Chain Transfer by an Addition–Substitution–Fragmentation Mechanism. 2.[1] Preparation of α,ω-Difunctional Telomers through a Radical Transfer Reaction on a Methacrylic-Type Cyclic Peroxyketal

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ABSTRACT: Ethyl 2-[1-((2-tetrahydrofuranyl)peroxy)ethyl]propenoate (ETPEP; see Chart 1) was used as a new chain transfer agent in the free radical polymerization of methyl methacrylate (MMA), styrene (St), and butyl acrylate (BA) to produce α,ω-difunctional telomers through a radical addition–substitution–fragmentation transfer reaction. The chain transfer constant obtained in the MMA polymerization at 60 °C ($C_{tr} = 0.096$) was very low compared to those obtained in styrene and butyl acrylate under the same conditions ($C_{tr} = 0.97$ and 1.02, respectively). Such a result was attributed to the bulkiness of the α-substituents of both monomer and transfer agent in the addition step of the transfer reaction. ETPEP behaves as an ideal transfer agent for styrene and butyl acrylate at 60 °C. The activation energy for the transfer reaction of ETPEP with PMMA radicals ($E_{a,tr} = 29.9$ kJ·mol^{-1}) was determined from transfer constants measured in MMA polymerization performed at 50, 55, 60, 70, and 80 °C. The thermal stability of peroxyketal ETPEP was estimated from the DSC measurements of the rate constants and from the activation energy of the thermolysis ($E_{a,th} = 130.1$ kJ·mol^{-1}) at various reaction temperatures.

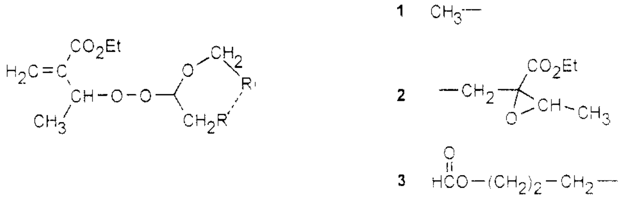
Introduction

Polymer chains bearing chemically distinct terminal groups make convenient building blocks for large structures, including block and graft copolymers, by condensation reactions.[2] The properties of these large structures are often sensitive to the molecular weights and polymolecularities of the telomer involved.[2] The use of suitable chain transfer agents (CTA) with transfer constants close to 1.0 is known to confer a narrow dispersity to the molecular weights of polymers.[3] Moreover, CTA able to involve functionalization of the formed telomers at both chain ends could be a good alternative to the design of sophisticated structures. The transfer properties of ETPEP developed in this paper are very close to those required.

For several years, free radical addition–fragmentation was identified as an effective means for controlling the molecular weight of vinyl polymers, avoiding the use of conventional chain transfer agents based on thio derivatives. The intermediate radical formed upon the addition of the propagating radical onto the transfer agent undergoes fragmentation, generating another radical entering into the polymerization cycle. Compounds of these types include allylic sulfides,[4] 2-((benzyloxy)methyl)acrylic derivatives,[5] alkyl ((alkylthio)methyl)propenoate,[6] *N*-hydroxypyridine-2-thione and *N*-hydroxy-4-methylthiazole-2-thione derivatives,[7] alkyl α-(halogenomethyl)propenoate,[6,8] etc. One attractive feature of this technique is the concomitant incorporation of a terminal functional group following fragmentation, the functional group being vinylic, ketonic, carboxylic, amino, etc., depending on the system. Meijs *et al.*[9] and Vertommen *et al.*[10] have reported a class of chain transfer agents that act via a two-step radical addition–substitution mechanism on allylic-type peroxides.[11]

We have recently reported that ethyl 2-[1-((1-*n*-butoxyethyl)peroxy))ethyl]propenoate (EBEPEP) was a useful transfer agent in the polymerization of MMA ($C_{tr} = 0.086$), St ($C_{tr} = 0.91$), and BA ($C_{tr} = 0.63$)[1] (see Chart 1).

Chart 1. EBEPEP and ETPEP Formula and End-Group Identification



EBEPEP: R = H and R' = -$(CH_2)_2CH_3$

ETPEP: R = R' = -CH_2-

The use of EBEPEP involved the preparation of one-end-functional polymers (see Scheme 1), avoiding undesirable sulfur-containing polymers. The regulation of molecular weights with EBEPEP involves addition of a growing macroradical to the activated olefinic center of the transfer agent and subsequent intramolecular homolytic substitution (SHi) of the intermediate radical on the peroxidic bond. This process leads to the formation of a glycidic ester group **2** at the end of the polymer and the expulsion of a 1-*n*-butoxyethoxy radical, which then β-fragments to yield butyl formate and a methyl radical. The latter can initiate further polymerization.

Examination of the ^1H and ^{13}C NMR spectra of a low-molecular-weight polystyrene prepared in the presence of EBEPEP provided evidence for the end groups **1** and **2** (see Chart 1) and showed that EBEPEP has no tendency to copolymerize.[1] This implies that the intramolecular step (SHi) is efficient.

We report now an investigation of the chain transfer activity of ethyl 2-[1-((2-tetrahydrofuranyl)peroxy)ethyl]-propenoate (ETPEP), which contains the same desirable methacrylic-type structure as EBEPEP but which bears a (2-tetrahydrofuranyl)oxy fragment on the other side of the O–O bond. The aim of the present study was to keep the formed carbonyl moiety on the expelled alkoxyl radical

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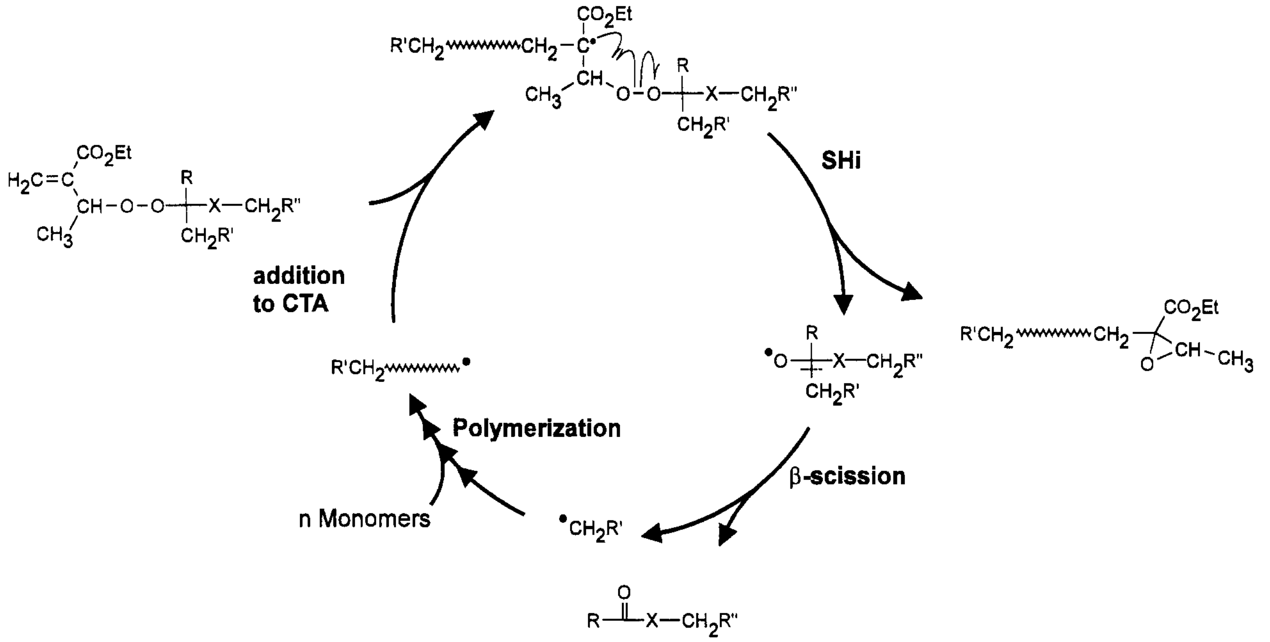
Scheme 1. Radical Mechanism of the Propagation Step in the Presence of a Peroxyketal



that was lost (butyl formate) when EBEPEP was used (see Chart 1). This was achieved by connected R and R′ moieties (R = R′ = $-CH_2-$). Then, the produced (2-tetrahydrofuranyl)oxy radical quickly β-fragments to yield an alkyl radical bearing a formate function.[12] This radical re-enters the cyclic reaction and re-initiates efficiently the chain polymerization. A consequence of this mechanism is that the resulting telomers are α,ω-functionalized by a formate fragment **3** and a glycidic ester group **2**.

The Mayo equation,[13], describing polymerization by a free radical mechanism, compares the overall termination rate with the rate of polymerization, to determine the number-average degree of polymerization (DP_n). In its general form, for polymerization in solvent (S), with chain transfer agent (CTA), initiator (I), and monomer (M) the equation may be written as

$$\frac{1}{DP_n} = \frac{1}{(DP_n)_0} + C_{tr(CTA)}\frac{[CTA]}{[M]} + C_{tr(S)}\frac{[S]}{[M]} + C_{tr(I)}\frac{[I]}{[M]} + C_{tr(M)} \quad (1)$$

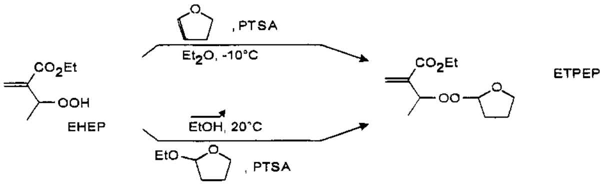
Experiments were run to minimize the contributions of the last three terms of eq 1, allowing the use of eq 2 as an approximation by inserting the three latter terms of eq 1 into $(DP_n)_0^{-1}$

$$\frac{1}{DP_n} = \frac{1}{(DP_n)_0} + C_{tr(CTA)}\frac{[CTA]}{[M]} \quad (2)$$

The assumptions made in this approximation are as follows: (1) the choice of bulk polymerization so [S] = 0 $mol{\cdot}L^{-1}$, and (2) the use of small amounts of initiator, minimizing the transfer constant $C_{tr(I)}$.

If the chain transfer constant for an added transfer agent is equal to unity, the latter is said to behave as an ideal regulator. Thus, when $C_{tr} = k_{tr}/k_p = 1.0$, the ratio of the rate constants of chain transfer and chain propagation is constant and equal to the ratio of the concentrations of monomer and transfer agent. In that case, transfer to CTA and propagation reaction predominate over the other reactions, and a large proportion of the macromolecules formed possesses the desired terminal functionality.

Scheme 2. Synthesis of ETPEP



ETPEP was prepared in high yield according to an efficient synthetic scheme[12] (Scheme 2).

Experimental Section

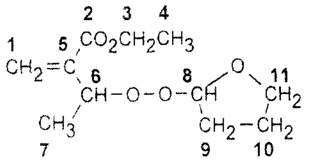
Instruments. NMR spectra were recorded on a Bruker AC 200 spectrometer, using $CDCl_3$ as solvent and internal reference. The molecular weights of the polymers were estimated by size exclusion chromatography (SEC) using a Waters instrument (Waters WISP710b automatic injector, Shimadzu LC6a pump) connected to four PL-Gel columns coupled with a Waters R401 refractometer, a Beckman 167 dual-UV detector, and a Chromatix CMX100 LS detector. Tetrahydrofuran (THF) was used as eluent at a flow rate of 1 mL/min, and the system was calibrated using narrow molecular weight distribution PMMA and PS standards (Waters). Thermal stability studies were performed using differential scanning calorimetry (DSC) (Perkin-Elmer DSC 4 instrument). Column chromatographic separations were carried out on Merck silica gel 60 (60-200 mesh).

Materials. Methyl methacrylate, styrene, and butyl acrylate (CdS Chimie) were purified by *vacuum* distillation over Na or CaH_2 *prior* to use and stored at -10 °C. Ethyl tiglate (Lancaster), 2,3-dihydrofuran, 2-ethoxytetrahydrofuran, and *p*-toluenesulfonic acid (PTSA) (Aldrich) were used as received. The solvents (THF, Et_2O, CCl_4, methanol, heptane, pentane, etc.) were reagent grade and used without further purification. The initiator 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich) was repeatedly crystallized from methanol.

Ethyl 2-[1-((2-Tetrahydrofuranyl)peroxy)ethyl]propenoate (ETPEP). This peroxyketal was obtained by two methods according to a previous work.[12] The starting material, ethyl 2-(1-(hydroxyperoxy)ethyl)propenoate (EHEP), was prepared by photooxygenation of ethyl tiglate according to a procedure adapted from Adam and Griesbeck.[14]

Method 1. A solution of ethyl 2-(1-(hydroperoxy)ethyl)propenoate[14] (4.8 g, 30 mmol) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) in Et_2O (50 mL) was stirred and cooled in an ice–salt bath (-10 °C). A solution of 2,3-dihydrofuran (3.0 g, 30 mmol) in Et_2O (10 mL) was then added dropwise under stirring. After 1 h, the stirred reaction mixture was allowed to

Chart 2. Carbon Naming for NMR Analysis



warm slowly to room temperature. The reaction mixture was then washed with an aqueous solution of Na_2CO_3 (10 mL) and with water (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure.

Method 2. To a mixture of 2-ethoxytetrahydrofuran (3.48 g, 30 mmol) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) was added ethyl 2-(1-(hydroperoxy)ethyl)propenoate (4.8 g, 30 mmol) little by little, and the ethanol formed was evacuated under reduced pressure (5–10 mmHg).

In both procedures, crude peroxyketal was purified by column chromatography on silica gel (method 1, 4.15 g, 60%; method 2, 6.3 g, 91%); R_f = 0.35, pentane/Et_2O = 85/15. The structure of ETPEP was checked by ^1H and ^{13}C NMR spectroscopy (see Chart 2).

^1H NMR ($CDCl_3$) δ 6.19 (s, 1H), 5.85–5.78 (s, 1H), 5.55–5.50 (m, 1H, OOC*H*O), 4.95 (qd, *J* = 6.5 Hz, 1H, CH_3CH), 4.10 (q, *J* = 7.1 Hz, 2H, CO_2CH_2), 3.85–3.72 (m, 2H, $CHOCH_2$), 2.05–1.54 (m, 4H, $OCH_2CH_2CH_2$), 1.20 (m, 3H, CH_3CH), 1.19 (t, *J* = 7.1 Hz, 3H, $CO_2CH_2CH_3$).

^{13}C NMR ($CDCl_3$) δ 165.8, 165.7 [C^2]; 141.1, 140.8 [C^5]; 125.0 [C^1]; 106.7, 106.1 [C^8]; 77.9, 77.3 [C^6]; 67.4, 67.3 [C^{11}]; 60.5, 60.4 [C^3]; 29.4, 29.3 [C^9]; 23.8 [C^{10}]; 19.1 18.7 [C^7]; 14.1 [C^4].

Found: C, 57.26; H, 7.83. $C_{11}H_{18}O_5$ required: C, 57.38; H, 7.88.

Polymerization Procedure. 2,2′-Azo-bis(isobutyronitrile) (40 mg, 2.44 × 10^{-4} mol) was dissolved in distilled styrene (40 mL). Aliquots (5.0 mL) were introduced into cleaned and dried Pyrex glass ampules. A solution of ETPEP (0.115 g, 5 × 10^{4} mol) in styrene (10 mL) was also prepared, and the required amounts of the chain transfer agent were added in the ampules. Generally, for a given ETPEP/monomer system, polymerizations were carried out with five concentrations of the transfer agent. The mixtures were degassed by three freeze–*vacuum*–thaw cycles and then sealed under reduced pressure (10^{-2} mmHg). After the polymerization for 1 h at 60 °C, (conversions were kept below 3% for styrene), the tubes were chilled and the contents of the ampules were poured into methanol. The precipitated polymers were filtrated, washed with methanol, and dried in a *vacuum* oven at 30 °C to constant weight. Each polymer was examined by size exclusion chromatography.

Polymerizations of methyl methacrylate were carried out in a similar manner at 60 °C for 1 h. 2,2′-Azobis(isobutyronitrile) (30 mg, 1.83 × 10^{-4} mol) was dissolved in freshly distilled methyl methacrylate (30 mL). Aliquots (3 mL) were withdrawn and added to ampules containing weighted amounts of a solution of ETPEP in MMA. After the polymerization had been stopped at <9% conversion, the contents of the ampules were precipitated into a large excess of *n*-heptane, isolated by filtration, dried under *vacuum* at 30 °C to constant weight, and examined as before.

Polymerizations of butyl acrylate were carried out using a solution of 2,2′-azobis(isobutyronitrile) (8 mg, 4.88 × 10^{-5} mol) in freshly distilled butyl acrylate (40 mL). Aliquots (5.0 mL) were introduced into ampules containing weighed amounts of a 5 × 10^{-2} M solution of ETPEP in butyl acrylate (10 mL). After degassing, the mixtures were polymerized at 60 °C for 10 min. The number-average degrees of polymerization of the telomers and the ratio of the polymerization rates with and without transfer (R_p/R_{p0}) were estimated by SEC measurements. The molecular weights of poly(butyl acrylate) were estimated from polystyrene calibration without consideration of the differences in hydrodynamic volumes between individual polymeric species.

Results and Discussion

This paper describes the use of a new addition–substitution–fragmentation regulator in the synthesis of the α,ω-difunctional telomers of methyl methacrylate, styrene, and butyl acrylate. Although free radical addition–fragmentation has been reported to be a new method for chain length control, it has seldom been identified as an effective means for generating functional polymers. However, methods for the preparation of α,ω-difunctional polymers using transfer agents which do not bear the potentially required two functions on their own structure are rare.

Table 1. Rate Constants of Thermolysis of ETPEP Obtained by DSC Measurements[a]

temp (°C)	k_{th} (s^{-1})	ln k_{th}	$1/T$ (K^{-1})
105	1.66 × 10^{-5}	-11.01	2.65 × 10^{-3}
110	3.33 × 10^{-5}	-10.31	2.61 × 10^{-3}
115	6.71 × 10^{-5}	-9.61	2.58 × 10^{-3}
120	1.10 × 10^{-4}	-9.11	2.54 × 10^{-3}
125	1.82 × 10^{-4}	-8.61	2.51 × 10^{-3}
130	2.58 × 10^{-4}	-8.26	2.48 × 10^{-3}
135	4.09 × 10^{-4}	-7.80	2.45 × 10^{-3}
140	6.58 × 10^{-4}	-7.33	2.42 × 10^{-3}
145	1.09 × 10^{-3}	-6.82	2.39 × 10^{-3}
150	1.84 × 10^{-3}	-6.30	2.36 × 10^{-3}
155	3.10 × 10^{-3}	-5.78	2.34 × 10^{-3}
160	5.13 × 10^{-3}	-5.27	2.31 × 10^{-3}
165	7.73 × 10^{-3}	-4.86	2.28 × 10^{-3}
170	1.24 × 10^{-2}	-4.39	2.26 × 10^{-3}

[a] Determined in a 1.5 M solution of triphenylmethane in diphenylmethane.

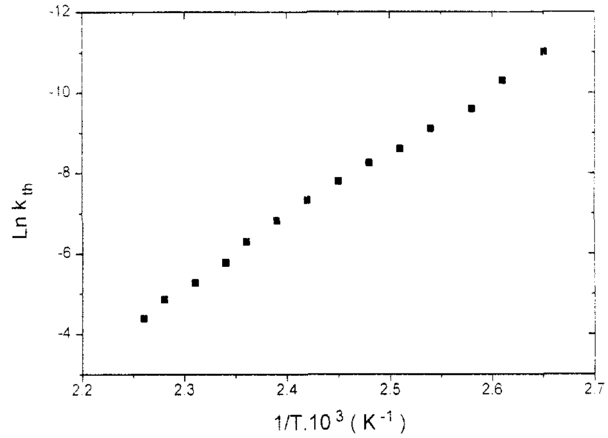


Figure 1. Napierian logarithm of the thermolysis rate constant as a function of the reciprocal reaction temperature.

Thermal Stability of ETPEP. The thermal stability of the unsaturated peroxyketal ETPEP was characterized according to the procedure developed by Maillard and co-workers.[15] Thermolysis of ETPEP was performed in a diphenylmethane–triphenylmethane solution to prevent side reactions of induced homolytic decomposition of the unsaturated peroxyketal by addition–substitution reactions. Then, oxyl and alkyl radicals formed in the reaction medium can efficiently abstract hydrogen on aromatic compounds to form strongly stable carbon-centered radicals which evolve essentially by addition to unsaturation.[15] In such cases, thermolysis of ETPEP was shown to be a true first-order reaction to yield rate constants k_{th} (Table 1), activation energy $E_{a,th}$ = 130.1 kJ·mol^{-1}, and frequency factor A_{th} = 1.5 × 10^{14} s^{-1} (Figure 1) of this homolytic dissociation.

Allylic peroxyketal ETPEP appeared to be as thermally stable as EBEPEP, $E_{a,th}$ = 133.5 kJ·mol^{-1} and A_{th} = 0.58 × 10^{14} s^{-1}. As mentioned previously,[1] reaction conditions of polymerization have to be controlled to minimize the thermolysis of the peroxyketal. This latter phenomenon is a minor side reaction whatever conditions were used in this study, and ETPEP could be considered

Table 2. Number-Average Degrees[a] of Polymerization and Conversions[b] of Isolated Polymers Obtained by the Use of ETPEP at 60 °C in the Polymerization of MMA, St, and BA

monomer	10^3[ETPEP] (mol·L^{-1})	DP$_n$[a] (mol^{-1})	10^4[ETPEP]/[M]	conv[b] (%)
MMA	0	5140	0	8.7
t = 60 min	0.5	5109	0.59	8.6
	2.5	4890	2.80	9.1
	5	4401	5.59	9.3
	10	3303	11.2	8.7
	25	2196	28.0	8.5
St	0	1706	0	2.1
t = 60 min	2.5	1228	2.81	2.0
	5	853	5.61	1.9
	10	630	11.2	1.6
	25	301	28.1	1.8
BA	0.5	6141	0.59	nd (1.00)[c]
(*t* = 10 min)	2.5	2219	2.96	nd (0.99)[c]
	5	1109	5.92	nd (0.97)[c]
	10	707	11.8	nd (0.95)[c]
	25	315	29.6	nd (0.95)[c]

[a] [AIBN] = 3.05 × 10^{-3} mol·L^{-1} in MMA and St and [AIBN] = 6.1 × 10^{-4} mol·L^{-1} in BA. [b] Ratio of the weight of recovered polymer to the initial weight of monomer. [c] nd = not determined; (R_p/R_{p_0}) = ratio of the rates of polymerization with and without ETPEP, determined from SEC data.

Table 3. Comparison of the Chain Transfer Constants (C_{tr}) of Methyl 2-((*tert*-Butylperoxy)methyl)propenoate[a] (MBPMP), ETPEP, and EBEPEP in the Polymerization of Vinylic Monomers at 60 °C

monomer	C_{tr}(MBPMP)	C_{tr}(ETPEP)	C_{tr}(EBEPEP)
MMA	0.63[b]	0.096[e]	0.086[e]
St	1.64[c]	0.97[e]	0.91[e]
BA	nd[d]	1.02[f]	0.63[f]

[a] Values from ref 9. [b] [AIBN] = 1.18 × 10^{-2} mol·L^{-1}. [c] [AIBN] = 8.51 × 10^{-3} mol·L^{-1}. [d] nd = not determined. [e] [AIBN] = 3.05 × 10^{-3} mol·L^{-1}. [f] [AIBN] = 6.1 × 10^{-4} mol·L^{-1}.

as "stable" under the conditions of the polymerization. Unreacted ETPEP could be recovered unchanged in the filtrates of the precipitations used to recover the polymers.

Chain Transfer Constants. The chain transfer constants of the allylic peroxyketal ETPEP were determined at 60 °C in the polymerization of MMA, styrene, and butyl acrylate in the presence of AIBN as the initiator. These polymerizations were carried out at constant AIBN concentration, while the transfer agent/monomer ratio was progressively increased. The number-average degrees of polymerization (DP$_n$) and the conversions of the precipitated polymers are presented in Table 2. According to the decrease of the DP$_n$ values, allylic peroxyketal ETPEP appears as an effective chain transfer agent. Similarly to EBEPEP, the yields of the obtained telomers of MMA, styrene, and butyl acrylate (ratio(R_p/R_{p_0}) based on SEC data) polymerizations were not significantly affected by the presence of ETPEP. This provided evidence for the process to be a true chain transfer rather than retardation (*i.e.*, termination of growing polymer chains without efficient re-initiation). These results will have to be confirmed by a kinetic study performed with higher concentrations of transfer agent. When samples of styrene containing various concentrations of ETPEP were polymerized in the bulk at 60 °C, the resulting polymers exhibited markedly lower molecular weights than those prepared in the absence of ETPEP (Table 3). The chain transfer constants (C_{tr}) were obtained from the slope of the linear plot 1/DP$_n$ *versus* [ETPEP]/[monomer] (Figure 2), according to the simplified Mayo equation (eq 2).

The chain transfer constant in styrene was C_{tr} = 0.97, which is very close to the ideal value[3] of 1.0. This result is in contrast with the case of thiols, which exhibit inconveniently high transfer constants in styrene polymerization (C_{tr} = 15–20)[16] and can lead therefore to the production of polymers with a broad distribution of molecular weights in batch polymerizations to high conversion. Similar experiments carried out with methyl methacrylate also led to the production of low-molecular-weight polymers. A chain transfer constant of 0.096 was derived from the experimental data. As mentioned for EBEPEP, the polymerizability of methacrylic-type monomers is strongly influenced by substituents in the allylic position.[17]

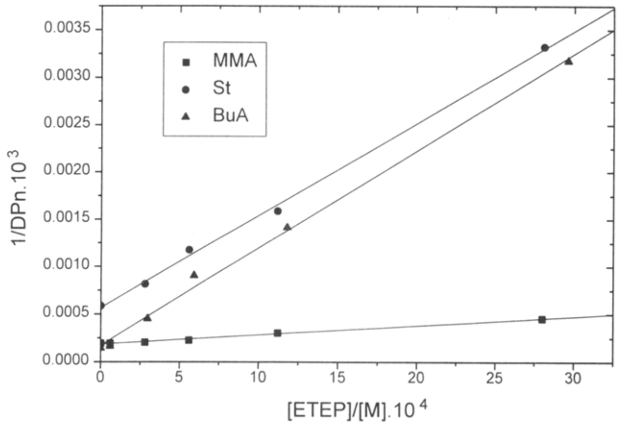
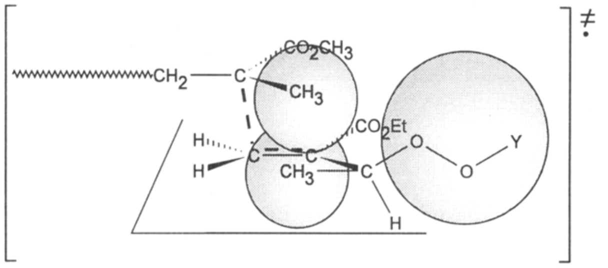


Figure 2. Reciprocal degrees of polymerization DP$_n$ of a monomer (M) as a function of the molar ratio of ETPEP to M. Values of DP$_n$ were determined by SEC. The line is a least-squares fit to the data represented by the corresponding filled symbols.

Scheme 3. Steric Hindrance in the Transition State of the Addition of a Growing PMMA Radical to the Chain Transfer Agents



The chain transfer constants observed with ETPEP in MMA were lower than those obtained with methyl 2-((*tert*-butylperoxy)methyl)propenoate (MBPMP) (Table 3).[9] This can be explained by a steric hindrance between the growing PMMA radical (methyl fragment) and the α-substituent on ETPEP (1-(2-tetrahydrofuranylperoxy)ethyl group) in the addition step of the transfer reaction (see Scheme 3). This phenomenon was found to be less important in BA polymerization (R′ = H), which explains the satisfactory chain transfer constant obtained in the latter case (C_{tr} = 1.02). The low difference of chain transfer constants observed between ETPEP and EBEPEP (Table 3) could be due to a greater bulkiness of the (1-*n*-butoxyethyl)peroxy group with respect to the 2-(tetrahydrofuranylperoxy)ethyl; the linear structure of EBEPEP involves more degrees of freedom than the blocked cyclic one for ETPEP, which disfavors the addition to the double bond by the allylic steric hindrance effect (see Scheme 3).

It can be concluded that substitution on the allylic position of methacrylic-type transfer agents seems to disfavor the possibility of addition to the unsaturation whereas substitution on the other side of the peroxidic bond—far away from the double bone—has less influence. Such phenomena will have to be confirmed by computer

Table 4. Number-Average Degrees[a] of Polymerization (DP_n), Conversions,[b] Rates of Polymerization (R_p), and Chain Transfer Constants (C_{tr}) of ETPEP in the Polymerization of MMA at Various Temperatures

polymerization conditions	DP_n[a] (mol^{-1})	10^4[ETPEP]/[M]	conv[b] (%)	$R_p \times 10^4$ ($mol \cdot L^{-1} \cdot s^{-1}$)	$C_{tr} \times 10^2$
	11447	0	4.2	0.70	9.1
temp = 50 °C	10581	0.55	4.4	0.73	
t = 90 min	8347	2.77	4.3	0.72	
[MAM][c] = 9.01 $mol \cdot L^{-1}$	6809	5.55	4.2	0.70	
[AIBN] = 3.05×10^{-3} $mol \cdot L^{-1}$	5041	11.1	4.0	0.67	
	2941	27.7	4.2	0.70	
	8845	0	nd[a]	(1.00)[e]	9.7
temp = 55 °C	8250	0.56	nd[d]	(0.98)[e]	
t = 90 min	6784	2.78	nd[d]	(0.97)[e]	
[MAM][c] = 8.98 $mol \cdot L^{-1}$	5834	5.57	nd[d]	(0.99)[e]	
[AIBN] = 3.05×10^{-3} $mol \cdot L^{-1}$	4412	11.1	nd[d]	(0.95)[e]	
	2586	27.8	nd[d]	(0.95)[e]	
	5140	0	8.7	2.15	10.6
temp = 60 °C	5109	0.56	8.8	2.18	
t = 60 min	4890	2.81	9.3	2.30	
[MAM][c] = 8.91 $mol \cdot L^{-1}$	4401	5.61	9.2	2.28	
[AIBN] = 3.05×10^{-3} $mol \cdot L^{-1}$	3303	11.2	8.7	2.15	
	2196	28.1	8.5	2.11	
	5131	0	6.7	3.27	11.6
temp = 70 °C	4950	0.57	7.1	3.46	
t = 30 min	4369	2.85	6.2	3.02	
[MAM][c] = 8.78 $mol \cdot L^{-1}$	3725	5.69	6.8	3.12	
[AIBN] = 1.52×10^{-3} $mol \cdot L^{-1}$	3038	11.4	6.5	3.17	
	1931	28.5	6.5	3.17	
	3458	0	7.1	6.83	12.4
temp = 80 °C	3357	0.58	7.0	6.74	
t = 15 min	3149	2.89	6.7	6.45	
[MAM][c] = 8.66 $mol \cdot L^{-1}$	2749	5.77	6.9	6.64	
[AIBN] = 1.52×10^{-3} $mol \cdot L^{-1}$	2312	11.5	7.0	6.74	
	1569	28.87	6.9	6.64	

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

calculations on space conformation energies. It was also observed recently in dialkyl itaconate polymerization.[18]

Moreover, we noted that, in the range of molecular weight studied, precipitation in heptane for PMMA or in methanol for PS did not alter significantly the number-average molecular weights or the molecular weight distribution of the polymers. In addition, no low-molecular-weight polymers were detected by ^1H NMR spectroscopy in the mother liquors of the precipitations. There was also a minor decrease in the conversion rate (Table 2, (R_p/R_{p0}) values) of the polymerization as the concentration of ETPEP increased; the data did, however, show that the primary process is chain transfer (*i.e.*, that re-initiation of chains is relatively efficient).

Although peroxidic type compounds generally do not show significant chain transfer activity ($C_{tr} = (2–3) \times 10^{-4}$ for di-*tert*-butyl peroxide and diisopropyl peroxide in styrene polymerization at 60 °C),[19] we can consider that the effectiveness of ETPEP as a chain transfer agent is probably due to (1) a high reactivity toward radical addition caused by an electron-deficient methacrylic-type double bond, (2) the presence of an intramolecular homolytically cleavable peroxidic bond on the favorable β-position[11] to the radical resulting from addition of the propagating polymer chain to ETPEP (see Scheme 1), and (3) the high re-initiation efficiency of alkyl radicals in the polymerization of the vinylic monomers used.

To determine the activation energy ($E_{a,tr}$) of the chain transfer reaction with ETPEP in the polymerization of MMA, the C_{tr} values of this unsaturated peroxyketal were measured at 50, 55, 60, 70, and 80 °C (Table 4).

Thermodynamics of the Transfer Reaction. The literature values of k_p are reported in Table 5 with the calculated k_{tr} values. Considering that the addition reaction is the limiting step of the transfer process, the rate constants, k_{tr}, can be considered as a good approximation of rate constants of addition, k_{add}, of the growing polymer radicals to the double bond of ETPEP. The Arrhenius equation for the chain transfer constant C_{tr} is

Table 5. Absolute Rate Constants k_{tr} for the Growing Polymer Radical Chain Transfer with ETPEP from 50 to 80 °C, in the Polymerization of MMA, St, and BA

monomer	reaction temp (°C)	k_p ($L \cdot mol^{-1} \cdot s^{-1}$)	C_{tr}	k_{tr} ($L \cdot mol^{-1} \cdot s^{-1}$)
MMA	50	560[a]	0.091	51
MMA	55	633[a]	0.097	61.5
MMA	60	705[a]	0.096	68
MMA	70	866[a]	0.116	100.5
MMA	80	1050[a]	0.124	130
St	60	176[b]	0.97	171
BA	60	2090[c]	1.02	2130

[a] Values from ref 20. [b] Value from ref 21. [c] Value from methyl acrylate.[21]

$$C_{tr} = \frac{k_{tr}}{k_p} = \frac{A_{tr}}{A_p} \exp\left(\frac{E_{a,p} - E_{a,tr}}{RT}\right) \qquad (3)$$

The experimental activation energy, $E_{a,p} - E_{a,tr} = -10.3$ $kJ \cdot mol^{-1}$, and the frequency factor, $A_{tr}/A_p = 4.1$, were calculated from the plot ln C_{tr} versus $1/T$ (Figure 3).

The absolute activation energy, $E_{a,tr} = 29.9$ $kJ \cdot mol^{-1}$, and the frequency factor, $A_{tr} = 35.7 \times 10^5$ $L \cdot mol^{-1} \cdot s^{-1}$, were determined from the experimental value of $E_{a,p} - E_{a,tr}$ using the literature values[22] of $E_{a,p}$, 19.6 $kJ \cdot mol^{-1}$, and A_p, 8.7×10^5 $L \cdot mol^{-1} \cdot s^{-1}$, respectively. The absolute activation energy $E_{a,tr}$ for termination of PMMA radicals by transfer on ETPEP is slightly higher than the activation energy $E_{a,p}$ for the propagation step of the monomer polymerization, but it is very low compared to 130.1 $kJ \cdot mol^{-1}$ for the thermal decomposition of the peroxyketal, $E_{a,th}$ (Table 2). The reduction in activation energy for transfer is

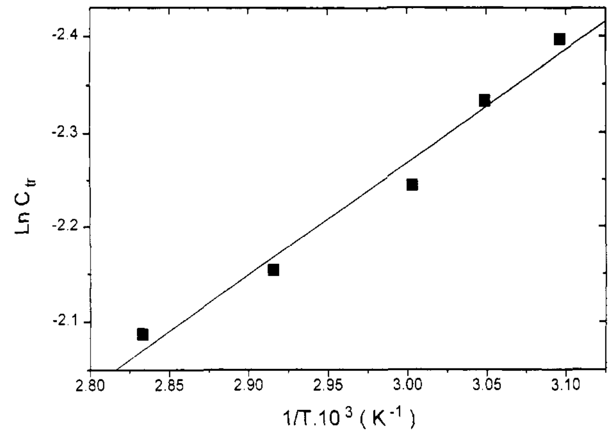


Figure 3. Napierian logarithm of the chain transfer constant as a function of the reciprocal reaction temperature. The line is a least-squares fit of the data represented by the filled squares.

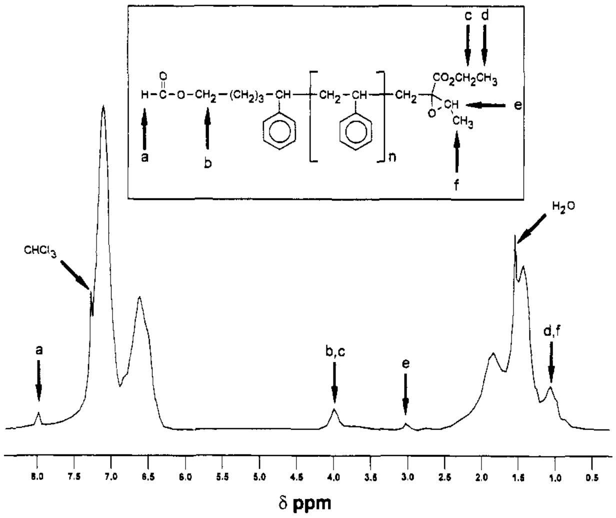


Figure 4. ^{1}H NMR (200 MHz) spectrum of polystyrene (M_n = 2040 g·mol^{-1}) prepared using ETPEP as a chain transfer agent.

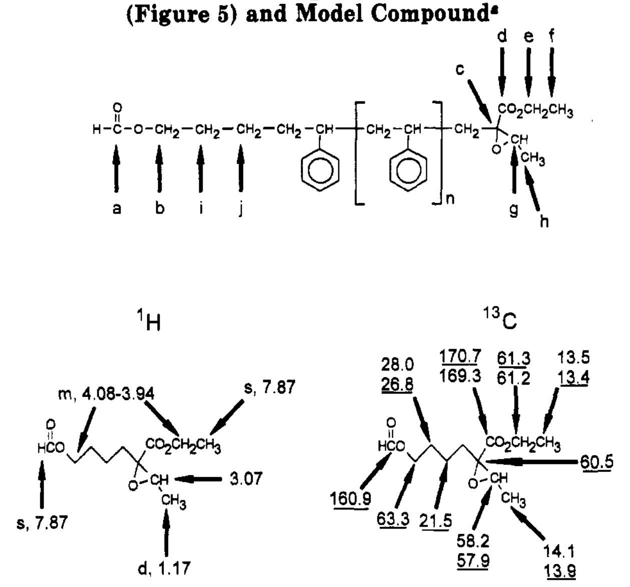
reasonable in terms of the homolytic intramolecular reaction shown in *Scheme 1* in which the scission of the peroxidic bond is enhanced by a carbon-centered radical in a favorable β-position from the O–O linkage.[11]

Spectroscopic Characterization of the Functionalized Polystyrene. The mechanism depicted in Scheme 1 leads to the expectation that the polymers prepared in the presence of allylic peroxyketal ETPEP be terminated by a glycidic ester end-group. To test this, a low-molecular-weight sample of polystyrene was prepared (M_n = 2040 g·mol^{-1}) using ETPEP in high amount ([ETPEP] = 0.65 mol·L^{-1}). The ^{1}H NMR spectrum (Figure 4) showed signals at 1.0–1.2, 3.0–3.1, and 3.9–4.1 ppm, consistent with the proton of the epoxide cycle and signals at 3.9–4.1 and 8.0 ppm for those of the ester group (see the model compound in Chart 3). The ^{13}C NMR spectrum of the same polymer (Figure 5) showed signals consistent with those expected for the formate and the glycidic ester end groups (the carbon naming for Figure 5 and model compound is in Chart 3).

Conclusion

The free radical addition–substitution–fragmentation reaction using ETPEP appears to be an elegant single-step method for the synthesis of α,ω-difunctional polymers. The current results highlight the efficiency of the activated allylic peroxyketal chain transfer agent ETPEP to regulate the molecular weight in vinylic monomer polymerizations. Further kinetic work and confirmation of the end group functionality are in progress.

Chart 3. Carbon Naming for ^{13}C NMR Spectrum (Figure 5) and Model Compound[a]



[a] Underlined chemical shifts are attributed to the major diastereoisomer.

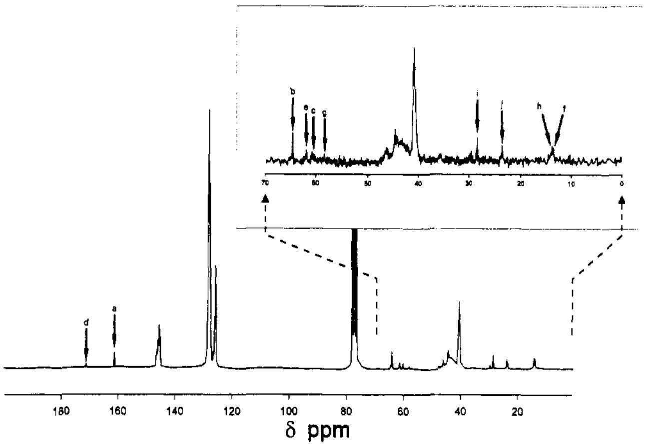


Figure 5. ^{13}C NMR (63 MHz) spectrum of polystyrene (M_n = 2040 g·mol^{-1}) prepared in the presence of ETPEP as a chain transfer agent (see carbon naming in Chart 3).

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