method to prepare end-functional polymers. We are currently investigating the possibility that appropriately substituted peroxyketals are useful for the preparation of low-molar-mass α,ω-functional polymers. Further kinetic work and confirmation of the end-group functionality are in progress.

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