

# Chain transfer by addition–substitution–fragmentation mechanism: 3. Access to low-molecular-weight telechelic polymers using ethyl 2-[1-(1-methoxy-1-cyclohexylperoxy)-ethyl]propenoate

Daniel Colombani\* and Philippe Chaumont\*

*Institut Charles Sadron (CRM-EAHP), UPR 22 CNRS, 6 rue Boussingault, 67083  
Strasbourg Cedex, France*

*(Received 3 February 1994; revised 3 May 1994)*

Low-molecular-weight di-end-functional (telechelic) telomers were prepared by radical addition–substitution–fragmentation transfer reactions on ethyl 2-[1-(1-methoxy-1-cyclohexylperoxy)ethyl]propenoate (EMCPEP), used as a new chain-transfer regulator in the free-radical polymerization of methyl methacrylate (MMA), styrene (St) and butyl acrylate (BA). The chain-transfer constant obtained in MMA polymerization at 60°C ( $C_{tr}=0.102$ ) was very low compared to those obtained in St and BA polymerization in the same conditions ( $C_{tr}=1.02$  and  $0.88$ , respectively). Such a result was attributed to the allylic steric effect of both monomer and transfer agent in the addition step of the transfer reaction. EMCPEP behaves as an ideal transfer agent for St and BA at 60°C. The activation energy for the transfer reaction of EMCPEP with poly(methyl methacrylate) radicals ( $E_{a_{tr}}=31.3\text{ kJ mol}^{-1}$ ) was determined from transfer constants measured in MMA polymerization performed at 50, 55, 60, 70 and 80°C. The differential scanning calorimetry study of the thermal stability of peroxyketal EMCPEP gave an estimation of the rate constants and the activation energy of the thermolysis ( $E_{a_{th}}=130.3\text{ kJ mol}^{-1}$ ) at various reaction temperatures.

(Keywords: radical polymerization; chain transfer agent; functionalized polymers)

## INTRODUCTION

Block and graft copolymers can be conveniently prepared by condensation reactions from telomers bearing terminal groups<sup>1</sup>. The properties of these large structures are often sensitive to the molecular weights and polymolecularities of the end-functionalized polymers involved<sup>1</sup>. The use of suitable chain-transfer agents (CTAs), with a transfer constant close to 1.0, is known to allow better control of the polymer functionality, even to very high conversion, and to confer to this polymer a narrow molecular weight distribution<sup>2</sup>. Moreover, a CTA able to involve di-end-functionalization of the formed telomers could be a good alternative to the design of complicated structures. The transfer properties of ethyl 2-[1-(1-methoxy-1-cyclohexylperoxy)ethyl]propenoate (EMCPEP) 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 CTAs based on thio-derivatives. The intermediate radical formed by the addition of the propagating radical on the transfer agent undergoes fragmentation, generating another radical entering into the polymer-

ization cycle. Compounds of these types include allylic sulfides<sup>3,4</sup>, 2-benzyloxymethylacrylic derivatives<sup>5,6</sup>, alkyl alkylthiomethylpropenoate<sup>7</sup>, *N*-hydroxypyridine-2-thione and *N*-hydroxy-4-methylthiazole-2-thione derivatives<sup>8</sup> and alkyl  $\alpha$ -halogenomethylpropenoate<sup>9–13</sup>. One attractive feature of this technique is the concomitant incorporation of a terminal functional group following fragmentation, the functional group being of vinylic, ketonic, carboxylic or amino type, depending on the system. Meijs *et al.*<sup>14</sup> and Vertommen *et al.*<sup>15</sup> have reported a class of CTAs that act via a two-step radical addition–substitution mechanism on allylic-type peroxides<sup>16</sup>.

We have recently reported<sup>17</sup> that ethyl 2-[1-(1-butoxyethylperoxy)ethyl]propenoate (EBEPEP) and ethyl 2-[1-(2-tetrahydrofuranylperoxy)ethyl]propenoate (ETPEP) (see *Scheme 1*) were useful transfer agents in the polymerization of methyl methacrylate (MMA) (chain transfer constant,  $C_{tr}=0.086\text{--}0.096$ ), styrene (St) ( $C_{tr}=0.91\text{--}0.97$ ) and butyl acrylate (BA) ( $C_{tr}=0.63\text{--}1.02$ ), respectively.

The use of EBEPEP and ETPEP involved the preparation of mono- and di-end-functional polymers, respectively (see *Scheme 2*). The regulation of molecular weight with these peroxyketals occurs by addition of a growing macroradical to the activated olefinic centre of the transfer agent and subsequent intramolecular

\* To either of whom correspondence should be addressed

homolytic substitution of the intermediate radical on the peroxidic bond (Scheme 2). This process leads to the formation of a glycidic ester group 2 at the end of the polymer and the expulsion of an oxy radical, which then evolves by  $\beta$ -scission to yield an alkyl radical, which can initiate further polymerization.

Examination of the  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (n.m.r.) spectra (see below) of a low-molecular-weight polystyrene (PS) prepared in the presence of EBEPEP or ETPEP provided evidence for the expected end-groups and showed that these unsaturated peroxyketals have no tendency to copolymerize<sup>17</sup>. This implies that the intramolecular homolytic substitution is efficient.

We report here an investigation of the chain transfer activity of EMCPEP which contains the same desirable methacrylic-type structure as those previously reported, but which bears a 1-methoxy-1-cyclohexyloxy fragment on the other side of the O–O bond. The aim of the present study was to attach to the expelled oxy radical a potentially available carboxylic acid function (by saponification and subsequent acidification of the graft ester function) (Scheme 2). This was realized by connecting R and R' moieties ( $\text{R} = \text{R}' = -(\text{CH}_2)_2-$ ) and designing the molecule in order to obtain the acetal fragment out of the cycle (the acetal was included in the cycle in ETPEP which led to a potentially available alcohol function, e.g. a formate fragment). The produced 1-methoxy-1-cyclohexyloxy radical can give fast  $\beta$ -scission to yield an alkyl radical bearing a methoxycarbonyl function<sup>18,19</sup>. This radical re-enters the cycle to re-initiate efficiently the polymer chain reaction. A consequence of this mechanism is that the resulting telomers are  $\alpha,\omega$ -functionalized by a

methoxycarbonylalkyl fragment 1 and a glycidic ester group 2.

## EXPERIMENTAL

### Materials

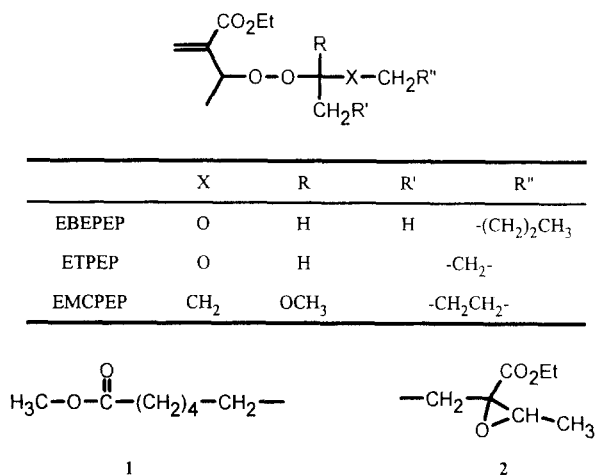
The three monomers (MMA, St and BA, from CdS Chimie) were distilled over Na or  $\text{CaH}_2$  prior to use and stored at  $-10^\circ\text{C}$ . Initiator 2,2'-azobisisobutyronitrile (AIBN, Aldrich) was repeatedly crystallized from methanol. Other products and solvents were reagent grade and were used without further purification: ethyl tiglate (Lancaster), cyclohexanone, *p*-toluenesulfonic acid (PTSA, Aldrich), tetrahydrofuran (THF), carbon tetrachloride, diethyl ether, methanol, heptane and pentane.

### Measurements

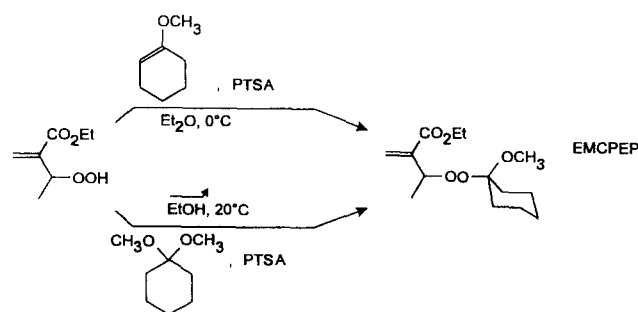
N.m.r. spectra were recorded on a Bruker AC 200 spectrometer, using  $\text{CDCl}_3$  as solvent and internal reference. The molecular weights of the polymer were estimated by size-exclusion chromatography (s.e.c.) using a Waters Instrument (Waters WISP710b automatic injector, Shimadzu LC6a pump), connected to four PL-Gel columns coupled with Waters R401 refractometer, Beckmann 167 Dual-UV detector and Chromatix CMX100 LS detector. THF was used as eluent at a flow rate of  $1\text{ ml min}^{-1}$  and the system was calibrated using a narrow distribution of poly(methyl methacrylate) (PMMA) and PS standards (Waters). Thermal stability was studied by differential scanning calorimetry (d.s.c.) performed on a Perkin-Elmer DSC 4 instrument. Column chromatographic separations were carried out on Merck Silicagel 60 (60–200 mesh).

### Synthesis of EMCPEP

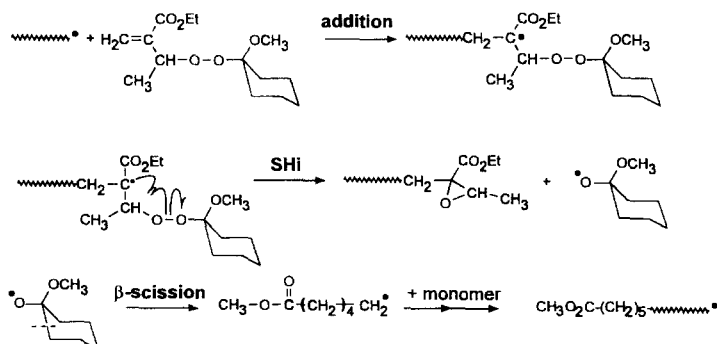
EMCPEP was easily obtained in good yields by two procedures according to previous work (Scheme 3)<sup>18,19</sup>.



Scheme 1 Formulae and end-group identification



Scheme 3 Synthesis of EMCPEP



Scheme 2 Radical polymerization in the presence of EMCPEP

**Method A.** To a stirred and cooled (0°C) solution of ethyl 2-(1-hydroperoxyethyl)propenoate<sup>20,21</sup> (4.0 g, 0.025 mol) and PTSA monohydrate (25 mg, 10<sup>-3</sup> mol) in Et<sub>2</sub>O (40 ml) was added dropwise a solution of 1-methoxy-1-cyclohexene<sup>22</sup> (2.8 g, 0.025 mol) in Et<sub>2</sub>O (10 ml). After 1 h, the stirred reaction mixture was allowed to warm slowly to room temperature. The reaction mixture was then washed with an aqueous solution of Na<sub>2</sub>CO<sub>3</sub> (10 ml) and water (2 × 10 ml). The combined organic layers were dried over anhydrous MgSO<sub>4</sub>, and the solvent was removed under reduced pressure.

**Method B.** Ethyl 2-(1-hydroperoxyethyl)propenoate (4.0 g, 0.025 mol) was added gradually to a mixture of 1,1'-dimethoxycyclohexane<sup>23</sup> (3.6 g, 0.025 mol) and PTSA monohydrate (25 mg, 10<sup>-3</sup> mol). The formed methanol was continuously eliminated under reduced pressure (5–10 mmHg).

In both methods, the crude peroxyketal was purified by chromatography on a column of silica gel (method A, 4.76 g, 70%; method B, 6.32 g, 93%); *R<sub>f</sub>* = 0.39, pentane: Et<sub>2</sub>O = 88:12.

The structure of EMCPEP was checked by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy (see Scheme 4). <sup>1</sup>H n.m.r.: (CDCl<sub>3</sub>) δ 6.20 (s, 1H), 5.84 (s, 1H), 4.90 (q, *J* = 6.6 Hz, 1H, CH<sub>3</sub>CH), 4.11 (q, *J* = 7.1 Hz, 2H, CH<sub>2</sub>CH<sub>2</sub>), 3.15 (s, 3H, OCH<sub>3</sub>), 1.60–1.25 (m, 10H, CH<sub>2</sub> cycle), 1.20 (d, 3H, CH<sub>3</sub>CH), 1.19 (t, *J* = 7.1 Hz, 3H, CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C n.m.r.: (CDCl<sub>3</sub>) δ 165.8 [C<sup>2</sup>], 141.3 [C<sup>5</sup>], 124.7 [C<sup>1</sup>], 104.7 [C<sup>8</sup>], 77.2 [C<sup>6</sup>], 60.5 [C<sup>3</sup>], 48.0 [C<sup>12</sup>], 31.6, 31.4 [C<sup>9,9'</sup>], 25.4 [C<sup>11</sup>], 22.7, 22.6 [C<sup>10,10'</sup>], 19.0 [C<sup>7</sup>], 14.0 [C<sup>4</sup>]. Found: C, 61.59; H, 8.73. C<sub>14</sub>H<sub>24</sub>O<sub>5</sub>, required C, 61.74; H, 8.88.

#### Polymerization

AIBN (40 mg, 2.44 × 10<sup>-4</sup> mol) was dissolved in distilled St (40 ml). Aliquots (5.0 ml) were removed and added to cleaned and dried Pyrex glass ampoules. A solution of EMCPEP (0.136 g, 5 × 10<sup>-4</sup> mol) in St (10 ml) was also prepared and used to add required amounts of CTA to the ampoules. Generally, for a given EMCPEP/monomer combination, polymerization was 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<sup>-2</sup> mmHg). After the polymerization (1 h at 60°C, conversions were kept below 3% for St), the tubes were chilled and the contents of the ampoules were poured into methanol and precipitated polymers were filtered, washed with methanol and dried in a vacuum oven at 30°C to constant weight. Each polymer was examined by s.e.c.

Polymerizations of MMA were carried out in a similar manner at 60°C for 1 h. AIBN (30 mg, 1.83 × 10<sup>-4</sup> mol) was dissolved in freshly distilled MMA (30 ml). Aliquots (3 ml) were withdrawn and added to ampoules containing

weighed amounts of a solution of EMCPEP in MMA. After the polymerization, stopped at less than 9% conversion, the contents of the ampoules were precipitated into a large excess of *n*-heptane, isolated by filtration and then dried in vacuum at 30°C to constant weight and examined as before.

Polymerizations of BA were carried out using a solution of AIBN (8 mg, 4.88 × 10<sup>-5</sup> mol) in freshly distilled BA (40 ml). Aliquots (5.0 ml) were removed and added to ampoules containing weighed amounts of a 5 × 10<sup>-2</sup> M solution of EMCPEP in BA (10 ml). After degassing, the mixtures were polymerized at 60°C for 10 min. The number-average degrees of polymerization (*DP<sub>n</sub>*) of the telomers and the ratio of the polymerization rates with and without transfer (*R<sub>p</sub>*/*R<sub>p0</sub>*) were estimated by s.e.c. measurements. The molecular weights of poly(butyl acrylate) were estimated from PS calibration without any consideration of differences in hydrodynamic volumes.

## 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 MMA, St and BA. Although free-radical addition–fragmentation has been reported as 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 from transfer agents that do not carry out the two functions potentially required are uncommon.

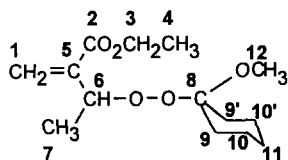
#### Thermal stability of EMCPEP

The thermal stability of the unsaturated peroxyketal EMCPEP was studied according to the procedure developed by Navarro *et al.*<sup>24</sup>. Thermolysis of EMCPEP was performed in a diphenylmethane–triphenylmethane solution to inhibit side-reaction of induced homolytic decomposition of the unsaturated peroxyketal by addition–substitution reactions. Then, oxyl and alkyl radicals liberated in the reaction medium can efficiently abstract hydrogens on aromatic compounds to form stable carbon-centred radicals which evolve essentially by termination reactions<sup>24</sup>. In such a case, thermolysis of EMCPEP was studied as a true first-order reaction to give rate constants (*k<sub>th</sub>*), activation energy (*E<sub>a,th</sub>* = 130.3 kJ mol<sup>-1</sup>) and frequency factor (*A<sub>th</sub>* = 2.1 × 10<sup>13</sup> s<sup>-1</sup>) of this homolytic dissociation. Δ*E<sub>a,th</sub>* and Δln *A<sub>th</sub>* were estimated to be 4.2 kJ mol<sup>-1</sup> and 1.0, respectively, with 99% confidence limits, according to Navarro *et al.*<sup>24</sup>.

Allylic peroxyketal EMCPEP appeared to be as stable as ETPEP (*E<sub>a,th</sub>* = 130.1 kJ mol<sup>-1</sup>) but slightly less stable than the linear peroxyketal EBEPEP (*E<sub>a,th</sub>* = 133.5 kJ mol<sup>-1</sup>). As mentioned previously<sup>17</sup>, polymerization conditions have to be controlled to minimize the thermolysis of the peroxyketal. This latter phenomenon remains a minor side-reaction whatever the conditions used in this study, and EMCPEP could be considered as 'stable' under the usual polymerization conditions.

#### Chain transfer constants

The chain transfer constants (*C<sub>tr</sub>*) of the allylic peroxyketal EMCPEP were determined at 60°C in the polymerization of MMA, St and BA in the presence of AIBN as the initiator. These polymerizations were carried



Scheme 4 Carbon identification for n.m.r. analysis

**Table 1** Number-average molecular weights ( $M_n$ ), conversions and rate of polymerization ( $R_p$ ) obtained by the use of EMCPEP at 60°C in the polymerization of MMA, St and BA

Polymerization conditions	[EMCPEP] $\times 10^3$ (mol l <sup>-1</sup> )	$M_n^a \times 10^{-3}$ (g mol <sup>-1</sup> )	Conversion <sup>b</sup> (%)	$R_p^c \times 10^5$ (mol l <sup>-1</sup> s <sup>-1</sup> )
MMA [MMA] <sup>d</sup> = 8.91 mol l <sup>-1</sup> [AIBN] = $3.05 \times 10^{-3}$ mol l <sup>-1</sup> $t = 60$ min	0	612	8.7	21.6
	0.5	581	8.7	21.6
	2.5	530	8.9	22.1
	5	480	8.9	22.0
	10	406	9.1	22.2
	25	221	8.9	22.1
St [St] <sup>e</sup> = 8.37 mol l <sup>-1</sup> [AIBN] = $3.05 \times 10^{-3}$ mol l <sup>-1</sup> $t = 60$ min	0	169	2.3	5.38
	0.5	137.5	2.4	5.63
	2.5	94	2.2	5.12
	5	83	2.4	5.63
	10	52.5	2.1	4.86
	25	26.5	2.4	5.63
BA [BA] <sup>f</sup> = 6.98 mol l <sup>-1</sup> [AIBN] = $6 \times 10^{-4}$ mol l <sup>-1</sup> $t = 10$ min	0	4550	n.d. <sup>g</sup>	(1.00)
	0.5	1823	n.d.	(0.99)
	2.5	495.5	n.d.	(0.98)
	5	253	n.d.	(0.96)
	10	105	n.d.	(0.97)
	25	49	n.d.	(0.96)

<sup>a</sup> Determined from s.e.c. data<sup>b</sup> Ratio of the weight of recovered polymer to the initial weight of monomer<sup>c</sup> Values in parentheses are  $R_p/R_{p0}$ , i.e. ratio of the rates of polymerization with and without EMCPEP, determined from s.e.c. data<sup>d</sup>  $d(\text{MMA}) = 0.968 - 1.225 \times 10^{-3} T$  ( $T$  in °C), where  $d$  is density<sup>e</sup>  $d(\text{St}) = 0.9224 - 8.69 \times 10^{-4} T$  ( $T$  in °C)<sup>f</sup> Based on MMA density<sup>g</sup> n.d., not determined**Table 2** Comparison of the chain transfer constants ( $C_{tr}$ ) of methyl 2-t-butylperoxymethylpropenoate (MBPMP), ETPEP, EMCPEP and EBEPEP in the polymerization of vinylic monomers at 60°C

	MMA <sup>a</sup>	St <sup>a</sup>	BA <sup>b</sup>	Ref. no.
$C_{tr}(\text{MBPMP})$	0.63 <sup>a</sup>	1.64 <sup>b</sup>	n.d. <sup>c</sup>	14
$C_{tr}(\text{ETPEP})$	0.096 <sup>d</sup>	0.97 <sup>d</sup>	1.02 <sup>e</sup>	17
$C_{tr}(\text{EMCPEP})$	0.102 <sup>d</sup>	1.02 <sup>d</sup>	0.88 <sup>e</sup>	This work
$C_{tr}(\text{EBEPEP})$	0.086 <sup>d</sup>	0.91 <sup>d</sup>	0.63 <sup>e</sup>	17

<sup>a</sup> [AIBN] =  $1.18 \times 10^{-2}$  mol l<sup>-1</sup><sup>b</sup> [AIBN] =  $8.51 \times 10^{-3}$  mol l<sup>-1</sup><sup>c</sup> n.d., not determined<sup>d</sup> [AIBN] =  $3.05 \times 10^{-3}$  mol l<sup>-1</sup><sup>e</sup> [AIBN] =  $6.1 \times 10^{-4}$  mol l<sup>-1</sup>

out at constant AIBN concentration, while the transfer agent/monomer ratio was progressively increased. The number-average molecular weights ( $M_n$ ) and the rates of polymerization ( $R_p$ ) are presented in Table 1. According to the significant decrease of the  $M_n$  values, allylic peroxyketal EMCPEP appears to be an effective CTA. Similarly to the cases reported previously<sup>17</sup> and under our reaction conditions, the rates of polymerization in MMA, St and BA (in the latter case,  $R_p/R_{p0}$  was based on s.e.c. data) appeared to be unaltered by the presence or absence of EMCPEP. This could provide evidence for the process being true chain transfer, rather than retardation (i.e. termination of growing polymer chains without efficient reinitiation).

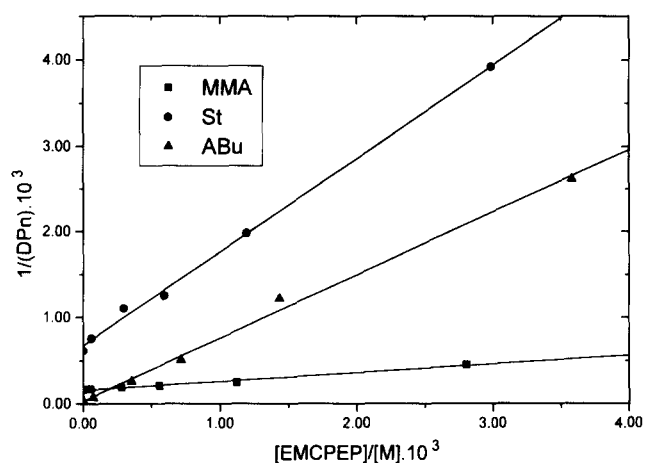
Kinetic studies of radical transfer reactions on allylic peroxyketals used in large amounts will be performed to check such behaviour. When samples of St containing various concentrations of EMCPEP were polymerized in bulk at 60°C, the resultant polymers had markedly lower molecular weight than those prepared in the absence of EMCPEP (Table 2). The  $C_{tr}$  values were obtained from the slope of the linear plot of  $(DP_n)^{-1}$  versus [EMCPEP]/[monomer] (Figure 1), according to the simplified Mayo relation (equation (2)). The Mayo equation<sup>25,26</sup> may be written as:

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_{tr(\text{CTA})} \frac{[\text{CTA}]}{[\text{M}]} + C_{tr(\text{S})} \frac{[\text{S}]}{[\text{M}]} + C_{tr(\text{I})} \frac{[\text{I}]}{[\text{M}]} + C_{tr(\text{M})} \quad (1)$$

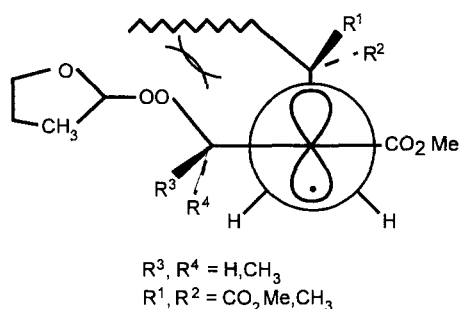
where S is solvent, I initiator and M monomer. This equation can be simplified by minimizing the contributions of the last three terms:

$$\frac{1}{DP_n} = \frac{1}{DP_{n0}} + C_{tr(\text{CTA})} \frac{[\text{CTA}]}{[\text{M}]} \quad (2)$$

The assumptions made in this approximation are: (1) the choice of bulk polymerization, so [S] = 0; (2) the use of micromolecular amounts of initiator minimizing the transfer constant  $C_{tr(\text{I})}$ .



**Figure 1** Reciprocal degree of polymerization of a monomer (M) as a function of the molar ratio of EMCPEP to M. Values of  $DP_n$  were determined by s.e.c. Lines are least-square fits to the data



**Scheme 5** Steric hindrance caused by addition of growing PMMA to EMCPEP (Newman's representation)

The chain transfer constant in St was 1.02, which is very close to the ideal value<sup>2</sup> of 1.0. This result contrasts with that of thiols, which have inconveniently high transfer constants in St polymerization ( $C_{tr} = 15\text{--}20$ )<sup>27</sup> and therefore can lead to the production of polymers with a broad distribution of molecular weights in batch polymerizations taken to high conversions. Similar experiments carried out with MMA also led to the production of low-molecular-weight polymers. A  $C_{tr}$  of 0.102 was derived from the experimental data. As mentioned for EBEPEP, the polymerizability of methacrylic-type monomers are greatly influenced by substituents in the allylic position of the double bond<sup>28,29</sup>.

The  $C_{tr}$  observed with EMCPEP in MMA was in between those obtained with EBEPEP and ETPEP (Table 2)<sup>14</sup>. It can be explained by a steric hindrance between the growing PMMA radical (methyl fragment) and the  $\alpha$ -substituent on EMCPEP (1-(1-methoxy-1-cyclohexylperoxy)ethyl group) in the addition step of the transfer reaction (see Scheme 5). This phenomenon was less important in BA polymerization ( $R' = H$ ) which may explain the intermediate  $C_{tr}$  value of EMCPEP obtained in the latter case ( $C_{tr} = 0.88$ ). This result, compared to those of EMCPEP and EBEPEP (Table 2), could be because the allylic strain effect of 1-methoxy-1-cyclohexylperoxy is intermediate to those of the 1-*n*-butoxyethylperoxy group and the 2-tetrahydrofuranylperoxy group.

**Table 3** Chain transfer constants ( $C_{tr}$ ) of EMCPEP in the polymerization of MMA at various temperatures

Temperature (°C)	$C_{tr}$
50	0.099
55	0.100
60	0.102
70	0.119
80	0.141

**Table 4** Absolute rate constant ( $k_{tr}$ ) for the PMMA radical chain transfer with EMCPEP from 50 to 80°C

Monomer	Reaction temp. (°C)	$k_p$ (l mol <sup>-1</sup> s <sup>-1</sup> )	$C_{tr}$	$k_{tr}$ (l mol <sup>-1</sup> s <sup>-1</sup> )
MMA	50	560 <sup>a</sup>	0.099	55
MMA	55	633 <sup>a</sup>	0.100	63.3
MMA	60	705 <sup>a</sup>	0.102	72
MMA	70	866 <sup>a</sup>	0.119	103
MMA	80	1050 <sup>a</sup>	0.141	148
St	60	176 <sup>b</sup>	1.02	179
BA	60	2090 <sup>c</sup>	0.88	1839

<sup>a</sup> Values from ref. 24

<sup>b</sup> Value from ref. 35

<sup>c</sup> Value from methyl acrylate, ref. 36

Effectively, the linear structure of EBEPEP involves many more degrees of freedom than the blocked cyclic fragment for EMCPEP. The latter, attached to the peroxidic bond by means of the quaternary carbon C8, seems bulkier than those of ETPEP. Substitution on the allylic position from methacrylic-type transfer agents disfavors the possibility of a large addition to the unsaturation, whereas substitution on the other side of the peroxidic bond (far away from the double bond) has less influence. Such a phenomenon will have to be confirmed by computer calculations on space conformation energies. It was also observed recently in the polymerization of dialkyl itaconates<sup>30</sup>.

The  $C_{tr}$  values of this unsaturated peroxyketal in MMA were determined at 50, 55, 60, 70 and 80°C (Table 3) to estimate the addition rate constants ( $k_{add}$ ) to EMCPEP. The propagation rate constants ( $k_p$ ) are reported in Table 4 with the calculated transfer rate constants ( $k_{tr}$ ). 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 the addition rate constants ( $k_{add}$ ) of the growing polymer radicals to the double bond of EMCPEP.

Precipitation of PMMA and PS in heptane and methanol, respectively, did not significantly alter the number-average molecular weights ( $M_n$ ) or the poly-molecularities ( $M_w/M_n$ ) of the telomers studied. Low-molecular-weight polymers were not detected by <sup>1</sup>H n.m.r. spectroscopy in the mixture from the precipitations. A minor decrease in the conversion rate (Table 1,  $R_p/R_{p0}$  values) of the polymerization of BA was observed as the concentration of EMCPEP increased; the data do, however, show that the primary process is chain transfer (i.e. that reinitiation of chains is relatively efficient).

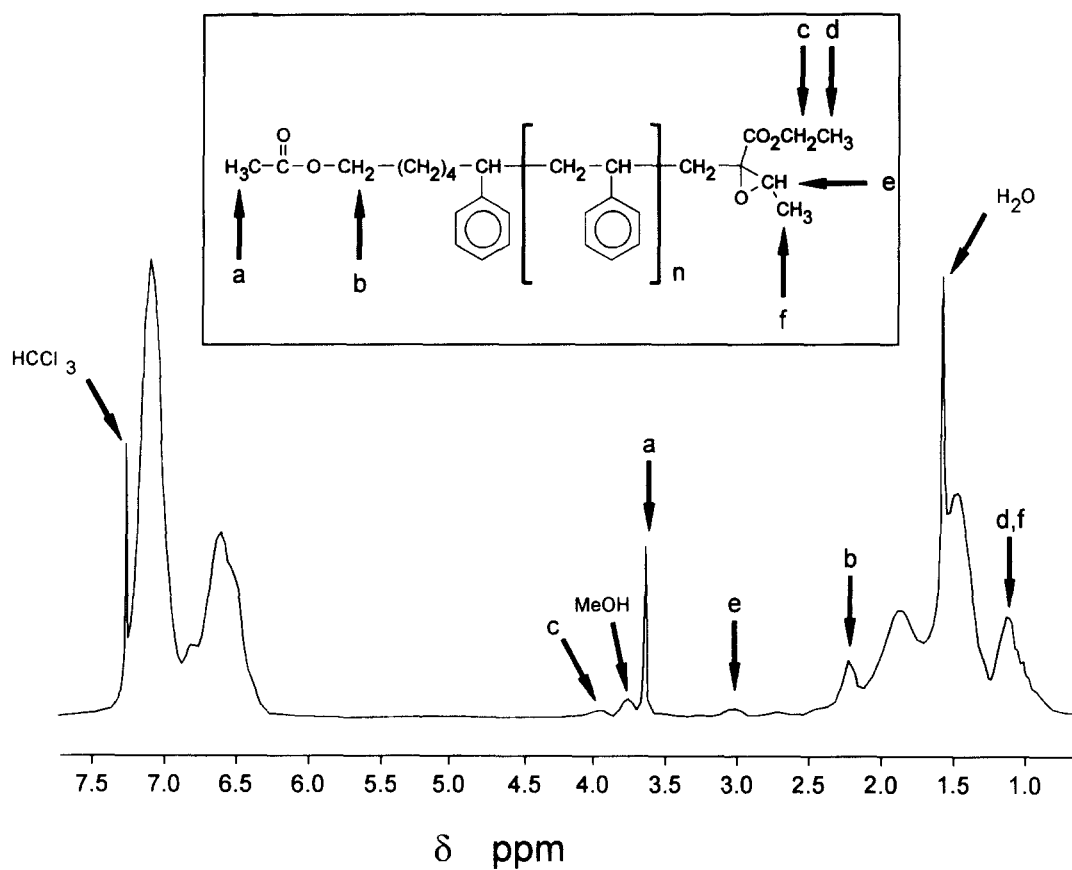


Figure 2  $^1\text{H}$  n.m.r. (200 MHz) spectrum of polystyrene ( $M_n = 2360 \text{ g mol}^{-1}$ ) prepared using EMCPEP as chain transfer agent

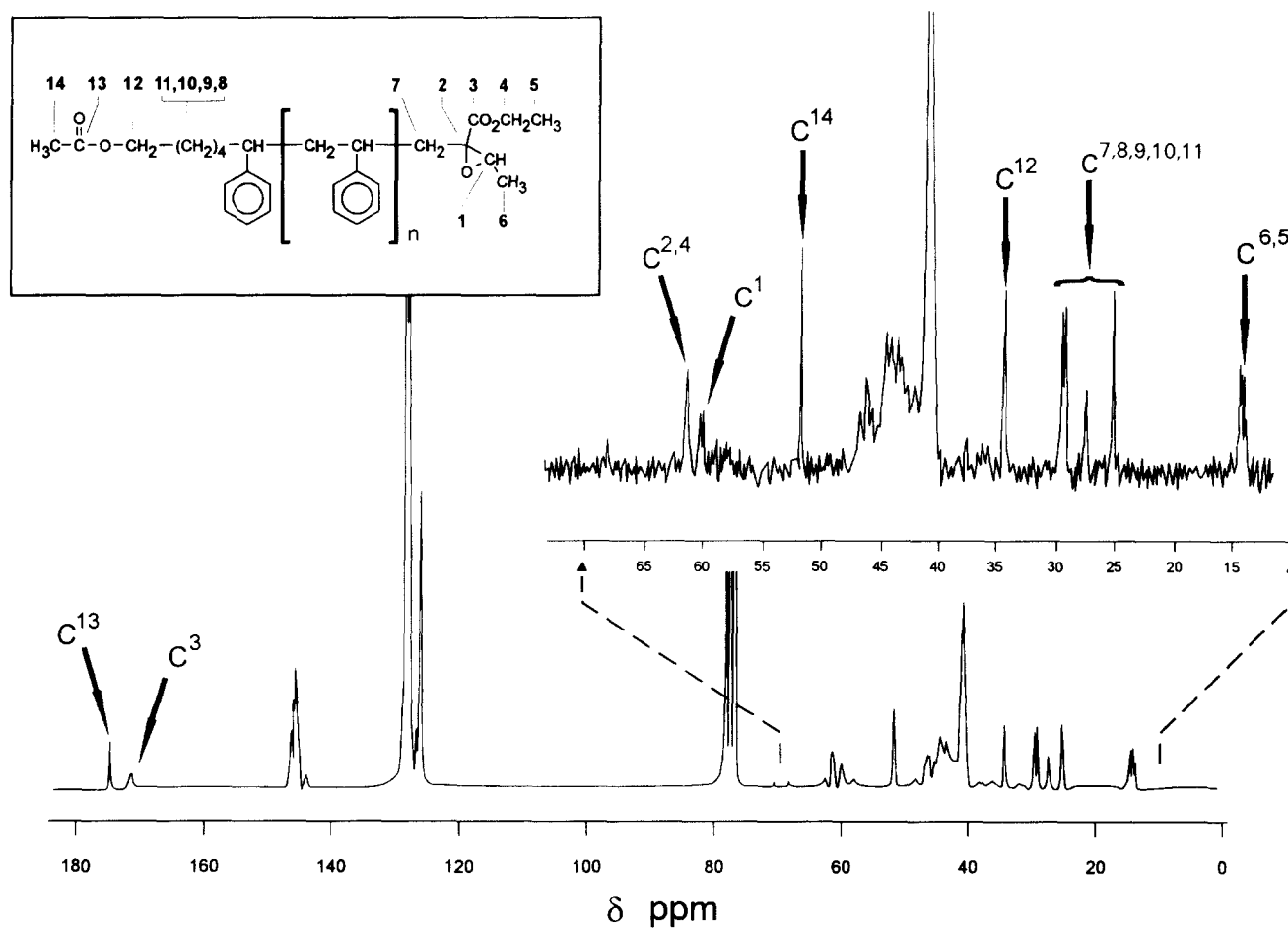
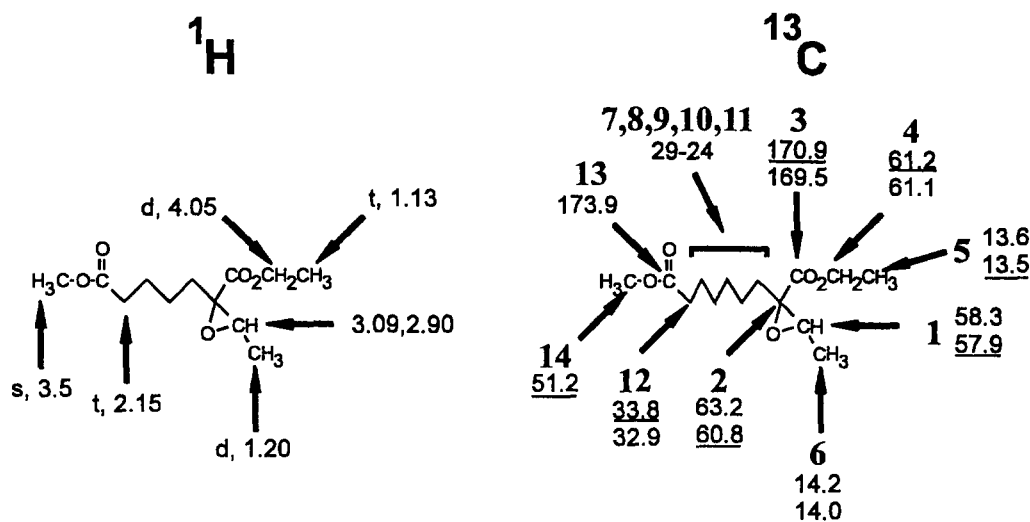


Figure 3  $^{13}\text{C}$  n.m.r. (63 MHz) spectrum of polystyrene ( $M_n = 2360 \text{ g mol}^{-1}$ ) prepared using EMCPEP as chain transfer agent



Scheme 6 N.m.r. of model compound. Underlined chemical shifts were attributed to the major diastereoisomers

### Thermodynamics of the transfer reaction

The activation energy ( $E_{a_{tr}}$ ) for the chain transfer reaction with EMCPEP in the polymerization of MMA was calculated from the plot  $\ln C_{tr}$  versus  $1/T$ , according to the Arrhenius equation for the chain transfer constants  $C_{tr}$ :

$$C_{tr} = \frac{k_{tr}}{k_p} = \frac{A_{tr}}{A_p} \exp\left(\frac{E_{a_p} - E_{a_{tr}}}{RT}\right) \quad (3)$$

The observed activation energy ( $E_{a_p} - E_{a_{tr}}$ ) and the ratio of the frequency factors ( $A_{tr}/A_p$ ) were estimated to be  $-11.5 \text{ kJ mol}^{-1}$  and 7.2, respectively.

The absolute activation energy ( $E_{a_{tr}} = 31.1 \text{ kJ mol}^{-1}$ ) and the frequency factor ( $A_{tr} = 6.3 \times 10^{-6} \text{ l mol}^{-1} \text{ s}^{-1}$ ) were determined from the experimental value of  $E_{a_p} - E_{a_{tr}}$  using the literature values<sup>31-33</sup> of  $E_{a_p}$  ( $19.6 \text{ kJ mol}^{-1}$ ) and  $A_p$  ( $8.7 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ ), respectively. The absolute activation energy ( $E_{a_{tr}}$ ) for termination of PMMA radicals by transfer on EMCPEP is slightly higher than the activation energy for the propagation step ( $E_{a_p}$ ) of the monomer polymerization, which can be explained by the allylic steric effect in the addition step of the transfer reaction, as mentioned earlier.

### Spectroscopic polymer characterization

The mechanism depicted in Scheme 2 leads to the expectation that the polymers prepared in the presence of allylic peroxyketal EMCPEP would be terminated by both methoxycarbonyl and glycidic ester end-groups (see Scheme 6).  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra (Figures 2 and 3) are in agreement with the expected structures. A low-molecular-weight sample of PS was prepared ( $M_n = 2360 \text{ g mol}^{-1}$ ) using a large amount of EMCPEP ( $[\text{EMCPEP}] = 7.02 \times 10^{-1} \text{ mol l}^{-1}$ ). The  $^1\text{H}$  n.m.r. spectrum (Figure 3) showed signals at 4.0, 3.5, 3.0 and 1.1 ppm, consistent with  $\text{CH}_2$  protons of the ethoxycarbonyl fragment, the methoxycarbonyl group, the hydrogen of oxirane, and other  $\text{CH}_3$  fragments, respectively. The  $^{13}\text{C}$  n.m.r. spectrum showed signals consistent with those expected for the methoxycarbonyl and the ethoxycarbonyloxirane functions.

### CONCLUSIONS

The free-radical addition-substitution-fragmentation reaction using EMCPEP appears to be an elegant single-step method for realizing  $\alpha,\omega$ -difunctional polymers. The current results highlight the efficiency of the activated allylic peroxyketal chain transfer agent EMCPEP for regulating molecular weight in vinylic monomer polymerizations. Further kinetic works and confirmation of the end-group functionality are in progress.

### REFERENCES

- Geothals, E. J. 'Telechelic Polymers: Synthesis and Applications', CRC, Boca Raton, 1989
- Corner, T. *Adv. Polym. Sci.* 1984, **62**, 95
- Meijs, G. F., Rizzardo, E. and Thang, S. H. *Macromolecules* 1988, **21**, 3122
- Meijs, G. F., Morton, T. C., Rizzardo, E. and Thang, S. H. *Macromolecules* 1991, **24**, 3689
- Meijs, G. F. and Rizzardo, E. *Makromol. Chem., Rapid Commun.* 1988, **9**, 547
- Meijs, G. F. and Rizzardo, E. *Makromol. Chem.* 1990, **191**, 1545
- Meijs, G. F., Rizzardo, E. and Thang, S. H. *Polym. Bull.* 1990, **24**, 501
- Meijs, G. F. and Rizzardo, E. *Polym. Bull.* 1991, **26**, 291
- Yamada, B., Kabatake, S. and Otsu, T. *Polym. J.* 1992, **24**, 281
- Yamada, B., Kabatake, S. and Otsu, T. *Macromol. Chem., Rapid Commun.* 1990, **11**, 513
- Yamada, B., Kabatake, S. and Otsu, T. *Makromol. Chem.* 1991, **192**, 333
- Yamada, B., Kato, E., Kabatake, S. and Otsu, T. *Polym. Bull.* 1991, **25**, 423
- Yamada, B., Kabatake, S. and Aoki, S. *Macromolecules* 1993, **26**, 5099
- Meijs, G. F., Rizzardo, E. and Thang, S. H. *Polym. Prepr.* 1992, **33**(1), 893
- Vertommen, L. L. T., Meijer, J. and Maillard, B. J. *PCT Int. Appl. WO 9 107 387*, 1991; *Chem. Abstr.* 1991, **115**, 160039q
- Montaudon, E., Rakotomanana, F. and Maillard, B. *Tetrahedron* 1985, **41**(13), 2727
- Colombani, D. and Chaumont, P. *Macromolecules* in press
- Colombani, D. and Maillard, B. *J. Chem. Soc., Perkin Trans II* 1994, 745
- Colombani, D. and Maillard, B. *J. Org. Chem.* 1994, **59**, 4765
- Adam, W. and Griesbeck, A. *Synthesis* 1986, 1050
- Orfanopoulos, M. and Foote, C. S. *Tetrahedron Lett.* 1985, **26**, 5991
- Wohl, R. A. *Synthesis* 1974, 38

- 23 McKenzie, C. A. and Stocker, J. H. *J. Org. Chem.* 1955, **20**, 1695
- 24 Navarro, C., Vertommen, L. and Maillard, B. *New J. Chem.* 1992, **16**(10), 987
- 25 Mayo, F. R. *J. Am. Chem. Soc.* 1943, **65**, 2324
- 26 Mayo, F. R. and Walling, C. *Discuss. Faraday Soc.* 1974, **2**, 328
- 27 Young, L. J. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 2nd edn, Wiley Interscience, New York, 1974, p. II-92
- 28 Cheng, J. S., Yamada, B. and Otsu, T. *J. Polym. Sci., Part A: Polym. Chem.* 1991, **29**, 1837
- 29 Penelle, J., Collot, J. and Rufflard, G. J. *J. Polym. Sci., Polym. Chem.* 1993, **31**, 2407
- 30 Otsu, T., Yamagishi, K., Matsumoto, A., Yoshioka, M. and Watanabe, H. *Macromolecules* 1993, **26**, 3026
- 31 Matheson, M. S., Auer, E. E., Bevilacqua, E. B. and Hart, E. J. *J. Am. Chem. Soc.* 1949, **71**, 497
- 32 Matheson, M. S., Auer, E. E., Bevilacqua, E. B. and Hart, E. J. *J. Am. Chem. Soc.* 1949, **71**, 2610
- 33 Walling, C. 'Free Radicals in Solution' (Ed. J. K. Kochi), Wiley, New York, 1957, p. 95
- 34 Masson, J. C. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 2nd edn, Wiley Interscience, New York, 1974, p. II-3
- 35 Volmann, D. H. and Graven, W. M. *J. Am. Chem. Soc.* 1953, **75**, 3111
- 36 Korus, R. and O'Driscoll, K. F. in 'Polymer Handbook' (Eds J. Brandrup and E. H. Immergut), 2nd edn, Wiley Interscience, New York, 1974, pp. II-45, 50