The in situ formation of a new initiator system for the syndiotactic anionic polymerization of methyl methacrylate in toluene at 0 °C

Thomas Zundel, Philippe Teyssie and Robert Jérôme

Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6, 4000, Liège, Belgium

Abstract

This paper reports on an efficient 'in-situ' one pot synthesis of an initiatior/ligand adduct, which can be used to initiate the anionic polymerization of methyl methacrylate in toluene at 0 °C. Predominantly syndiotactic PMMA is formed.

Keywords: Anionic polymerization; Polymerization; Methyl methacrylate; Ligand

Recent years have witnessed considerable effort towards achieving 'living' polymerization of (meth)acrylic esters [1]. These monomers are, in principle, good candidates to undergo anionic polymerization. However, this method suffers severe limitations when applied to (meth)acrylates, under the usual conditions of solvent and temperature. These problems arise from the possible nucleophilic attack of the active species on the carbonyl groups along the chain and the potential abstraction of the α-hydrogen atom of the acrylates. It has been previously shown in this laboratory, that ligated anionic polymerization is a very effective strategy in preventing the anionic polymerization of hindered alkyl acrylates from being disturbed by sidetransfer and termination reactions. Thus, the application of polydentate lithium alkoxides as ligands, in combination with a sterically hindered stabilized carbanion such as diphenylhexyl lithium (DPHLi) as initiator, has allowed synthesis of highly syndiotactic poly(methyl methacrylate) (PMMA) in toluene, at temperatures as high as 0 °C [2-4]. However, this procedure involves the separate synthesis of both the polydentate lithium alkoxide and DPHLi, the use of the latter being economically prohibitive. The purpose of this communication is to report on the discovery of a new concept which allows an efficient 'in situ' one-pot synthesis of ligand and initiator adduct, a possible answer to that economical problem.

It is well known that α-lithio esters are very effective initiators for the polymerization of (meth)acrylates [5-7]. These compounds have as yet been prepared in the pure state, mostly by metalation of esters using substituted metal amides in aliphatic or aromatic hydrocarbon solvent even at room temperature [8-9]. On the other hand, some authors [10-12] reported in the literature, that the acidity of alcohols rapidly decreases as the $[RO^-]/[ROH]$ molar ratio is increased, and reaches a constant value of $pK_a=31$ for ratios higher than two. This value is about 7×10^3 times that one of dimethyl sulfoxide (DMSO) (i.e. $pK_a=34.8$ [13-14]) and is, within experimental error, the same for the commonly used alcohols (i.e. EtOH, *t*-BuOH, and *n*-BuOH). Accordingly, we found that the lithiation of ethyl isobutyrate (EIB) ($pK_a=30$, by comparison to the pK_a of the $CH_3COOCH_2CH_3$ parent compound [15]) can be carried out advantageously using a solution of a bidentate alcohol ($HOCH_2CH_2OCH_3$) (i.e. HOEM) in the presence of an excess of lithium metal in toluene, and that, in some cases, the LiOEM/lithio ester (EIBLi) adduct can be used to initiate the anionic polymerization of MMA. The general idea is sketched in Fig. 1.
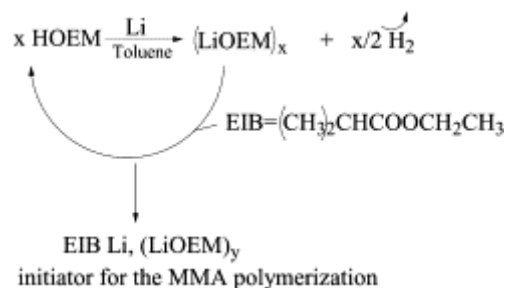

Fig. 1. New initiator system for the anionic polymerization of MMA, using lithium, HOEM and EIB as promoter.

The reaction was conducted in a previously flamed glass apparatus, under inert atmosphere. Toluene was purified by refluxing over fresh sodium-benzophenone complex and distilled just prior to use. HOEM (ALDRICH) was used as received without further purification. EIB (ALDRICH) and methyl methacrylate (MMA) (JANSSEN) were added with a 10 wt% AIEt$_3$ solution in hexane until a persistent yellowish color was observed, and distilled before polymerization. Dimethyl sulfoxide was distilled and stored over dry molecular sieves (3 Å grade) under a nitrogen atmosphere. The standard technique consists in introducing an excess of lithium (granular, grain size ca. 2.5 mm, JANSSEN; [Li]>[HOEM]+[EIB]), 5 ml toluene and HOEM into the flask. After quantitative conversion of HOEM to LiOEM (90 min to 20 °C), the desired amount of EIB was added into the mixture, and allowed to react over t_2 h at T_2 °C. It was noticed that upon addition of EIB the color of the reaction medium progressively changed from colorless to yellow-green, and that an insoluble product was formed, which could be lithium ethanolate (LiOEt, cfr. infra). Furthermore, 80 ml toluene were added to the reaction medium and 4.2 g of MMA were polymerized at 0 °C. The polymer was recovered by precipitation into methanol and dried under vacuum at 70 °C for 24 h. Size exclusion chromatography (SEC) was performed with a HEWLETT PACKARD 1090 apparatus equipped with 4 PLgel columns (10^5, 10^4, 10^3 and 10^2 Å) using tetrahydrofuran as eluent and a HP 1030 A refractive index detector. The flow rate was 1.0 ml/min. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were calculated from size exclusion chromatograms on the basis of a polystyrene calibration. Polymer chain tacticity was determined by ^{1}H NMR spectroscopy using a BRUKER AN-400 spectrometer.

Table 1 lists the results of polymerizations performed under various conditions. Predominantly syndiotactic PMMA (i.e. mr~70%) is formed with a monomodal molecular weight distribution (MWD) (i.e. $M_w/M_n \sim 1.7$; SEC trace on Fig. 2). MMA polymerization is usually close to completion, and the polymer molecular weight can be modified by changing either the [EIB] whenever [Li]>[HOEM]+[EIB] (runs 2–4) or [Li] (run 1). The initiator efficiency F calculated with respect to EIB or Li is however low ($F<6\%$; runs 1–5). This observation indicates that a large part of the initiator is either killed in the reaction medium or inactive.

Table 1. Characteristic data for the polymerization of MMA in toluene at 0 °C using the {Li+HOEM+EIB+PhCH$_3$} system as initiator

Code	Li (mmol)	HOEM (mmol)	T_1/t_1 (°C/min)	EIB (mmol)	T_2/t_2 (°C/min)	DMSO (mmol)	t_3 (min)	ρ (%)	M_n GPC	M_w/M_n	F (%)
1	4.46	2.53	20/35	3.74	20/1545	0	30	88	210000	1.7	0.92
2	18.40	10.10	20/35	7.40	20/1260	0	30	100	75000	1.6	0.75
3	4.01	1.26	40/45	1.56	40/110	0	2	94	200000	1.8	1.24
4	8.77	2.53	20/40	3.74	40/110	0	2	92	100000	2.3	1.03
5	7.48	2.53	20/95	3.00	40/155	0	2	100	22500	1.7	6.07
6	8.47	2.53	20/100	3.00	40/165	28	2	94	44500	1.4	2.93
7	8.47	2.53	20/100	1.20	40/165	28	2	99	98000	1.4	3.48
8	8.17	2.53	20/115	3.00	40/160	14	2	100	45000	1.5	3.11

The HOEM solution is first mixed with Li in toluene for t_1 min at T_1 °C, before addition of EIB at T_2 °C for t_2 min; t_3=propagation time; ρ=polymer yield; F=initiator EFFICIENCY=100×(grams of PMMA/moles of initiator)/Not-$found_n$ GPC. The theoretical amount of initiator corresponds either to [EIB] if ([Li]−[HOEM])>[EIB] or to ([Li]−[HOEM]) (run 1). *Not-found$_n$* of PMMA was determined by SEC with polystyrene calibration. Hence, F correlation should be considered approximate.
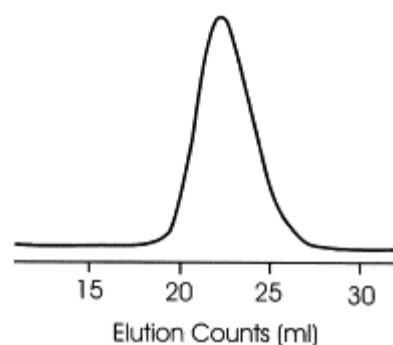

Fig. 2. GPC trace of MMA polymerization product, using lithium, HOEM and EIB as initiator in toluene at 0 °C, run 2 in Table 1.

If the active species were sparingly soluble and therefore of low efficiency, the polarity of the solvent should obviously be a critical parameter for improving that situation. However, if addition of dimethyl sulfoxide prior to

MMA polymerization, somewhat decreases the MWD, it has no beneficial effect on F (runs 6–8), which strongly suggests that the loss of active species results from side reactions.

The experimental results show an enhancement of the initiator efficiency F upon increasing the T_2 and t_2 parameters from 0 up to a limiting value (Fig. 3). The best results (F=6%) are obtained for T_2=40 °C and t_2=155 min. This dependence of F can be accounted for as follows. According to Lochmann et al. [7] esters of α-lithioisobutyric acid have a limited stability in hydrocarbons and they react by self-condensation (i.e. $2LiMe_2CCOOEt \rightarrow LiMe_2CCOCMe_2COOEt+LiOEt$) and by condensation with the parent non-metalated ester (i.e. $LiMe_2CCOOEt+HMe_2CCOOEt \rightarrow HMe_2CCOCMe_2COOEt+LiOEt$) at room temperature. Because this ketoester ($HMe_2CCOCMe_2COOEt$) is acidic enough ($pK_a \approx 21$, by comparison to the pK_a of the parent compound ($(CH_3)_3CCOCH_3$ [16]), it is more likely metalated in α position by LiOEM (i.e. $HME_2CCOCMe_2COOEt+LiOEM \rightarrow LiMe_2CCOCMe_2COOEt+HOEM$), which leads to the same α-lithio ketone as formed by self-condensation. Consistent with the insolubility of LiOEt, precipitation occurs in the polymerization medium. Because LiOEt is not able to initiate the MMA polymerization, EIB and lithium are partly lost, which contributes to a limited efficiency F. In contrast, α-lithio ketones are known for efficiency in initiating MMA polymerization, which is further enhanced by lithium *tert*-butoxide [17-18]. Therefore, it seems reasonable that the α-lithio ketone–ester/LiOEM adduct is the actual initiator for the MMA polymerization rather than the EIBLi/LiOEM one. The decrease in the initiator efficiency F when T_2 and t_2 exceed some critical value, is strong indication that the lithiated species (EIBLi and α-lithio ketone–ester) have a limited stability in the reaction medium as result of slow condensation reactions. As far as $LiMe_2CCOCMe_2COOEt$ is concerned, a cyclic product, such as tetramethyl-1,3-cyclobutanedione (TMCB), could be formed by intramolecular condensation with release of LiOEt.

To sum up, these preliminary results illustrate an obviously promising situation that paves the way toward the in situ one-pot synthesis of a new and cheap initiator system. As an indirect evidence that α-lithio ketone–ester is the actual initiator and that the concept is liable to improvement, 2,4-dimethyl 3-pentanone (DMP) has been used instead of EIB in scheme 1. The initiator efficiency F calculated with respect to Li then increases up to 35%. Further work is in progress to confirm and exploit these results for practical applications.
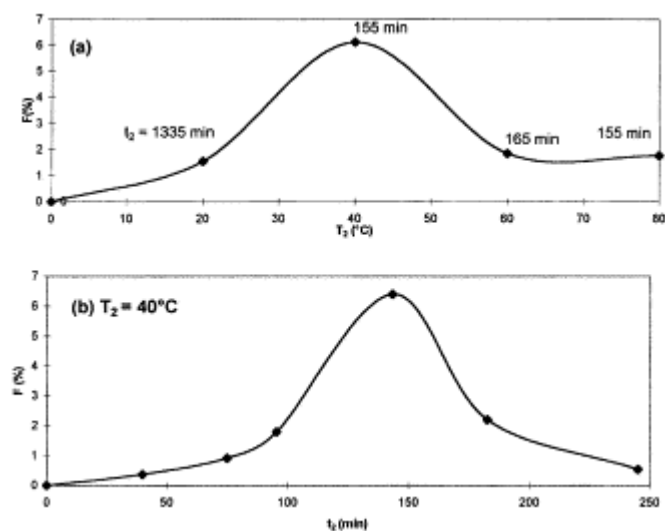

Fig. 3. Anionic polymerization of MMA using an initiator solution prepared in situ by reaction of LiOEM with EIB in the presence of an excess of lithium. Effect of the reaction temperature T_2 (a) and the reaction time t_2 at T_2=40 °C (b) on the initiator efficiency F. F=100×(grams of PMMA/[EIB])/$\bar{M}_{n\,GPC} = 2.53$ mmol of [HOEM]; of 8 mmol Li; 3.00 mmol of EIB; reaction TIME=5 min; polymer YIELD=100%.

Acknowledgements

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