Synthesis and characterization of anionic 2,3-epoxypropyl methacrylate polymers and of related random and block copolymers with methyl methacrylate

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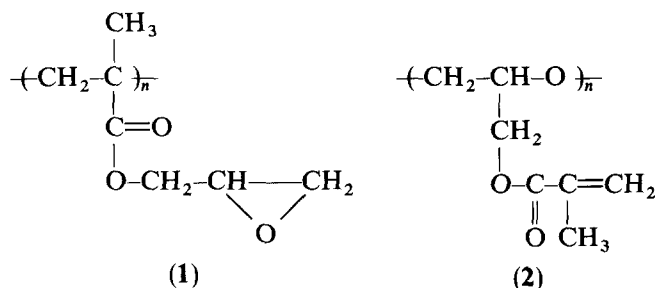
Glycidyl methacrylate polymers and their random or block copolymers with methyl methacrylate have been synthesized anionically with a lithium organic initiator in tetrahydrofuran solution, at low temperature, with lithium chloride added to the reaction medium. In all cases, initiation and propagation involved exclusively methacrylic unsaturation, without touching the oxirane group of glycidyl methacrylate. The macromolecular species formed were characterized by titration of the epoxide groups, ^{1}H n.m.r., i.r. spectroscopy, s.e.c. and light scattering measurements. The determination of compositions, average molecular weight and polydispersity indices of the various samples were in agreement with the values expected.

INTRODUCTION

2,3-Epoxypropyl methacrylate (or glycidyl methacrylate, GMA) is an interesting monomer exhibiting a polymerizable methacrylic unsaturation and an oxirane function of potential reactivity.

This monomer has been homopolymerized by means of free-radical initiators[1,2] (organic peroxides or azo-catalysts) known to selectively attack the methacrylic double bonds. The repeat units (1) thus contain pendant epoxy substituents, whereas polymerization of GMA through its epoxide functions would lead to polymer (2)[3]. If methacrylic polymerization and epoxy-ring-opening polymerization occurred simultaneously, a crosslinked polymer would be formed[4].

$$
\begin{array}{cc}
\underset{\text{(1)}}{
\begin{array}{l}
\quad\; \text{CH}_3 \\
\quad\; | \\
\text{+CH}_2\text{-C }\text{)}_n \\
\quad\; | \\
\quad\; \text{C=O} \\
\quad\; | \\
\text{O-CH}_2\text{-CH}\text{---CH}_2 \\
\qquad\qquad \backslash\;\;/ \\
\qquad\qquad \text{O}
\end{array}}
&
\underset{\text{(2)}}{
\begin{array}{l}
\text{+CH}_2\text{-CH-O)}_n \\
\quad\;\; | \\
\quad\;\; \text{CH}_2 \\
\quad\;\; | \\
\quad\;\; \text{O-C-C=CH}_2 \\
\qquad\;\; \| \;\; | \\
\qquad\;\; \text{O CH}_3
\end{array}}
\end{array}
$$

Free-radical random copolymerizations of GMA with conventional monomers[1,5] have been widely investigated for their potential applications (i.e. functionalization with amines[1], hydrophilic polymers[6,7], polyelectrolytes[8]).

Free-radical polymerization methods do not allow accurate control of the molecular weight distributions. The anionic polymerization of GMA has therefore been

considered with great interest as a possible route to well defined macromolecular species: homopolymers of known molecular weight and low polydispersity, ω-functional polymers (including macromonomers) and block copolymers. To allow molecular weight control, the polymerization has to be performed at low temperature. To control the reactivity of the carbanionic sites and to minimize side reactions, Teyssie and co-workers[9,10] have suggested carrying out the polymerization of acrylic monomers in the presence of specific ligands such as lithium chloride. It was established that LiCl modifies the environment of the growing sites by decreasing their nucleophilicity: the polymerization rate is lowered but the 'shelf-time' of the living species is increased. In spite of its efficiency, the role of LiCl in the polymerization mechanism is still not well understood[11].

A priori, both functions of GMA are liable to attack by carbanions. Methacrylic unsaturations do not require highly nucleophilic initiators to undergo polymerization. Sterically hindered carbanionic initiators such as diphenylmethyl- or diphenylhexyl-lithium are preferable to prevent side reactions onto the ester carbonyl[12]. Anionic initiators are also able to induce the ring-opening polymerization of oxirane, under specific experimental conditions, which depend mainly upon the counterion used. However, even if the experimental conditions chosen (low temperature, Li counterion) are inadequate for oxirane propagation, initiation can still occur. The resulting alkoxide sites are not sufficiently nucleophilic to attack a methacrylic unsaturation. Consequently, any side reaction affecting the epoxide cycle will lower the number of growing sites. Consequences are to be expected on molecular weight, polydispersity and availability for further reactions.

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Few publications have dealt with the anionic polymerization of GMA. Iwakura et al.[13] have reported on the stereospecific anionic polymerization of GMA and of 2,3-epoxythiopropyl methacrylate, but no details are given on the molecular weight distribution of the polymers formed. Recently, controlled 'living' anionic polymerization of GMA has been performed by Leemans et al.[14]. Block copolymers of GMA and α-methylstyrene have also been synthesized. These experiments, carried out in the absence of LiCl, yielded block copolymers of rather narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.16$).

The first aim of the present work is to evaluate the ability of very pure GMA to polymerize anionically via its methacrylic double bond, with the pendant oxirane function remaining unaffected.

The second aim was to synthesize and characterize block and random copolymers of methyl methacrylate (MMA) (A) and GMA (B), in the presence of LiCl. The challenge is to determine whether the living species arising from the anionic polymerization of monomer A are able to initiate quantitatively the polymerization of monomer B, and vice versa (monomer A attacked by active sites B^-). These experiments were aimed at the synthesis of di- and triblock copolymers constituted of poly(GMA) (PGMA) and poly(MMA) (PMMA) sequences. Finally, the anionic polymerization of a mixture of these two monomers was attempted, with the aim of obtaining random copolymers.

EXPERIMENTAL

Materials

Solvent. Tetrahydrofuran (THF) of high purity, free of protonic impurities, was obtained by two successive distillations, the first on sodium wire and the second from a fresh benzophenone-sodium adduct solution.

Monomers. Methyl methacrylate (Fluka) was dried over $CaCl_2$ and stored at low temperature. Before use, the monomer was distilled twice under reduced pressure over sodium wire and finally over calcium hydride powder.

The ultimate purification of GMA is not easy to achieve, but it is a prerequisite for successful anionic polymerization. In fact, commercial GMA (Aldrich Chemical Co.) contains impurities such as epichlorhydrin (originating from its industrial monomer synthesis), as proved by elemental analysis. Distillation in the presence of triethylaluminium, used for various alkyl methacrylates[15], has to be disregarded, because the monomer exhibits a strong tendency to polymerize spontaneously. Our investigations have demonstrated that two careful distillations of GMA over CaH_2 powder eliminated the inhibitors and yielded epichlorhydrin-free monomer. The purification of GMA must be carried out just before its polymerization, the distillate being recovered in a Schlenk vessel to avoid any contact with air or moisture.

Initiators. The anionic polymerization initiators were prepared in THF or benzene solution, by methods described in the literature[16,17].

Sec-butyllithium was formed in benzene solution by reaction of 2-chlorobutane with an excess of lithium metal pieces, at room temperature under dry argon atmosphere. The yield was about 70% after 3 days. Just before use,

the molarity of the initiator solution was determined by titration with acetanilide, the molar concentration of sec-BuLi being of the order of 0.6 M.

The preparation of 1,1-diphenyl-3-methylpentyllithium (DPHLi) was performed in situ inside the polymerization reactor, by stoichiometric reaction of sec-BuLi onto 1,1-diphenylethylene (DPE) in THF, under dry argon atmosphere. The process, which yielded a deep red solution in THF, was carried out at $-30°C$, to avoid possible side reactions between sec-BuLi and THF. DPHLi is formed instantaneously and quantitatively.

Lithium chloride (Merck Co.) was used as received.

Synthesis

PGMA homopolymers. The anionic polymerization of GMA was carried out in a tight glass reactor equipped with magnetic stirrer, temperature control, argon inlet, sampling device and specific entry for sec-BuLi. The other reagents (THF, DPE and GMA) were added from graduated Schlenk vessels fitted with stopcocks at both ends to prevent contact with air. The entire experiment was conducted under a slight argon over-pressure (about 70 mmHg above atmospheric pressure).

The required amount ($[LiCl]/[sec-BuLi] = 5$) of dry lithium chloride was introduced first. The reactor was then heated to 120–130°C and subjected to several argon–vacuum cycles to minimize residual moisture. The apparatus was cooled to $-40°C$ by a dry ice–isopropanol mixture, and a given volume of very pure THF was introduced, followed by the chosen amount of DPE. The protonic impurities of the reaction medium were neutralized with sec-BuLi (generally, two or three drops were sufficient for a THF volume of about 100 ml). Subsequently, the required volume of sec-BuLi solution was introduced under stirring and the mixture was cooled to $-60°C$. The chosen amount of pure GMA was added all at once, rather than dropwise, so that initiation would proceed rapidly. The reaction medium turned immediately from deep red to light yellow, characteristic of methacrylic anions, and the temperature increased by about 30°C in a few seconds. These observations indicate fast polymerization. The temperature was kept at around $-40°C$ (below that temperature the polymer tends to precipitate) for 30 min to ensure complete polymerization. Protonic deactivation of the living sites of PGMA was achieved with methanol. The polymer was precipitated from its THF solution by a methanol–water (85/15 v/v) mixture at $-15°C$, rather than with cold heptane. It was dried under vacuum, at room temperature for several days to constant weight. Gravimetric yields were found to be quantitative. The resulting polymers were soluble in organic solvents such as THF, acetone, dioxane, dimethylformamide, slightly soluble in benzene or toluene and insoluble in water, heptane and methanol.

Block copolymers of MMA and GMA. To synthesize di- and triblock copolymers containing at least one PGMA sequence, MMA and GMA were submitted to sequential anionic copolymerization.

Diblock PMMA-*b*-PGMA copolymers were prepared using a procedure similar to that described above. The anionic polymerization of MMA was conducted first using a sterically hindered initiator (DPHLi) in an aprotic solvent (THF), at low temperature ($-60°C$), under argon atmosphere, in the presence of LiCl. When the polymerization of MMA was complete, an aliquot of the

polymer solution was sampled out and deactivated protonically. The polymer formed was recovered by precipitation into a MeOH/H$_2$O (80/20 v/v) mixture and used to characterize the PMMA sequence. In the second step, GMA was added in one shot to the rest of the 'living' PMMA solution, under efficient stirring. A temperature increase was observed, the magnitude of which depended upon the amount of GMA added. The macromolecular species formed were either deactivated with methanol and isolated as above, or considered as a truly 'living' precursor for further polymerization. The overall yields of the copolymer formed were of the order of 98%.

To yield PMMA–PGMA–PMMA triblock copolymers, further MMA was added to the reaction medium. The reaction between MMA and the carbanionic sites of the 'living' PMMA-*b*-PGMA precursor involved a noticeable increase in temperature. The purification of the triblock copolymer formed did not involve special difficulties, although the final gravimetric yields did not exceed 90%.
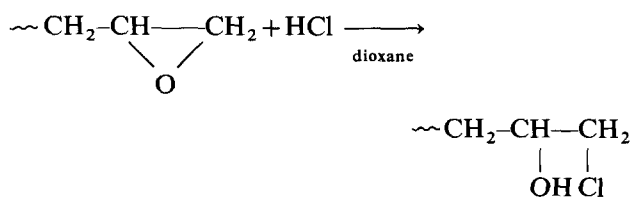
Random copolymers of GMA and MMA. If a mixture of two polymerizable monomers is reacted with an anionic initiator, the process does not usually yield random copolymers. Nevertheless, we have attempted the anionic synthesis of copolymers of MMA and GMA, because it has been shown that cross-additions are possible either way (A$^-$ + B and B$^-$ + A), owing to the fact that GMA and MMA exhibit similar electroaffinities. Random copolymer formation could thus be expected.

GMA–MMA mixtures of various compositions were added at $-60°C$ to a DPHLi solution in THF, in the presence of the required amount of LiCl. The reactions were carried out using the same experimental conditions as above. The monomer mixture was added in one shot. A greater temperature increase was observed when there was a high proportion of MMA in the mixtures. In each case, the gravimetric yields were above 95%.

Characterization of GMA (co)polymers

All the materials prepared were characterized using functional analysis of oxirane groups, ^{1}H n.m.r., i.r. spectroscopy, size exclusion chromatography (s.e.c.) in most cases with double detection, i.e. light scattering and differential refractometry.

Functional analysis of oxirane functions. Accurate determinations of the epoxy contents allowed evaluation of the degree of purity of GMA monomer and of its homopolymers. The same method served to determine the composition of the copolymers formed with MMA. The analytical determination of 1,2-epoxides is based upon the hydrochlorination of the cycle, producing chlorohydrin[18]:

$$\sim CH_2\text{-}CH\underset{O}{\diagdown\diagup}CH_2 + HCl \xrightarrow{\text{dioxane}}$$

$$\sim CH_2\text{-}CH\text{—}CH_2$$
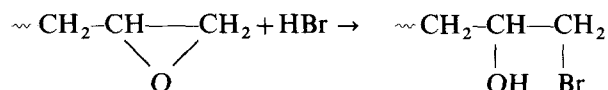$$\qquad\quad |\quad\ |$$
$$\qquad\quad OH\ Cl$$

Determination of the residual hydrochloric acid by back-titration with standard sodium hydroxide is the

most common procedure used in epoxide analysis. We have established that this method is inadequate, as it yields erratic results, even with model molecules (i.e. 1,2 epoxy-hexane or 1,2 epoxy-5 hexene). A kinetic investigation of the hydrochlorination reaction demonstrated that the epoxide content found was time dependent, and higher than the expected values. It seems that the HCl–dioxane reagent deteriorates with time. To overcome this difficulty, we have used a method described by Jay[19], involving nascent hydrobromic acid, formed by an exchange reaction between perchloric acid and tetraethylammonium bromide:
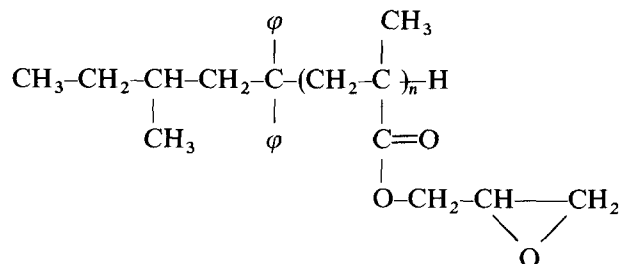
$$HClO_4 + (C_2H_5)_4N^+Br^- \rightarrow HBr + (C_2H_5)_4N^+ClO_4^-$$
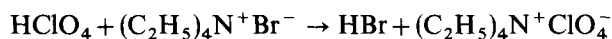
The reaction with oxirane functions is selective and instantaneous:

$$\sim CH_2\text{-}CH\underset{O}{\diagdown\diagup}CH_2 + HBr \rightarrow \quad \sim CH_2\text{-}CH\text{—}CH_2$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |\quad\ \ |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ OH\ Br$$

The following procedure has been used: the epoxide-containing polymer (100 mg) was dissolved in an acetone (10 ml)–acetic acid (15 ml) mixture and treated with a 40% solution (10 ml) of tetraethylammonium bromide in acetic acid, prepared previously. Perchloric acid in acetic acid solution (0.1 N) was added and the hydrobromic acid reacted instantaneously with the epoxide groups, leading to bromohydrin. The epoxide contents were obtained by direct titration of the bromide formed, the end-point being determined potentiometrically. The relative error was estimated to be about ±0.4%, the epoxide content found for GMA monomer being 28.40% (theoretical 28.16%).

Let us now consider the structure of PGMA homopolymers:

$$CH_3\text{-}CH_2\text{-}CH\text{-}CH_2\text{-}\overset{\overset{\varphi}{|}}{\underset{\underset{CH_3}{|}}{C}}\text{-}(CH_2\text{-}\overset{\overset{CH_3}{|}}{\underset{\underset{C=O}{|}}{C}})_{\overline{n}}\text{-}H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\ O\text{-}CH_2\text{-}CH\underset{O}{\diagdown\diagup}CH_2$$

obtained with 1,1-diphenyl-3-methylpentyllithium (M = 237) as the anionic initiator. The actual molecular weight of the species formed is $\bar{M}_a = \bar{M}_{PGMA} + 237$. Consequently, the theoretical weight per cent epoxide content of GMA homopolymers is related to the molecular weight of the polymer by:

$$\underset{O}{\diagdown\diagup}\% = \frac{28.16}{1 + (237/\bar{M}_{PGMA})}$$

If the molecular weight of PGMA increases from 2000 to 50 000, the corresponding epoxy weight content varies from 25.1 to 28.0%. A rough evaluation of the PGMA molecular weight is thus possible. Similar considerations about copolymers of MMA and GMA yielded the relation:

$$\underset{O}{\diagdown\diagup}\% = \frac{28.16}{(\bar{M}_{PMMA}/\bar{M}_{PGMA}) + (237/\bar{M}_{PGMA}) + 1}$$

which, knowing the average molecular weight of the PMMA 'precursor', allowed evaluation of the copolymer composition.

Spectroscopy. The epoxide content was also characterized qualitatively by i.r. spectroscopy, using a Perkin-Elmer 983 apparatus. The spectra obtained from THF solutions exhibited a strong characteristic absorption at $840 \, cm^{-1}$.

The copolymer composition was determined in $CDCl_3$ at 25°C by ^1H n.m.r., using a Brucker AC 200 spectrometer.

Size exclusion chromatography. S.e.c. measurements were carried out using a Waters g.p.c. apparatus equipped with a Waters R 401 differential refractometer fitted with six microstyragel columns exhibiting various porosities (10^6, mixture, 10^5, 10^4, 10^3 and 500 Å). The measurements were performed with THF as eluent, at a flow rate of $1 \, ml \, min^{-1}$ and at a temperature of 25°C. Various standard samples of PMMA with low polydispersity and known molecular weight (3000, 10000, 52500, 164000, 310000) were used for calibration. The number- and weight-average molecular weights of the GMA polymers and copolymers were determined from the corresponding calibration curve.

From the simultaneous measurements of the scattered light intensity and index of refraction increment, it was possible to calculate the molecular weight of the polymer as it was eluted from the s.e.c. columns. The molecular weight averages $\bar{M}_w$ and $\bar{M}_n$, as well as the polydispersity index, could thus be calculated. These values were also compared with those arising from the sole refractometric detection, using a calibration curve established with standard polystyrenes.

RESULTS AND DISCUSSION

GMA homopolymers

Glycidyl methacrylate was polymerized anionically at low temperature with 1,1-diphenyl-3-methylpentyllithium as initiator in the presence of LiCl (at least five times the

molar amount of initiator). Under these experimental conditions, initiation was instantaneous, as shown by the colour change of the reaction medium. The polymerization induced an increase in temperature and the polymer yields were quantitative.

The average molecular weight of PGMA (3639) determined by light scattering ($\bar{M}_{w,LS} = 20900$) and by s.e.c. using PMMA calibration ($\bar{M}^*_{w,PMMA} = 20200$) were in satisfactory agreement with the values expected ($\bar{M}_w = 20000$) from the mole ratio of monomer to initiator (*Table 1*). The molecular weight distributions were very narrow ($\bar{M}_w/\bar{M}_n = 1.05$) as shown by the s.e.c. chromatogram (*Figure 1*). Polymerizations of GMA, carried out under similar experimental conditions, but without LiCl (3629), yielded polymers exhibiting a very
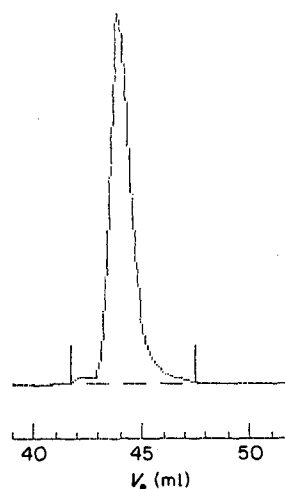

Figure 1 Size exclusion chromatography diagram of PGMA homopolymer (3639) in THF using standard PMMA calibration. The sample was prepared in THF at −60°C with DPHLi as anionic initiator in the presence of LiCl, $\bar{M}_w = 20300$, $\bar{M}_w/\bar{M}_n = 1.05$

Table 1 Average molecular weights and polydispersity indices of glycidyl methacrylate polymer and of its random and block copolymers

Samples	Yields (%)	dn/dc (exp)	$\bar{M}_{w,th}$ [a]	$\bar{M}_{w,LS}$ [b]	$(\bar{M}_w/\bar{M}_n)_{LS}$	$\bar{M}^*_{w,PS}$ [c] (s.e.c.)	$\bar{M}^*_{w,PMMA}$ [d] (s.e.c.)	$(\bar{M}_w/\bar{M}_n)_{PMMA}$	$\dfrac{\bar{M}_{w,LS}}{\bar{M}^*_{w,PMMA}}$	$\dfrac{\bar{M}_{w,LS}}{\bar{M}^*_{w,PS}}$
3639 PGMA homopol.[e]	100	0.0935	20000	20900	1.10	13800	20200	1.05	1.03	1.59
3629 PGMA homopol.[f]	~50	0.0935	9000	–	–	–	7150	1.59	–	–
3642-I PMMA homopol.[e]	100	0.0873	6000	–	–	–	6500	1.03	–	–
3642-II sequential copol. PMMA-b-PGMA[e]	>97	0.0918	10000	10700	1.03	7900	11800	1.03	0.91	1.35
3642-III sequential copol. PMMA-PGMA-PMMA[e]	>89	0.0880	20000	19300	1.04	14300	21400	1.03	0.90	1.35
3640 random copol. PMMA-PGMA[e]	>95	0.8930	12000	14100	1.05	9700	14700	1.04	0.96	1.46
3631 random copol. PMMA-PGMA[e]	>95	–	15000	–	–	–	18100	1.12	–	–
3641 random copol. PMMA-PGMA[e]	>92	0.0920	12000	13100	1.02	11200	16800	1.03	0.79	1.17
Standard PMMA[f]	100	0.0873	–	64700	–	56200	–	–	–	1.15

[a] Calculated from the monomer-to-initiator mole ratio
[b] By light scattering in THF
[c] By s.e.c. using standard polystyrenes calibration in THF
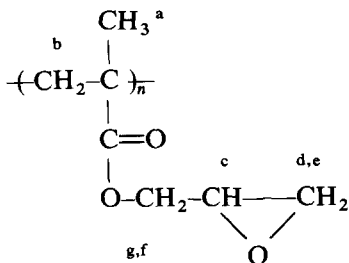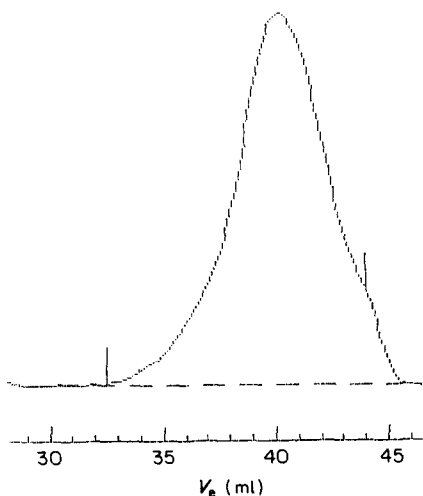[d] By s.e.c. using standard PMMA calibration in THF
[e] In the presence of required amount of LiCl:([LiCl]/[sec-BuLi] = 5)
[f] In the absence of LiCl
dn/dc, experimental refractive index increment

broad molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.59$, *Figure 2*).

A typical ^{1}H n.m.r. spectrum of PGMA (3639) is shown in *Figure 3*. Within experimental accuracy, each monomer unit carries a dangling oxirane group:

CH₃ ᵃ

b |

+CH₂–C)ₙ

|

C=O

| c   d,e

O–CH₂–CH——CH₂

g,f   \ /
            O

a: doublet at 0.94 and 1.10 ppm characterizing CH₃ protons

Figure 2 Size exclusion chromatography diagram of PGMA homopolymer (3629) in THF using standard PMMA calibration. The sample was prepared in THF at −60°C with DPHLi as anionic initiator in the absence of LiCl. $\bar{M}_w = 7150$, $\bar{M}_w/\bar{M}_n = 1.59$

b: peaks at 1.90 and 1.98 ppm of the methylene protons of the polymer chain

c, d, e: three peaks at 2.64, 2.84 and 3.24 ppm evidencing the epoxy-ring protons

f, g: set of peaks between 3.77–3.88 ppm and 4.27–4.33 ppm characterizing CH₂ protons next to the ester function

Functional oxirane analysis confirmed the results obtained by ^{1}H n.m.r. Hydrobromic acid reacted quantitatively with the oxirane groups present in the polymer. It can be concluded that, within experimental accuracy, the epoxy functions are not affected by the anionic polymerization. From the analytical titration of bromine in PGMA fitted at one chain end with DPHLi, the weight content of epoxy was found to be 27.55% (the theoretical value being 27.50% and 27.83% for $\bar{M}_w$ values of 10^4 and 2×10^4, respectively). These results are summarized in *Tables 1* and *2*.

It can be concluded that GMA is polymerizable anionically to linear macromolecules exhibiting low polydispersity indices, the oxirane functions remaining untouched. In other words, the shelf-time of this 'living' polymer is sufficiently long to allow polymerization to be completed without noticeable deactivation of the sites. These results should be compared with those of Leemans *et al.*[14], who did not add LiCl to the reaction medium. Obviously, the molecular weight control is better and the polydispersity slightly lower in our experiments.

Di- and triblock copolymers involving PGMA blocks

Many alkyl methacrylates exhibit electrophilicities close enough to enable reciprocal cross-initiation[20]: each monomer can be attacked by the carbanion arising from the other. This observation does not mean that their anionic copolymerization will necessarily yield a random copolymer. Because the rates of homopolymerization are strongly influenced by the bulkiness of the alkyl
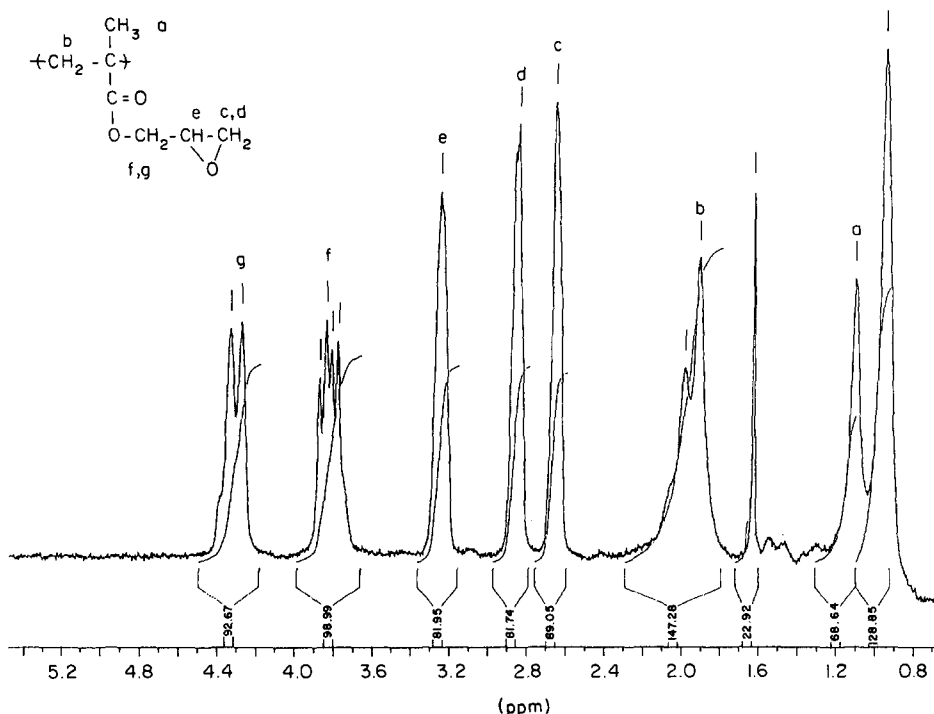

Figure 3 Typical ^{1}H n.m.r. spectrum of PGMA homopolymer (3639) in CDCl₃ at 25°C

Table 2 Compositions of block and random copolymers of glycidyl methacrylate and methyl methacrylate

Samples	$\bar{M}_{w,LS}$	GMA in the initial mixture (%)	PGMA in the copolymer formed (%)			
			^{1}H n.m.r.[a]	^{1}H n.m.r.[b]	O (%)[c]	Analysis
3639 PGMA homopol.	20900	100	100	100	27.50	100
3629 PGMA homopol.	–	100	100	100	26.78	100
3642-I PMMA homopol.	–	0	0	0	0	0
3642-II sequential copol. PMMA-b-PGMA	10700	46.5	45.75	47.35	14.73	50.53
3642-III sequential copol. PMMA-PGMA-PMMA	19300	30.0	21.20	23.80	7.99	28.37
3640 random copol. PMMA-PGMA	14100	28.8	23.80	28.35	7.97	28.30
3631 random copol. PMMA-PGMA	–	48.0	43.50	49.00	12.82	45.52
3641 random copol. PMMA-PGMA	13100	75.0	70.01	80.50	20.77	73.75

[a] By taking into account the –CH——CH$_2$ protons (c, d, e) and –O–CH$_3$ protons (h)
                \ /
                 O

[b] By taking into account the protons corresponding to c, d, e, f, g peaks
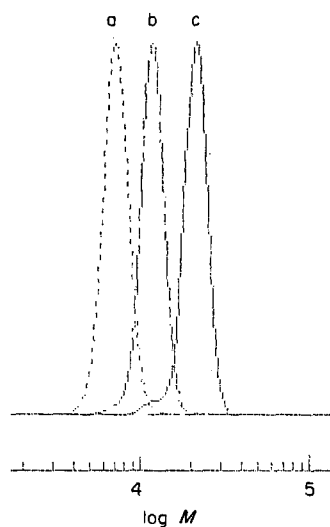[c] Analytical titration of epoxy functions by the method of Jay[19]

Figure 4 Size exclusion chromatography diagrams of (a) PMMA homopolymer (3642-I), (b) PMMA-b-PGMA block copolymer (3642-II) and (c) PMMA-PGMA-PMMA block copolymer (3642-III) in THF using standard PMMA calibration. All the samples were prepared in THF at −60°C with DPHLi as anionic initiator in the presence of LiCl

substituents, the reactivity ratios are necessarily close to unity.

We have demonstrated that cross-additions are possible between GMA and MMA. A 'living' PMMA (3642-I) is able to initiate the polymerization of GMA. The corresponding 'living' diblock copolymer PMMA-b-PGMA$^{(-)}$ (3642-II) does initiate the polymerization of MMA, leading to triblock copolymer PMMA–PGMA–PMMA (3642-III). In both cases, in the presence of LiCl the overall copolymer yields were close to quantitative (*Table 1, Figure 4*).

The ^{1}H n.m.r. spectrum of PMMA-b-PGMA block copolymer (*Figure 5*) enabled the copolymer composition

to be determined. It exhibits specific peaks due to methoxy protons (h) of the PMMA units (between 3.54 and 3.60 ppm). The α-methyl protons (a) of PMMA were shifted with respect to those of PGMA (0.88 and 1.02 ppm instead of 0.94 and 1.10 ppm), which provides an additional chance to calculate the copolymer composition (*Table 2*).

From these results it can be concluded that the ability of active sites originating from one monomer to initiate the polymerization of the other, and vice versa, is well established under the experimental conditions chosen. The synthesis of A–B and A–B–A block copolymers containing PGMA B sequences is thus possible. The copolymers exhibited no detectable fluctuations in composition. The copolymer yields were quasi-quantitative and the molecular weight distributions were unimodal and very narrow.

'Random' copolymers of GMA and MMA

The above conclusions on the cross-addition of MMA and GMA open new vistas on the possibility of preparing 'random' copolymers as a result of the polymerization of a mixture of the two monomers under appropriate conditions.

Experiments (3640 and 3641) were carried out: MMA–GMA mixtures (71.2/28.8 w/w and 25/75 w/w, respectively) were added in one shot to DPHLi solution in THF, at −60°C, with the required amount of LiCl. The colour of the reaction medium changed instantaneously from deep red to clear yellow, and the temperature increased noticeably. Thus, initiation was fast and propagation ensued. The gravimetric yields were practically quantitative.

The copolymers formed are free of PMMA and PGMA homopolymers as evidenced by the s.e.c. characterization. The molecular weights attained are close to those expected (around 15000). The chromatograms (*Figure 6*) are unimodal and characteristic for very narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.03-1.04$).
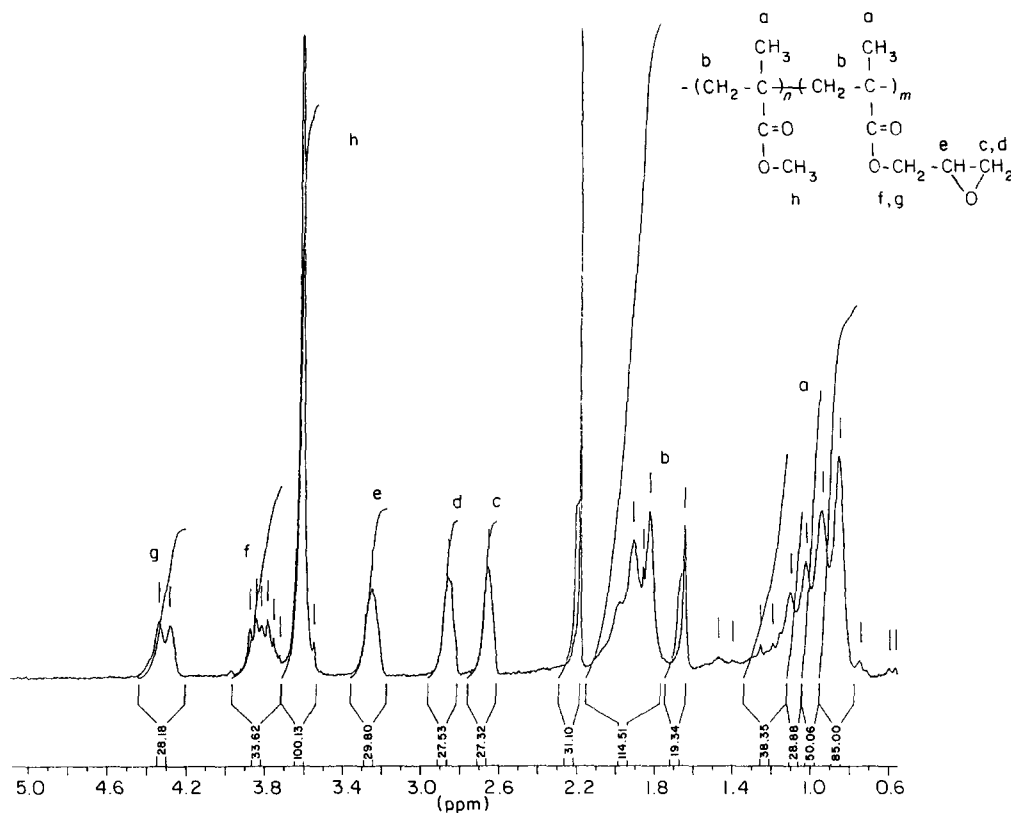
Figure 5 ¹H n.m.r. spectrum of PMMA-*b*-PGMA block copolymer (3642-II) in CDCl₃ at 25°C
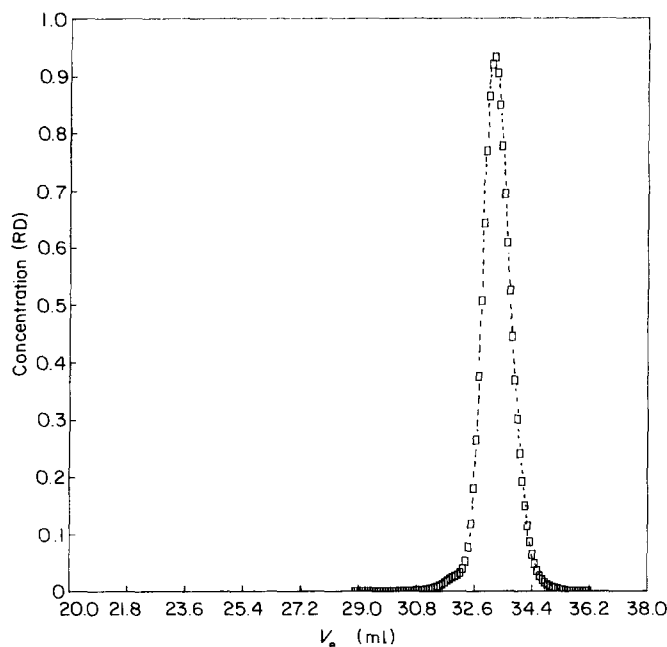

Figure 6 Size exclusion chromatography diagram of PMMA–PGMA random copolymer (3641) using polystyrene calibration. The sample was prepared in THF at −60°C with DPHLi as anionic initiator, in the presence of LiCl. $\bar{M}_{w,LS} = 13\,100$, $\bar{M}_w/\bar{M}_n = 1.02$

This is a valuable check of the 'living' character of this copolymerization.

The ¹H n.m.r. spectra (*Figure 7*) show the simultaneous presence of methoxy protons (h) and of oxiranyl protons (c,d,e). The overall copolymer compositions can be accurately determined. The striking fact is that the ¹H

n.m.r. spectra exhibit two α-methyl peaks at 0.88 and 1.03 ppm, whereas in the corresponding homopolymers these peaks have different locations, as already mentioned. In the case of block copolymers, these four peaks are well separated as a consequence of the presence of homopolymeric blocks of either type. It can be concluded that the copolymers formed do not contain homopolymeric blocks of any length. This conclusion is a good argument in favour of random placement of the monomer units along the chain. Another experiment (3631) was performed, in which the monomer mixture was added dropwise into the reaction mixture. In this case, the composition of the monomer mixture is kept approximately constant, and it can be anticipated that, in spite of possible differences in the growth rates, the distribution of monomeric units is random. The ¹H n.m.r. spectrum of this copolymer also exhibits only two α-methyl proton absorption peaks, confirming the above statement.

The synthesis of copolymers in which the two monomer units are randomly distributed along the polymer chain is thus possible. The samples formed exhibit low fluctuations in molecular weights and in composition. The ultimate structure of such macromolecular species will be studied in a forthcoming work using ¹³C n.m.r.

CONCLUSION

It is confirmed that GMA undergoes anionic polymerization exclusively on its methacrylic double bond, the oxirane function remaining unaffected. When carried out in the presence of lithium chloride the process can be considered as 'living': the molecular weights obtained are close to the values arising from the monomer-to-initiator mole ratio. The polymers exhibit unimodal and very
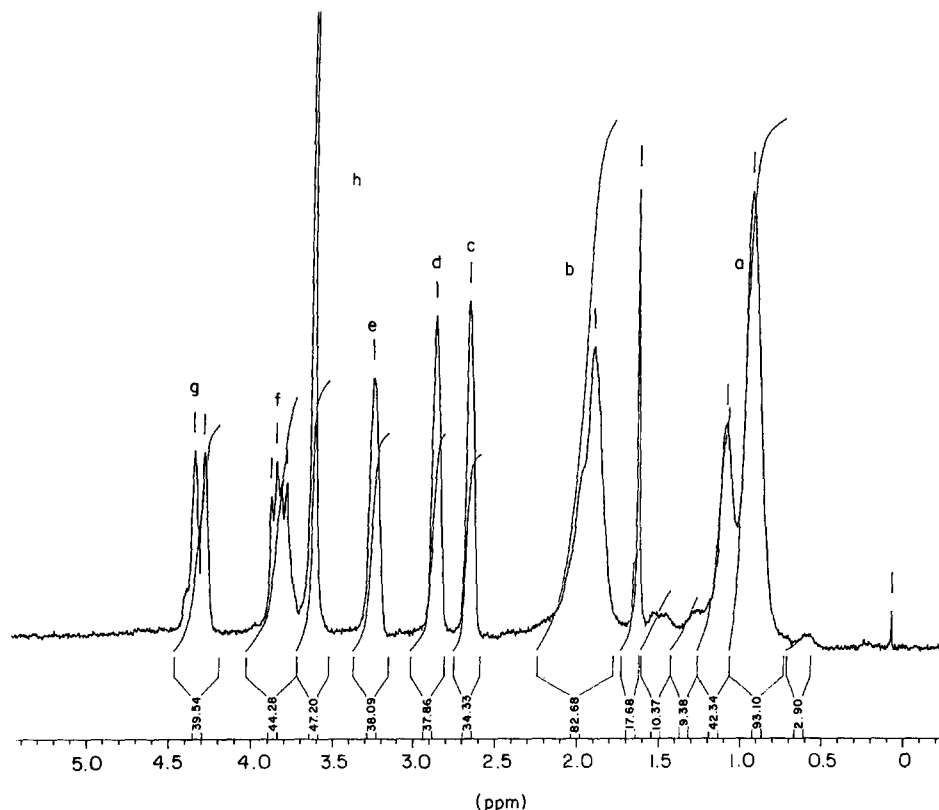
Figure 7 ¹H n.m.r. spectra of PMMA–PGMA random copolymers (3641) in CDCl₃ at 25°C

narrow molecular weight distribution, indicating that initiation is fast and that the carbanionic sites are not subject to transfer or termination under the experimental conditions chosen.

A second conclusion can be drawn, concerning the cross-addition reactions between GMA and MMA, which are possible in both ways (A⁻ + B or B⁻ + A). Well defined block copolymers with low fluctuations in molecular weight and composition can be obtained in quasi-quantitative yields. Triblock copolymers have even been obtained by sequential addition of MMA, GMA and MMA.

Finally, mixtures of both monomers polymerize anionically to high yields, leading to copolymers in which the distribution of monomer units is close to random.

These results confirm earlier investigations by Leemans et al.[14]. However, they show that LiCl addition is effective in lowering the nucleophilicity of the carbanionic sites, thus helping to eliminate side reactions and enhancing the 'living' character of the process.

The synthesis and characterization of new copolymers containing PGMA and other poly(alkyl methacrylate) sequences will be considered in a future paper.

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