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ORIGINAL PAPER

Synthesis of hydroxy-functionalized star-branched PMMA by anionic polymerization

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Abstract Living anionic polymerization has been exploited to synthesize hydroxy end-functionalized PMMA star-branched polymers. 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 used to cross-link ethylene glycol dimethacrylate (EGDMA) in order to form star-branched polymers with cross-linked EGDMA core via 'arm-first' method. The linear arms and the star molecules have been characterized by ^{1}HNMR, GPC, and light scattering. Variation in the number of arms with arm molecular weight and cross-linker loading has been studied. Star-branched PMMA-OH with as many as ~10 arms could be successfully made. Increased molecular weight of PMMA-OH led to decrease in the number of arms incorporated due to increased steric hindrance on the core. Increase in EGDMA concentration slightly increased the arm incorporation.

Keywords Anionic polymerization · Star-branched PMMA · Star polymers

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Introduction

'Living Anionic Polymerization' free of termination and transfer reactions, is one of the most important living polymerization techniques that has enabled synthesis of various architectural polymers as well as functional polymers and macromonomers with high purity, well-defined structures, low compositional heterogeneity, and low polydispersity [1–5]. Functionalization of chain ends using anionic polymerization have drawn lot of interest as it helps in further modification of the polymer chain ends by post-polymerization reactions such as cross-linking or chain extension [6–13]. This enables one to prepare block, graft or star-branched polymers by proper choice of polymerization method depending on the functionality. Recently, polystyrene macromonomers with two or three end functionalities have been made by living anionic polymerization and used for synthesizing branched polymers by polycondensation [14–16]. In general, such functionalities have been introduced either by electrophilic termination of living chains or by using suitable functionalized anionic initiators. Star-shaped polymers exhibit the simplest form of branching and are particularly interesting due to their unique solution and rheological properties [5, 9, 17–19]. Living anionic polymerization enables synthesis of star-branched polymers with narrow MWD and predictable arm length. Well-defined structures make these polymers the best materials for investigations into structure-property relationship of branched polymers. The three generally applied methodologies of preparing star-branched polymers are (1) using multifunctional organometallic compounds to initiate polymerization of several branches, (2) linking living anionic polymers to an electrophilic multifunctional coupling agent, (3) using bis-unsaturated compounds e.g. divinyl benzene to link the living chains.

Anionic polymerization has been successfully utilized to prepare star polymers with high compositional homogeneity and well-controlled structures of the arms and core. The past decade has witnessed intense research on synthesis of well defined star-branched polymers by anionic polymerization using non-polar monomer e.g. styrene and dienes [20–25]. A majority of these have been accomplished by using multifunctional electrophilic linking agents e.g. chlorosilanes. However, synthesis of PMMA star-branched polymers using linking reactions of living PMMA chains with using multifunctional electrophilic linking agents has proved to be challenging [26, 27]. Anionic polymerization of MMA is rendered living only at lower temperatures under stringent reaction conditions that ensures minimum extent of termination [1, 2, 28, 29] and under such conditions many of these linking reactions do not occur efficiently. Possibly, the bulky nature of the methacrylate chain ends also plays a role in preventing easy synthesis of star-branched polymers using multifunctional linking agents. Moreover, in such techniques, the maximum number of arms in the star-molecule is dictated by the number of electrophilic sites available for coupling. Keeping these various drawbacks in mind, majority of the PMMA stars, a few of them bearing hydroxyl functionalities at the chain termini, have been synthesized either by GTP, or using living chains of predetermined arm length to initiate anionically the cross-linking of the core by "arm-first" method [10, 11, 30–32]. Simms et al. [30] reported synthesis of star-branched copolymers of methyl and ethyl methacrylates by group transfer polymerization of MMA and by subsequent linking of the living arms using ethylene glycol dimethacrylate (EGDMA). GTP enabled the reaction to be performed at 25 °C resulting in a star polymer with large number of arms, but the polydispersity was high and the viscosity increased upon storage. Later, PMMA stars were prepared by anionically polymerizing MMA and linking the living chains with EGDMA [31]. The effect of arm length and EGDMA concentration on the degree of branching was studied. Using functional initiators for anionic polymerization of MMA and coupling the living chains using EGDMA, Quirk et al. [10, 11] prepared PMMA stars with hydroxy group at the end of each chain. However, no detailed study was done and polymerization data was limited.

Recently, we have reported the synthesis of hydroxyl-functionalized PMMA by using hydroxyl-functional initators [33]. We had also demonstrated the successive utilization of these functionalized PMMA chains as anionic macro-initators to make PMMA-*block*-PEO copolymers with relatively high purity and low polydispersity. In the present work, we have explored the synthesis of star-branched polymers using the hydroxy-functional PMMA as a precursor and EGDMA as cross-linker. Initiators with protected hydroxyl functions have been used to synthesize the hydroxyl functionalized PMMA living chains. Both primary –OH as well as phenolic –OH group were introduced at the PMMA chain ends using the respective initiators and subsequently the living chains were used to cross-link EGDMA. The effects of increase in arm length and concentration of EGDMA on the number of arms have been investigated.

Experimental

Materials and purification

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. Required amount was distilled into ampoules just prior to polymerization reaction.

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 pre-purified 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.

Cross-linkers

Ethylene glycol dimethacrylate (Aldrich, USA) was fractionally distilled over CaH_2 under reduced pressure and stored over activated molecular sieves. Before adding to the polymerization system, it was distilled under high vacuum over CaH_2.

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.

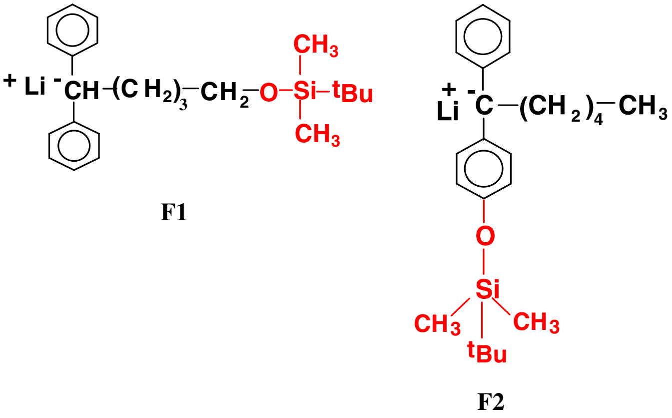
Synthesis of hydroxy-functionalized initiators

Synthesis of **F1** (Scheme 1) involved reaction between 3-(*t*-butyldimethylsilyloxy) propyllithium (FMC, USA) with DPE in THF at −40 °C [32]. The protected hydroxy-functional initiator 1-[*p*-(*tert*-butyldimethylsilyloxy)]phenyl-1′-phenylhexyllithum (**F2**, Scheme 1) was prepared from 4-hydroxy benzophenone as reported earlier [12]. All the initiators were standardized by Gilman's double titration method [34].

Polymerization procedure

Procedure for synthesis of hydroxy-functionalized star-branched polymer

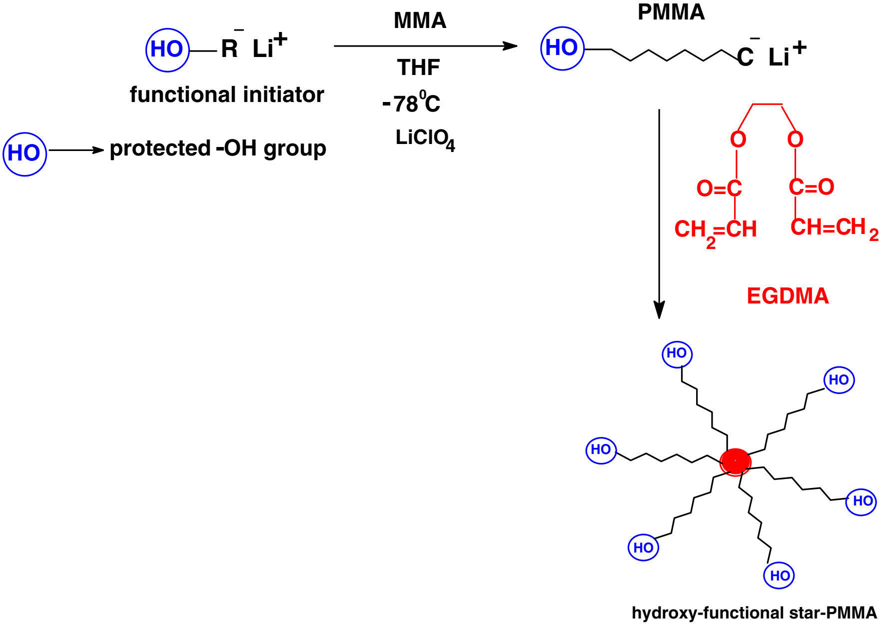
Anionic polymerization of MMA was done in a bench-top single-neck glass reactor under nitrogen pressure. Transferring of reagents was done under nitrogen pressure using syringes and cannulas. THF was freshly distilled over Na–K alloy and transferred to the reactor with the help of a flame-dried cannula. $LiClO_4$



Scheme 1 Hydroxy-functional initiators for synthesis of precursor hydroxy-PMMA used for preparing PMMA star-branched polymers

[10×(initiator)] solution in THF was transferred to the reactor by syringe. The temperature of the flask was then brought down to −78 °C followed by addition of required amount of the functional initiator (**F1** or **F2**). Finally MMA was added within 5–6 s using a flamed cannula into the initiator solution. Details of the polymerization have also been discussed in our previous publication [33]. For a typical polymerization, 3.5 g 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 in ten times excess (moles) over DPHLi and acts as additive to control the polymerization [28]. The ratio of monomer to initiator was adjusted according to the targeted molecular weight. The polymerizations were continued for 10–15 min and then to the living solution was added freshly distilled EGDMA diluted with THF dropwise under constant stirring. The reaction is represented in Scheme 2. The molar concentration of EGDMA was maintained at 3:1 or 6:1 ratio with respect to the initiator. Typically, 0.16 mL of EGDMA (9×10^{-3} mol/L) dissolved in 0.5 mL THF was added when a 3:1 ratio over the initiator was maintained. The reaction was continued at −78 °C for another 30 min before it was quenched by methanol. The polymers were precipitated in *n*-hexane and dried in vacuum-oven to determine the conversion gravimetrically. The polymers were desilylated using tetrabutylammonium fluoride (TBAF, 1 M solution in THF) in dry THF to liberate the free hydroxy group.

Purification of the star polymers was necessary to remove contamination by a small amount of linear polymer corresponding to the arms. This was done in the usual manner by solvent–non-solvent fractionation by adding methanol to a dilute (~1.0% by weight) solution of the star in toluene.



Scheme 2 Preparation of hydroxy-PMMA and star-branched PMMA

Analysis

All polymers were characterized by Gel Permeation Chromatography (GPC, 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 1 mL/min. Standard monodisperse poly(methyl methacrylate)s (Polymer Standards Service) were used for calibration.

The functionality of the linear protected-hydroxy PMMA was determined by ^{1}H NMR (Bruker, 200 MHz). The star-branched PMMA were characterized by light scattering using Malvern Photon Correlation Spectrophotometer, Model 4700, at a wavelength of 488 nm using THF as solvent. The weight average molecular weights were obtained using a Debye plot. The dn/dc value of PMMA in THF was 0.088 as obtained from literature. Titration of the hydroxy group (ASTM Standard E222-73, 1979) was done to determine the average number of arms of the star.

Results and discussion

Synthesis of star-branched hydroxy-PMMA: coupling of living chains of silyl-protected hydroxy-PMMA chains by EGDMA gave PMMA star polymers with protected-hydroxy group at the end of each arm of the star. The results of synthesis of living PMMA using protected hydroxy-functionalized initiators have been thoroughly discussed in our previous publication [33]. The presence of a protected hydroxy-function at the precursor PMMA chain-end was determined by ^{1}H NMR of an aliquot taken before adding the EGDMA solution. For example, Fig. 1 shows the ^{1}H NMR spectrum for the linear hydroxy-PMMA ($\overline{M}_{w,sec} = 11,700$) precursor of PMMA star, F1–S3 (Table 1) prepared using initiator **F1**. The chemical shift at δ 7.1–7.4 corresponds to ten phenyl protons from the initiator moiety, and that at δ 0.0 is due to the six protons of two Si–Me groups of the hydroxy-protecting group. The absorption at δ 3.58 is due to the –OMe protons of the methacrylate chain. Thus the spectrum is consistent with quantitatively functionalized hydroxy-PMMA. Functional initiator **F1** was used for the first five runs in Table 1 and the arm molecular weights were varied from 7,000 to 20,000 by changing the molar concentration of monomer versus initiator. The molar ratio of the cross-linker EGDMA to the initiator was usually maintained at 3:1, with one reaction being performed using 6:1 ratio (sample F1–S5, Table 1). Initiator **F2** was used to prepare the precursor hydroxy-PMMA for the star polymers F2–S1 and F2–S2 (Table 1), using 3:1 and 6:1 molar ratio of EGDMA to initiator, respectively.

The GPC analysis of the all the unfractionated stars showed contamination by small amount of residual arm material. The chromatograms for the star-PMMA samples F1–S2 and F1–S3 are shown in Figs. 2a and 3a, respectively. The presence of unreacted linear chains along with the star-branched polymer has been earlier reported during synthesis of PMMA star-branched polymers using EGDMA as cross-linking agent [31]. The authors attributed this phenomenon to steric effect rather than chain-deactivation due to introduction of impurities during or before

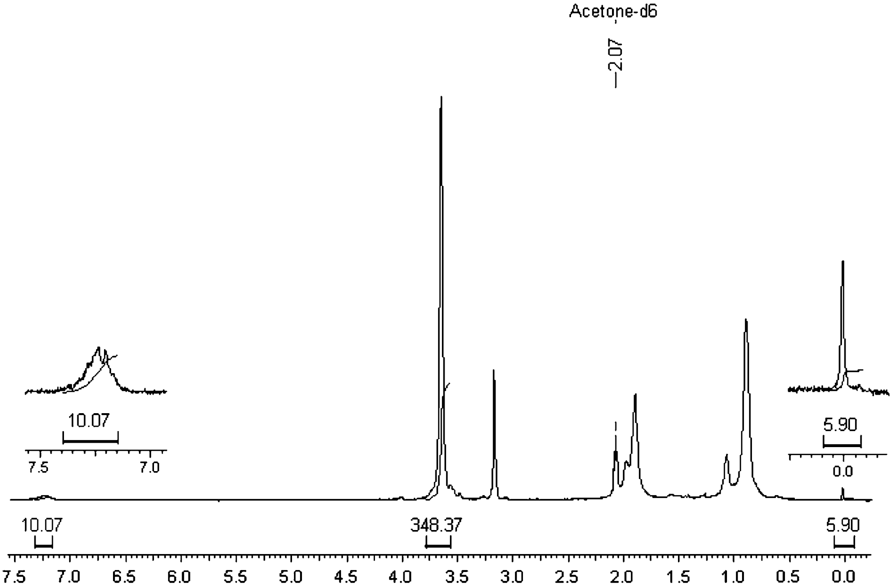


Fig. 1 ^{1}H NMR spectra (200 MHz, acetone-d_6) for linear silyl-protected hydroxy-PMMA prepared using functional initiator F1. Subsequent linking by EGDMA produces hydroxy-functionalized star-PMMA (sample F1–S3, Table 1)

Table 1 Molecular weights, polydispersities and degree of branching of hydroxy-PMMA stars and precursor PMMA-OH

Sample	EGDMA/ initiator	Linear-PMMA			Star-PMMA				No. of arms (by –OH titrn.)
		$\overline{M}_n$ (sec)	$\overline{M}_w$ (sec)	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w$ (sec) $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$ (sec)	$\overline{M}_w$(LS) $\times 10^{-3}$	$\bar{f}_w$[a]	
F1–S1	3:1	7,000	7,600	1.09	55.0	1.11	74.6	9.8	9.3
F1–S2	3:1	8,500	9,100	1.07	54.5	1.12	70.0	7.7	7.4
F1–S3	3:1	11,000	11,700	1.07	60.0	1.09	75.4	6.4	6.0
F1–S4	3:1	19,700	21,000	1.07	97.8	1.15	120.0	5.7	–
F1–S5	6:1	8,600	9,400	1.08	75.0	1.10	90.0	9.5	9.0
F2–S1	3:1	5,100	5,500	1.08	35.0	1.10	39.0	7.1	–
F2–S2	6:1	5,000	5,500	1.09	48.0	1.12	–	–	9.4

[a] $f_w = \overline{M}_{w,LS}(\text{star})/\overline{M}_{w,\text{sec}}(\text{arm})$

addition of cross-linker. In fact, with increase in the number of arms, the central cross-linked core becomes sterically more congested and resists further incorporation of arms. Hence, some unreacted chains are usually left behind along with the required star-branched polymer. The protected hydroxy end-functions were deprotected by treatment with tetrabutylammonium fluoride to form the stars with free hydroxy groups at the chain-ends. This was then followed by fractionation of the star polymers to separate the pure star from the residual arms. The GPC chromatogram of the pure hydroxy-PMMA star polymers F1–S2 and F1–S3 are

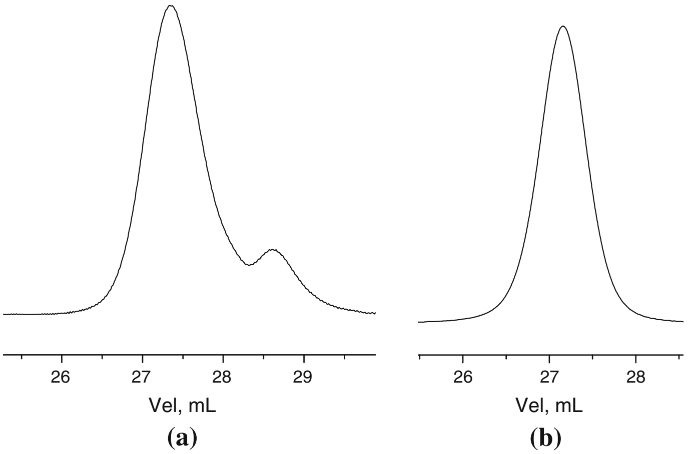


Fig. 2 GPC chromatograms of PMMA star (sample F1–S2, Table 1); **a** unfractionated PMMA star with residual arm material where $\overline{M}_{w,\,sec}$ (arm) = 9,100; **b** pure PMMA star after fractionation

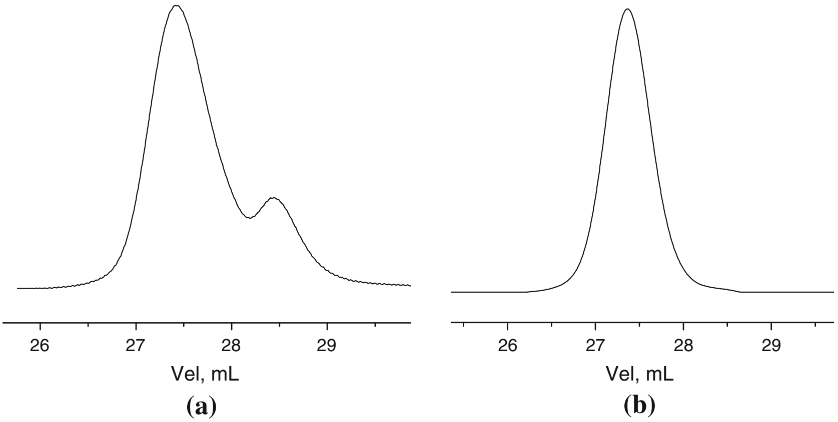


Fig. 3 GPC chromatograms of PMMA star (sample F1–S3, Table 1); **a** unfractionated PMMA star with residual arm material where $\overline{M}_{w,\,sec}$ (arm) = 11,700; **b** pure PMMA star after fractionation

shown in Figs. 2b and 3b, respectively. No peak corresponding to residual linear PMMA could be detected in the chromatogram of the fractionated star, which proved that the purification of the stars polymers could be successfully done using solvent/non-solvent fractionation. In fact, the presence of hydroxy end-groups obtained after desilylation aids in the separation of the star from the linear polymer. The solubility of the hydroxy-PMMA stars in the mixed solvent of methanol and toluene is a function of molecular weight. The linear hydroxy-PMMA is sufficiently soluble in the alcoholic medium, but the star polymer is insoluble. Hence the separation becomes convenient. Table 1 shows the molecular weights, polydispersities and degree of branching of the pure hydroxy-PMMA star-branched polymers as analyzed by GPC, light scattering and end-group titration methods. The molecular weight and MWD of the arms of each star-branched PMMA sample were determined by GPC analysis of PMMA recovered from a aliquot taken from the PMMA living solution prior to EGDMA addition. Syringing out of aliquots prior to EGDMA addition was usually avoided in order to prevent quenching of the active centers due to additional manipulation.

The molecular weight distribution of the arms is seen to be quite narrow, usually $1.07 \leq \overline{M}_w/\overline{M}_n \leq 1.09$. The polydispersity indices of the star polymers are also less, typically in the range of $\overline{M}_w/\overline{M}_n \sim 1.1$–$1.2$, in contrast to polydispersity indices greater than 2.0 reported earlier for PMMA stars [31]. The weight average number of arms, f_w is calculated by dividing the $\overline{M}_w$ of the star as measured by light scattering, with that of the $\overline{M}_{w,\mathrm{sec}}$ of the respective arm. Titration of the –OH groups present at the terminus of each arm of the fractionated hydroxy-PMMA star was done for most of the samples, and the degree of branching calculated therefrom was found to be close to those calculated on the basis of light scattering data. Thus star-branched PMMA with as high as nine arms and low PDI could be obtained by using the functional initiators followed by EGDMA as cross-linker.

Effect of arm length

The results for the first four samples F1–S1 to F1–S4 in Table 1 show that for a given ratio of EGDMA to initiator, the number of arms increases with a decrease in the arm molecular weight. Compared to smaller arms, the larger arms shield the core to a greater extent, i.e. they exert greater steric hindrance to incoming chains and thereby allow lesser number of arms to get linked to the core. Due to the same reason, a greater amount of the residual or unreacted arms in the star polymer are seen in case of higher arm length, as shown in Fig. 4, as compared to the residual arm concentration shown in Figs. 2 and 3.

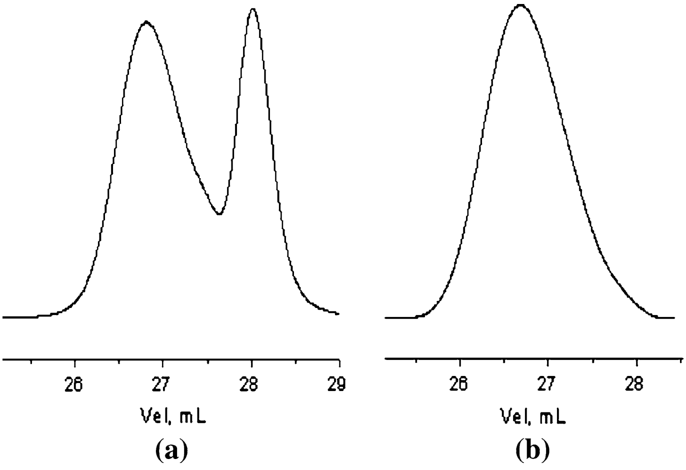


Fig. 4 GPC chromatograms of PMMA star sample F1–S4 (Table 1); **a** unfractionated PMMA star with residual arm material where $M_{w,sec}$ (arm) = 21,000; **b** pure star after fractionation

This effect of arm molecular weight on the degree of branching was observed by Mays et al. [31] while synthesizing PMMA stars. The authors observed a decrease in the number of arms from 18.7 to 6.7 for an increase in the arm molecular weight from 10,000 to 40,000. However, the number of arms of the PMMA stars observed by them is significantly greater than those observed by us for hydroxy-PMMA stars, for a similar arm length and ratio of EGDMA to initiator. In fact, our results agree well with those of Quirk et al. [10, 11] who have reported results of only one polymerization using hydroxy-PMMA of $M_{n,sec} = 8{,}000$ and obtained almost 10.7 arms for the corresponding star using EGDMA as cross-linker. A lower number of arms observed for hydroxy-functionalized star-branched PMMA than for unfunctionalized star-branched PMMA [31] can be explained on basis of additional shielding of the core surface by the bulky terminal functionality. Unlike a simple PMMA molecule, each hydroxy end-functionalized PMMA chain, in our case, contains a bulky *t*-butyldimethylsilyl group protecting the hydroxy function. It is possible that the functionalized PMMA chains that were already incorporated onto an EGDMA core caused greater steric crowding at the core surface compared to unfunctionalized PMMA of similar molecular weight, due to the bulky terminal group attached to each chain. As a consequence, further approach of any linear PMMA chain toward the core would be resisted to a greater extent, resulting in star molecules containing relatively lower number of arms compared to those in case of unfunctionalized PMMA [31].

Effect of EGDMA to initiator ratio

The molar ratio of EGDMA to the initiator at a given arm length is also seen to have some effect on the degree of branching. An increase in this ratio for a given arm molecular weight leads to a small but finite increase in the number of arms of the hydroxy PMMA star polymer. As evident from Table 1, for PMMA star polymers F1–S2 and F1–S5 prepared using **F1**, the number of arms increases from 7 to 9 on increasing the ratio from 3:1 to 6:1, for an arm molecular weight of about 9,000–9,500. A similar observation is made with the samples F2–S1 and F2–S2 prepared using initiator **F2** and adding EGDMA at 3:1 and 6:1 mole ratio, respectively with respect to the initiator. This is due to the fact that an increase in the amount of the bis-unsaturated monomer with respect to the chain-end concentration leads to greater size of the core and, hence, provides more space for accommodating a greater number of arms.

Conclusion

Well-defined star-branched PMMA with protected hydroxy groups at the outer end of each arm have been successfully prepared by one-pot synthesis, using protected hydroxy-functional initiators followed by cross-linking of the living PMMA anions by bis-unsaturated monomer, EGDMA. Subsequent deprotection using TBAF solution generated the free hydroxyl functionalities at the end of each arm. Both phenolic as well as primary –OH groups could be successfully introduced at the chain-ends by using the corresponding initiators. The number of arms has been varied by changing either the arm molecular weight or the molar ratio of EGDMA to initiator. Smaller arms exert less steric hindrance to incoming arms, thus leading to an increase in the number of arms per core, leaving a relatively smaller amount of unreacted linear chains in the system. Also, an increase in the cross-linker concentration with respect to the active centers, led to a larger core size and hence more space for accommodating higher number of arms. However, in reactions performed under nitrogen atmosphere where reagent transfers were done by syringes and cannulas, it was difficult to maintain the perfect livingness of the system during and after addition of a reagent. Thus, addition of EGDMA solution is THF is sure to introduce a small, but finite amount of impurities that quenched some of the active centers. Consequently the number of arms obtained are restricted and do not show any significant increase on increasing the concentration of the cross-linking agent even to twice the original amount. This problem may be circumvented by using high vacuum techniques. The terminal hydroxyl functionalities at the periphery of the star molecule can induce better solubility characteristics to the PMMA star-branched molecule. Moreover these hydroxyl groups may be further transformed to the respective oxyanion and used to initiate anionic polymerization of new monomers e.g. anionic ring-opening polymerization of ethylene oxide to form PMMA-PEO star-block copolymers.

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