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Anionic functional polymers, triblock copolymers and model networks derived from 2,3-epoxypropyl methacrylate

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This paper is devoted to the anionic polymerization of glycidyl methacrylate (GMA), using 1,1,4,4-tetraphenyl-1,4-dilithiobutane as the bifunctional initiator, at low temperature, in an aprotic solvent, and in the presence of the required amount of lithium chloride. This polymerization yields well defined polymers, exhibiting molar masses close to the expected ones, and narrow molar mass distributions. The oxirane ring remaining unaffected, the polymerization involves exclusively the methacrylic unsaturation of the monomer. Using this difunctional initiator, the synthesis of poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA) triblock copolymers can be achieved. The central block of poly(MMA) (poly(methyl methacrylate)) is synthesized first, followed by the outer poly(GMA) blocks. All these materials have been characterized by analytical determination of the oxirane content, by size exclusion chromatography and by proton nuclear magnetic resonance, the latter method leading to the copolymer composition. The species formed are free of the corresponding homopolymers and their molar mass distributions are narrow and unimodal. Finally, new polymeric model networks have been synthesized by endlinking, upon addition of a small amount of ethylene dimethacrylate to the above bifunctional living precursor polymers.

(Keywords: anionic polymerization; endlinking reactions; triblock copolymers)

INTRODUCTION

The present paper is an extension of previous research[1] on the synthesis and characterization of well-defined homopolymers, block and random copolymers arising from 2,3-epoxypropyl methacrylate (or glycidyl methacrylate).

The anionic synthesis of methacrylic ester polymers[2,3] has not been developed extensively, while well-defined polymer species derived from hydrocarbon monomers such as styrene or dienes have already been obtained[4]. Two main reasons explain this slow development. First, terminating protonic impurities (e.g. alcohols) are often present in commercial-grade monomers, preventing anionic polymerization. Secondly, the undesirable side reaction of the living carbanions with ester functions during the process involves premature termination.

During the last decade, considerable progress has enabled these difficulties to be overcome[5-8]. A new purification methodology[9] involving complexation with various trialkylaluminium reagents yielded monomers that can be polymerized anionically. The attack of ester carbonyls by strongly nucleophilic carbanions can be prevented by the use of bulky, resonance-stabilized carbanions such as those of diphenylmethyllithium[10-12]. Recently, Teyssié and co-workers[13-16] reported on the beneficial effect of specific ligands (such as LiCl) on the anionic polymerization of methyl methacrylate (MMA) and of *t*-butyl acrylate. Side reactions are minimized, allowing better control of the polymerization at low temperature and in a polar aprotic solvent. On studying the kinetics of the effect of LiCl on these anionic polymerizations, Kunkel *et al.*[17] concluded that the nucleophilic character of the growing sites is attenuated and the rate of propagation is lowered noticeably. These polymerizations involve neither transfer nor spontaneous termination[13,15], and can be described as 'living'.

We focused our attention on the anionic polymerization of glycidyl methacrylate (GMA). This monomer exhibits a polymerizable methacrylic unsaturation and an epoxy function of potential reactivity towards nucleophilic sites. While free-radical polymerization and copolymerization of this monomer have been widely investigated[18-25], few papers deal with its anionic polymerization, probably because of the difficulties involved in efficient purification of this monomer (see Experimental section). In 1967, Iwakura *et al.*[26] studied the stereospecific polymerization of GMA and of the corresponding thiirane, but no details are given of the molar mass of the polymers obtained. Recently, Leemans *et al.*[27,28] succeeded in anionically polymerizing GMA and in synthesizing diblock copolymers with MMA in the absence of LiCl.

We have recently[1] optimized the experimental conditions for the anionic polymerization of highly pure GMA. We obtained well-defined poly(GMA) samples by operating in a polar solvent, tetrahydrofuran, at low temperature, under dry argon atmosphere, with a

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monofunctional, resonance-stabilized lithium organic initiator (1,1-diphenyl-3-methylpentyl lithium), lithium chloride being added to the reaction medium. We have established that anionic polymerization proceeds exclusively on the methacrylic unsaturation of GMA, its oxirane cycle remaining unaffected. In the presence of LiCl, the process is truly living, the obtained average molar masses being close to the theoretical values arising from the molar ratio of monomer to initiator. Mixtures of GMA and MMA were copolymerized to high yields, and it was established that either monomer can be attacked by the carbanion derived from the other. As a consequence, diblock copolymers and triblock copolymers of these two monomers could be prepared by sequential addition of the corresponding monomers to the solution of an appropriate monofunctional initiator.

The present paper is the continuation of the research programme on GMA, with three objectives.

1. Our first goal was to widen the domain of molar masses accessible. A bifunctional lithium organic initiator was used at a steady rate. The living poly(GMA)s obtained were thus fitted with carbanions at both chain ends, and they constituted the precursor polymers for further polymerizations.
2. The second aim was to synthesize triblock copolymers from MMA and GMA using a bifunctional initiator, and starting with living poly(MMA). The living triblock copolymer can also be considered as a precursor for further developments.
3. The final goal was to evaluate the ability of these living species to yield new types of model networks, upon using polymerizable crosslinking agents.

EXPERIMENTAL

Materials

Solvent. Tetrahydrofuran (THF) was made free of protonic impurities by two successive distillations, the first on Na wire and the second from a dilute solution of benzophenone–Na adduct.

Monomers. Triethylaluminium (from Aldrich) was diluted to a 1 M solution in cyclohexane.

Methyl methacrylate (MMA) (from Fluka) was dried over $CaCl_2$, made free of inhibitors by distillation over sodium or over calcium hydride and stored at low temperature. Just before use, triethylaluminium was added dropwise to the monomer, under stirring, until a faint yellow colour appeared, as described by Allen *et al.*[9]. After distillation, MMA was collected in a Schlenk vessel to prevent access of air or moisture, and stored in a dry-ice/isopropanol bath until use.

Glycidyl methacrylate (GMA) was not easy to purify extensively. Commercial GMA (from Aldrich) contains various impurities: inhibitors, methacrylic acid, epichlorhydrin or glycidol, the latter originating from the industrial GMA synthesis. Careful distillation in the presence of triethyl aluminium[9] has to be rejected, because of the high tendency of the monomer to polymerize. To eliminate the inhibitor and to get epichlorhydrin-free monomer, GMA was distilled twice over CaH_2 powder. The resulting monomer can be polymerized with a monofunctional initiator such as 1,1-diphenyl-3-methyl pentyllithium (DPHLi)[1]. In the present case, we have added an ultimate purification step: it was distilled under vacuum in the presence of a small amount of DPHLi. No polymerization was observed and the ultra-pure monomer was collected in a Schlenk vessel and kept at low temperature until use.

Ethylene dimethacrylate (DME) (from Interscience or Aldrich) was selected as the bisunsaturated monomer. Two successive distillations under vacuum were carried out over CaH_2 and the monomer was recovered and kept in a Schlenk vessel until use.

Initiators. They were prepared according to methods already described in the literature[10–12].

s-Butyllithium (BuLi) was supplied by Aldrich (as 1.4 molar solution in cyclohexane), or it was prepared in the laboratory by reaction of 2-chlorobutane with an excess of Li metal pieces, in benzene solution, at room temperature and under argon atmosphere. After 72 h of reaction the yield is about 70%. The BuLi solution is titrated by the acetanilide method to determine its molarity (around 0.6 M).

1,1-Diphenyl-3-methylpentyl lithium (DPHLi) was prepared *in situ* by stoichiometric reaction of 1,1-diphenylethylene (DPE) with BuLi. DPHLi is formed quantitatively and exhibits a typical deep red colour.

1,4,4,-Tetraphenyl-1,4-dilithiobutane was selected as the bifunctional initiator to be used whenever polymers carrying sites at both chain ends were desired. This initiator was prepared from DPE and an excess of Li metal in THF, at room temperature. The reaction was completed with 24 h. The initiator solution was titrated by the acetanilide method. It cannot be kept for more than 5 days because of its rather low stability in THF.

Lithium chloride (from Merck) was used as received.

Syntheses

Poly(GMA) homopolymers. The anionic polymerization of GMA was performed under a slight argon overpressure, in a tight reactor, equipped with magnetic stirrer, temperature control, sampling device, and special entries for solvent, monomer and initiator. A chosen amount of LiCl ([LiCl]/[living sites] = 5) was introduced first into the reactor which was heated to 130°C and submitted to several argon/vacuum cycles. After cooling, the chosen quantity of pure THF was introduced and cooled to approximately −50°C. A few drops of the initiator were added to neutralize the residual protonic impurities (usually two or three drops were sufficient for 100 ml of THF). The calculated amount of the bifunctional initiator solution was introduced next, under stirring. The selected quantity of purified GMA was then added at once (rather than dropwise) to the initiator solution. The red colour of the medium vanished immediately, the solution becoming faint yellow or colourless. The temperature increased by 20°C within a few seconds, indicating fast propagation. The temperature was then kept at around −37°C, since below this temperature the poly(GMA) formed tends to precipitate because of its poor solubility in THF at low temperature.

A given volume of the polymer solution was sampled out and deactivated protonically (with methanol). The polymer formed was precipitated with a methanol/water mixture (85/15 v/v) at −15°C. It was then dried under vacuum to constant weight. The gravimetric yields were determined and found to be quasi-quantitative.

The rest of the polymer solution constituted the living precursor for further polymerizations, such as endlinking experiments.

Poly(GMA)-b-*poly(MMA)*-b-*poly(GMA) triblock copolymers.* The difunctional initiator was again used to obtain B-A-B triblock copolymers – A being poly(MMA) and B being poly(GMA) – with only two successive monomer additions (two-step process). The anionic polymerization of MMA was conducted using 1,1,4,4-tetraphenyl-1,4-dilithiobutane as the initiator, at −60°C, under argon atmosphere, in the presence of a known amount of LiCl. The purified MMA was added slowly to the initiator solution whereupon the central block of the triblock copolymer was formed. Sufficient time was allotted to allow completion of the MMA polymerization. An aliquot was then sampled out and deactivated protonically with methanol. The poly(MMA) was precipitated from its solution by a methanol/water mixture (85/15 v/v) at −15°C or with cold heptane. In the latter case, the polymer has to be redissolved in benzene to allow separation of LiCl, and it is then recovered by freeze-drying. This latter method is preferable for molar masses smaller than 10 000.

To the remaining reaction medium, ultra-pure GMA was added in one shot, under efficient stirring, to form B-A-B triblock copolymers. A noticeable temperature increase was observed, the magnitude of which depended on the amount of GMA added. The copolymers were found to be more soluble in cold THF than poly(GMA) homopolymers, and the medium remained homogeneous at low temperature, except when the GMA content was very high. The triblock copolymer was either isolated as described above, or kept living as a precursor for further polymerizations. The yields of the reaction are higher than 95% after precipitation.

Model networks derived from poly(GMA) and from poly(GMA)-b-*poly(MMA)*-b-*poly(GMA) triblock copolymers.* The living precursors (homopoly(GMA) and B-A-B triblock copolymer) were used in endlinking experiments to obtain polymer networks. Purified DME, selected as bisunsaturated monomer, was added at once to the precursor solution under efficient stirring, which was discounted soon afterwards. The temperature was kept at −35°C for one night, under argon atmosphere. The reaction medium gelled after about 12 h of reaction. The gels were quenched with methanol, and subsequently swollen to equilibrium in excess THF.

Characterization

The copolymers formed were characterized by functional analysis of their epoxy functions, by size exclusion chromatography (s.e.c.) and by proton nuclear magnetic resonance (^{1}H n.m.r.).

Functional analysis of oxirane functions. The analytical determination of epoxy rings in the block copolymers was carried out according to a method already described[1]. The procedure used is based on the quantitative reaction of oxirane groups with nascent HBr. The theoretical weight percentage of epoxy in poly(GMA) homopolymers is related to their molar mass by the following relation:

$$\text{wt\% oxirane} = \frac{28.16\bar{M}_{\text{PGMA}}}{360 + \bar{M}_{\text{PGMA}}} \qquad (1)$$

360 being the molar mass of the bifunctional initiator used in these experiments. Similar considerations on the block copolymers containing poly(GMA) blocks yielded the relation:

$$\text{wt\% oxirane} = \frac{28.16\bar{M}_{\text{PGMA}}}{\bar{M}_{\text{PMMA}} + \bar{M}_{\text{PGMA}} + 360} \qquad (2)$$

knowing the molar mass of the central poly(MMA) block, it is possible to evaluate the composition of the copolymer.

Size exclusion chromatography. The s.e.c. experiments were performed using a Knauer apparatus equipped with a Waters R 401 differential refractometer and fitted with six styragel columns of various porosities (10^6 to 500 Å). THF was used as eluent at a flow rate of 1 ml min^{-1}. Standard poly(MMA) samples of known molar mass (3×10^3 to 3×10^5 g mol^{-1}) and narrow molar mass distribution were used for calibration.

^{1}H nuclear magnetic resonance. ^{1}H n.m.r. was used to determine the composition of the samples of triblock copolymer. The spectra were taken at 25°C using a Brucker AC 200 spectrometer.

RESULTS AND DISCUSSION

Poly(GMA) homopolymers

Ultra-pure GMA was polymerized anionically in a polar solvent (THF) at −50°C, using 1,1,4,4-tetraphenyl-1,4-dilithiobutane as the bifunctional initiator, in the presence of added lithium chloride (five-fold molar excess with respect to initiating sites).

Initiation was found to be fast and quantitative. The red colour of the initiator solution vanishes at once and the temperature increases by at least 20°C. The polymer yields were quasi-quantitative (>98%) after precipitation in a methanol/water mixture. A series of poly(GMA) samples was synthesized.

Table 1 shows that the average molar masses determined experimentally by s.e.c. are in good agreement with the expected values, calculated from the monomer to initiator molar ratio. It should be pointed out that the experimental $\bar{M}$ values arising from s.e.c. are apparent values, given in terms of poly(MMA) equivalents. It is, however, reasonable to assume that poly(GMA) and poly(MMA), with the same degree of polymerization, exhibit similar hydrodynamic volumes in THF. The calibration curves for these polymers should thus be similar, at least in the range of molar masses covered (<40 000). The polydispersity of the various samples (characterized by the $\bar{M}_w/\bar{M}_n$ ratio) extends from 1.08 to 1.19. They are slightly higher than those found for poly(GMA) synthesized with a monofunctional initiator[1]. This may be due to the difficulty of purifying the monomer, and to the fact that difunctional initiators are more sensitive to protonic impurities than their monofunctional homologues.

A typical s.e.c. chromatogram (3771) is shown in *Figure 1*. It exhibits a unimodal and quasi-symmetric distribution, indicating that the carbonionic sites are

Table 1 Average molar masses and polydispersity indices of poly(glycidyl methacrylate) homopolymers

Samples[a]	$\overline{M}_{th}$[b]	$\overline{M}_w$[c]	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]
3764	10 000	9600	8200	1.17
3771	10 000	12 000	11 100	1.08
3761	15 000	16 600	13 900	1.19
3760	15 000	16 400	14 500	1.13
3769	20 000	20 000	18 000	1.11
3772	20 000	24 100	20 600	1.17
3776	30 000	35 100	29 300	1.19
3779	40 000	42 700	32 700	1.13

[a] All the samples were prepared at −50°C using 1,1,4,4-tetraphenyl-1,4-dilithiobutane as bifunctional initiator, in the presence of the required amount of LiCl ([LiCl]/[living sites] = 5)
[b] Theoretical calculated values from monomer to initiator molar ratio
[c] Experimental values determined by s.e.c., using standard poly(MMA) calibration curve

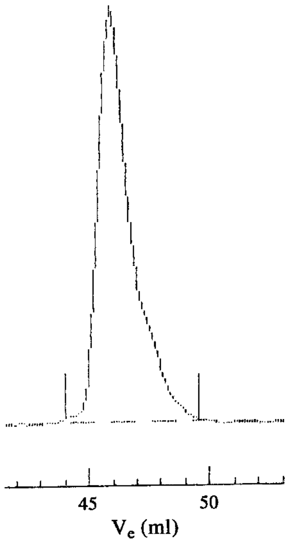

Figure 1 Size exclusion chromatography diagram of poly(GMA) homopolymer (3771) in THF. $\overline{M}_w = 12000$; $\overline{M}_n = 11000$; polydispersity ratio = 1.08

subject to very few accidental deactivations during the polymerization.

A typical ^{1}H n.m.r. spectrum of a poly(GMA) homopolymer (3760) is shown in *Figure 2*. Taking into account the structure of the macromolecule formed, the spectrum exhibits the following characteristics:

- absence of peaks corresponding to the methacrylic unsaturation;
- a: two peaks at 0.98 and 1.14 ppm characterizing the α-methyl protons;
- b: a doublet at 1.95 and 2.01 ppm corresponding to the methylene protons of the main chain;
- c, d, e: three characteristic peaks at 2.69, 2.88 and 3.28 ppm, evidencing the oxiranyl protons:
- f and g: a set of peaks between 3.82 and 3.92 ppm and between 4.31 and 4.37 ppm corresponding to the methylene protons of the side chains.

Integration of the peaks is self-consistent. It is thus demonstrated that within experimental accuracy each monomer unit of poly(GMA) carries a dangling epoxy group. The anionic polymerization of this monomer exclusively involves the methacrylic unsaturation.

It is theoretically possible to calculate the number average molar mass from the analytical determination of oxirane functions in the polymer. In fact, it ensues from equation (1) that the weight percentage of epoxy varies from 27.18 to 27.90% over the range of molar masses (10^4 to 4×10^4) covered in our experiments. The accuracy of the experimental titration method is insufficient to achieve accurate molar mass determination.

It can be concluded that GMA can be polymerized anionically using a bifunctional lithium organic initiator, in the presence of LiCl. The epoxy cycles remain unaffected; initiation as well as propagation affect exclusively the methacrylic unsaturations. The polymer is formed to quantitative yields; it exhibits molar masses close to those expected, and a rather narrow polydispersity. These results confirm the living character of the anionic GMA polymerization, which has already been proposed[1,28]. It is confirmed that the use of a sterically hindered carbanionic initiator prevents side reactions onto ester carbonyls. It was also established that the presence of LiCl has a beneficial effect on the anionic polymerization of methacrylic monomers. Poly(GMA) synthesized without LiCl exhibits a broad molar mass distribution[1].

Poly(GMA)-b-*poly(MMA)*-b-*poly(GMA) triblock copolymers*

In our previous work[1], we have used a monofunctional initiator to synthesize A-B-A triblock copolymers by sequential additions of monomer A, monomer B and monomer A again, taking advantage of the fact that the nucleophilicity of methacrylic monomers is very similar. This procedure involves the intermediate formation of diblock copolymers, but the macromolecules formed carry an active site at one chain end only. The method developed here for the synthesis of living triblock copolymers with active sites at both chain ends requires a bifunctional initiator. The central sequence is made first and it is fitted with living sites at both ends. The latter serve as initiators for the polymerization of the second monomer. The central block was of poly(MMA) and the two outer blocks were of poly(GMA). *Table 2* schematizes the synthesis performed.

The anionic polymerizaton of MMA was conducted at low temperature (−60°C), with 1,1,4,4-tetraphenyl-1,4-dilithiobutane, in THF, and in the presence of dry LiCl ([LiCl]/[living sites] = 5). This LiCl-assisted polymerization yielded well-defined living poly(MMA) precursor chains. The latter were used in turn to initiate the polymerization of GMA, from both ends of the poly(MMA) block. The triblock copolymers were deactivated protonically, and precipitated in a methanol/water mixture. Alternatively the living triblock copolymers can be considered as precursors for further polymerizations as crosslinking experiments.

The yields of the copolymers were close to quantitative. A series of such B-A-B block copolymers were prepared using this 'two-step' procedure, in the presence of LiCl. *Table 3* summarizes the characterization results. The poly(MMA) precursors exhibit number average molar masses close to the theoretically expected ones. It has to be kept in mind that the experimental values of $\overline{M}_n$ include the mass of the initiator (360). Under the experimental conditions selected, the polydispersity

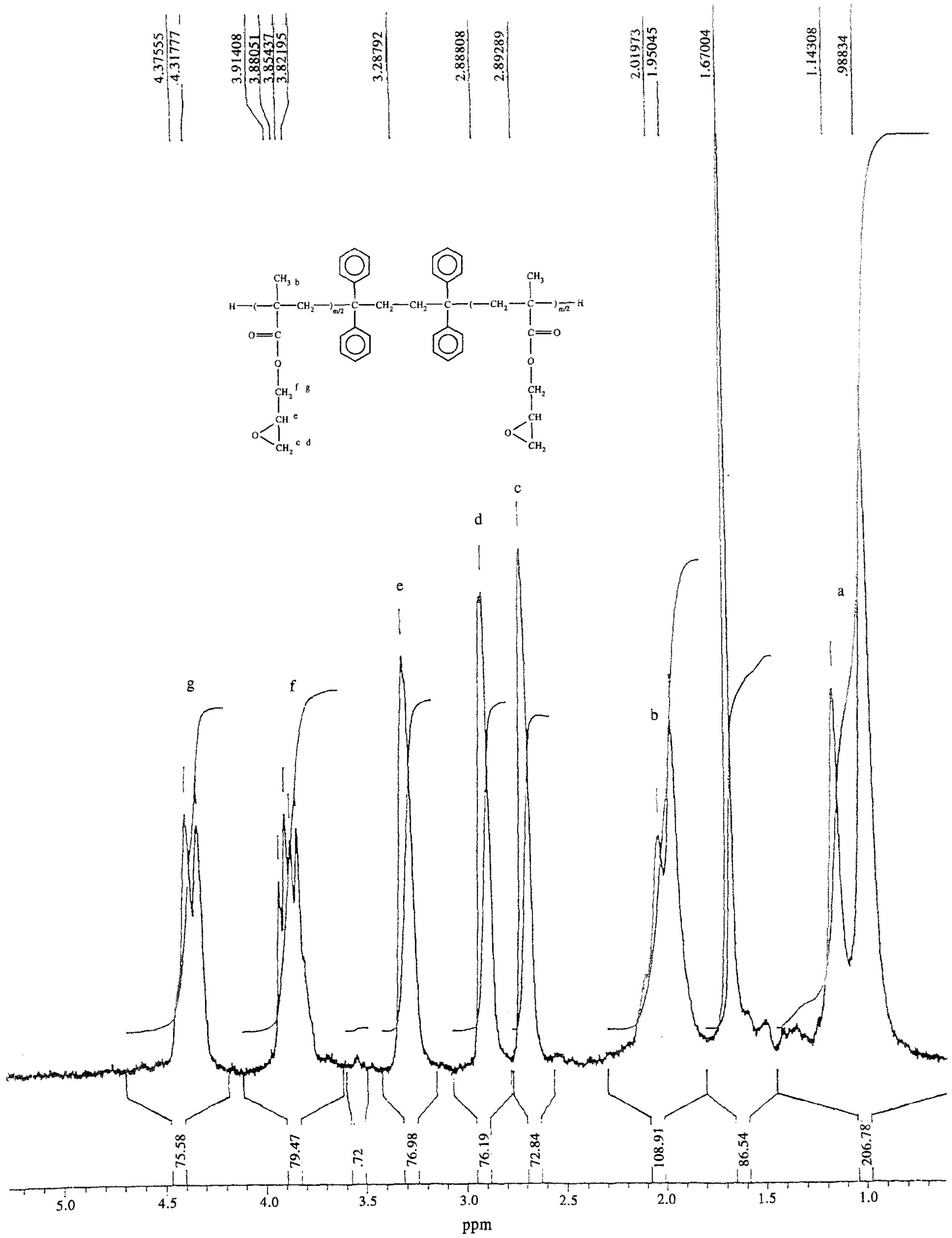

Figure 2 Typical ^{1}H n.m.r. spectrum of poly(GMA) homopolymer (3760) in $CDCl_3$, at 25°C

ratios range from 1.05 to 1.09 over the entire range of molar masses (6000 to 25 000) investigated. These results are quite satisfactory.

The results displayed in *Table 4* show that the sequential addition of MMA and GMA yielded the expected triblock copolymers. The experimental molar masses determined by s.e.c. (using poly(MMA) calibration) are in good agreement with the theoretical values. If it is assumed that the hydrodynamic volumes of poly(MMA) and poly(GMA), with the same degree of polymerization, are similar in THF, and if the incompatibility between them is not very large, the poly(MMA) calibration of the s.e.c. data can be used to characterize the block copolymers.

Table 2 Schematic anionic synthesis of poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA) block copolymers

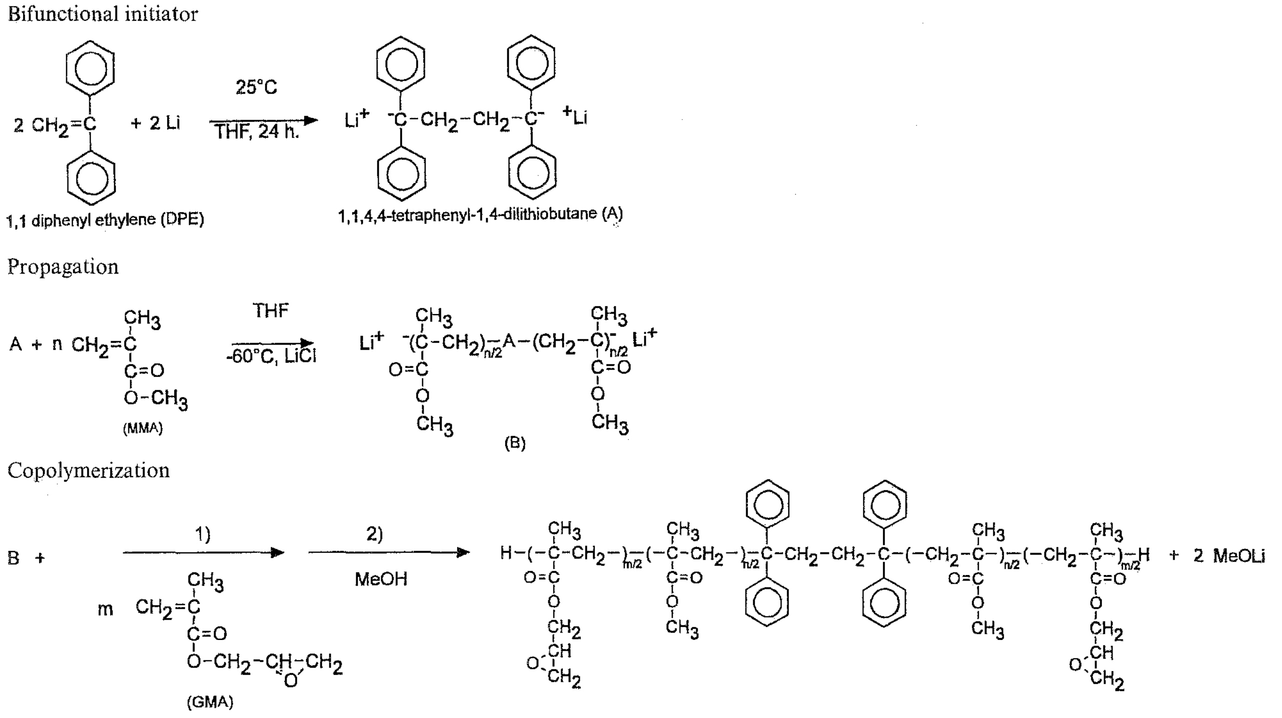

Table 3 Average molar masses and molar mass distributions of poly(MMA) precursors, in the presence of lithium chloride

Samples[a]	$\overline{M}_{th}$[b]	$\overline{M}_w$[c]	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]
3782	6000	7000	6600	1.06
3783	7500	7500	7050	1.06
3781	11 000	11 700	11 000	1.06
3784	12 000	13 300	12 400	1.07
3786	8000	8050	7350	1.09
3787	25 000	25 500	24 300	1.05
3785	15 000	16 700	15 800	1.05

[a] All the samples were prepared at −60°C using 1,1,4,4-tetraphenyl-dilithiobutane as bifunctional initiator, in the presence of the required amount of LiCl ([LiCl]/[living sites] = 5)

[b] Theoretical calculated values from the monomer to initiator molar ratio

[c] Experimental values determined by s.e.c., using standard poly(MMA) calibration curve

Table 4 Average molar masses, polydispersity indices and compositions of poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA) block copolymers

Samples[a]	$\overline{M}_{th}$[b]	$\overline{M}_w$[c]	$\overline{M}_n$[c]	$\overline{M}_w/\overline{M}_n$[c]	$(GMA)_{\overline{M}_n}$ (%)[d]
3782	10 000	10 550	9750	1.08	32.50
3783	18 000	20 100	18 100	1.11	61.64
3781	20 000	21 100	18 900	1.12	41.79
3784	33 000	37 200	32 150	1.15	61.43
3786	35 000	39 500	30 650	1.29	76.01
3787	35 000	38 750	34 700	1.11	29.97
3785	45 000	55 800	43 700	1.27	63.83

[a] All the triblock copolymers were synthesized in a two-step process using 1,1,4,4-tetraphenyl-1,4-dilithiobutane as bifunctional initiator, in the presence of LiCl

[b] Theoretical values calculated from monomer to initiator molar ratio

[c] Experimental values determined by s.e.c. measurements, using standard poly(MMA) calibration curve

[d] Experimental values of the proportions of poly(GMA) in the copolymers formed with respect to $\overline{M}_n$

The polydispersity indices of the triblock copolymers are rather low (ranging from 1.06 to 1.13) and are similar to those of the corresponding poly(MMA) precursors. The two exceptions are the cases in which the weight percentage of GMA in the copolymers was very high (63 and 76%, respectively). This may be connected with their lower solubilities in THF at low temperature. Similar observations have been made for homopoly(GMA)s[1,28] and show that every precursor molecule gives rise to a triblock copolymer.

In *Figure 3*, the s.e.c. diagrams of a poly(MMA) precursor and of the corresponding triblock copolymer (3783) are compared. The molar mass distributions are narrow and unimodal, and the copolymer is free of the corresponding homopolymers.

It is thus confirmed that if the reaction is carried out with the bifunctional initiator selected, in the presence of LiCl, the sequential copolymerization does not involve spontaneous transfer or termination: the process is living.

The compositions of the block copolymers were determined by ^1H n.m.r. spectroscopy. A typical spectrum (3783), shown in *Figure 4*, exhibits the following resonance peaks:

- a: four peaks between 0.85 and 1.09 ppm (α-methyl protons);
- b: three peaks between 1.82 and 1.97 ppm (methylene protons);
- c, d, e: peaks at 2.64, 2.84 and 3.24 ppm (oxiranyl protons);
- f, g: sets of peaks at 3.77–3.86 ppm and 4.27–4.33 ppm (CH_2 protons between ester and oxiranyl groups);
- h: a peak at 3.60 ppm (methoxy protons);
- no peaks between 5.0 and 5.2 ppm (unsaturations).

There are differences between the ^1H n.m.r. spectra of

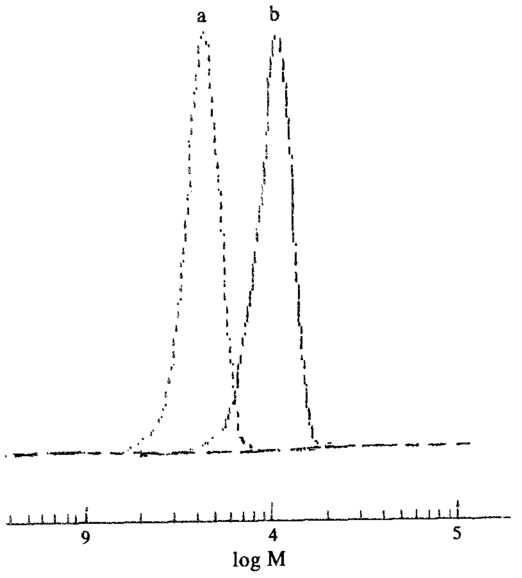

Figure 3 Size exclusion chromatography diagrams (3783). (a) Poly(MMA) precursor: $\bar{M}_w = 7500$; $\bar{M}_n = 7050$; $\bar{M}_w/\bar{M}_n = 1.06$. (b) Triblock copolymer: $\bar{M}_w = 20100$; $\bar{M}_n = 18000$; $\bar{M}_w/\bar{M}_n = 1.11$

poly(GMA) (*Figure 2*) and those of the triblock copolymer (*Figure 4*). In the latter case, four well-separated α-methyl peaks are found, indicating the presence of blocks of either type. *Figure 4* also shows the simultaneous presence of oxiranyl protons (c,d,e) and of methoxy protons (h). The compositions of the triblock copolymers have been determined from these spectra by three different methods. In the first one, the oxiranyl protons are compared with the α-methyl protons. In the second one, the methoxy protons are compared with the α-methyl protons. The third takes into consideration the ratio of the oxiranyl protons to the sum of the oxiranyl and methoxy protons. The results are shown in *Table 5*. They can be compared with those arising from the s.e.c. measurements and from analytical determinations of the oxirane contents. The agreement is quite satisfactory, if account is taken of the fact that the weight percentage of oxirane analytically determined (by nascent HBr titration) may be slightly overestimated.

It can be concluded that the synthesis of our triblock copolymers can be achieved anionically by sequential addition of the two monomers considered, using a bifunctional initiator, in the presence of the appropriate

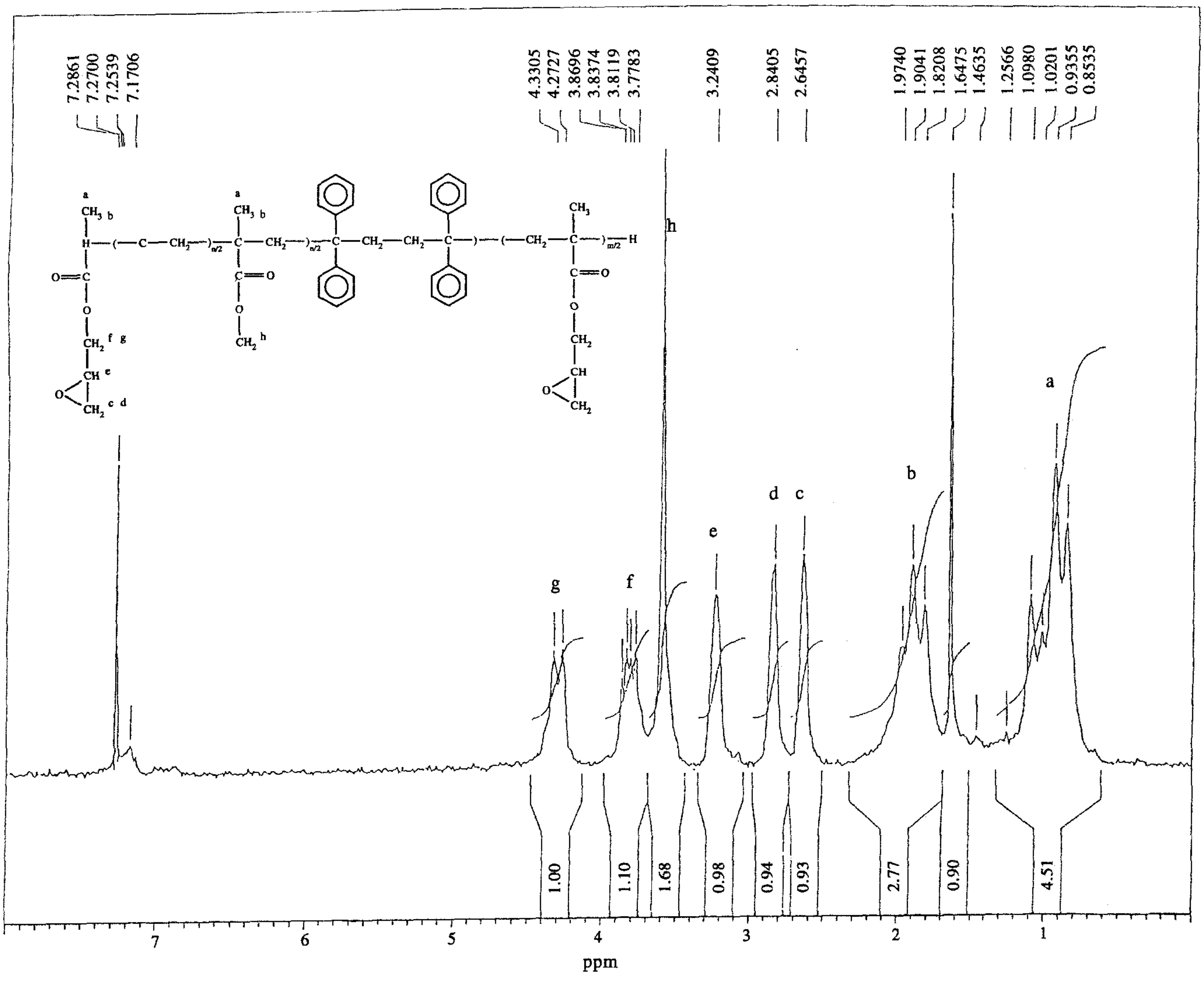

Figure 4 Typical ^{1}H n.m.r. spectrum of poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA) triblock copolymer (3783) in CDCl^3 at 25°C

Table 5 Composition of poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA) block copolymers determined by ^{1}H n.m.r., by s.e.c. and by analytical titration of oxirane rings

	^{1}H n.m.r.			S.e.c.	Analytical titration		
Samples	GMA/CH$_3$ (%)^a	OCH$_3$/CH$_3$ (%)^b	GMA/GMA + OCH$_3$ (%)^c	(GMA)$_{\overline{M_n}}$(%)^d	(%)^e	(GMA)$_{AN}$ (%)^f	(GMA)$_{AV}$ (%)^g
3782	(46.72)^h	31.98	40.72	32.30	–	–	–
3783	62.45	63.38	62.67	61.04	17.55	62.34	62.48
3781	41.91	41.71	41.75	41.79	–	–	–
3784	59.22	59.66	59.31	61.43	17.75	63.03	59.90
3786	82.56	77.06	77.21	76.01	22.82	81.05	78.19
3787	33.22	28.76	31.83	29.97	11.07	(39.31)^h	30.94
3785	61.30	63.14	62.45	63.43	19.20	68.18	62.56

[a] By taking into account oxirane protons (c,d,e) with respect to α-methyl protons (a)
[b] By taking into account methoxy protons (h) compared to α-methyl protons (a)
[c] Direct comparison of oxiranyl protons with the sum of oxiranyl and methoxy protons
[d] Values obtained from average number molar masses by s.e.c. measurement
[e] Analytical titration of oxirane rings by the method of Jay[39]
[f] Values obtained from analytical titration of oxirane groups
[g] Average values of the proportions of poly(GMA) in the triblock copolymers formed
[h] Overestimated values

amount of LiCl. Well-defined copolymers are obtained in quantitative yields, with low fluctuations in molar mass and in composition.

*Model networks arising from poly(GMA) homopolymers and from triblock copolymers poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA)*

A model network is a crosslinked system exhibiting ν linear elements (elastically effective chains, of supposedly known length and low polydispersity) connected by means of $\mu = 2\nu/f$ effective crosslinks, f being the functionality of the crosslinks (i.e. the average number of elastic chains connected to one crosslink site). These elastic chains are supposed to be connected by their two ends to two different branch points. Such networks should be homogeneous, macroscopically as well as microscopically. No syneresis[29] (solvent expulsion, inducing turbidity) should take place during the network formation, lowering the mechanical properties of the material. However, some structural defects are to be found in the networks, such as dangling chains, loops, double connections and trapped entanglements.

In this laboratory, several syntheses of model networks have been developed[30,31].

1. Sequential anionic copolymerization of a monovinylic (or methacrylic) monomer with a suitable bisunsaturated monomer: polystyrene[29], polyisoprene[32], poly(2-vinylpyridine)[32], poly(isopropylideneglyceryl methacrylate)[33], poly(trimethylsilyloxyethyl methacrylate)[34] networks.
2. Network formation by anionic polymerization, followed by deactivation with a plurifunctional reagent: polystyrene networks[30].
3. Network formation by reacting polymer precursors fitted with reactive functions at both chain ends with a plurifunctional antagonist compound: poly(dimethylsiloxane) networks[35].
4. Network formation by step-growth polymerization involving pre-existing linear polymer chains and appropriate plurifunctional reagents: poly(ethylene oxide) networks[36,37], poly(1,3-dioxolane) networks[38].

The synthesis of model networks arising from poly(GMA) or block copolymer precursors, fitted with active sites at both chain ends, has been carried out by anionic endlinking processes using a suitable bisunsaturated monomer, DME. The living precursor solutions were treated with a small amount of DME (4 mol per living site). The temperature plays an important role, as poly(GMA) has a limited solubility in THF at low temperature. The crosslinking copolymerizations were carried out at low temperature (−40 to −32°C). At these temperatures, the reaction is very slow. After a few hours, the viscosity of the reaction medium increases noticeably and after approximately 12 h, gelation has occurred. It was not easy, however, to establish whether complete conversion had been attained.

The results are summarized in *Table 6*. Regardless of the molar mass of the precursor, the process steadily yielded turbid gels, which remained opaque even after they had been placed in excess THF. This may be due to the fact that the swelling degree of the nascent networks

Table 6 Model networks derived from glycidyl methacrylate polymers and triblock copolymers

Samples^a	$\overline{M_w}$^{b}	GMA (%)^c	$(\mathrm{G\overline{M}A})_{\mathrm{AV}}$^{d}	Characteristics
Homopolymers				
3771	12 000	97.00		
3760	16 400	97.80		Syneresis opaque gels
3761	16 600	97.83		
3769	20 000	98.20		
Triblock copolymers				
3872	7000		–	
3781	11 700		41.79	Optically transparent gels
3874	13 300		59.90	
3787	25 000		30.94	

[a] All the samples were prepared by anionic block copolymerization with ethylene dimethacrylate as bisunsaturated comonomer (four molecules of DME per living end)
[b] Average molar masses determined by s.e.c. measurements
[c] Proportions of poly(GMA) taking into account the presence of the initiator ($M = 360$)
[d] Values arising from *Table 5*

was larger than that of the gels swollen to equilibrium in THF. Consequently, solvent was expelled, leading to spongy macroporous materials exhibiting poor mechanical properties. In an attempt to prevent these drawbacks, living triblock copolymer was used as the polymeric precursor, since the solubility of these species in THF at low temperature increased considerably as the weight percentage of GMA decreased. As a matter of fact, the crosslinking reaction could be performed under conditions more favourable for anionic polymerization of methacrylic monomers, staying beyond the cloud point. The reaction remained very slow, however, but it led to gelation of the reaction medium. The gels arising from precursors with molar masses between 6000 and 25 000 were homogeneous and optically transparent. Protonic deactivation was achieved by addition of a small amount of methanol, which diffused slowly through the gel. These materials are mechanically weak but stayed transparent when swollen to equilibrium in THF. Their swelling and mechanical behaviour is presently under investigation.

It can be concluded that the synthesis of model networks derived from poly(GMA) and from poly(GMA)-*b*-poly(MMA)-*b*-poly(GMA) triblock copolymers is possible by sequential copolymerization with ethylene dimethacrylate. The gels obtained are characterized by the length of their elastic chains. With triblock copolymers, syneresis can be avoided.

CONCLUSION

The synthesis of well-defined functional poly(GMA) by anionic polymerization can be achieved, in THF, at low temperature, provided lithium chloride is added to the reaction medium. 1,1,4,4-Tetraphenyl-1,4-dilithiobutane was chosen as a bifunctional, sterically hindered initiator of moderate nucleophilicity. Under the experimental conditions chosen, GMA undergoes polymerization exclusively on the methacrylic unsaturation, the oxirane group remaining untouched. The average molar masses of the polymers formed are close to the values arising from the molar ratio of monomer to initiator. The living character of the anionic GMA polymerization is thus well established.

The synthesis of poly(GMA) containing triblock copolymers could thus be considered. A two-step method has been used: the central poly(MMA) block is made first using the bifunctional initiator. The living species thus obtained, fitted at both chain ends with carbanionic sites, served as polymeric initiators for the subsequent polymerization of GMA. The presence of LiCl has a beneficial effect on the polymerization process. Well-defined triblock copolymers have been obtained, the molar masses of which are in good agreement with the values expected. The molar mass distributions are unimodal and rather narrow.

Finally, anionic crosslinking block copolymerization (endlinking) of the above living species (homopoly(GMA) as well as triblock copolymers) by means of a small amount of an appropriate bisunsaturated monomer, DME, yielded model networks. Due to the poor solubility of poly(GMA) in THF, at low temperature, the process leads to opaque gels when the homopolymer is used as polymer precursor. Homogeneous and optically transparent gels are obtained from living triblock copolymers, especially when their poly(GMA) content is low.

The materials investigated are considered to be of great interest. They constitute a possible route towards new attractive functional intermediates of controlled architecture, exhibiting oxirane functions that can be used, in turn, for further reactions.

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