

Diblock copolymers, triblock copolymers and model networks synthesized by sequential anionic polymerization of styrene and 2,3-epoxypropyl methacrylate

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Diblock and triblock copolymers were synthesized, under standard conditions, by sequential anionic polymerization of styrene and 2,3-epoxypropyl methacrylate or glycidyl methacrylate (GMA). In both cases, suitable initiators were selected. The ‘living’ carbanions originating from the polymerization of styrene are able to attack GMA. The reverse reaction (attack of styrene monomer by poly (glycidyl methacrylate) anions) cannot occur. Consequently, styrene was polymerized first, yielding well defined poly (styrene) ‘precursors’. The high reactivity of poly (styryl) carbanions was reduced by the addition of 1,1-diphenylethylene. The polymer thus, fitted at chain end(s) with diphenylmethyl anions, served as macroinitiator for the subsequent polymerization of GMA. The synthesis of poly (styrene)-b-poly (GMA) diblock copolymers were carried out using *sec*-butyllithium as the monofunctional initiator, in the presence of lithium chloride. Potassium-naphthylide was chosen as the bifunctional initiator whenever a poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymer is desired. The poly (styrene) ‘precursors’ and the block copolymers were characterized by size exclusion chromatography, proton nuclear magnetic resonance and analytical titration of the oxirane functions. These methods allowed us to determine the weight- and number-average molar mass of each block, the molar mass distribution and the copolymer composition. The above ‘living’ bifunctional species were used as polymeric ‘precursors’, leading to the formation of model networks by an endlinking process, upon addition of a bisunsaturated monomer, such as ethylene dimethacrylate. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The present paper is devoted to new developments of a research programme, focused on functional homopolymers, ‘random’ or block copolymers and model networks, derived from 2,3-epoxypropyl methacrylate or glycidyl methacrylate (GMA), using anionic ‘living’ polymerization. In recent publications^{1–3}, the data already obtained have been summarized.

As shown by Szwarc^{4,5}, the anionic polymerization of vinylic and methacrylic monomers leads to ‘living’ polymers. The corresponding carbanionic ‘living’ sites themselves may be used in turn to initiate the polymerization of a second monomer to yield block copolymers. The latter species exhibit two or three sequences, depending upon the chemical nature of the initiator, either monofunctional or bifunctional. This process is not quite general, since it implies that the electroaffinity of the second monomer be equal or greater than that of the first monomer^{6,7}. Therefore, a prerequisite to the formation of block copolymers is that the anionic polymerization of monomer B be initiated fast and quantitatively by the ‘living’ sites of poly (A)[–]. The reverse reaction (attack of monomer A by the carbanionic sites of poly (B)[–] arising from the polymerization of monomer B) often cannot take

place. These basic observations generate two different experimental situations.

(1) If the cross-addition reaction is possible both ways, the formation of poly (A)-b-poly (B) or poly (B)-b-poly (A) diblock copolymers, and of poly (A)-b-poly (B)-b-poly (A) or poly (B)-b-poly (A)-b-poly (B) triblock copolymers can be achieved. In 1960, Graham *et al.*⁸ showed that the sequential anionic polymerization of methyl methacrylate (MMA) and of hexyl methacrylate (HMA) yielded the formation of diblock copolymers both ways. These results were confirmed by Ailhaud *et al.*⁹ upon copolymerizing anionically MMA with hexyl, lauryl and stearyl methacrylates, respectively. In all cases, the order of addition of methacrylic esters is inconsequential^{8,9}. Later, *tert*-butyl methacrylate was polymerized anionically with either 2-ethylhexyl methacrylate or *n*-hexyl methacrylate in the presence of 1,1-diphenyl-3-methylpentyllithium (DPHLi), as a monofunctional initiator¹⁰. Several other couples of polymerizable monomers undergo sequential anionic polymerization, such as methyl methacrylate (MMA) and *tert*-butyl acrylate as described by Varshney *et al.*¹¹, and MMA and glycidyl methacrylate, as shown by us in previous papers^{1,2}. In the two latter cases, well defined diblock and triblock copolymers were synthesized by cross-addition reaction, both ways. Under selected experimental conditions, it was shown that these processes are perfectly ‘living’.

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Diblock and triblock copolymers, arising from 2-vinylpyridine and *tert*-butyl acrylate or *tert*-butyl methacrylate, respectively, were prepared by Klein *et al.*¹² and by Yin and Hogen-Esch¹³. In these experiments, 2-vinylpyridine was introduced first, since it is assumed that the meth (acrylic) esters exhibit a higher electrophilicity. Similarly, diblock copolymers derived from 4-vinylpyridine were obtained by Bringuier *et al.*¹⁴, this latter monomer being polymerized as the first block. Alternatively, Riess and co-workers¹⁵ claimed that poly (MMA)-*b*-poly (4-vinylpyridine) diblock copolymers can arise from the polymerization of 4-vinylpyridine when initiated quantitatively by the 'living' poly (MMA) carbanions. Schulz *et al.*¹⁶ also showed that poly (*tert*-butyl methacrylate) carbanions are able to initiate the polymerization of 4-vinylpyridine.

(2) More commonly, the reverse reaction (attack of monomer A by the carbanionic sites of poly (B)⁻) is either quite impossible or extremely slow. The anionically polymerizable monomers were classified according to increasing nucleophilicity⁷. Thus, it is well known that 'living' poly (styrene) or poly (isoprene) are able to initiate the anionic polymerization of alkyl methacrylates, whereas the reverse reaction does not take place. Therefore, as shown by Rempp and co-workers¹⁷⁻¹⁹, it was only possible to synthesize anionically poly(A)-*b*-poly (B) diblock copolymers and poly (B)-*b*-poly (A)-*b*-poly (B) triblock copolymers, the latter species consisting of a central poly (styrene) block surrounded by two outer poly (MMA) sequences. Similar considerations prevailed for styrene-*tert*-butyl acrylate monomer system^{12,20-22}. Diblock copolymers were obtained using monofunctional initiator upon polymerization of the acrylic ester initiated by the poly (styryl) anions^{12,20,22}. Owing to their insufficient basicity, these 'living' macromolecular species are unable to initiate again the polymerization of styrene. Therefore, if triblock copolymers are desired, a bifunctional initiator (i.e. lithium- or potassium-naphthylide) is required: the α,ω -difunctional poly (styrene) 'precursor' initiates efficiently the subsequent polymerization of *tert*-butyl acrylate^{12,20}. The situation is similar for the monomer system isoprene-*tert*-butyl methacrylate²³. Triblock copolymers were synthesized in the presence of a soluble bifunctional initiator (product of the reaction of 1,3-bis (phenylethenyl) benzene onto *sec*-butyllithium). Isoprene was polymerized first, in cyclohexane at 60°C. After completion, pure *tert*-butyl methacrylate was added to the 'living' bifunctional poly (isoprene) chains in a cyclohexane-THF mixture at low temperature, leading to the expected triblock copolymer.

Actually, many extensive studies on anionic polymerization of hydrocarbon monomers (i.e. styrene and dienes) were performed with success^{24,25}, after the discovery of Szwarc concerning a 'living' mechanism^{4,5} (absence of spontaneous transfer or termination reactions) for this type of polymerization. However, for a long time, controlled 'living' polymerization of polar vinyl monomers, such as acrylic and methacrylic esters, in aprotic solvents and at low temperature, was difficult to achieve. Most of these commercial-grade monomers contain impurities to some extent, which may perturb the course of their anionic polymerization. Sometimes homopolymers were formed which contaminated the expected block copolymers. Consequently, the purification of polar vinyl monomers is a prerequisite for their anionic polymerization. For this purpose, Allen *et al.*²⁶ demonstrated that various trialkylaluminium reagents are usually very efficient as purification agents. This new methodology, involving

complexations between the crude monomers and the reagent, yielded ultra-pure monomers after careful distillation. Another difficulty is connected with the existence of undesirable side reactions, during either the initiation step or the propagation reaction. 'Living' nucleophilic carbanions may sometimes react onto the ester carbonyl of the alkyl meth (acrylate) used, whereupon the conversion is limited. The use of bulky, resonance-stabilized carbanions, such as those derived from diphenylmethyl lithium allowed us to prevent efficiently the occurrence of such side reactions¹⁸⁻²⁸.

During the last decade, several strategies such as metal-free polymerizations, or group-transfer polymerizations (GTP)^{29,30} have opened new vistas into the controlled anionic polymerization and block copolymerization of polar vinyl monomers. Among these new procedures, the so-called 'ligated polymerization'²² seems to be the most promising. It leads to a better control of the reactivity of the 'living' sites at low temperature and to a minimization of the side reactions (i.e. transfer and/or termination reactions). This approach is based upon the introduction into the reaction medium of appropriate ligands, which are able to form 'adducts' with the growing ion pairs³¹. Thus, the nucleophilic character of the growing sites is reduced, the propagation rate is noticeably lowered, but the 'shelf-time' of the 'living' species is greatly increased.

In 1987, it was reported by Teyssié and co-workers³² that alkali-metal halides, such as lithium chloride, are able to form μ -type complexes with the growing ion pairs. The resulting initiating system is quite efficient to promote 'living' polymerizations of methyl methacrylate³³ and of *tert*-butyl acrylate^{32,34}, provided lithium organic initiators are used. In recent papers¹⁻³, we have shown that the anionic polymerization of ultra-pure glycidyl methacrylate is a truly 'living' process, provided it is carried out in the presence of LiCl in the required amount. These polymerizations yield well defined homopolymers, exhibiting average molar masses close to the theoretical values (arising from the mole ratio of monomer to initiator) and narrow molar mass distributions. Moreover, by its beneficial effect, LiCl allows the elimination of the side reactions associated with the ester carbonyl of various acrylic and methacrylic esters.

In our research programme, glycidyl methacrylate (GMA) is considered as the basic monomer. A priori, it can undergo polymerization by its two chemical functions i.e. the methacrylic double bond and the oxirane function. Homopolymerization and copolymerization of GMA, by means of free-radical initiator (i.e. azobisisobutyronitrile) were extensively investigated³⁵⁻⁴¹. These processes usually yielded macromolecular species arising from the selective polymerization of GMA via its methacrylic unsaturation. Obviously, due to the potential reactivity of the remaining epoxy functions present along the polymer chain, specific modifications of these polymers were developed in various ways: synthesis of graft copolymers with polyalkylene oxides⁴¹, reactions with amines^{35,37} or sulfonic acid groups³⁸, formation of hydrophilic polymers⁴² or networks⁴³.

In contrast, few papers were devoted to the anionic polymerization of glycidyl methacrylate. The stereospecific anionic polymerization of GMA, of 2,3-epithiopropyl methacrylate and of cyclopropanemethyl methacrylate was investigated⁴⁴, but no detailed characterization of the polymers was given. Leemans *et al.*⁴⁵ anionically synthesized poly (GMA), as well as poly (MMA)-*b*-poly (GMA)

diblock copolymers in the absence of lithium chloride. It was established^{46,47} on these block copolymers that conversion of the dangling oxirane functions into β -hydrosulfonate groups is possible subsequently by the method already described by Paul and Ranby³⁸, yielding hydrophilic blocks. Recently, Zhang *et al.*⁴⁸ anionically polymerized GMA in the absence of lithium chloride. The experiments performed by the latter authors were not convincing, since no control of the average molar mass of the polymers formed was achieved. In no case can the process used be considered as perfectly 'living', as shown recently in our comments⁴⁹ about this paper.

In our recent papers¹⁻³, we have optimized the experimental conditions to obtain functional polymers, block copolymers and model networks of well defined structure derived from the anionic polymerization of GMA (ultra-pure monomer, dry argon atmosphere, aprotic solvent, low temperature). In the presence of sterically hindered initiators of moderate nucleophilicity, such as 1,1-diphenyl-3-methylpentyl lithium (monofunctional initiator)¹ and 1,1,4,4-tetraphenyl-1,4-dilithiobutane (bifunctional initiator)², the anionic polymerization of GMA was found to be perfectly 'living', provided lithium chloride, in the required amount, had been added to the reaction medium. The oxirane function remains unaffected by the carbanions, the polymerization occurring only via the methacrylic double bond of GMA. Diblock and triblock copolymers of methyl methacrylate and GMA, exhibiting controlled architecture, were synthesized to quasi-quantitative yields. In these syntheses, the cross-addition between MMA and GMA is possible both ways. It was established^{2,3} that the 'living' species formed (homopolymers and triblock copolymers), fitted at both chain ends with carbanionic sites, yielded novel model networks. In these endlinking processes a bisunsaturated monomer, such as ethylene dimethacrylate, was used as a crosslinking agent.

The present paper aims at a further discussion of the ability of glycidyl methacrylate towards anionic synthesis of block copolymers exhibiting two or three sequences, using polymerizable vinylic (or methacrylic) comonomers other than methyl methacrylate. For this purpose, styrene was selected and its sequential anionic polymerization was performed with glycidyl methacrylate as the second monomer.

EXPERIMENTAL

Materials

Solvent. Tetrahydrofuran (from S.D.S.) was used as a polymerization solvent. To obtain highly pure THF, two successive distillations were carried out: the first over sodium wire (or calcium hydride), and the second from a dilute solution of the benzophenone-sodium adduct.

Monomers. Styrene (from Aldrich or Lancaster) was dried over calcium chloride and stored at low temperature. It was made free of inhibitor by a first distillation over sodium wire. After a second distillation (again over sodium wire), styrene was collected in a Schlenk vessel to prevent access of air or moisture, and stored in a dry-ice/isopropanol mixture prior to polymerization.

Glycidyl methacrylate (GMA) is a commercial monomer (from Aldrich), contaminated by low amounts of impurities (i.e. inhibitor, methacrylic acid, glycidol, epichlorohydrin) resulting from its synthesis. The usual purification method,

useful for various meth (acrylic) monomers, described by Allen *et al.*²⁶, involves the use of triethylaluminium as complexing agent. This procedure cannot be applied to the purification of GMA^{1,2}, since triethylaluminium reacts rapidly with the oxirane functions, inducing a spontaneous and ill-timed polymerization. Therefore, the crude monomer was distilled twice carefully over calcium hydride powder, under vacuum, the first and last fractions being eliminated. The middle fraction was redistilled in the presence of a small amount of *sec*-butyllithium, under vacuum, which yielded highly pure GMA. The latter was collected in a Schlenk vessel, at low temperature, prior to use.

1,1-Diphenylethylene (DPE) was prepared in the laboratory by dehydration of 1,1-diphenylethanol, in an alumina column, at 300°C. The product obtained was distilled twice over sodium wire, under vacuum ($E_{0.2} = 60^\circ\text{C}$).

Ethylene dimethacrylate (DME) is a commercially available bisunsaturated monomer (from Aldrich). Two successive distillations over calcium hydride powder yielded a monomer of high purity, the distillate being recovered and kept in a Schlenk vessel, at low temperature, until use.

Initiators. The *sec*-butyllithium was prepared by reaction of 2-chlorobutane with an excess of lithium, in cyclohexane. The reaction was carried out at room temperature, for 72 hours, under a dry argon atmosphere, the yield being about 70%. The molarity of the initiator solution was determined by titration with acetanilide, in dimethyl sulfoxide medium, in the presence of triphenylmethane, as titration indicator. The endpoint was obtained by a persistent faint red colour. As the molarity (about 0.6 M) decreased slowly, the initiator solution was used only for 10 days.

1,1-Diphenyl-3-methylpentyllithium (DPHLi) was used as a monofunctional initiator. It was prepared in situ by the stoichiometric reaction between D.P.E. and *sec*-butyllithium. In polar solvents such as THF the reaction is almost instantaneous and quantitative at -30°C .

Alkali-metal naphthylides (Na, K, Li) used as bifunctional radical-ionic initiators, were obtained by the stoichiometric reaction between metal and naphthalene at room temperature overnight, in THF medium and under dry argon atmosphere. The molarity of sodium-naphthylide and of potassium-naphthylide (about 0.5 M) was found to remain constant for 1 week, whereas lithium-naphthylide lacks stability in THF. It was therefore necessary to use the latter initiator solution within a 3 day period, the molarity being determined before each experiment.

Lithium chloride (from Merck) was used as received. It was heated to about 120–130°C in the polymerization reactor and submitted to several vacuum-argon cycles.

Synthesis

Diblock and triblock copolymers. The polymerization set-up was as described previously^{1,2}. When the use of lithium chloride was considered necessary (see Results and discussion section), it was introduced first into the glass reactor, in the required amount (usually, $[\text{LiCl}]/[\text{Living sites}] \geq 5$) and dried, as indicated above. The polymerization solvent (THF) was then transferred, at room temperature, into the reactor and cooled slowly in a dry-ice/isopropanol bath to about -55°C . A few drops of anionic initiator were usually necessary to neutralize the remaining protonic impurities of the LiCl-THF solution

(or of pure THF). For the monofunctional initiation, a drop of styrene was added prior to the introduction of *sec*-butyllithium, yielding a persistent faint red colour at the endpoint. The reaction medium was stirred for several minutes, the time required for the mixture to reach a temperature of about -75 to -78°C . Usually, one further drop of initiator was necessary to complete neutralization at low temperature. The calculated volume of initiator solution was then introduced at once into the reactor, under efficient stirring. Purified styrene was then added dropwise (for about 10–15 min for a charge of about 13 cc of styrene). After the addition of some drops of styrene, the solution becomes immediately red, due to the formation of poly (styryl) carbanions. This observation indicates fast initiation. The temperature was maintained around -70°C , the polymerization of styrene being complete within a few minutes. An aliquot was sampled out and deactivated protonically with methanol. To the rest of the solution, pure 1,1-diphenylethylene (more than 1 mole per 'living' site) was added, yielding a deep red colour. The second monomer (ultra-pure GMA) was subsequently added slowly, under efficient stirring. After the addition of few drops of GMA, the reaction medium turned to faint yellow. The temperature was kept around -70°C for 20 min to ensure complete polymerization.

This process is expected to lead to the formation of a 'living' diblock (or triblock) copolymer. The species formed was either deactivated protonically and isolated or it was considered as the 'living precursor' for further polymerization. The poly (styrene) homopolymer (first block) and the corresponding diblock (or triblock) copolymer were precipitated from their THF solution by a methanol–water mixture (85/15 v/v).

Model networks. The above 'living' triblock copolymers can be considered as 'precursors' to the formation of model networks via endlinking processes. For this purpose, pure ethylene dimethacrylate (DME) was selected as the bisunsaturated monomer. The latter was added (usually 4–10 mol per 'living' end) rapidly to the triblock copolymer solution under efficient stirring which was discontinued soon afterwards. At -60°C , the viscosity of the reaction medium increased slowly and gelation occurred after several hours. After quenching with methanol, THF was used as the swelling solvent, allowing the determination of the equilibrium volume swelling degree of the network formed, after extraction of the sol-fraction, if any.

Characterization of the block copolymers

The diblock and triblock copolymers obtained were thoroughly characterized by size exclusion chromatography (s.e.c.), by proton nuclear magnetic resonance (^1H n.m.r.) and by analytical titration of the epoxy functions of the poly (GMA) blocks.

Size exclusion chromatography. The first characterization experiments on the poly (styrene) 'precursors' and on the block copolymers were performed by s.e.c. using three different detection methods: differential refractometry (Ref.), ultra-violet (u.v.) spectroscopy and light scattering (LS).

The set-up was equipped with an automatic injector and a differential refractometer Shimazu RID-GA; it was fitted with five poly (styrene) gel columns (Polymer Laboratory) of various porosities. Distilled THF was used as an eluent, at a flow rate of about 1 ml min^{-1} , at room temperature. Linear

poly (styrene) standards of known average molar mass (from 1.9×10^3 to 1.33×10^6) and of narrow polymolecularity were used for calibration purposes. The values of the weight-average molar mass $\bar{M}_{w,\text{ref.}}$ and of the number-average molar mass $\bar{M}_{n,\text{ref.}}$ of the poly (styrene) block and of the block copolymers were determined from the calibration curve, using computer calculations.

Ultra-violet spectroscopy was used concurrently at a wavelength of 254 nm.

The computer program allowed accurate determination of the values $S_{\text{ref.}}$ and $S_{\text{u.v.}}$ of the areas of the chromatograms arising from refractometric detection and from u.v. spectroscopy for the poly (styrene) 'precursor'. Similarly, $S'_{\text{ref.}}$ and $S'_{\text{u.v.}}$ were the values of the corresponding areas for the block copolymer. The refractive index increments $(dn/dc)_{\text{P.S.}}$ and $(dn/dc)_{\text{cop.}}$ of the two species were also determined by the computer treatment. From the data obtained, one can evaluate for the poly (styrene) 'precursor' the ratio A of the species as:

$$A = \frac{S_{\text{u.v.}}}{S_{\text{ref.}}} \quad (1)$$

If the block copolymer is concerned, the $S'_{\text{ref.}}$ value, originating from refractometric detection, must be corrected by the ratio $(dn/dc)_{\text{P.S.}}$ to $(dn/dc)_{\text{cop.}}$, yielding the actual $S_{\text{ref., corr.}}$, expressed as:

$$S_{\text{ref., corr.}} = S'_{\text{ref.}} \frac{(dn/dc)_{\text{P.S.}}}{(dn/dc)_{\text{cop.}}} \quad (2)$$

Therefore, the ratio B of the areas is given by the relation:

$$B = \frac{S'_{\text{u.v.}}}{S'_{\text{ref.}} \frac{(dn/dc)_{\text{P.S.}}}{(dn/dc)_{\text{cop.}}}} \quad (3)$$

From these expressions, the ratio B/A gives access to the weight percent of poly (styrene) present in the block copolymer, and thus to the copolymer composition.

The third detection method was low-angle laser light scattering (LALLS), using a chromatix GMX 100, allowing the determination of the weight-average molar mass $\bar{M}_{w,\text{L.S.}}$. A prerequisite for light scattering analysis of the samples is knowledge of two parameters: the concentration c of the polymeric eluate and the refractive index increment d_n/dc , at the wavelength λ_0 of the light used. The light scattering equation is usually expressed as:

$$\frac{Kc}{R_\theta} = \frac{1}{\bar{M}_{w,\text{L.S.}}P(\theta)} + 2A_2c \quad (4)$$

with

$$K = \frac{4\pi^2}{N_A\lambda_0^4} \left(n_0 \frac{dn}{dc} \right)^2$$

where R_θ is the Raleigh ratio of the scattered light at an angle θ , $P(\theta)$ is the particle scattering factor, A_2 is the second virial coefficient and N_A is Avogadro's number.

For the poly (styrene) 'precursors' in THF solution, the standard value of $(dn/dc)_{\text{P.S.}} = 0.186(5)\text{ cm}^3\text{ g}^{-1}$ was chosen. As shown in a previous paper¹, we determined experimentally the refractive index increment of poly (GMA) homopolymers in THF solution, yielding $(dn/dc)_{\text{P.GMA}} = 0.093(1)\text{ cm}^3\text{ g}^{-1}$. For block copolymers, it is assumed that the rule of weighted additivity is valid. For block copolymers of styrene and GMA, the corresponding

$(dn/dc)_{\text{cop}}$ is given by the expression:

$$(dn/dc)_{\text{cop}} = \omega_{\text{P.GMA}}(dn/dc)_{\text{P.GMA}} + \omega_{\text{P.S.}}(dn/dc)_{\text{P.S.}} \quad (5)$$

with

$$\omega_{\text{P.GMA}} + \omega_{\text{P.S.}} = 1. \quad (6)$$

$\omega_{\text{P.GMA}}$ and $\omega_{\text{P.S.}}$ being the weight fractions of poly (GMA) and poly (styrene) in the block copolymer, respectively. From the two latter expressions, we calculated the composition of the block copolymer using experimental values $(dn/dc)_{\text{cop}}$ supplied by the computer.

As shown first by Benoit and Froelich⁵⁰, it has been established that the weight-average molar mass $\bar{M}_{w, \text{L.S.}}$ of the block copolymer determined by light scattering is an *apparent* value (especially when the refractive index increments of the two blocks are quite different).

Following Kratochvil and co-workers⁵¹, the value of $\bar{M}_{w, \text{L.S.}}$ can be expressed in a rather practical form:

$$\bar{M}_{w, \text{L.S.}}$$

$$= \frac{1}{\nu^2} [\nu_A \nu_B M_w + \nu_A (\nu_A - \nu_B) \omega M_\omega^A + \nu_B (\nu_B - \nu_A) (1 - \omega) M_\omega^B]$$

in this relation ν_A , ν_B and ν (expressed in $\text{cm}^3 \text{g}^{-1}$) are the refractive index increments in a *given solvent* of homopolymer A, of homopolymer B and of block copolymer, respectively (these parameters are *experimentally accessible*); ω is the average chemical composition expressed as the mass fraction of the poly(A) block in the copolymer and M_ω^A , M_ω^B and M_w are the *true* average-weight molar masses of the poly (A) block, of the poly (B) block and of the block copolymer, respectively. These three parameters are unknown. *A priori*, to calculate M_ω^A , M_ω^B and M_w , the light scattering should be performed in *three different* solvents. In our experiments, the determination of $\bar{M}_{w, \text{L.S.}}$ was carried out *only* in THF. Consequently the values of M_ω^A , M_ω^B and M_w remain unknown. However, in the case of poly (styrene)-b-poly (GMA) diblock copolymers and poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers, styrene was always polymerized first (see Synthesis section). Before the subsequent addition of GMA, an aliquot of the poly (styrene) 'precursor' was sampled for characterization purposes, yielding the corresponding *true* value M_ω^A . Therefore, to obtain the M_ω^B and M_w values, it would be necessary to carry out light scattering experiments in an additional solvent.

Proton nuclear magnetic resonance. The characterization of the block copolymers by ^1H n.m.r. was performed using a Bruker AC200 spectrometer. The copolymer composition was determined at 1% concentration in deuterated chloroform (from Aldrich), at room temperature. The resonance peaks of each block of the copolymer are well separated in the ^1H n.m.r. spectrum. The two large peaks, corresponding to the five aromatic protons (h, i) of the poly (styrene) sequence, are located between 6.5 and 7.1 ppm. The peaks, evidencing the five characteristic protons of poly (GMA) block (three oxiranyl protons (c, d, e) and two methylene protons (f, g) located between the ester function and the oxirane ring) appear between 2.5 and 4.4 ppm (for more details, see Results and discussion). The integration of the peaks is thus easy and the overall copolymer composition can be accurately determined by direct comparison of the corresponding protons.


Functional analysis of oxirane functions. The epoxy function content in the block copolymers was determined by an analytical titration derived from the method of Jay⁵², as previously described¹. It is based upon the instantaneous, selective and quantitative reaction of nascent hydrobromic acid on the oxirane functions carried by the poly (GMA) block. The epoxy content y was obtained by a direct titration of the bromide formed upon opening the oxirane ring, the endpoint being determined potentiometrically.

The weight percent of epoxy cycles y present in the block copolymer can be related to the average molar mass of the poly (GMA) block of the block copolymer by the expression:

$$y (\%) = \frac{\left(\frac{40}{142} * 100\right) M_{\text{Poly(GMA)}}}{M_{\text{cop.}} + m} \quad (7)$$

where m is the molar mass of the initiator incorporated in the block copolymer. The parameter

$$\left(\frac{40}{142} * 100\right) = 28.16$$

corresponds to the weight percent epoxy in *pure* poly (GMA), 40 being the molar mass of the epoxy cycle  and 142 the molar mass of GMA.

Obviously, the weight percent x of poly (GMA) present in the block copolymer is given by the relation:

$$x (\%) = \frac{y (\%)}{28.16} \quad (8)$$

The experimental determination of y by analytical titration of the oxirane functions of poly (GMA) block gives direct access to the x value and thus to the copolymer composition.

RESULTS AND DISCUSSION

As the methacrylic ester exhibits a higher electroaffinity than styrene, it was always added *last* in the polymerization procedure to yield only poly (styrene)-b-poly (GMA) diblock copolymer or poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymer. In other words, the glycidyl methacrylate carbanions are not able to initiate the anionic polymerization of styrene. On the other hand, it is known that at room temperature, the carbanionic sites of a 'living' poly (styrene) can react on the ester carbonyl, carried by methyl methacrylate^{17,18}. In principle, this reaction does not occur at low temperature. However, owing to their high nucleophilicity, the poly (styryl) carbanions can be involved in this side reaction, yielding branched structure. To prevent the occurrence of that reaction, we replaced the terminal 'living' sites of poly (styrene) by less reactive carbanions, still able to initiate the polymerization of GMA, but preventing the undesirable reaction on the ester carbonyl. For this purpose, 1,1-diphenylmethyl carbanions of lower nucleophilicity were thus formed at chain ends by addition of DPE. It was checked that this reaction does not induce a detectable variation of the average molar mass of the polymer formed. Subsequently, GMA was added to this endcapped poly (styrene). Diblock and triblock copolymers were thus synthesized and characterized, the latter species exhibiting a central poly (styrene) block surrounded by two outer poly (GMA) sequences.

Poly (styrene)-b-poly (GMA) diblock copolymers

The sequential anionic polymerization of styrene and

GMA, yielding diblock copolymer, was conducted in two steps. First, the 'living' poly (styrene) block, fitted at one chain end with a carbanion, was synthesized under standard conditions. For this purpose, *sec*-butyllithium was used as an initiator, in the presence of lithium chloride, in the required amount. 1,1-Diphenylethylene was then added. In the second step, GMA was introduced slowly and the red colour of the poly (styrene) solution turned immediately to faint yellow, indicating fast initiation. After 20 min, the diblock copolymer was deactivated protonically, precipitated from its solution by a methanol–water mixture (85/15 v/v) and dried under vacuum to constant weight.

As shown in *Table 1*, the monofunctional poly (styrene) 'precursors' exhibit weight-average molar masses $\bar{M}_{w, L.S.}$ (determined by light scattering, using $(dn/dc)_{P.S.} = 0.186$) which are slightly higher than the values $\bar{M}_{th.}$ calculated from the monomer to initiator mole ratio. In contrast, the number-average molar masses $\bar{M}_{n, ref.}$ arising from s.e.c. with refractometric detection are slightly lower than the expected $\bar{M}_{th.}$ values. The polymolecularities of poly (styrene) arising from s.e.c. are rather narrow, the $(\bar{M}_w/\bar{M}_n)_{ref.}$ ratio being located between 1.10 and 1.20.

The values of the refractive index increments (theoretical and experimental), of the average molar masses and of the polymolecularities of a series of poly (styrene)-*b*-poly (GMA) diblock copolymers are displayed in *Table 2*. First, the block copolymers were characterized by s.e.c. using refractometric detection, with poly (styrene) calibration. However, the hydrodynamic volumes of poly (styrene) and of poly (GMA) of the same degree of polymerization cannot be considered similar, as was the case with the poly (methyl methacrylate) and poly (GMA) homopolymers examined previously^{1,2}. The hydrodynamic volume of block

copolymers which determines the s.e.c. retention volume in the s.e.c. columns depends strongly upon the interactions between the two sequences⁵³. For the styrene–GMA system, the two homopolymers exhibit different affinities for the eluting solvent (THF) and thus different calibration curves. Therefore, it should be expected that the weight-average molar mass $\bar{M}_{w, ref.}$, arising from s.e.c. with refractometric detection, differs from the apparent weight-average molar mass $\bar{M}_{w, L.S.}$ measured by light scattering.

As shown in *Table 2*, this situation is experimentally observed. $\bar{M}_{w, L.S.}$ values are systematically larger than $\bar{M}_{w, ref.}$. Comparisons of $\bar{M}_{w, L.S.}$, $\bar{M}_{w, ref.}$ and $\bar{M}_{n, ref.}$ with the calculated values $\bar{M}_{th.}$ (arising from the molar mass of the poly (styrene) 'precursor' and of the proportion of GMA added to it) evidence significant differences. The values of the weight-average molar mass, determined by light scattering are larger than the expected ones ($\bar{M}_{th.}$), whereas both are lower than the ($\bar{M}_{th.}$) values. The molar mass distributions of the diblock copolymers are rather narrow ($1.12 < (\bar{M}_w/\bar{M}_n)_{ref.} < 1.22$) and are comparable to those (*Table 1*) of the corresponding poly (styrene) 'precursors' ($1.10 < (\bar{M}_w/\bar{M}_n)_{ref.} < 1.20$). The 'theoretical' refractive index increments $(dn/dc)_{th.}$, arising from the weight percents of styrene and GMA initially introduced in the reactor, were calculated from equations (5) and (6) using $(dn/dc)_{P.S.} = 0.186$ and $(dn/dc)_{P.GMA} = 0.093$. These values were compared with the corresponding experimental values $(dn/dc)_{cop.}$ of the block copolymers determined by computer calculation. In some cases, slight differences between the two values of the refractive index increment are observed.

The information provided by s.e.c., using both refractometric and ultra-violet methods of detection, is summarized in *Table 3*. The values of $S_{ref.}$ and $S_{u.v.}$ of the areas of the

Table 1 Weight- and number-average molar masses and polymolecularities of poly (styrene) "precursors" prepared using a monofunctional initiator

Sample ^a	$\bar{M}_{th.}^b$	$\bar{M}_{w, L.S.}^c$	$\bar{M}_{w, ref.S.}^d$	$\bar{M}_{n, ref.S.}^e$	$(\bar{M}_w/\bar{M}_n)_{ref.}^e$
3824	20 000	21 000	20 000	18 100	1.10
3825	20 000	26 600	23 600	19 600	1.20
3830	20 000	21 000	18 700	16 200	1.15
3831	10 000	12 600	11 900	9 900	1.20
3832	10 000	13 100	12 000	10 400	1.15

^aAll samples were prepared at -78°C using *sec*-butyllithium as a monofunctional initiator, in the presence of required amount of LiCl

^bTheoretical values of the molar mass calculated from monomer to initiator mole ratio

^cExperimental values of the weight-average molar mass determined by light scattering

^dExperimental values of the weight- and number-average molar masses determined by s.e.c. using refractometric detection

^eExperimental values of the molar mass distribution determined by s.e.c. using refractometric detection

Table 2 Refractive index increments, weight- and number-average molar masses and polymolecularities of poly (styrene)-*b*-poly (GMA) diblock copolymers

Sample ^a	$\bar{M}_{P.S., th.}^b$	$\bar{M}_{th.}^c$	$(dn/dc)_{th.}^d$	$(dn/dc)_{exp.}^e$	$\bar{M}_{w, L.S.}^f$	$\bar{M}_{w, ref.}^g$	$\bar{M}_{n, ref.}^g$	$(\bar{M}_w/\bar{M}_n)_{ref.}^h$
3824	20 000	30 000	0.1557	0.1545	30 600	27 900	24 900	1.12
3825	20 000	50 000	0.1308	0.1308	59 500	44 500	37 000	1.20
3830	20 000	40 000	0.1402	0.1366	40 800	31 400	27 400	1.14
3831	10 000	15 000	0.1561	0.1468	18 800	15 900	13 900	1.14
3832	10 000	40 000	0.1171	0.1163	57 700	32 500	26 500	1.22

^aAll the diblock copolymers were synthesized using monofunctional "living" poly (styrene) "precursors"

^bTheoretical values of the molar mass of the poly (styrene) "precursors"

^cTheoretical values of the molar mass of the diblock copolymers, calculated from the proportion of GMA added

^dTheoretical values of the refractive index increment. ($\text{in cm}^3 \text{g}^{-1}$)

^eExperimental values of the refractive index increment. ($\text{in cm}^3 \text{g}^{-1}$)

^fExperimental values of the weight-average molar mass determined by light scattering

^gExperimental values of the weight- and number-average molar masses determined by s.e.c. using refractometric detection

^hExperimental values of the polymolecularity determined by s.e.c. using refractometric detection

Table 3 Compositions of poly (styrene)-b-poly (GMA) diblock copolymers by s.e.c. using refractometric and ultra-violet methods of detection

Sample	GMA ^a (%)	S _{ref.} ^b	S _{u.v.} ^b	S _{ref.} ^c	S _{u.v.} ^c	(dn/dc) _{cop.} ^d	Poly (GMA) ^e (%)	Poly (GMA) _{dn/dc} ^f (%)
3824	32.87	4403	5955	3546	3866	0.1545	33.20	34.22
3825	59.50	4341	6016	3045	2485	0.1308	58.78	59.78
3830	49.48	4327	15 906	3131	7855	0.1366	50.02	53.36
3831	32.42	4307	–	3469	10 135	0.1468	–	42.45
3832	74.22	4268	15 600	2680	4617	0.1163	70.62	74.65

^aProportion of G.M.A. present initially in the reaction mixture

^bValues of the areas of the s.e.c. chromatograms arising from refractometric and ultra-violet detections (arbitrary units) for poly (styrene) 'precursors'

^cValues of the areas of the s.e.c. chromatograms arising from refractometric and ultra-violet detections (arbitrary units) for poly (styrene)-b-poly (GMA) diblock copolymers

^dExperimental values of the refractive index increment. (in cm³ g⁻¹)

^eExperimental values of the proportion by weight of poly (GMA) present in the diblock copolymers obtained from equations (1)–(3)

^fExperimental values of the proportion by weight of poly (GMA) present in the diblock copolymers obtained from refractive index increment values using equations (5) and (6)

chromatograms arising from poly (styrene) 'precursors' are listed, as well as the areas S_{ref.} and S_{u.v.} related to the corresponding diblock copolymers. The weight percents of poly (GMA) present in the diblock copolymers have been calculated from the ratio B/A arising from equations (1)–(3). The use of equations (5) and (6) gives access to a second method to determine the weight percents ω_{P,GMA} (referred to as poly (GMA)_{dn/dc} (%) in Table 3) of poly (GMA) present in the block copolymer, provided that the values of the three refractive index increments (dn/dc)_{P,S.}, (dn/dc)_{P,GMA} and (dn/dc)_{cop.} are experimentally determined. The two methods investigated yield ω_{P,GMA} values which are almost identical. Comparison of these latter values with the weight percent of GMA introduced initially in the reactor during the polymerization process, leads to a satisfactory agreement, within the accuracy of the measurements.

Figure 1 shows typical traces of a poly (styrene) 'precursor' and of the corresponding poly (styrene)-b-poly (GMA) diblock copolymer (sample 3824). A peak shift is clearly observed from one sample to another. The diagrams are quasi-symmetric, indicating that the carbanionic sites are not subject to accidental deactivation during the process. The molar mass distributions of the two species are

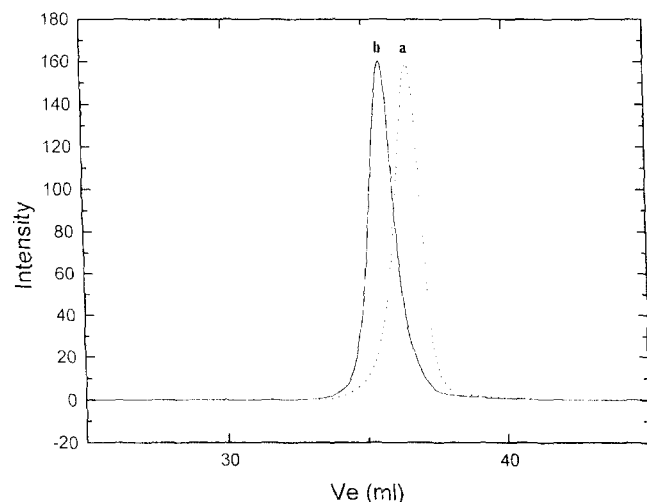
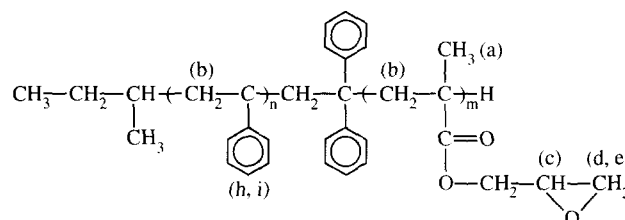


Figure 1 Size exclusion chromatography diagrams (sample 3824). (a) Poly (styrene) 'precursor': $\bar{M}_{w,ref.} = 20\,000$, $\bar{M}_{n,ref.} = 18\,100$, $(\bar{M}_w/\bar{M}_n)_{ref.} = 1.10$. (b) Poly (styrene)-b-poly (G.M.A.) diblock copolymer: $\bar{M}_{w,ref.} = 27\,900$, $\bar{M}_{n,ref.} = 24\,900$, $(\bar{M}_w/\bar{M}_n)_{ref.} = 1.11$. The calibration curve was obtained from linear poly (styrene) standards of known average molar mass and of narrow polymolecularity

unimodal and narrow ($\bar{M}_w/\bar{M}_n = 1.11$ and 1.12 for sample 3824), attesting that the diblock copolymer is not contaminated by any homopolymer.

The use of ¹H n.m.r. spectroscopy also allowed us to determine the copolymer composition. For this purpose, let us consider the chemical structure of the poly (styrene)-b-poly (GMA) diblock copolymer, including the monofunctional initiator (*sec*-butyllithium) and 1,1-diphenylethylene:



A typical ¹H n.m.r. spectrum (sample 3832) of a block copolymer is shown in Figure 2. It exhibits the following resonance peaks and characteristics:

a: two peaks characterize the α-methyl protons –CH₃ of the poly (GMA) block at 0.93 and 1.08 ppm.

b: a doublet corresponds to the methylene protons >CH₂ of the main chain of the block copolymer at 1.89 and 1.95 ppm.

c, d, e: three well defined peaks evidence the oxiranyl protons of the epoxy rings $\begin{matrix} \text{CH} \\ \diagdown \\ \text{O} \\ \diagup \\ \text{CH}_2 \end{matrix}$ of the poly (GMA)

sequence at 2.63, 2.82 and 3.24 ppm.

f, g: two sets of peaks allow characterization of the methylene protons >CH₂ located between the ester functions and the oxirane functions of the poly (GMA) block, around 3.76–3.86 ppm and 4.25–4.31 ppm.

h, i: two large peaks characterize the five aromatic protons –C₆H₅ of poly (styrene) block and the aromatic protons of 1,1-diphenylethylene at 6.57 and 7.06 ppm.

No peak appears around 5.00 and 5.30 ppm, which indicates the absence of the protons corresponding to the methacrylic unsaturation.

The resonance peaks being well separated, their integration is self-constant. These data confirm that the anionic polymerization of GMA exclusively involves its methacrylic double bond¹. The copolymer composition was therefore determined by a direct comparison between the five characteristic protons (c, d, e, f, g) of the poly (GMA) block and the five aromatic protons (h, i) of the poly

(styrene) sequence. However, the aromatic protons arising from 1,1-diphenylethylene were taken into account in the copolymer composition calculation.

As shown in Table 4, the overall composition of the diblock copolymers (i.e. the weight percent of poly (GMA) $\omega_{P,GMA}$ present in the copolymer) was determined independently by s.e.c. (using equations (1), (3), (5) and (6)), by ^1H n.m.r. as described above and by analytical titration of the oxirane functions (using equation (8)). The four $\omega_{P,GMA}$

values obtained were compared with the expected ones arising from the weight percent of GMA introduced initially in the reactor. Within the accuracy of the measurements, the $\omega_{P,GMA}$ values arising from the titration of the oxirane functions are in good agreement with the expected ones. They agree satisfactorily with the values obtained in s.e.c. analysis. However, the $\omega_{P,GMA}$ values determined from the ^1H n.m.r. spectra are systematically somewhat lower than the other values, possibly resulting from insufficient accuracy.

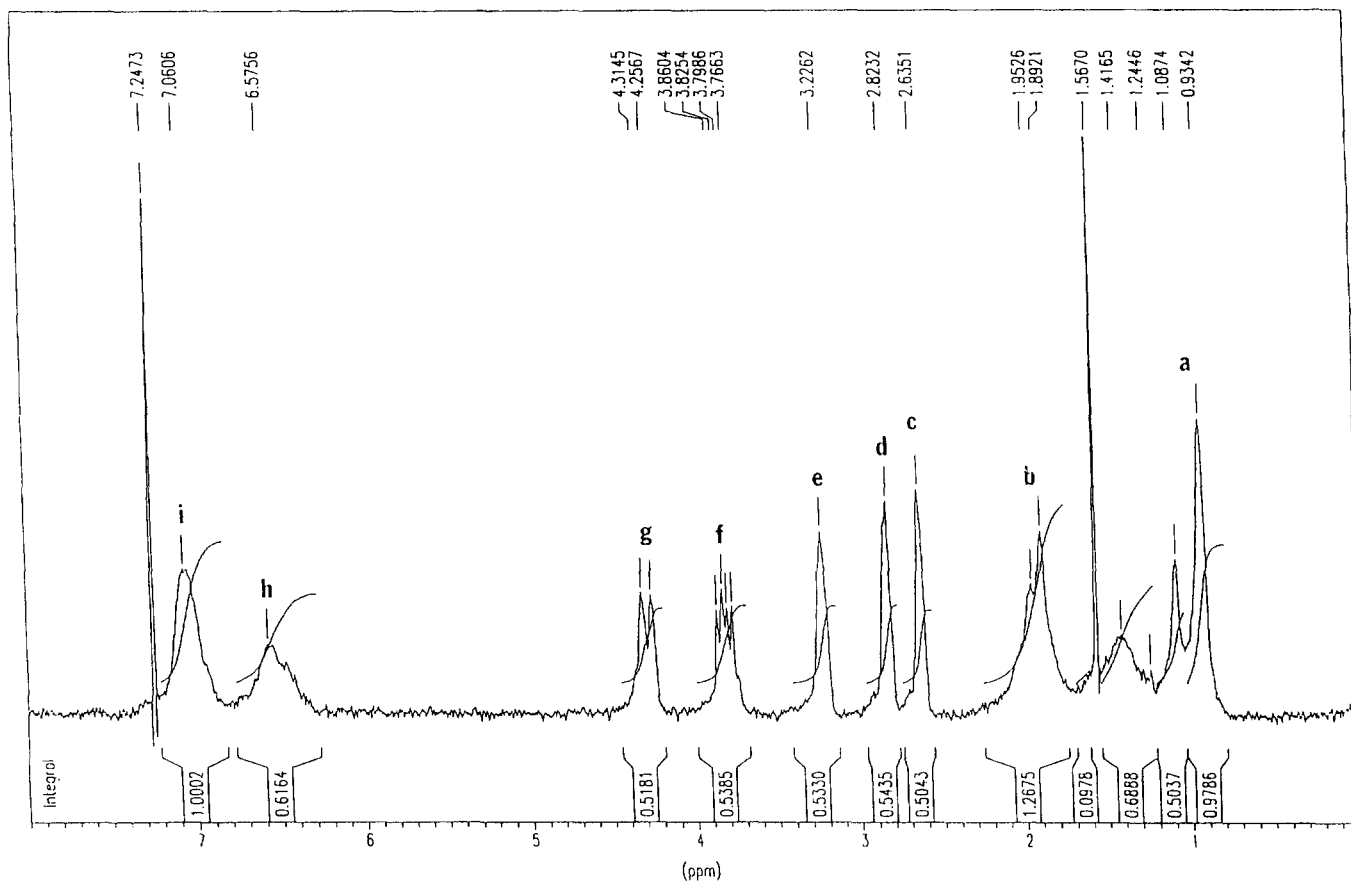


Figure 2 Typical proton nuclear magnetic resonance spectrum of poly (styrene)-b-poly (GMA) diblock copolymer (sample 3832), in deuterated chloroform, at room temperature. The copolymer composition was calculated by comparison between the protons (c, d, e, f, g) of poly (GMA) block and the protons (h, i) of poly (styrene) sequence

Table 4 Compositions of poly (styrene)-b-poly (GMA) diblock copolymers determined by s.e.c., ^1H n.m.r. and analytical titration of the oxirane functions

Sample	s.e.c.			^1H n.m.r.	Analytical titration	
	GMA ^a (%)	Poly (GMA) ^b (%)	Poly (GMA) ^c _{dn/dc} (%)	Poly (GMA) ^d (%)	Epoxy cycles ^e (%)	Poly (GMA) ^f (%)
3825	32.87	33.20	34.22	24.68	9.97	35.40
38.26	59.50	58.78	59.78	50.59	16.67	59.19
3830	49.48	50.02	53.36	39.66	13.97	49.60
3831	32.43	—	42.45	25.32	9.66	34.30
3832	74.22	70.62	74.65	62.48	19.77	70.20

^aProportion of GMA present initially in the reaction mixture

^bExperimental values of the proportion of poly (GMA) present in the diblock copolymers determined by s.e.c. using equations (1) and (3)

^cExperimental values of the proportion of poly (GMA) present in the diblock copolymers obtained from the refractive index increment values using equations (5) and (6)

^dExperimental values of the proportion of poly (GMA) present in the diblock copolymers determined by ^1H n.m.r.

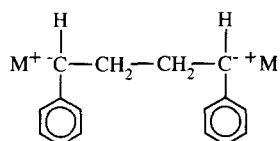
^eExperimental values of the proportion of oxirane functions ($\text{C}=\text{C}=\text{O}$) in the diblock copolymers determined by analytical titration

^fExperimental values of the proportion of poly (GMA) present in the diblock copolymers determined by analytical titration of the oxirane functions using equation (8)

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

The synthesis of triblock copolymers involving styrene and GMA requires the use of suitable bifunctional initiators. Since carbanions arising from glycidyl methacrylate are unable to initiate the anionic polymerization of styrene, 'living' poly (styrene) was synthesized first, endcapped with 1,1-diphenylethylene at both chain ends. This species was used to initiate the polymerization of GMA. The obtained block copolymers is thus constituted of a central poly (styrene) sequence surrounded by two outer poly (GMA) blocks.

Alkali-metal naphthylides (Li, Na, K) were selected as bifunctional radical-ionic initiators. The initiation proceeds by electron transfer from [naphthalene]⁻ to the monomer, followed by a fast dimerization by coupling of the radicals, whereupon the dianionic dimer is formed⁷:



When sodium-naphthylide or potassium-naphthylide were used as bifunctional initiators, no lithium chloride was introduced in the reaction medium. If initiated by

lithium-naphthylide, the polymerization of styrene was carried out in the presence of the required amount of LiCl, as a stabilizing additive. The sequential anionic polymerization of styrene and GMA was conducted using a procedure similar to that described for the synthesis of the diblock copolymers, except for the use of a bifunctional initiator.

The achievement of the anionic polymerization of styrene was tested with respect to the three bifunctional radical-ionic initiators. It was checked first that the use of sodium-naphthylide, as initiator, was quite inadequate. It was confirmed that the average molar masses of the polymers formed are much larger than those expected from the monomer to initiator mole ratio and that non-realistic polymolecularity values are obtained (of the order of 1.8–2.0), as shown earlier⁵⁴. The lithium chloride-assisted polymerization of styrene, initiated by lithium-naphthylide, did not allow to synthesize well defined poly (styrene) 'precursor', as shown in Table 5 (sample 3821). Finally, we chose to carry out the polymerization of styrene with potassium-naphthylide as the bifunctional initiator (samples 3827–3829 and 3833–3838). This procedure allowed a better control of the average molar masses and rather satisfactory polymolecularities ($1.08 < (\bar{M}_w/\bar{M}_n)_{\text{ref.}} < 1.21$) of the poly (styrene) 'precursors'. In most cases, $\bar{M}_{w, \text{L.S.}}$ and $\bar{M}_{w, \text{ref.}}$ exhibit similar values (by about 10%) and they

Table 5 Weight- and number-average molar masses and polymolecularities of poly (styrene) "precursors" prepared using bifunctional initiators

Sample	\bar{M}_{th}	$\bar{M}_{w, \text{L.S.}}$	$\bar{M}_{w, \text{ref.}}$	$\bar{M}_{n, \text{ref.}}$	$(\bar{M}_w/\bar{M}_n)_{\text{ref.}}$
3821 ^a	10 000	(27 000)	(24 800)	(14 300)	(1.73)
3822 ^a	10 000	16 000	16 000	13 500	1.18
3827 ^b	20 000	29 300	27 700	24 300	1.14
3828 ^b	20 000	23 300	21 300	19 000	1.12
3829 ^b	20 000	25 500	27 200	23 300	1.17
3833 ^b	30 000	38 500	34 900	30 600	1.14
3834 ^b	30 000	36 500	32 300	26 700	1.21
3835 ^b	30 000	31 500	28 900	24 800	1.16
3836 ^b	30 000	32 300	29 600	26 900	1.10
3837 ^b	19 000	19 100	19 700	18 300	1.08
3838 ^b	40 000	48 000	53 100	48 600	1.09

^aSamples prepared at -78°C using lithium-naphthylide as bifunctional initiator in the presence of lithium chloride

^bSamples prepared at -78°C using potassium-naphthylide as bifunctional initiator

All the symbols have the same significance as in Table 1

Table 6 Refractive index increments, weight- and number-average molar masses and polymolecularities of poly (GMA)-*b*-poly (styrene)-*b*-poly (GMA) triblock copolymers

Sample	$\bar{M}_{\text{P.S., th.}}$	$\bar{M}_{\text{th.}}$	$(dn/dc)_{\text{th.}}$	$(dn/dc)_{\text{cop.}}$	$\bar{M}_{w, \text{L.S.}}$	$\bar{M}_{w, \text{ref.}}$	$\bar{M}_{n, \text{ref.}}$	$(\bar{M}_w/\bar{M}_n)_{\text{ref.}}$
3822 ^a	10 000	40 000	0.1172	0.1163	62 600	43 900	35 300	1.24
3827 ^b	20 000	30 000	0.1555	0.1624	54 200	44 600	33 400	1.33
3828 ^b	20 000	40 000	0.1403	0.1495	52 000	40 000	27 600	1.44
3829 ^b	20 000	50 000	0.1309	0.1509	49 700	44 000	29 500	1.49
3833 ^b	30 000	40 000	0.1634	0.1435	63 200	50 200	40 200	1.25
3834 ^b	30 000	50 000	0.1494	0.1476	70 900	51 900	38 000	1.41
3835 ^b	30 000	70 000	0.1334	0.1170	77 900	53 700	34 800	1.54
3836 ^b	30 000	90 000	0.1339	0.1226	72 200	51 400	37 400	1.37
3837 ^b	19 000	23 750	1.1685	0.1730	23 300	25 300	22 200	1.15
3838 ^b	40 000	70 000	0.1465	0.1595	64 100	61 300	55 600	1.14

^aThe starting initiator was lithium-naphthylide in the presence of the required amount of lithium chloride

^bThe starting initiator was potassium-naphthylide

All symbols have the same significance as in Table 2

Table 7 Compositions of poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers determined by s.e.c. using refractometric and ultra-violet methods of detection

Sample	GMA (%)	$S_{ref.}$	$S_{u.v.}$	$S'_{ref.}$	$S'_{u.v.}$	$(dn/dc)_{cop.}$	Poly (GMA) (%)	Poly (GMA) $_{dn/dc}$ (%)
3822	74.04	4483	6775	2775	1685	0.1163	74.53	75.08
3827	32.76	4560	12413	3761	11359	0.1624	—	25.77
3828	49.26	4357	15725	3478	9711	0.1495	37.99	39.57
3829	59.38	4454	15557	3447	9630	0.1509	34.44	38.07
3833	24.68	4384	15516	3310	10415	0.1435	(31.60)	(45.98)
3834	39.59	4265	6137	3585	4037	0.1176	33.66	41.60
3835	56.72	4071	5561	2810	2722	0.1170	(57.82)	(74.33)
3836	66.28	4200	5949	3123	2965	0.1390	52.01	56.25
3837	19.57	4479	6323	4223	5427	0.1730	15.53	14.43
3838	42.54	4174	5895	3889	4780	0.1595	25.57	28.87

All symbols have the same significance as in Table 3

are both larger than the expected molar mass $M_{th.}$ arising from monomer to initiator mole ratio. It has to be noted that the values of $\bar{M}_{n, ref.}$ and $M_{th.}$ are usually in satisfactory agreement.

The average molar masses of the triblock copolymers (determined either by s.e.c. with refractometric detection or by light scattering), the polymolecularities and the 'theoretical' and experimental refractive index increments are displayed in Table 6. The s.e.c. calibration curves of poly (styrene) and of poly (GMA) being quite different, as indicated above, the values of $\bar{M}_{w, L.S.}$ are larger than the weight-average molar mass $\bar{M}_{w, ref.}$ arising from s.e.c. with refractometric detection. Here again, differences between 'theoretical' and experimental refractive index increments are observed. Moreover, the polymolecularities of the triblock copolymers are broader ($1.14 < (\bar{M}_w/\bar{M}_n)_{ref.} < 1.54$). Apparently, the use of lithium chloride helps to keep the poly (GMA) sites 'living', since the data on diblock copolymers are obviously better those on triblock copolymers.

In Table 7, the values of the areas of the s.e.c. chromatograms $S_{ref.}$ and $S_{u.v.}$ for poly (styrene) 'precursors', $S'_{ref.}$ and $S'_{u.v.}$ for the corresponding triblock copolymers are presented, as well as the experimental values $(dn/dc)_{cop.}$. Using equations (1)–(3) and equations (5) and (6), the values of the weight percent of poly (GMA) present in the block copolymers can be calculated. The agreement between the two values obtained can be considered as rather satisfactory, except for two samples. Nevertheless, differences are observed with the values of the weight percent of GMA present initially. The data obtained show that in all cases the poly (GMA) content in the triblock copolymers is lower than anticipated, which can be attributed to incomplete conversion. Moreover, the data arising from ultra-violet detection are not reliable. The poly (styrene) 'precursors' exhibit—at quasi-constant concentration—u.v. areas which can change by a factor of 2 or more, which might indicate the presence of strongly absorbing impurity (naphthalene?).

Typical s.e.c. chromatograms of poly (styrene) 'precursor' and of the corresponding triblock copolymer (sample 3828) are shown in Figure 3. As expected, there is a peak shift between the two samples. A single and rather symmetrical curve (even though a slight tail towards higher masses is observed) shows that the triblock copolymer is not contaminated by poly (styrene) or poly (GMA) homopolymers. The two species considered exhibit

unimodal molar mass distributions, the \bar{M}_w/\bar{M}_n values being 1.12 for the poly (styrene) 'precursor' and reaching 1.44 for the corresponding triblock copolymer. This broadening may be attributed to the fact that some 'living' sites have been deactivated during the growth of the poly (GMA) blocks, thus increasing slightly the polymolecularity and the compositional heterogeneity of the triblock copolymer.

As shown in Table 8, the discrepancies already observed using s.e.c. experiments (Table 7) are confirmed by the data arising from 1H n.m.r. and from the analytical titration of the epoxy groups. The values of the weight percent of poly (GMA) present in the block copolymers are systematically lower than those expected. Under the experimental conditions chosen, it seems that the sequential anionic polymerization of GMA, initiated by endstanding diphenylmethyl carbanions fitted at both chain ends of the poly (styrene) 'precursor' chains is not always quantitative. In some cases up to at least 30% of GMA present initially has not polymerized. In future experiments, the time allowed for the polymerization of GMA should be increased.

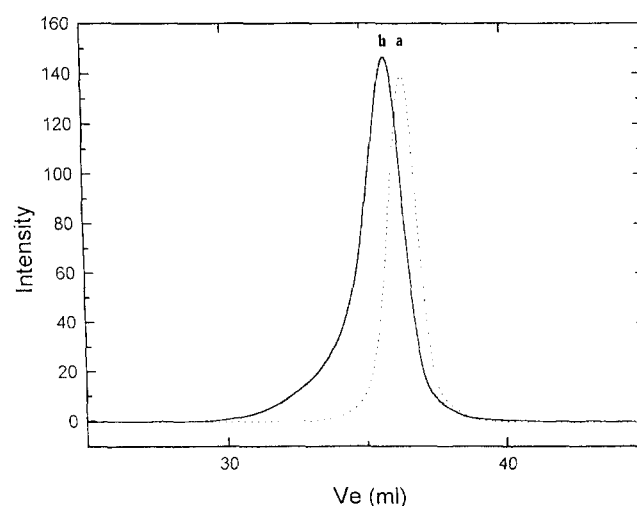


Figure 3 Size exclusion chromatography diagrams (sample 3828). (a) Poly (styrene) 'precursor': $\bar{M}_{w, ref.} = 21\,300$, $\bar{M}_{n, ref.} = 19\,000$, $(\bar{M}_w/\bar{M}_n)_{ref.} = 1.12$. (b) Poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymer: $\bar{M}_{w, ref.} = 40\,000$, $\bar{M}_{n, ref.} = 27\,600$, $(\bar{M}_w/\bar{M}_n)_{ref.} = 1.44$. The calibration curve was obtained from linear poly (styrene) standards of known average molar mass and of narrow polymolecularity

Table 8 Compositions of poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers determined by s.e.c., ¹H n.m.r. and analytical titration of the oxirane functions

Sample	GMA (%)	s.e.c.		¹ H n.m.r.	Analytical titration	
		Poly (GMA) (%)	Poly (GMA) _{dn/dc} (%)	Poly (GMA) (%)	Epoxy cycles (%)	Poly (GMA) (%)
3822	74.04	74.53	75.08	68.25	21.29	75.60
3827	32.76	—	25.77	22.15	9.33	33.13
3828	49.36	37.99	39.57	31.99	12.44	44.17
3829	59.38	34.44	38.07	28.45	11.38	40.41
3833	24.68	(31.60)	(45.98)	19.87	7.26	25.78
3834	39.59	33.66	41.60	27.56	10.84	38.49
3335	56.72	(57.82)	(74.33)	40.71	12.53	44.49
3836	66.28	52.01	56.25	43.86	14.79	52.52
3837	19.57	15.53	14.43	10.54	4.88	17.38
3838	42.54	25.57	28.87	18.65	7.11	25.24

All symbols have the same significance as in Table 4

Model networks arising from 'living' poly (styrene) 'precursor' and from 'living' poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers

It is well known that the sequential anionic polymerization of a vinylic (or methacrylic) monomer and an appropriate bisunsaturated monomer results in network formation⁵⁵. A 'living' bifunctional 'precursor' was synthesized first. This species initiates the polymerization of the bisunsaturated monomer, whereupon crosslinks are formed, each of them being connected with *f* chains ends which have participated in its initiation. As shown earlier^{56,57}, such procedure was used with 'living' bifunctional poly (styrene) and divinylbenzene as bisunsaturated comonomer. Such anionic endlinking processes are smooth and yield model networks, provided it can be assumed that each network chain connects two different crosslinks. Furthermore, the amount of solvent present should be compatible with the swelling degree of the 'nascent' network (i.e. in the 'reference' state at which the network is formed).

As shown recently^{2,3}, it was attempted to use 'living' triblock copolymers as 'precursors' in endlinking processes, the biunsaturated monomer being ethylene dimethacrylate (DME), chosen because of its high electroaffinity. In such networks, each elastic chain is constituted by three blocks: their swelling properties as well as the mechanical response to an applied stress are expected to be influenced by the interactions between the individual blocks.

In the present work, it was first checked that a poly (styrene) 'precursor', fitted at both chain ends with 'living' sites (sample 3826, initiator: potassium-naphthylide, $\bar{M}_w = 20\,000$), can initiate the anionic polymerization of highly pure DME (8 mol per 'living' end) at low temperature (–60°C). Upon endlinking, gelation of the reaction medium took place. The model network formed is characterized by the average molar mass \bar{M}_w of its elastic chains, by the overall polymer volume fraction ($v_c = 0.07$) upon crosslinking, and by the average functionality *f* of the crosslinks. The optically transparent model network obtained was placed in excess of THF to determine its sol-fraction (i.e. the extractable part of the material) and then its equilibrium volume swelling degree. The gel formed is not sticky and exhibits an 'apparent' satisfactory elasticity.

Subsequently, experiments were performed, at low temperature using 'living' poly (GMA)-poly (styrene)-b-poly

(GMA) triblock copolymers, fitted at both chain ends with active sites. Again DME was used as the bisunsaturated monomer. The formation of model networks was found to be slower than that observed for the poly (styrene) 'precursor'. The 'apparent' viscosity of the reaction medium increased slowly over several hours, until gelation took place, yielding a transparent crosslinked network. The 'syneresis' phenomenon, which is observed^{2,58} when the mesh size of the networks is compatible with the amount of solvent present, was not been observed in these experiments as a consequence of the relatively high molar mass of the elastic chains (triblock copolymers). Beyond the gel point, the glass reactor was kept at low temperature for three additional hours, to allow completion of the endlinking process. Finally, protonic deactivation of the gel obtained was carried out by addition of a small volume of methanol, the latter diffusing slowly through the material. Homogeneous and optically transparent model networks were obtained by this method. Even if they are still mechanically weak, these gels remain transparent when they are placed in an excess of THF. Several days were necessary to reach the swelling equilibrium.

In a forthcoming paper, the equilibrium volume swelling degree *Q* of these model networks will be discussed. The data will be compared with those arising from the affine and 'phantom' models, as has been done recently for poly (styrene) and poly (dimethylsiloxane) model networks⁵⁸.

CONCLUSION

The syntheses of diblock and triblock copolymers, arising from styrene and glycidyl methacrylate (GMA), were performed by sequential anionic polymerization, in tetrahydrofuran, at low temperature, under dry argon atmosphere and using appropriate monofunctional or bifunctional initiators.

Poly (styrene)-b-poly (GMA) diblock copolymers were synthesized first, using a monofunctional lithium organic initiator, such as *sec*-butyllithium. To control the reactivity of the carbanionic sites, lithium chloride was added to the reaction medium. Styrene was polymerized first leading to well defined 'living' poly (styrene). Initiation was fast and quantitative. The highly nucleophilic carbanions were reacted with 1,1-diphenylethylene in order to prevent any side reaction between the growing chains and the ester

functions. This 'living' poly (styrene) fitted at both ends with less reactive diphenylmethyl carbanions, served as the macroinitiator for the subsequent polymerization of GMA. It is necessary to do the addition in this order (styrene, DPE, GMA) because the reverse reaction is impossible.

The synthesis of poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers were investigated next. Alkali-metal naphthylides, and especially potassium-naphthylide, were selected as bifunctional initiators. Here again, the polymerization of glycidyl methacrylate was initiated by the endstanding diphenylmethyl carbanions of the poly (styrene) 'precursors' yielding the expected triblock copolymers.

The poly (styrene) 'precursors' and the corresponding block copolymers were thoroughly characterized by size exclusion chromatography (with refractometric, ultra-violet and light scattering detectors), by proton nuclear magnetic resonance and by analytic titration of the oxirane functions (in the block copolymers).

The weight-average molar masses of the diblock and triblock copolymers determined by light scattering are larger than those arising from s.e.c. with refractometric detection using calibration (poly (styrene) standards). These data are not surprising. They can be explained, knowing that the hydrodynamic volumes of poly (styrene) and poly (GMA) are quite different, the two homopolymers exhibiting also different affinities for the eluting solvent (THF). This explains, at least in part, the fact that the agreement between the experimental average molar mass is not always in good agreement with the expected value arising from monomer to initiator mole ratio.

The molar mass distributions characterizing the poly (styrene) 'precursors', as well as than those of the poly (styrene)-b-poly (GMA) diblock copolymers, originating from refractometric detection, are unimodal and rather narrow ($(\bar{M}_w/\bar{M}_n)_{ref.} < 1.20$). For the poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers, the corresponding polymolecularities are larger ($1.14 < (\bar{M}_w/\bar{M}_n)_{ref.} < 1.54$). However, even in these cases, the s.e.c. chromatograms are almost symmetric and unimodal, confirming that the triblock copolymers are not contaminated either by homopoly(styrene) or by poly(GMA) homopolymer.

The overall compositions of the block copolymers were determined independently by the three methods of characterization mentioned. In several cases (especially when ^1H n.m.r. is considered), the weight percent of poly (GMA) effectively present in the block copolymers is lower than the proportion of GMA introduced. In other words, these data indicated that the sequential anionic polymerization of GMA may not always be quantitative. These effects do not clearly happen in the diblock copolymer formation, which confirms that the presence of lithium chloride in such sequential polymerization is quite helpful.

Finally, homogeneous and optically transparent model networks were prepared by endlinking processes. In these crosslinking reactions, either 'living' poly (styrene) or 'living' poly (GMA)-b-poly (styrene)-b-poly (GMA) triblock copolymers, fitted at both chain ends with active sites, were used as macroinitiators for the polymerization of ethylene dimethacrylate, yielding model networks of controlled architecture. It is thus confirmed that this bisunsaturated monomer reacts readily with the endstanding 'living' poly (GMA) sites, the 'precursor' chains (poly (styrene) or poly (GMA)-b-poly (styrene)-b-poly (GMA)

triblock copolymers) becoming the elastically effective network chains.

The same procedure could be applied to 'living' poly (styrene)-b-poly (GMA) diblock copolymers and DME, and it should provide access to 'star-shaped' block copolymers, i.e. macromolecules in which each branch is constituted of an outer poly (styrene) block and an inner poly (GMA) block. Hydrolysis of the oxirane functions of the poly (GMA) block may lead to amphiphilic 'star'-block copolymer, the properties of which should be of interest.

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