

# Controlled "Living" Anionic Polymerization of Glycidyl Methacrylate

L. LEEMANS, R. FAYT, and Ph. TEYSSIÉ,\* *Laboratory of Macromolecular Chemistry and Organic Catalysis University of Liège, B6, Sart Tilman, 4000 Liège, Belgium*, and H. UYTTERHOEVEN and W. DE WINTER, *Agfa-Gevaert R & D Laboratories, 2510 Mortsel, Belgium*

## Synopsis

The living anionic polymerization of glycidyl methacrylate (GMA) in THF at low temperature initiated with diphenyl hexyl lithium, 9-anthracenyl methyl lithium, and  $\alpha$ -methylstyryl lithium leads to well characterized homo- and block copolymers, with predictable  $\overline{M}_n$  and narrow molecular weight distributions and with all the oxirane groups intact. Broadening of the molecular weight distributions above a certain and very critical  $\overline{M}_n$  supported the idea that the living polymerization at low temperature might proceed in micelle-like structures. Diffusional restriction of the monomer access towards the living centers, due to lesser solvation and increasing compactness of the polymer coils is thought to give rise to broadening of the molecular weight distribution of PGMA homo- and block copolymers.

## INTRODUCTION

Although an overwhelming number of articles and patents have been published concerning the radical homo- and copolymerization of glycidyl methacrylate (GMA), literature references to its anionic polymerization are still scanty. Arbuzova et al. merely state a polymer yield of 11% with 80% of the epoxy groups unreacted, in a butyl lithium initiated polymerization.<sup>1</sup> Iwakura et al. reported the similarly initiated polymerization of GMA among other methacrylates in THF at  $-78^\circ\text{C}$ ,<sup>2</sup> but attempts in this laboratory to obtain polymer this way failed, a negative conclusion also reached by G. D. Andrews and L. R. Melby of Du Pont de Nemours. These authors explored diphenyl hexyl lithium, methyl methacrylate capped diphenyl hexyl lithium, and lithium diisopropylamide as initiators for homo- and copolymerization of GMA, obtaining rather low molecular weight ( $\overline{M}_n = \text{ca. } 2000$ ) PGMA's.<sup>3</sup> Considering the need for preparation of PGMA homo- and copolymers with well defined molecular weights and narrow molecular weight (MW) distributions,<sup>4</sup> we wish to report here on a truly living anionic polymerization process for glycidyl methacrylate. It must be stressed that the group transfer polymerization method proposed by Du Pont de Nemours is of course very efficient for the living polymerization of such  $\alpha,\beta$ -unsaturated carbonyl monomers, yielding polymer of narrow distribution and predictable  $\overline{M}_n$ ; unfortunately it does not allow for the direct synthesis of block copolymers with monomers lacking carbonyl conjugated groups, i.e., in particular with styrenes and dienes.<sup>5</sup>

\* To whom correspondence should be addressed.

However, such block polymers become now readily accessible by the straightforward anionic polymerization process described hereafter, their PGMA blocks being easily functionalized, thus leading to new materials with very interesting properties.<sup>6,7</sup>

## EXPERIMENTAL

### Monomer

Glycidyl methacrylate was dried over calcium hydride under a high purity nitrogen atmosphere for several days. It was fractionally vacuum distilled from finely divided calcium hydride, and the first and last fractions discarded. Just before polymerization the pure monomer was finally vacuum distilled in high yield from a toluene solution that contained a small amount of poly styryl lithium.

### Solvent

Tetrahydrofuran (THF) was dried by refluxing over sodium benzophenone for several days, and distilled therefrom under a high purity nitrogen atmosphere.

### Initiation and Polymerization of GMA

Initiation of this anionic polymerization in THF at low temperature ( $-78^{\circ}\text{C}$ ) was carried out with various initiators such as diphenyl hexyl lithium (DPHLi),<sup>8</sup>  $\alpha$ -methyl styryl lithium,<sup>9</sup> and 9-anthracenyl methyl lithium,<sup>10,11</sup> all of them known to be excellent for the anionic polymerization of a large number of methacrylates. Indeed the anionic polymerization of GMA in THF at  $-78^{\circ}\text{C}$  readily proceeded with these initiators to give a soluble polymer with a narrow MW distribution and an  $\overline{M}_n$  as predicted by the monomer to initiator molar ratio, at least within certain limits. All polymerizations were carried out in ordinary laboratory glassware. The reaction flask was put under vacuum and thoroughly flame-dried. Solvent and monomer were transferred to the polymerization flask through a stainless steel capillary. In a typical polymerization experiment, a 500 mL Pyrex flask, fitted with a rubber septum equipped stopcock was loaded with 250 mL dry THF solvent. A DPHLi solution in THF was added into the polymerization flask until the deep red colour of the diphenyl hexyl carbanion persisted;  $1.74 \times 10^{-3}$  mol of DPHLi solution was then transferred into the reactor as the required initiator amount for a 5980 calculated  $\overline{M}_n$ . The flask was cooled down to  $-78^{\circ}\text{C}$  in a dry ice-acetone mixture before GMA (10.4 g;  $7.32 \times 10^{-2}$  mol) was added; the colour of the solution changed from deep red to faint yellow. The polymerization was terminated by addition of methanol after 45 min at  $-78^{\circ}\text{C}$ . The yield was quantitative ( $\overline{M}_{n\text{ exp}} = 6120$ ;  $\overline{M}_w / \overline{M}_n = 1.07$ ).

### Measurements

GPC measurements were carried out in THF at  $45^{\circ}\text{C}$  using a Hewlett-Packard 1090 liquid chromatograph equipped with four Polymer Laboratories PL

Gel Columns ( $10^5$ ,  $10^3$ ; 500, and 100 Å) and a Hewlett-Packard 1037 A Refractive Index Detector. A PMMA calibration curve allowed  $\overline{M}_w/\overline{M}_n$ , and MW distributions to be calculated from the chromatogram.

## RESULTS AND DISCUSSION

First, homo-PGMA prepared by initiation with DPHLi or 9-anthracenyl methyl lithium was treated for 4 hours with an aqueous HCl in DMF solution, at 65°C and the excess chloride anions titrated with standardized  $\text{AgNO}_3$  solution after reaction of the oxirane units.<sup>12</sup> The data revealed that within experimental error no oxirane units were opened during the anionic polymerization of GMA; titrated oxygen content was 11.2 wt %, i.e., equal to the theoretically calculated value. Thus, in practice, it may safely be said that under these conditions, GMA anionic polymerization occurs only through the vinylic double bond, while oxirane units remain unaffected.

Figure 1 shows the typical monomodal GPC chromatogram of homo-PGMA I ( $\overline{M}_n = 6120$  and  $\overline{M}_w/\overline{M}_n = 1.07$ ) that was initiated with DPHLi. In contrast to this result, researchers from Du Pont Co. reported in the above-mentioned

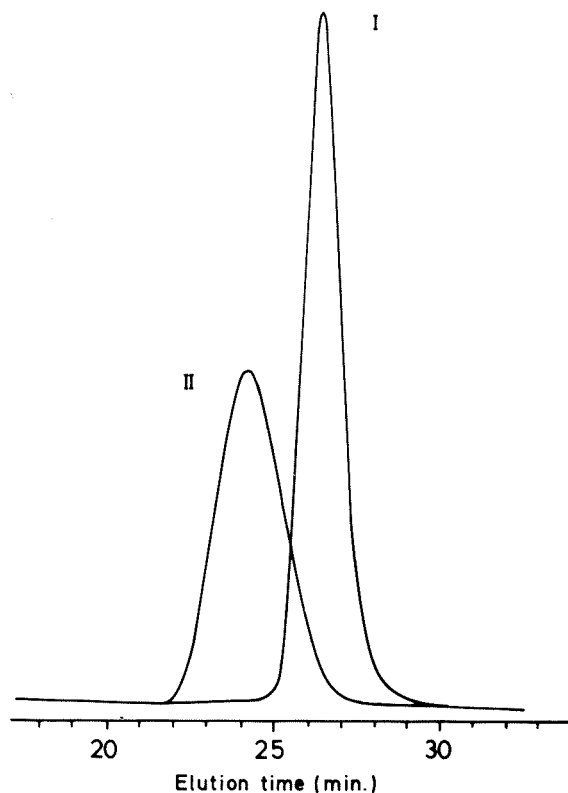


Fig. 1. GPC chromatogram of homo-PGMA I (10.4 g) initiated with DPHLi in THF (250 mL) at  $-78^\circ\text{C}$ ;  $\overline{M}_{n\text{exp}} = 6120$ ;  $\overline{M}_w/\overline{M}_n = 1.07$ . GPC chromatogram of homo-PGMA II (5.2 g) initiated by DPHLi in THF (250 mL) at  $-78^\circ\text{C}$ ;  $\overline{M}_{n\text{exp}} = 18200$ ;  $\overline{M}_w/\overline{M}_n = 1.42$ .

paper that the MW distribution for a 2000 MW homo PGMA as initiated with DPHLi was much broader than expected for an orderly living polymerization ( $\bar{M}_w/\bar{M}_n = 1.9$ ).<sup>3</sup> The authors claim capping of DPHLi with methyl methacrylate, so generating a weakly nucleophilic methacrylate enolate ion, as necessary to avoid destruction of the initiator by reactions with oxirane groups.

However, we rather believe that under our conditions, the problem of MW distribution is associated with the limited solubility of PGMA at the low temperature needed for living anionic polymerization. Indeed, homo-PGMA solutions at low temperature in THF often display intense light scattering, indicating possible formation of aggregates, their solvation depending on the  $\bar{M}_n$  of the polymer. For higher molecular weight, less solvated polymer coils, slower monomer diffusion towards the living center might thus interfere with the regular propagation of the polymer chains in solution, resulting in a broadening of the MW distribution.

Figure 1 shows as well the GPC chromatogram of the homo-PGMA II that was synthesized under exactly the same experimental conditions as the aforementioned monodisperse sample I, except for the initiator over monomer ratio that was only one third, thus yielding an 18K  $\bar{M}_n$ . One clearly sees indeed that just increasing the chain length has a dramatic effect on the broadening of the MW distribution. Table I summarizes the experimental conditions for the performed anionic polymerizations.

By using poly  $\alpha$ -methyl styryl lithium, also a much more nucleophilic initiator than the methacrylate anion (e.g., it initiates the anionic polymerization of styrenes and dienes), block polymers of  $\alpha$ -methylstyrene and GMA were synthesized in which the influence of the length of the PGMA block on the MW distribution was examined. Figure 2 shows the GPC chromatograms of PGMA initiated by a poly  $\alpha$ -MeStLi (IIIa;  $\bar{M}_n = 4400$ ,  $\bar{M}_w/\bar{M}_n = 1.09$ ) precursor. The GMA monomer was added in two successive crops to this living precursor (cf. Table I). Upon adding the first one, the red poly  $\alpha$ -MeStLi solution immediately turned pale yellow, the characteristic color of the methacrylic anion, and re-

TABLE I  
Characteristic Data for the Anionic Polymerization of GMA in THF<sup>a</sup> at  $-78^\circ\text{C}$

Sample	Initiator <sup>b</sup>	GMA <sup>c</sup> (g)	$\bar{M}_{n_{\text{theor}}}$ <sup>d</sup>	$\bar{M}_{n_{\text{exp}}}$ <sup>e</sup>	$\bar{M}_w/\bar{M}_n$	Yield (%)
I	DPHLi 1.74 mmol	10.4	5980	6120	1.07	100
II	DPHLi 0.29 mmol	5.2	17930	18200	1.42	98
IIIa	P $\alpha$ MeSt 4.4K				1.09	
IIIb		IIIa + 5.2	9440	10130	1.16	
IIIc		IIIb + 6.2	15840	15280	1.40	98
IVa	P $\alpha$ MeSt 5.0K				1.05	
IVb		IVa + 11.4	16450	17200	1.36	97
V	PMMA 24.6K		48200	51100	1.16	97

<sup>a</sup> Solvent for polymerization: THF, 250 mL.

<sup>b</sup>  $\bar{M}_n$  of living poly  $\alpha$ -MeStLi precursor as determined by GPC.

<sup>c</sup> Added quantities of GMA.

<sup>d</sup> Calculated from monomer to initiator molar ratio.

<sup>e</sup> GPC data on HP Liquid Chromatograph in THF at  $45^\circ\text{C}$  using a PMMA calibration curve.

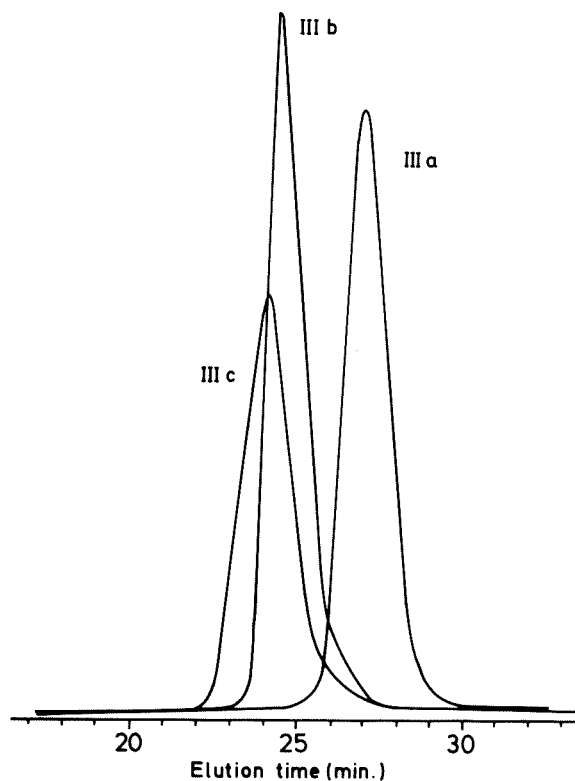


Fig. 2. GPC chromatograms of P $\alpha$ -MeStLi precursor IIIa ( $\overline{M}_{n\text{exp}} = 4400$ ); IIIb ( $\overline{M}_{n\text{exp}} = 10130$ ) upon addition of 5.2 g GMA to IIIa; IIIc ( $\overline{M}_{n\text{exp}} = 15280$  upon addition of 6.2 g GMA to IIIb).

mained transparent during polymerization. After 90 min of polymerization time an aliquot for GPC analysis was taken out of the reaction flask: the resulting poly( $\alpha$ -MeSt-*b*-GMA) IIIb had a  $\overline{M}_n = 10130$ , close to the calculated one, and its MW distribution was still narrow ( $\overline{M}_w/\overline{M}_n = 1.16$ ) as expected for a truly living polymerization with fast initiation rate. A further addition of GMA to this living block polymer significantly broadened the MW distribution of the resulting IIIc block polymer. The solution shifted progressively to a turbid and finally to a milky white one in the course of the polymerization. Nevertheless the yield was quantitative.

In addition, the experiment described above was repeated with all conditions equal, except that the entire quantity of GMA was now added at one time to the living poly  $\alpha$ -MeStLi (IVa) precursor (cf. Table I). The obtained block polymer (IVb) had also a significantly increased MW dispersity as can be seen from Figure 3: since those two chromatograms do not superimpose at all, broadening of the block polymer MW distribution due to a deactivation of living centers with resulting homopolymer formation can be ruled out. Again, the low temperature ( $-78^\circ\text{C}$ ) red poly  $\alpha$ -MeStLi solution shifted to pale yellow upon addition of the GMA and finally also became milky white after all of the GMA had polymerized, as it was the case for IIIc.

Thus, an increasing PGMA chain length in the same block polymer leads to a significant broadening of the MW distribution from a certain composition

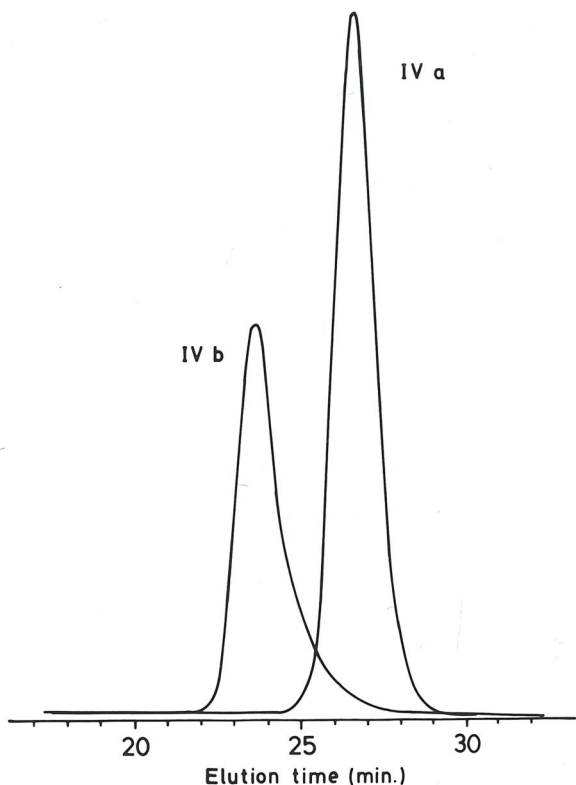


Fig. 3. GPC chromatograms of  $P\alpha$ -MeStLi precursor IVa ( $\overline{M}_{n\text{exp}} = 5040$ ); IVb ( $\overline{M}_{n\text{exp}} = 17200$ ) upon addition of 11.4 g GMA to IVa.

on. Obviously, if that phenomenon is indeed due to decreased solvation, the nature and length of the other block should also be important in controlling that MW distribution; conclusively, a more soluble block copolymer V (PMMA-*b*-PGMA,  $\overline{M}_n = 51100$ ) having a PGMA block of 26500 still retains a narrow MW distribution ( $\overline{M}_w/\overline{M}_n = 1.16$ ).

Since increasing PGMA content and  $\overline{M}_n$  leads to pronounced light scattering of the solutions at low temperatures (going from clear transparent to milky white), the possible influence of solvation was also probed by gradually increasing temperature; indeed, solutions of PGMA in THF become progressively less turbid, and finally even completely transparent (ca.  $-10^\circ\text{C}$ ), unfortunately a too high temperature for performing a truly living anionic polymerization of such monomers. It is however noteworthy that this appearance of turbidity at low temperature is a perfectly reversible process.

## CONCLUSION

These observations support the idea that the living polymerization of GMA in THF at low temperature might proceed in micelle-like structures, above a certain and very critical  $\overline{M}_n$  (ca. 10K under polymerization conditions described here), the more soluble PMMA or  $P\alpha$ -MeSt block stabilizing a colloidal dis-



persion of the growing block polymer. This is somehow analogous to an anionic dispersion polymerization process wherein the disperse phase monomer is added in order to continue chain growth from the living end of a soluble polymer block. Aggregates of block copolymer are formed when the insoluble portion reaches the size at which critical micelle concentration is exceeded; dispersion polymerization then proceeds within the aggregate.<sup>12</sup> So if there is diffusional restriction of the monomer access towards the living centers, due to lesser solvation and increasing compactness of the polymer coils, broadening of the MW distribution of the block is likely to occur.

Nevertheless, in the present case, proper control of experimental conditions and precise tailoring of the chain-length and composition of these homo- and copolymers allow the performing of perfectly living polymerization in true solution, using this attractive monomer so rich in interesting potentialities. In that prospect, it should be emphasized again that the many possibilities to co-react to crosslink, or transform into other structures (i.e., polyelectrolytes), the PGMA sequences of di- and, particularly, tri-block copolymers, certainly pave the way for many exciting applications.

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