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Selective Ring-Opening Polymerization of Glycidyl Methacrylate: Toward the Synthesis of Cross-Linked (Co)polyethers with Thermoresponsive Properties

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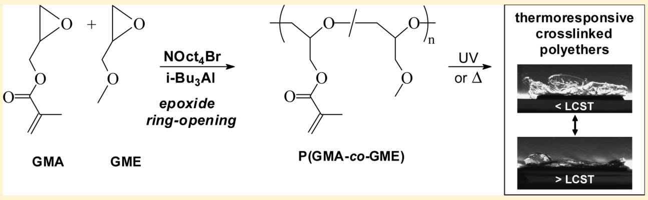
S *Supporting Information*

ABSTRACT: Selective polymerization of glycidyl methacrylate (GMA), which has two polymerizable functional groups such as epoxide and methacrylate, was achieved by the monomer-activated anionic approach using tetraoctylammonium bromide/triisobutylaluminum initiating system in toluene at 20 °C. Quantitative and controlled synthesis of poly(glycidyl methacrylate ether), up to about 20 000 g/mol, with pendant methacrylate functions, was obtained by ring-opening of the epoxide. The copolymerization of glycidyl methacrylate with glycidyl methyl ether (GME) in similar conditions, the resulting copolyether structures, and their properties were investigated as a function of feed composition. Reactive poly(glycidyl methyl ether-*co*-glycidyl methacrylate ether)s P(GME-*co*-GMA) with lower critical solubility temperature depending on the ratio [GME]/[GMA] were prepared and analyzed by NMR spectroscopy and differential scanning calorimetry. Postpolymerization cross-linking reactions of PGMA and random P(GME-*co*-GMA) copolymers were investigated by infrared spectroscopy and water contact angle measurements under heating or UV irradiation.



■ INTRODUCTION

Glycidyl ethers constitute an interesting and broad family of monomers as a great diversity of polymeric materials can be obtained by varying the nature of the ether side group attached to the epoxide. Polyethers with tunable hydrophilic/hydrophobic character (solubility, lower critical solubility temperature (LCST)) as well as reactivity for postpolymerization reactions can be prepared.[1,2]

Glycidyl methacrylate (GMA) is a monomer of particular interest since it possesses two polymerizable groups: the epoxide and the methacrylate functions. If GMA can be selectively polymerized or copolymerized via one of the two functions, reactive polymers of interest for many applications such as epoxy resins,[3] biopolymers immobilization,[4] reactive supports,[5] etc., could be obtained. A major concern is to find polymerization conditions that allow a selective reaction of one of the functional groups, thus avoiding cross-linking reaction and the formation of ill-defined materials. Literature data concerning GMA polymerization reports almost exclusively reaction mechanisms involving, more or less selectively, the methacrylate function while the epoxide ring remains unreacted. Indeed, the use of nucleophilic *s*-BuLi as initiator results in very low conversions and uncontrolled GMA polymerization,[6] whereas hindered alkyllithium or systems allowing charge delocalization, such as diphenylhexyllithium[7,8] associated with LiCl in polar medium, were reported to selectively polymerize GMA by the methacrylate function. In the same way, the anionic block copolymerization of GMA with acrylates[7] or styrene[9] was also described. The pendant epoxide functions of the resulting copolymers were then used for postpolymerization ring-opening reactions used for cross-linking, functionalization by various nucleophiles,[5,10,11] or grafting of living polystyrene and polyisoprene[12,13] or polyaniline.[14] Radical polymerization of glycidyl methacrylate was also largely investigated. Whereas free radical polymerization leads to ill-defined poly(glycidyl methacrylate) (PGMA),[15] atom transfer radical polymerization[11,16,17] and reversible addition−fragmentation chain transfer[18] systems were found to allow the controlled polymerization of GMA selectively by the methacrylate function. Nitroxide-mediated radical polymerization[19] and group transfer polymerization[20] methods were also investigated, but no information is available about the structure of the resulting polymers.

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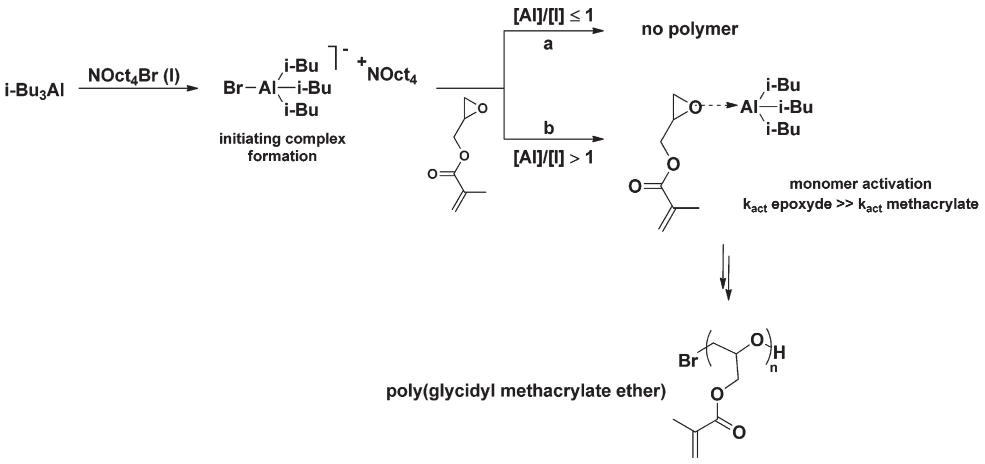
Table 1. Polymerization of Glycidyl Methacrylate (GMA) and Its Copolymerization with Glycidyl Methyl Ether (GME) Initiated by $NOct_4Br$ (I) in the Presence of i-Bu_3Al (Toluene, 20 °C)

run	monomer(s)	[Al]/[I]	[M] (mol/L)	time (h)	yield (%)	Th composition[a] $DP_{GME}-DP_{GMA}$ (DP_{GME}/DP_{GMA})	DP_{GME}/DP_{GMA} exp[b]	$\overline{M}_{n,th}$[c] (g/mol)	$\overline{M}_{n,exp}$[d] (g/mol)	$\overline{M}_w/\overline{M}_n$[d]
1	GMA	0	1.5	24	0			9500		
2	GMA	1	1.5	24	0			9500		
3	GMA	1.3	1.5	3	100			5000	5500	1.14
4	GMA	1.5	1.5	2	100			9500	9700	1.10
5	GMA	2.6	1.5	4	100			30000	22700	1.13
6	GME/GMA	1.5	1.5/0.15	2	100	101–10 (10.1)	10.3	10300	10800	1.07
7	GME/GMA	1.5	1.5/0.45	2	100	78–22 (3.55)	3.6	10000	10600	1.10
8	GME/GMA	1.5	1.5/1.40	2	100	44–42 (1.05)	1.0	9800	10100	1.11
9	GME/GMA	2.5	1.0/0.60	2	100	114–70 (1.63)		20000	e	

[a] DP = [M]/[$NOct_4Br$]. [b] Determined by ^1H NMR. [c] $\overline{M}_{n,th} = [GMA]_0/[NOct_4Br] \times M_{GMA} \times$ yield or $\overline{M}_{n,th} = ([GME]_0/[NOct_4Br] \times M_{GME} + [GMA]_0/[NOct_4Br] \times M_{GMA}) \times$ yield. [d] Determined by size exclusion chromatography in tetrahydrofuran using a calibration with polystyrene standards. [e] Nonsoluble polymer.

Scheme 1. Polymerization of Glycidyl Methacrylate Initiated by Tetraoctylammonium Bromide Depending on the Amount of Triisobutylaluminum



Polymerization of GMA by its epoxide function was mainly conducted by a cationic way. Using the $BF_3 \cdot Et_2O$ initiating system, Yan et al.[21] prepared poly(ethylene oxide-*b*-glycidyl methacrylate ether) block copolymers by initiation of the GMA polymerization from an hydroxyl-terminated poly(ethylene oxide). However a very limited number of GMA units were added (less than 10). Indeed, the cationic polymerization of epoxides is accompanied by side reactions which strongly limit the possibility in polymer synthesis. No mention was made about the selective homopolymerization of GMA by this approach. Using trimethylsilyltriflate, Bicak and Karagoz reported the synthesis of low molar mass poly(cyclohexene oxide-*co*-glycidyl methacrylate ether) copolymers carrying pendant methacrylate groups which were reactive for postpolymerization reactions under UV irradiation using benzoin as photoinitiator.[22] Copolymerization of GMA and succinic anhydride in the presence of zinc succinate was also described to give oligoesters with methacrylate pendant groups.[23]

We have recently shown that new anionic polymerization systems, based on the association of alkali metal salts[24] or ammonium salts[25−29] with trialkylaluminum, allow the controlled high-speed anionic polymerization of epoxides. In this paper, we report the use of tetraoctylammonium bromide/triisobutylaluminum system for the (co)polymerization of GMA. Homopolymerization of GMA and its random and block copolymerizations with glycidyl methyl ether are investigated. The structure of the polymers and copolymers, their postreaction by thermal or light irradiation of the pendant methacrylate functions, and the thermoresponsive properties of P(GME-*co*-GMA) copolymers are described.

■ EXPERIMENTAL PART

Materials. Triisobutylaluminum (i-Bu_3Al, 1 M in toluene, Aldrich) was used without further purification. Tetraoctylammonium bromide ($NOct_4Br$, 98%, Aldrich) was dried under dynamic vacuum for 2 h and then solubilized in toluene to the desired concentration. Glycidyl methacrylate (GMA, 96%, Janssen Chemicals) was dried two times under vacuum over CaH_2. It was then distilled under vacuum over *sec*-butyllithium for a few minutes and finally distilled under vacuum in a flask. The purified monomer was kept in a fridge until use. Glycidyl methyl ether (GME, >85%, TCI) was first distilled under atmosphere pressure, then dried and distilled under vacuum over calcium hydride and two times over triethylaluminum, and finally stored in a fridge and

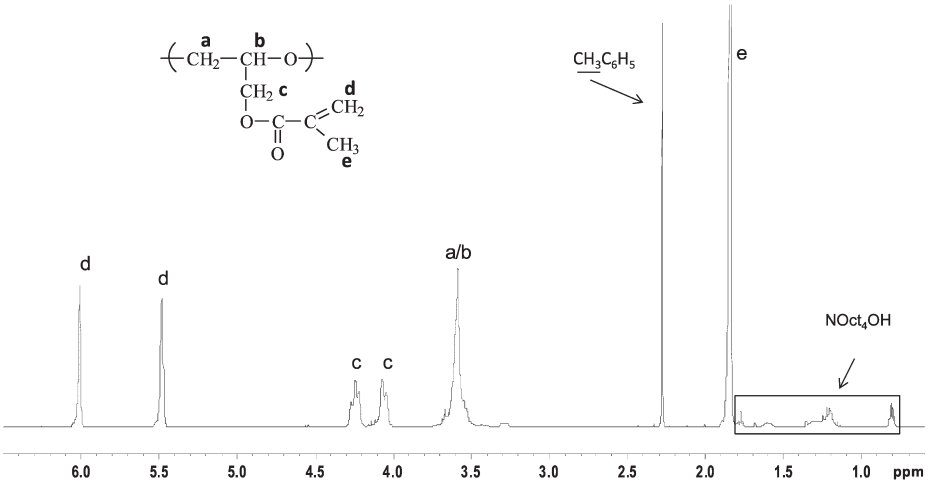


Figure 1. ^{1}H NMR spectrum in toluene-d_8 of poly(glycidyl methacrylate ether) (run 4, Table 1) initiated by $NOct_4Br$ in the presence of 1.5 equiv of i-Bu_3Al.

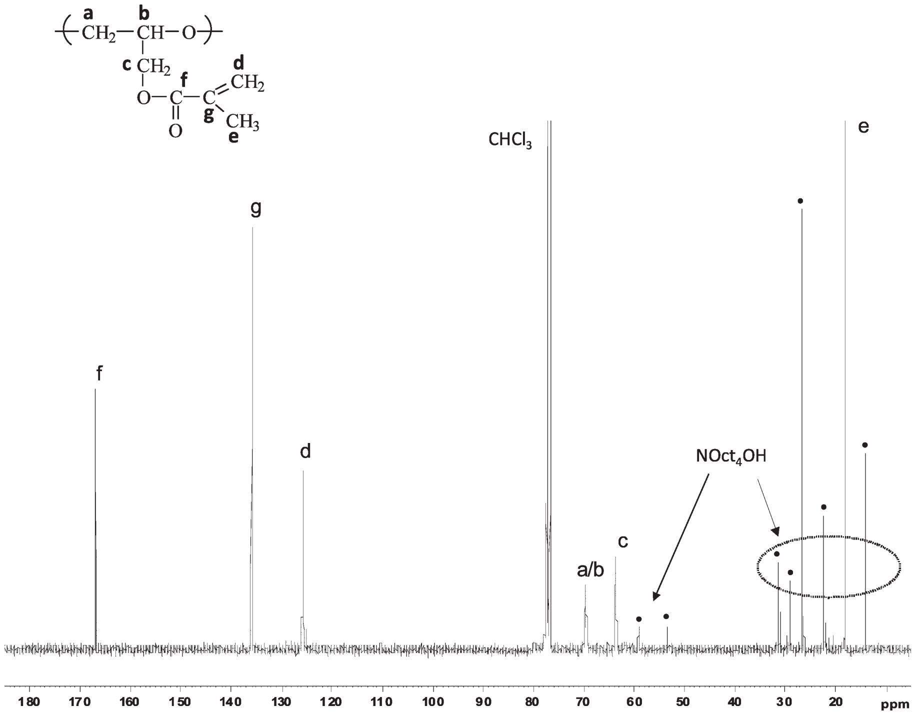


Figure 2. ^{13}C NMR spectrum in $CDCl_3$ of poly(glycidyl methacrylate ether) (run 3, Table 1) initiated by $NOct_4Br$ in the presence of 1.5 equiv of i-Bu_3Al.

distilled under vacuum in a graduated flask before use. Toluene (99%, J.T. Baker) was purified over polystyryllithium seeds and distilled under vacuum before use. Irgacure 819 (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide, BASF) was used without purification.

Procedures. All (co)polymerizations were performed in dark conditions, under argon in a glass reactor equipped with a magnetic stirrer, fitted with PTFE stopcocks, and previously flamed under vacuum. As an example, 6.7 mL of toluene was first introduced in the reactor under vacuum through a connected glass tube, and temperature was decreased to −30 °C before adding 2 mL of GMA (14.7 mmol) via a syringe under argon. Then, 0.95 mL (0.21 mmol) of a toluene solution of $NOct_4Br$ (C = 0.22 M) followed by 0.31 mL (0.31 mmol) of i-Bu_3Al solution in toluene (C = 1 M) were added via a syringe under argon. The polymerization was allowed to proceed for 2 h at 20 °C and then stopped by addition of ethanol. The yield was determined gravimetrically after complete drying of the polymer under vacuum at room temperature or by ^{1}H NMR. $\overline{M}_n$(SEC) = 9700 g/mol, I_p = 1.10. ^{1}H NMR of PGMA: $-O-CH_2(1)-CH(2)[CH_2(3)-O-CO-CCH_2(4)CH_3(5)]$: 1 and 2, 3.6 ppm; 3, 4.05, and 4.25 ppm; 4, 5.5, and 6.0 ppm; 5, 1.85 ppm.

A typical copolymerization of GME and GMA was carried out with 1.7 mL (18.9 mmol) of GME, 0.74 mL (5.4 mmol) of GMA, 8.4 mL of toluene, 1.1 mL (0.24 mmol) of $NOct_4Br$ solution in toluene (C = 0.22 M), and 0.26 mL (0.26 mmol) of i-Bu_3Al solution in toluene (C = 1 M) for 2 h at 20 °C (first minutes at −30 °C). Yield: 100%, $\overline{M}_n$(SEC) = 10 600 g/mol, I_p = 1.10, DP_{GME}/DP_{GMA} (NMR) = 3.6. ^{1}H NMR of P(GME-*co*-GMA): $O{-}CH_2(1){-}CH(2)[CH_2(3){-}O{-}CH_3(4)]$-*co*-$O{-}CH_2(5){-}CH(6)[CH_2(7){-}O{-}CO{-}CCH_2(8)CH_3(9)]$: 1, 2, 3, 5, and 6, 3.3−3.7 ppm; 4, 3.25 ppm; 7, 4.05, and 4.25 ppm; 8, 5.5, and 6.0 ppm; 9, 1.85 ppm.

Analysis. ^1H NMR spectra of the copolymers were recorded at room temperature on a Bruker Avance 400 MHz spectrometer using the residual proton resonance of the deuterated solvent as an internal standard.

(Co)polymers molar masses were determined by size exclusion chromatography (SEC) at 20 °C using tetrahydrofuran (THF) as eluent on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU, a dual refractive index/UV Varian detector, and fitted with three TSK columns (G4000HXL with particles of 5 μm, pore size of 200 Å and exclusion limit of 400 000 Da, G3000HXL with particles of 5 μm, pore size of 75 Å and exclusion limit of 60 000 Da and G2000HXL with particles of 5 μm, pore size of 20 Å and exclusion limit of 10 000 Da) at an elution rate of 1 mL/min. Polystyrene standards were used as reference.

Fourier transformed infrared (FTIR) spectra were obtained using a Perkin-Elmer Spectrum One spectrometer combined with a "Golden Gate" single-reflection ATR system equipped with a diamond cell. The IR spectra were recorded at 20 ± 1 °C in the spectral range of 650−4000 cm^{-1}.

Differential scanning calorimetry (DSC) measurements were performed on a DSC Q100 apparatus from TA Instruments. Samples were measured at temperatures ranging from −100 to 170 °C at heating and cooling rates of 10 °C min^{-1}. A second series of MTDSC (modulated DSC) experiments were also performed on a TA Q100. Standard modulation conditions, in both experimental series, are a rate of 1 °C/min with a period of 50 s and an amplitude of 0.5 °C.

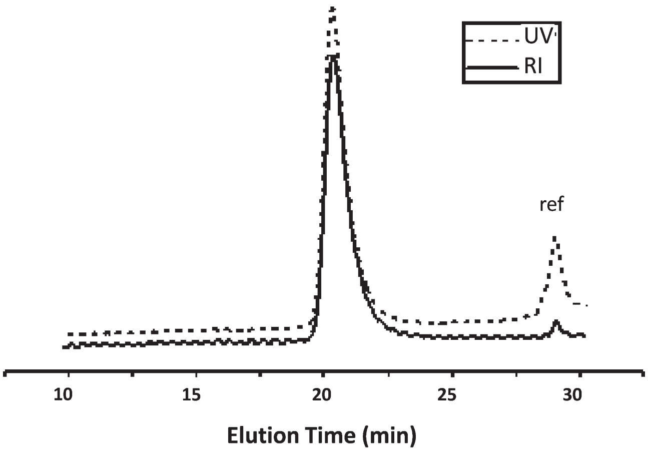


Figure 3. SEC chromatogram of a P(GME_{78}-*stat*-GMA_{22}), initiated by $NOct_4Br$ in the presence of 1.5 equiv of *i*-Bu_3Al (run 7, Table 1).

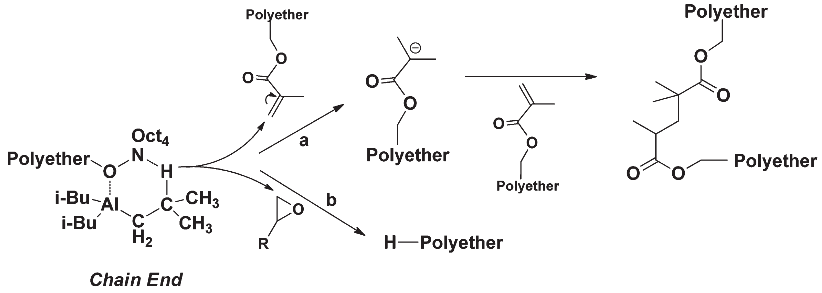
Contacts angles of water were determined using a Krüss DSA100 contact angle measuring system at room temperature. A charge coupled device camera was used to capture the images of the water droplets (2 μL) for the determination of the contact angles.

RESULTS AND DISCUSSION

Synthesis of (Co)polyethers Based on Glycidyl Methacrylate. Triisobutylaluminum/tetraalkylammonium halide (*i*-Bu_3Al/NR_4X) systems (R = Bu and Oct and X = halogen and N_3), when used in the presence of a slight excess of the aluminum derivative with respect to the ammonium salt, are very effective initiators for the activated anionic polymerization of propylene oxide and other oxiranes.[25−29] In a similar way and in dark conditions, polymerization of glycidyl methacrylate (GMA) proceeded rapidly in the presence of *i*-$Bu_3Al/NOct_4Br$ at ratio $[R_3Al]/[\text{initiator}]$ between 1.3 and 2.5 (Table 1, runs 3−5), while in the absence of triisobutylaluminum or at a ratio $[R_3Al]/[\text{initiator}]$ lower than or equal to one the polymerization does not proceed (Table 1, runs 1 and 2, and Scheme 1a). Complete GMA conversion into soluble polymer is achieved in 2−4 h at 20 °C, even when a polymer with a molar mass of 30 000 g/mol is targeted. The polymers show narrow molar mass distributions (<1.15), and their molar masses increase with the increase of the [monomer]/[initiator] ratio, although some deviation is observed for the highest polymer, suggesting some transfer reaction. These results are in agreement with a relatively well controlled polymerization process and the selective incorporation of GMA via one of its two anionically polymerizable groups.

^1H NMR (Figure 1) shows characteristic peaks corresponding to protons of methylene (a) and methine (b) groups of the polyether backbone $-CH_2{-}CH{-}O-$ at 3.6 ppm, whereas no signal corresponding to residual epoxide functions between 2.6 and 3.3 ppm is observed. In addition, the resonance signal of the methyl group of a polymerized methacrylate function is observed in the literature between 0.9 and 1.3 ppm.[30] This region of the experimental spectrum did not show such signals but was slightly polluted by signals coming from residual counterion ($NOct_4OH$ after termination reaction). Because the nonwashed polymer being preferably analyzed to avoid any polymer separation, doubts about the selectivity of the reaction could still exist. ^{13}C NMR was therefore used (Figure 2). It allowed to identify all the signals corresponding to the GMA polymerized through the epoxide function, especially to the pendant methacrylate function at 167 ppm for the carbonyl group (f), 136 ppm for the quaternary carbon (g), 126 ppm for the $=CH_2$ (d), and the methyl group (e) at 18 ppm. Chloroform was preferred as

Scheme 2. Possible Side Reactions at High [*i*-Bu_3Al]/[Initiator] Ratio



a = crosslinking due to hydride formation and reaction with methacrylate functions
b = transfer to hydride of i-Bu_3Al

deuteriated solvent to avoid any contaminant signals in the concerned chemical shift region. As referred to the literature,[30] no signal attributable to the polymer obtained through the methacrylate function was observed, like 176 ppm for the C═O, 52 ppm for the methylene, or 44 ppm for the quaternary carbon. These results confirm the selective polymerization of GMA through the epoxide function giving a polyether with reactive pendant methacrylate groups (Scheme 1b). It is believed that stronger activation of the epoxide function, with respect to the methacrylate one, via complexation with trialkylaluminum reverse the generally observed monomer reactivity order.[7,8] The low nucleophilicity and basicity of aluminate complexes involved as initiating and propagating species is too low in nonpolar media to induce methacrylate polymerization and minimize other potential side reactions.

The copolymerization of GMA with glycidyl methyl ether (GME) was then investigated in similar reaction conditions. To that aim, a series of statistical copolymerizations of GME in the presence of various amounts of GMA (up to 50 mol %) were performed. As shown in Table 1, copolymerizations (runs 6−8) proceed up to complete conversion and in a controlled way as indicated by the experimental molar mass values and the low dispersities obtained. A typical SEC chromatogram is shown in Figure 3. The UV and RI signals reveal an homogeneous distribution of GMA units (absorbance at 250 nm) into the whole copolymer, in agreement with a statistical copolymerization. Selective incorporation of the two monomers via epoxide opening is confirmed by the observed signals of both monomers in the ^{1}H NMR spectrum (see Supporting Information S1) and the absence of residual epoxide functions as already mentioned.

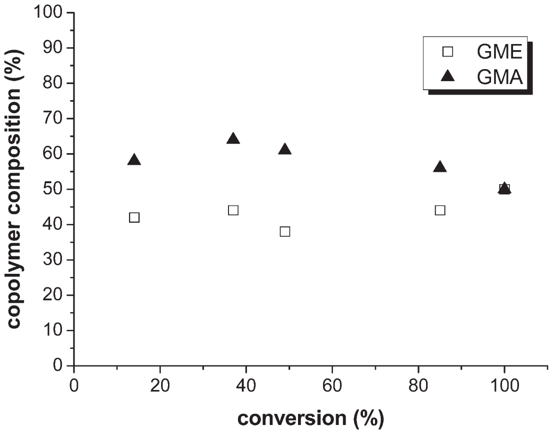


Figure 4. Evolution of the glycidyl methyl ether and glycidyl methacrylate copolymer composition with conversion starting from a 50/50 molar comonomer feed ([GME] = 1.5 mol L^{-1}, [GMA] = 1.5 mol L^{-1}, [NOct$_4$Br] = 3.43 × 10^{-2} mol L^{-1}, [i-Bu$_3$Al] = 5.14 × 10^{-2} mol L^{-1}, toluene, −30 °C).

It should be noticed that the selectivity toward GMA ring-opening was partly lost when the amount of trialkylaluminum in the system was increased, in particular when targeting copolymers of higher molar masses which requires the use of higher [Al]/[I] ratio (Table 1, run 9, 20 000 g/mol, 38%$_{\text{mol.}}$of GMA, [Al]/[I] = 2.5). In these conditions, the formation of a non-soluble polymer fraction is observed, suggesting the formation of hydrides, coming from isobutyl groups of trialkylaluminums, able to attack the double bonds of the methacrylate functions. These new pendant active centers, along the polyether backbones, can then react with other pendant methacrylate functions and give the cross-linked structure (Scheme 2a). Such a reaction was already mentioned by Müller et al. for the anionic polymerization of n-butyl acrylate in the presence of a cesium fluoride—triisobutylaluminum complex.[31]

A series of copolymerization experiments between GMA and GME at various initial comonomer compositions were performed to scale the reactivities of the two monomers according to the Kelen−Tüdos method.[32,33] To get low monomer conversions (between 5 and 15%), in order to limit the influence of the comonomers composition drift with conversion, experiments were performed in toluene at −30 °C. Reactivity ratios are r_{GME} ($k_{\text{GME-GME}}/k_{\text{GME-GMA}}$) = 0.37 and r_{GMA} ($k_{\text{GMA-GMA}}/k_{\text{GMA-GME}}$) = 1.24. These values indicate a slightly higher reactivity of GMA with respect to both GMA and GME active polymer ends. Monitoring of the copolymerization reaction by ^{1}H NMR, starting from a 50/50 molar composition feed, allowed us to determine the composition of the resulting copolymer for different conversions (Figure 4). In agreement with obtained reactivity ratios, GMA units are incorporated in the copolymer slightly faster than GME ones, but the drift in monomer composition remains very limited. These results confirm that, globally, the copolymers will exhibit a quite uniform and random composition of the two monomers.

As one of the main interest and application of the living polymerizations, the block copolymerization of GMA with GME by sequential monomer addition was investigated. As previously shown, the polymerization of GME proceeds in a controlled manner.[27] GME was first added, followed by GMA. Results presented in Table 2 show that the sequential polymerization of the two monomers is quantitative after 6 h at 20 °C, yielding copolymers with molar masses up to 43 000 g/mol. SEC chromatograms of the recovered polymers are presented in Figure 5. They show the evolution of the molar masses before and after GMA polymerization. The presence of a shoulder at high elution time indicates uncomplete reinitiation upon addition of GMA. Reinitiation efficiency estimated by deconvolution of the SEC chromatograms goes from about 90% to 70% for a

Table 2. Synthesis of Block Copolymers by Sequential Addition of Glycidyl Methyl Ether and Glycidyl Methacrylate Initiated by NOct$_4$Br (I) in the Presence of i-Bu$_3$Al (Toluene, 20 °C, 100% Conversion, Time for Each Polymerization = 3 h)

			$\overline{M}_{\text{n,th}}$[a] (g/mol)		$\overline{M}_{\text{n,exp}}$[b] (g/mol)			
run	[Al]/[I]	[M] (mol/L)	1st block (DP$_{\text{GME}}$)	2nd block (DP$_{\text{GMA}}$)	1st block	copolymer	f[c] (%)	$\overline{M}_{\text{w}}/\overline{M}_{\text{n}}$[d]
1	2.0	1.2/0.6	5100 (58)	4800 (34)	5300	10300	90	1.14
2	2.5	0.9/0.6	10000 (114)	10000 (70)	16000	38000	79	1.05
3	3.0	1.1/0.6	15300 (174)	15000 (106)	15700	43000	70	e

[a] Theoretical number-average molar mass calculated by ([monomer]/[initiator]) × conversion. [b] Number-average molar mass measured by SEC. [c] Reinitiation efficiency calculated by deconvolution of SEC peaks. [d] Dispersity given by SEC. [e] Value not determined due to peak overlap.

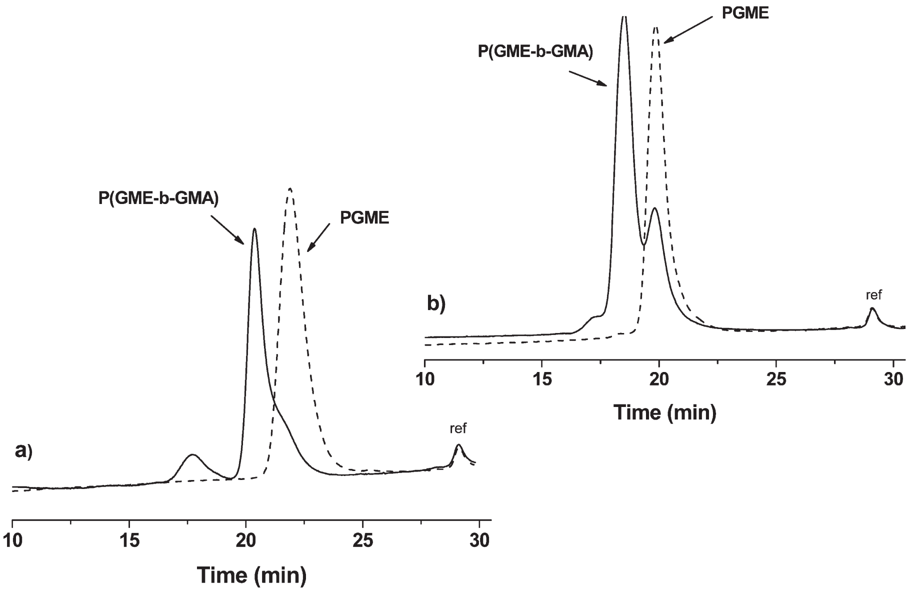


Figure 5. SEC traces corresponding to the different polymerization stages during the synthesis of P(GME-*b*-GMA) diblock copolymers initiated by $NOct_4Br$ in the presence of *i*-Bu_3Al in toluene at 20 °C (a, run 1; b, run 3; Table 2).

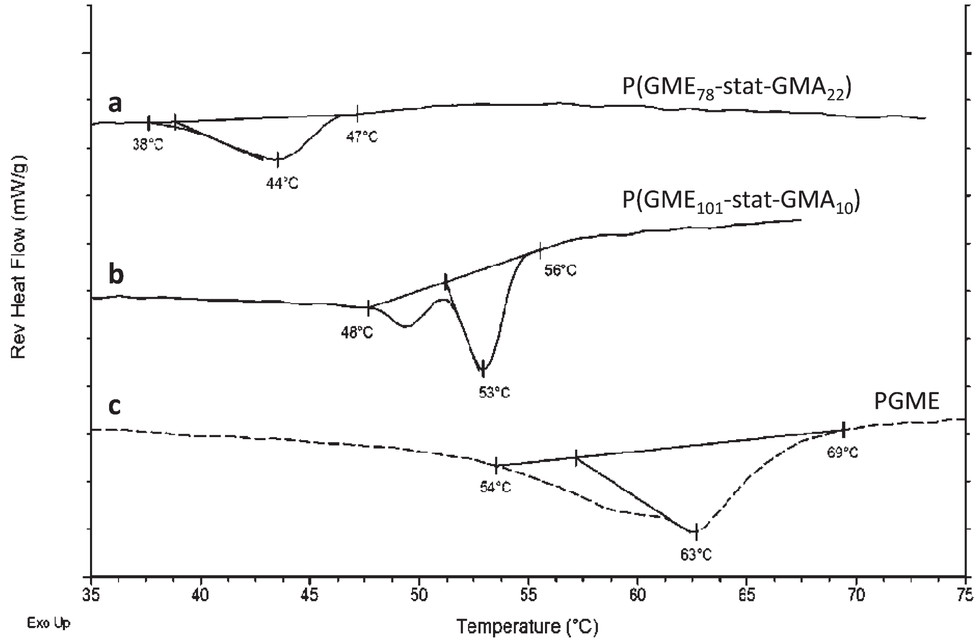


Figure 6. Modulated differential scanning calorimetry analysis (third run) of random P(GME−GMA) copolymers (22 mol % (a) and 9 mol % (b) of GMA) and homoPGME (c).

first PGME block of 5000 g/mol (Table 2, run 1) and 15 000 g/mol (Table 2, run 3), respectively. Reinitiation efficiency decreases when higher molar masses are targeted. This might be attributed to some transfer reaction to *i*-Bu_3Al which has to be used in larger excess with respect to the initiator[25,29,34] due to competitive complexation of the GMA and GME polymer units[27,29] (Scheme 2b). In addition, the presence of a small peak, or shoulder, at shorter retention times can be attributed to the formation of a copolymer fraction with branches resulting from the reaction of some of the pendant methacrylate functions of the copolymer units. However, the formation of a nonsoluble fraction was not observed, indicating that this side process still remains limited. It was noticed also that the presence of light inside the reactive medium enhanced this undesired phenomenon giving cross-linked materials.

Study of Solubility Characteristics (LCST) of P(GME-*stat*-GMA). We recently reported that PGME exhibits a lower critical solubility temperature, monitored by UV absorbance, in the range 56−61 °C depending on the polymer molar mass.[27] This property was investigated by different methods as a function of composition of P(GME-GMA) random copolymer and for PGME with number-average molar mass close to 10 000 g/mol

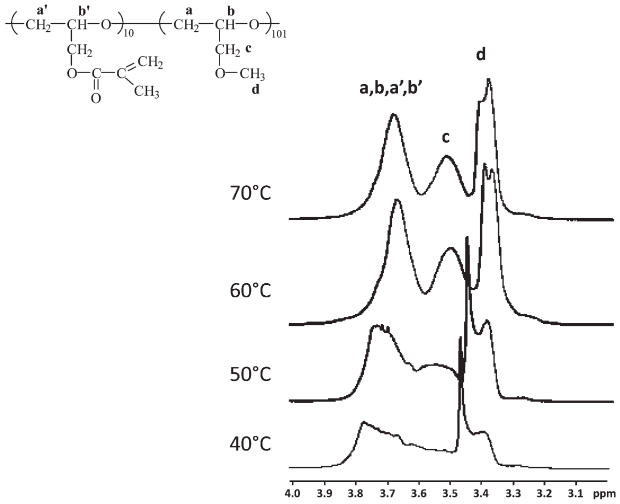


Figure 7. ^{1}H NMR spectra in D_2O of P(GME_{101}-*stat*-GMA_{10}) at various temperatures (expansion between 3.0 and 4.0 ppm).

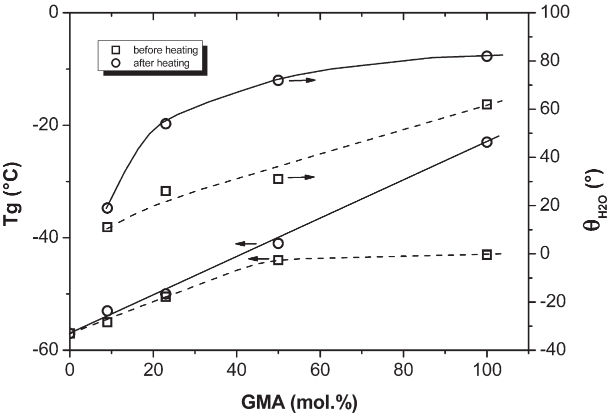


Figure 8. Influence of glycidyl methacrylate content into poly(glycidyl methyl ether) over glass transition temperatures and water contact angle before and after heat treatment.

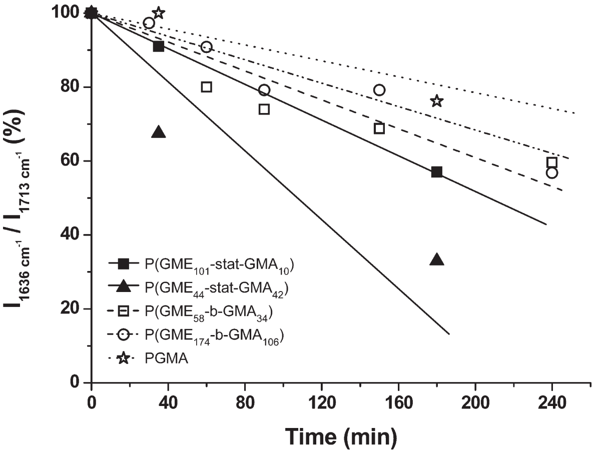


Figure 9. Evolution of the normalized intensity ratio $I_{1636\ \mathrm{cm}^{-1}}/I_{1713\ \mathrm{cm}^{-1}}$ (100% at t = 0) versus time for PGMA and random or block P(GME–GMA) copolymers (heat treatment = 110 °C).

and low dispersity (≈1.1). The thermal behavior was first investigated in water solution by modulated differential scanning calorimetry (DSC). Both PGME and copolymers thermograms show an endothermic signal, sometimes split in two peaks, attributed to the LCST transition (Figure 6). Increasing amount of GMA units into the copolymer shifts the LCST value to lower temperature range. The endotherm which covers a temperature range of 10 °C or more indicates that the LCST process proceeds in different stages although PGME and the copolymers exhibit narrow molar mass distributions. Influence of temperature on the ^{1}H NMR spectrum of the copolymers in D_2O was also investigated. Results observed for a P(GME_{101}-*stat*-GMA_{10}) copolymer are shown Figure 7. As it may be seen, methylene (a, a′, and c) and methine (b and b′) signals remain similar at various temperatures. The methoxy one (d) of GME units is split in two signals centered at 3.39 and 3.48 ppm. Their proportion varies with the temperature. Indeed, the signal at 3.48 ppm, which predominates below 60 °C, can be attributed to water-solvated methoxy groups, whereas above 50 °C the signal at 3.39 ppm becomes more and more intense when increasing temperature, in agreement with preferential hydrophobic polymer–polymer interactions. Again the interaction changes proceeds over a broad temperature range (50–60 °C).

Postpolymerization Reactions of GMA-Based Polyethers. As previously described for poly(glycidyl methacrylate) with pendant epoxide functions,[5,10–14] the present PGMA and random or block GMA-based copolymers bearing side methacrylate are attractive reactive materials owing to the high reactivity of this group toward free radicals. These polymers and copolymers show potential application as curing resin, for coating of organic and inorganic surfaces, and as adhesives as well as precursors for the formation of hydrophilic, hydrophobic, or thermosensitive gels depending on the nature of the associated comonomer. Cross-linking of GMA homo- and copolymers was investigated both under heating and UV-irradiation.

The thermal conditions allowing the reaction of GMA units was investigated by DSC using a random P(GME–GMA) copolymer with an equimolar composition (T_g = −44 °C). No reaction is detected up to 110 °C, where takes place an exothermic process attributed to thermally initiated radical reaction of methacrylate groups (see Supporting Information Figure S2). Measurement of glass transition temperature and contact angles with water before and after heating for 4 h at 110 °C was performed on PGMA-based polymer films. Results collected in Figure 8 show both a significant increase of the T_g and a decrease of the hydrophilic character of the cross-linked materials, in agreement with a loss of polymer chains mobility and rigidity increase.

The extent of the cross-linking reaction was monitored by following the disappearance of the methacrylate double bond at 1636 cm^{-1} by FTIR using an attenuated total reflectance (ATR) while the 1713 cm^{-1} carbonyl group band present in the methacryloyl moiety was used as internal reference. The decrease of the normalized intensity ratio (at t = 0 it corresponds to 100% of double bonds) between the two bands (I_{1636}/I_{1713}), as a function of time, is shown Figure 9 for PGMA-based random and block copolymers. Kinetics are affected by the polymer structure, the homoPGMA leading surprisingly to the slowest consumption of methacrylate double bonds, the highest rates being observed for the random copolymers. It agrees with a decrease of chain mobility and reactive functions accessibility for PGMA or PGMA-based block copolymers and a better accessibility in the random structures due to GME neighboring monomer units.

Table 3. Influence of P(GME-*stat*-GMA) Composition toward the Cross-Linking Efficiency Cured by UV Light (20 W, 254 nm, 16 h)

polymer composition	without photoinitiator		Irgacure 819	
	residual double bonds $I_{1636\ \mathrm{cm}^{-1}}/I_{1713\ \mathrm{cm}^{-1}}$[a] (%)	water contact angle (deg)	residual double bonds $I_{1636\ \mathrm{cm}^{-1}}/I_{1713\ \mathrm{cm}^{-1}}$[a] (%)	water contact angle (deg)
P(GME_{101}-*stat*-GMA_{10})	86	11	54	13
P(GME_{78}-*stat*-GMA_{22})	84	26	51/28[b]	50/53[b]
P(GME_{44}-*stat*-GMA_{42})	89	46	54	63
PGMA	89	69	75	83

[a] Intensity ratio between C═C and C═O IR bands normalized to 100% at t = 0. [b] UV light 400 W, 15 min.

FTIR-ATR methods as well as water contact angle measurements were applied to follow the reaction of the methacrylate function under UV-irradiation in the absence and in the presence of Irgacure 819 as photoinitiator (Table 3). Activation by Irgacure 819 allows the reaction to proceed in a few minutes. Indeed, relatively low double bond conversion values (I_{1636}/I_{1713} = 84−89% residual double bonds after 16 h) are observed using a 20 W UV lamp at 254 nm in the absence of a photoinitiator where much higher ones were obtained in the presence of Irgacure 819. Again, the result concerning homoPGMA agrees with previous results seen with heat treatment corresponding to a decrease of chain mobility and reactive functions accessibility. Using a 400 W UV lamp allows high conversions in limited time (15 min). Water contact angle results showed a similar trend as the values are higher with the use of a photoinitiator. As observed previously, the hydrophobicity increased with increasing PGMA content with or without Irgacure 819.

Combining the thermoresponsive property of PGME in water and the cross-linking one of PGMA via the pendant methacrylate functions, thermoresponsive polyether hydrogels were prepared.

CONCLUSION

Monomer-activated anionic polymerization of glycidyl methacrylate (GMA) using a binary initiating system consisting of tetraoctylammonium bromide and triisobutylaluminum allows the synthesis of polyethers with pendant methacrylate functions. Selective ring-opening of GMA epoxide function yields reactive polyethers with controlled molar masses up to 20 000 g/mol and low dispersities. As in previously reported epoxide polymerization studies involving monomer activation by trialkylaluminum, the formation of 1:1 initiating and propagating complexes of weak basicity is believed to strongly limit side reactions. The excess of Lewis acid with respect to the initiating salt allows selective or at least highly preferential complexation/activation of the epoxide groups despite the presence of the methacrylate function. Thanks to this selectivity, copolymerization of glycidyl methyl ether with GMA permits the synthesis of corresponding random and block copolyethers combining interesting characteristics such as tunable LCST and chain reactivity allowing the preparation of thermoresponsive polyether hydrogels. The very broad variety of glycidyl ethers that can be associated with GMA offers large opportunities to design reactive polyethers with various properties.

ASSOCIATED CONTENT

Supporting Information. Figures S1 and S2. This material is available free of charge via the Internet at http://pubs.acs.org.

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