Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Dhara, Mahua Ganguly and Sivaram, Swaminathan(2009) 'Synthesis of Hydroxy-Functional PMMA Macromonomers by Anionic Polymerization', Journal of Macromolecular Science, Part A, 46: 10, 983 — 988
To link to this Article: DOI: 10.1080/10601320903158610
URL: http://dx.doi.org/10.1080/10601320903158610

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2009) **46**, 983–988

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320903158610

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Synthesis of Hydroxy-Functional PMMA Macromonomers by Anionic Polymerization

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Received January 2009, Accepted April 2009

Living anionic polymerization has been utilized to synthesize hydroxy end-functionalized PMMA macromonomers with styryl or allyl functionalities as the polymerizable end-groups. Protected hydroxy-functionalized alkyl lithium initiators have been used to initiate anionic polymerization of MMA. Subsequently the living chains with protected hydroxyl function have been terminated using 4-vinylbenzyl chloride (4-VBC) or allyl methacrylate (ALMA) to form α-hydroxy-ω-styryl and α-hydroxy-ω-allyl PMMA, respectively. These protected hydroxy-functionalized PMMA macromonomers have been characterized by GPC and ^{1}H-NMR. Termination using 4-VBC led to 50% functionalization, whereas that using allyl methacrylate led to 100% functionalization of the hydroxy-PMMA.

Keywords: Anionic polymerization, macromonomer, functionalized initiator.

1 Introduction

"Living" polymerizations with minimum extent of termination and transfer reactions have been the most extensively used techniques for synthesis of various architectural polymers, functional polymers, macromonomers, stars and block copolymers with well-defined structures and low polydispersity (1–6). Living anionic polymerization has been one of the most efficient living polymerization techniques for synthesis of functional polymers with high purity and low compositional heterogeneity (1, 5–13). These functionalities have been introduced either by i) electrophilic termination of living chains, or by ii) using suitable functionalized anionic initiators to initiate living polymerization of the desired monomer. Modification of the terminal functionality by post-polymerization reactions such as crosslinking or chain extension enabled synthesis of block, graft or star-branched polymers by proper choice of polymerization method depending on the functionality (8, 9, 14–16).

Macromonomers are reactive prepolymers with polymerizable end-group. The advent of macromonomers has provided an efficient and facile means to the synthesis of well-defined graft copolymers (6, 7, 17–20). Macromonomers of amphiphilic nature have also attracted considerable attention as stabilizers in emulsion polymerization, providing an alternative to use of surfactants (21). In general, macromonomers with styryl, vinyl or allyl functionalities have been synthesized by termination of living polymeric anions by electrophilic reagents containing the corresponding polymerizable group. Compared to a vast amount of literature available on macromonomers synthesized from non-polar hydrocarbon monomers (3–6, 22–26) e.g. styrene, isoprene, butadiene, few reports based on methacrylate-based macromonomers are available (27–30). This could be partly due to the inherent problems associated with methacrylate polymerization, e.g. the side-reactions involving the ester group, under classical conditions of initiation and propagation (1, 31, 32). Anionic polymerization of MMA is rendered living only at lower temperatures under stringent reaction conditions that ensures minimum extent of termination and under such conditions many of these reactions required for functionalization do not occur efficiently. Andrews et al. synthesized PMMA macromonomers with allylic and styrenic end-function by polymerizing MMA using DPHLi as initiator at -78°C followed by deactivating the living chains by allyl bromide, and vinylbenzyl iodide or bromide respectively (27). Vinylbenzyl chloride failed to react with the living PMMA anion. Synthesis of PMMA macromonomers by termination of living chains by benzaldehyde or 4-vinylbenzoyl chloride have also been reported (28). Highly syndiotactic PMMA of low polydispersity (1.11–1.17) have

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been prepared with Ph_3CLi in THF or THF-PhMe, and coupled with p-(chloromethyl)styrene at −78° yielding PMMA macromonomers with one vinylbenzyl group per polymer chain **(29)**. Hatada et al. polymerized MMA with o-vinylbenzylmagnesium chloride in toluene and in THF at −78° producing PMMA macromonomers with one vinylbenzyl group at the α -end of the chain (30). Recently, we have reported the synthesis of hydroxyl-functionalized PMMA by using functionalized initators and subsequent utilization of the hydroxy-PMMA chains as anionic macroinitators to make PMMA-*block*-PEO copolymers with relatively high purity and low polydispersity (15). We have also reported synthesis of functionalized star-branched PMMA by post-polymerization reaction of the linear hydroxy-PMMA living chains with EGDMA (16). In the present work, we have explored the possibility of synthesis of α-hydroxy-ω-styryl PMMA and α-hydroxy-ω-allyl PMMA macromonomers by using functionalized anionic initiators for synthesis of hydroxy-PMMA and subsequent reaction of the living chains with 4-vinylbenzyl chloride and allyl methacrylate.

2 Experimental

2.1 Materials and Purification

2.1.1. *Solvents*

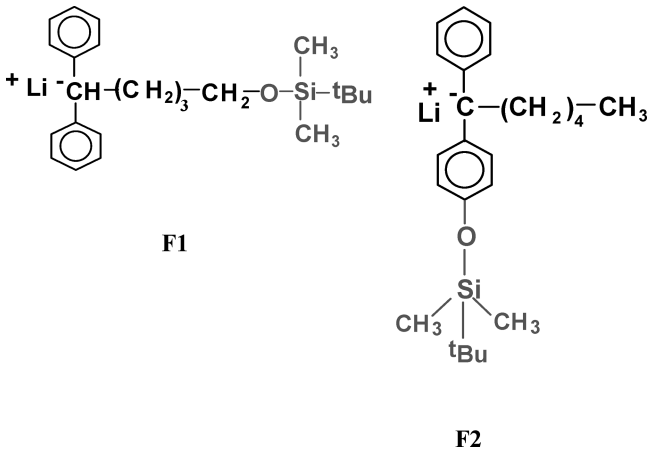
Tetrahydrofuran (THF, S. D. Fine Chem., India) used as solvent for anionic polymerization was first refluxed over calcium hydride and then fractionally distilled and stored over activated molecular sieves. It was further refluxed and then distilled over Na-benzophenone complex. The distilled solvent was then stored under high vacuum over Na-K alloy in graduated solvent storage flasks. The required amount was distilled into ampoules just prior to polymerization reaction.

2.1.2. *Monomer*

Methyl methacrylate (MMA, Schuchardt, Germany) was vacuum-distilled over CaH_2 after proper stirring and stored under N_2 at 0–4°C. Before polymerization, this prepurified monomer was titrated by triethylaluminium (TEA, Schering, Germany) till a persistent greenish yellow color of the TEA- MMA complex indicated the end-point of impurity titration. MMA was then immediately distilled under vacuum into a graduated ampoule portion of a monomer distillation unit before addition to the reactor.

2.1.3. *Initiators*

Diphenylethylene (DPE, Aldrich, USA) was purified by distillation over small amounts of *n*-BuLi. 3-*tert*-butyldimethylsilyloxypropyllithium was purchased from FMC Lithium Division, USA.



Sch. 1. Hydroxy-functional initiators for synthesis of hydroxy-PMMA used for preparing PMMA macromonomers.

2.1.4. *Synthesis of hydroxy-functionalized initiators*

Synthesis of **F1** (**Sch. 1**) involved reaction between 3-(*t*-butyldimethylsilyloxy) propyllithium (FMC, USA) with diphenylethylene in THF at −40°C (15). The protected hydroxy-functional initiator 1-[*p*-(*tert*-butyldimethylsilyloxy)]phenyl-1'-phenyl-hexyllithum or **F2** (**Sch. 1**) was prepared from 4-hydroxy benzophenone as reported earlier (12). All the initiators were standardized by Gilman's double titration method (33).

2.1.5. *Chain-terminators*

4-Vinylbenzyl chloride (4-VBC, Aldrich) and allyl methacrylate (ALMA, Aldrich) were fractionally distilled over CaH_2 under reduced pressure and stored over activated molecular sieves. Before adding to the polymerization system, each of them was freshly distilled under high vacuum over CaH_2.

2.2 Polymerization Procedure

2.2.1. *Preparation of hydroxy-functional PMMA macromonomer*

Anionic polymerization of MMA was done in a bench-top single-neck glass reactor under nitrogen pressure. Transferring of reagents was done under nitrogen pressure using syringes and cannulas. THF was freshly distilled over Na-K alloy and transferred to the reactor with the help of a flame-dried cannula. $LiClO_4$ (10x[moles of initiator]) solution in THF was transferred to the reactor by syringe (31, 32). The temperature of the flask was the brought down to −78°C followed by the addition of the required amount of the functional initiator (**F1** or **F2**). Finally, MMA was added within 5–6 seconds using a flamed cannula into the initiator solution. Details of the polymerization have also been discussed in our previous publication (15). For a typical polymerization, 3.5 gms of MMA (0.33 mol/L), 3 mL of

0.1[M] functional initiator (3×10^{-3} mol/L) were taken in 100 mL THF. $LiClO_4$ was added as an additive to control the polymerization. The polymerizations were continued for 10–15 mins. Subsequently, to the living solutions was added freshly distilled 4-VBC or ALMA in almost equimolar amounts with respect to the initiator. Reactions were continued for additional 2 h in the case of 4-VBC and 0.5 h in the case of ALMA. The reactions were quenched with methanol and the polymers precipitated in *n*-hexane. Subsequently, the polymers were desilylated using tetrabutylammonium fluoride (1[M] solution in THF) in dry THF to liberate the free hydroxy group.

2.3 Analysis

All polymers were characterized by Gel Permeation Chromatography (Thermoseparation Products), equipped with two detectors, UV and RI, and two 60 cm PSS SDV-gel columns: 1 × 100 Å and 1 × linear (10^2 – 10^5 Å) at room temperature. THF was used as eluent at a flow rate of 1mL/min. Standard monodisperse PMMA were used for calibration.

The presence of silyl-protected hydroxy group at one chain-end and styryl or allyl group at the other chain-end of the PMMA macromonomer was determined by ^{1}H NMR (Bruker, 500 MHz) using acetone-d_6 as solvent.

3 Results and Discussion

3.1 Synthesis of Hydroxy-PMMA Macromonomers:

The hydroxy-functionalized PMMA macromonomers were prepared by anionic polymerization of MMA using protected hydroxy-functional initiators, **F1** and **F2 (**Sch. 1**)** in THF as solvent.

α-Hydroxy-ω-styryl PMMA (sample F1-PMVB in Table 1) was synthesized by anionic polymerization of MMA using protected hydroxy-functionalized initiator **F1** at −40°C, followed by termination of the living PMMA chains by **4-VBC**. On the other hand, α-hydroxy-ω-allyl PMMA was synthesized by using protected hydroxy-functionalized initiator **F2** to initiate living anionic polymerization of MMA at −78°C and subsequent reaction of the living chains with ALMA (F2-PMAM in Table 1) such that only one mole of ALMA is reacted with one mole of polymer, followed by quenching of the anionic chain end with methanol. The results of GPC analysis are shown in Table 1. The polymerizations are seen to be sufficiently well-controlled as the resulting polymers show quite narrow molecular weight distribution and a good agreement between observed and targeted molecular weight, i.e., the initiator efficiency is close to 1.0. The yield of the final polymer was usually found to be quantitative as determined gravimetically.

3.2 Reaction with 4-Vinylbenzyl Chloride

Termination of PMMA living chains by 4-VBC was done at −40°C and the reaction was continued for almost 2 h. However, only 50% of the chains were coupled as evident from ^{1}H-NMR (500 MHz, Bruker) of the sample F1-PMVB before deprotection of the hydroxy-function, as shown in Figure 1. The characteristic absorption at δ 5.1–5.8 (two doublets) correspond to the two terminal vinyl protons [marked (a)] of the styryl end-function. The peak at δ 0.0 corresponds to the 6 protons [marked (d)] of the $Si(Me)_2$ group attached to the initiator-end of PMMA chain. The peak intensity per proton of the vinyl group is exactly half of that of the $Si\text{-}(Me)_2$ group, which makes it clear that only half of the hydroxy-PMMA chains have reacted with **4-VBC**. The intensity of ∼2.5 at δ 6.8 is due to one proton (marked b) of the $-CH{=}CH_2$ group and the two phenyl protons (marked c) in **Figure 1**. The remaining 7 phenyl protons of the initiator and the 4 phenyl protons of the styryl end-function appear together near δ 7.0–7.4.

The most probable reason for such partial functionalization is a slow reaction between the enolate ion-pair with **4-VBC** at a temperature of −40°C. Earlier, Andrews et al. (27) had reported that living PMMA chains did not react with **4-VBC**. However, reaction with the corresponding bromide or iodide gave >90% yield of the macromonomer. Later, Ishizu et al. prepared PMMA macromonomers by reacting $Ph_3C^-\ Li^+$ initiated PMMA chains by **4-VBC**, and obtained almost 92% functionalization (29). However, they observed a MWD ∼ 1.1, which was slightly broader than those obtained by us. They explained the failure of this reaction by the previous group as due to insufficient purification of the chloride. However, unlike the polymerization reported by these authors, our polymerization was conducted in the presence of $LiClO_4$ as an additive added in 10 mole excess of the initiator. This enabled us to prepare polymers with sufficiently narrow molecular weight distribution (MWD ∼ 1.07). $LiClO_4$ being a strong Lewis acid complexes effectively with the enolate ion-pairs and establishes

Table 1. Characterization of α -hydroxy-ω - styryl and α -hydroxy-ω -allyl PMMA macromonomers

Sample	$[I]_0 \times 10^{-3}$ *m/L*	$[M]_0 \times 10$ *m/L*	*Temp.* °*C*	*Time of rxn. (mins)*	*Yield %*	$M_{n,theo}$	$M_{n,sec}$	*MWD*	*polymerizable functionality %*
F1-PMVB	6.8	2.54	−40	120	100	3730	4100	1.07	50
F2-PMAM	3.0	1.75	−78	30	100	5800	6000	1.09	∼100

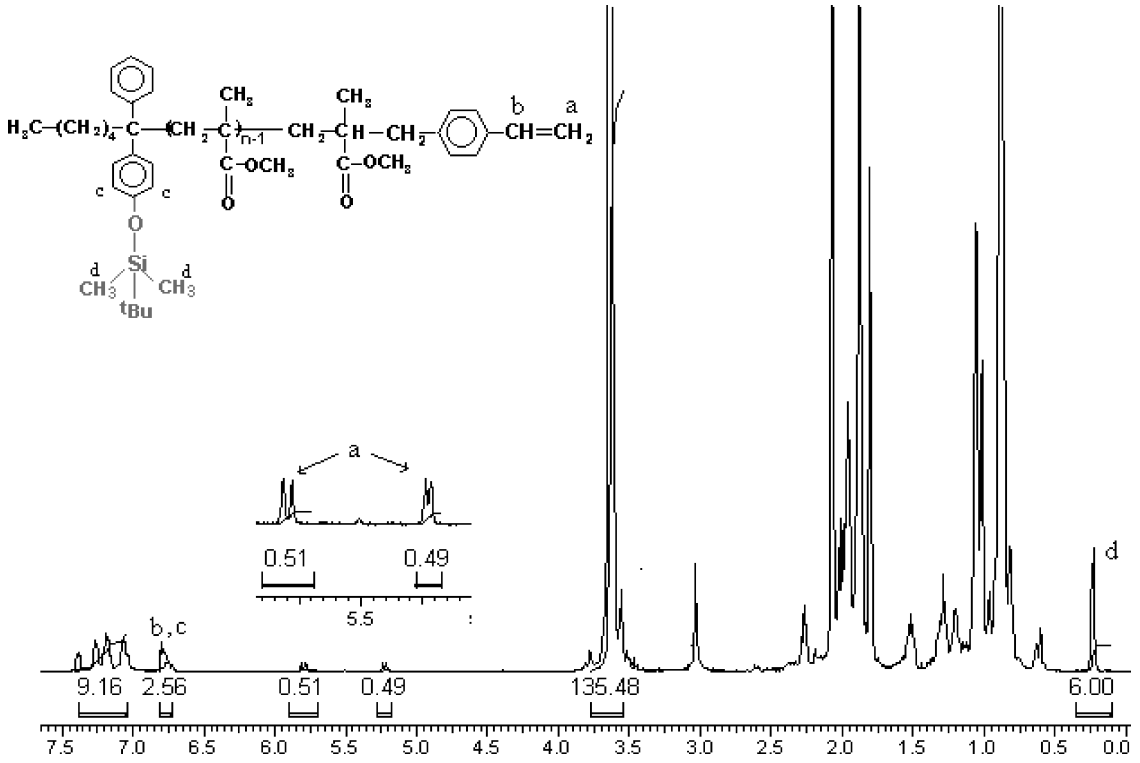


Fig. 1. ^{1}H-NMR (500 MHz, acetone-d_6) of silyl-protected hydroxy-PMMA macromonomer with styryl end-function using functional initiation by F1 followed by electrophilic termination by **4-VBC** (sample F1-PMVB, Table 1)

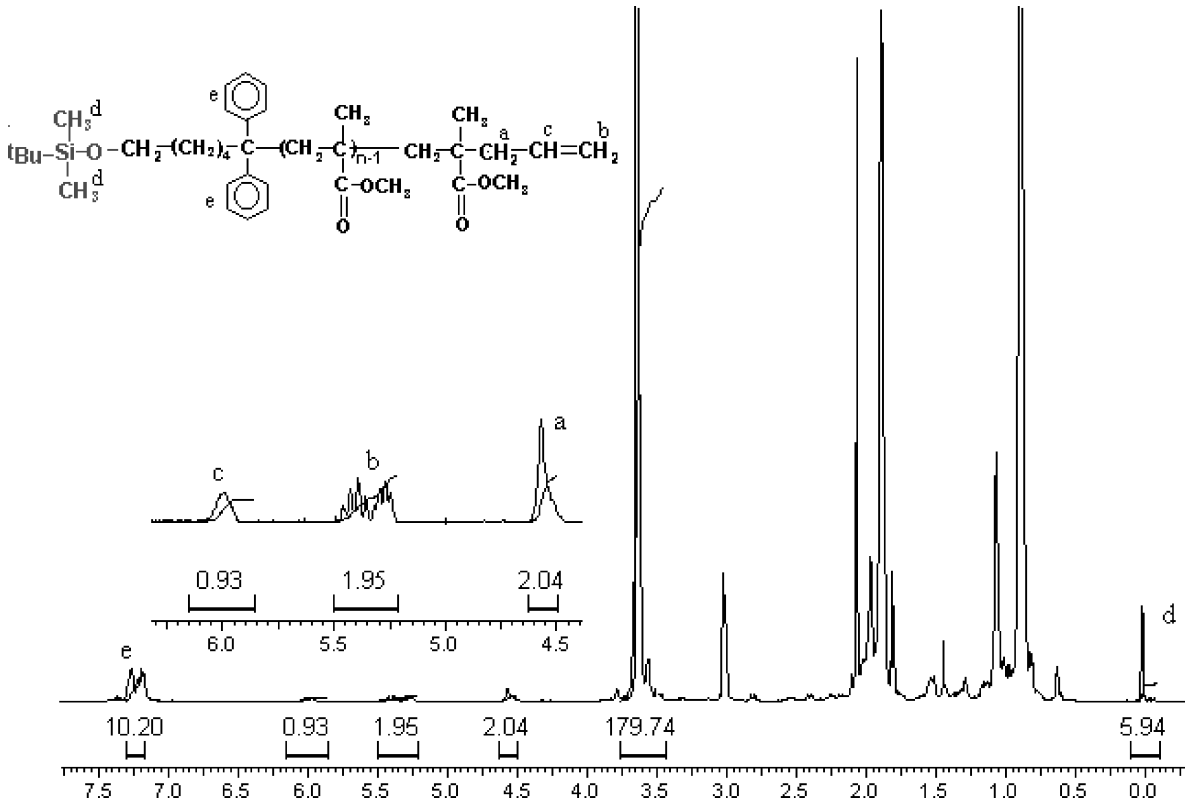


Fig. 2. ^{1}H-NMR (500 MHz, acetone-d_6) of silyl-protected hydroxy-PMMA macromonomer with allyl end-function using functional initiation by **F2** followed by electrophilic termination by ALMA (sample F2-PMAM, Table 1)

a relatively faster equilibrium between the different mixed complexes in solution, thus narrowing down the MWD (31, 32). However, the reason for partial functionalization could not be explained. It is probable that the complexation of the propagating anion with $LiClO_4$ created a sterically hindered environment around the anion that reduced the rate of the nucleophilic substitution reaction with the added chloride. Deprotection of the hydroxy group by TBAF in THF gave PMMA with phenolic hydroxy group at one end and a polymerizable styrene function at the other end.

3.3 Reaction with Allyl Methacrylate

Living chains of protected hydroxy-functionalized PMMA were deactivated by ALMA at −78°C and the reaction was allowed to proceed for 30 min to yield protected hydroxy-PMMA with allyl end-function. The reaction led to almost 100% functionalization by the allyl group, as clearly seen in the ^{1}H-NMR spectra (Fig. 2) of sample F2-PMAM (Table 1).

The characteristic absorption at δ 4.55, δ 5.2–5.5 (two doublets) and δ 6.0 correspond to the allylic protons marked (a), (b), and (c), respectively in structure shown in **Figure 2**. The absorption at δ 0.0 correspond to the 6 protons of -Si(Me)$_2$ groups and at δ 7.1–7.4 is due to the 10 phenyl protons of the initiator moiety attached to the other end of the PMMA chain. The intensity per proton of the phenyl and Si-Me group was almost equal to the peak intensity per proton of the allylic group. This proved the presence of one allyl group per chain of protected hydroxy-PMMA, confirming a quantitative functionalization. Desilylation by TBAF in THF led to liberation of the free hydroxy group yielding α-hydroxy-ω-allyl PMMA macromonomer.

4 Conclusions

Controlled anionic polymerization of MMA with protected hydroxy-functional initiator followed by deactivation of living chains by 4-vinylbenzyl chloride and allyl methacrylate yielded protected hydroxy-PMMA macromonomers with styryl and allyl end-functions, respectively. The propagating enolate ion-pairs reacted with 4-VBC, but the reaction seemed to be slow possibly due to the presence of complexing $LiClO_4$ ligand around the active center. This resulted in only partial (50%) introduction of styryl groups at the chain termini at the end of 2 h. In contrast, allyl end-functionalization reactions using ALMA occurred relatively faster resulting in quantitative functionalization. Such α-hydroxy-ω-styryl/allyl PMMA macromonomers can act as useful precursors for further synthesis of novel block-copolymers and graft-copolymers by utilizing the hydroxy function for further initiation (15, 16) and the polymerizable function for further copolymerization using radical or anionic polymerization methods.

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