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Reactive Polymers Bearing Styrene Pendants through Selective Anionic Polymerization of 4-Vinylbenzyl Methacrylate

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S *Supporting Information*

ABSTRACT: Selective anionic polymerization of 4-vinyl-benzyl methacrylate at methacrylate site has been achieved using resonance stabilized anionic initiators such as 1,1-diphenylhexyllithium (DPHLi) and tritylpotassium (TritylK) in tetrahydrofuran (THF) at -78 °C. Polymerization proceeded selectively through methacrylate functionality of the monomer in a controlled manner and produced polymers and copolymers with narrow molecular weight distribution at low temperatures (≤ -40 °C). ^{1}H NMR of the polymer showed the presence of styrene pendants in every monomeric repeating unit. The polymerization results confirm that the resonance stabilized carbanions with an optimum pK_a ($30 \leq pK_a \leq 32$) of their conjugate acids such as DPHLi and TritylK do not react with styrene functionality at -78 °C. The selective initiation without cross-linking is attributed to the differences in the electronegativity between polar methacrylate and styrene functionalities and an attenuation of initiator reactivity at low temperature. Poly(4-vinylbenzyl methacrylate) and its copolymers with the vinyl pendant in close proximity with ester linkage are very reactive and unstable, readily undergoing cross-linking in solution or in solid state with or without a radical initiator.
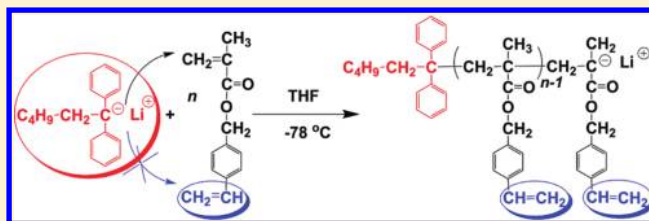
INTRODUCTION

Polymers having polymerizable functional groups at their repeat units are of significant interest as they can be used as thermally reactive polymers in many applications such as cross-linked adsorbents, controlled postgrafting, immobilization of bioactives, and thermal cross-linking agent in the production of high-refractive-index transparent organic glass.[1−3] However, synthesis of polymers with reactive vinyl group at every repeating unit remains a challenge for chemists, and only in a few cases have such polymers been synthesized.[4−6]

Reactive vinyl group containing polymers can be made via either postattachment of a monomer moiety at the repeat units or selective initiation of divinyl monomers. Selective polymerization of one vinyl group in divinyl monomers is a straightforward method. Nevertheless, the reactivity of vinyl groups present in the difunctional monomer must be drastically different otherwise cross-linking will dominate the course of the polymerization.[1,7−10] The difunctional monomers such as divinylbenzene (1,3- and 1,4-isomers),[11−13] diisopropylbenzene (1,3- and 1,4-isomers),[4,14−16] allyl methacrylate,[17] 4-(α-alkylvinyl)styrene,[18] 4-(1-alkynyl)styrenes,[19] and 4-vinylbenzyl methacrylate[9] have been used for selective initiation in the past. Although the reactivity of the vinyl groups in these difunctional monomers differs considerably, reactive radical initiators do not allow initiation of one of the vinyl groups selectively.[20−22] Linear polymers of ethylene glycol dimethacrylate, and ethylene glycol 4-vinylbenozate methacrylate have been prepared with a pendant vinyl group through protection of methacrylate functionality with cyclodextrin via inclusion complex.[23] One of the double bonds of 2,5-norbornadiene has been copolymerized with ethylene successfully using metallocene catalyst as an initiator.[24]

Synthesis of linear polymer from difunctional monomers is possible in some cases with anionic initiators.[4,14] Polymerization of 1,3-diisopropenylbenzene using n-butyllithium as anionic initiator in tetrahydrofuran (THF) at a low temperature produced polymer with pendant vinyl groups.[14] Recently, Hirao and co-workers have successfully polymerized 1,4-divinylbenzene selectively through one of its vinyl groups using oligo(α-methylstyryl)lithium initiator complexed with 11-fold excess of potassium *tert*-butoxide.[13] In these cases, the reactivity modulations were achieved through stabilization of anions and ion-pair complexation.

Zhang and Ruckenstein reported selective anionic polymerization of 4-(vinylphenyl)-1-butene at its styrene functionality.[6] The reactivity of the two vinyl groups is substantially different, the olefinic unsaturation being nonreactive. It was possible to selectively initiate styrene polymerization using an anionic initiator. Group transfer polymerization (GTP) using silylketene acetal is effective for polar vinyl monomers such as alkyl (math)acrylates and is ineffective for the polymerization of nonpolar monomer such as styrene.[25] Pugh and Percec polymerized 4-vinylbenzyl methacrylate (VBMA) through its methacrylate double bond using GTP and obtained polymers

Scheme 1. Anionic Polymerization of 4-Vinylbenzyl Methacrylate Using DPHLi as Initiator in THF at −78 °C
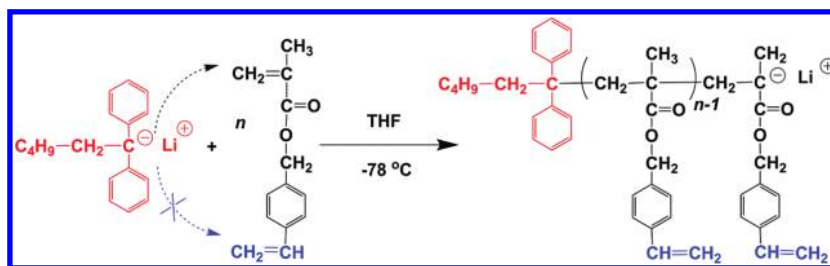
with bimodal molecular weight distribution ($M_w/M_n = 8.3$) and incomplete monomer conversion.[9] Nonetheless, they prepared successfully controlled molecular weight copolymers of VBMA with methyl methacrylate (MMA). It is also known, based on the relative pK_a values of conjugate acids of propagating enolate (~30) and styryl anions (~44),[26] that the propagating methacrylate anion is not nucleophilic enough to initiate the polymerization of styrene.[27−29] Therefore, a selective initiation is critical in the anionic polymerization of VBMA to produce polymer with styrene pendants.

Herein, we report selective anionic polymerization of VBMA at its polar vinyl functionality using 1,1-diphenylhexyllithium (DPHLi) and tritylpotassium (TritylK) as initiators in THF at −78 °C (Scheme 1).[30] Although DPHLi is routinely used as the initiator for the anionic polymerization of acrylates and methyl methacrylates, it is also known to initiate styrene polymerization in THF at 0 °C.[31] At lower temperature, the reactivity of stabilized anions such as diphenylhexyl or trityl carbanions can be moderated to selectively polymerize VBMA at its methacrylate site.

■ EXPERIMENTAL SECTION

Materials. Tetrahydrofuran (THF, SD Fine Chemicals, India) was fractionated, refluxed over K metal, and stored over fresh Na−K alloy in a vacuum line. N_2 gas (Industrial Oxygen, Pune) was purified by passing through a heated column containing Cu (200 °C) (2 × 1 m) and a column containing A4 molecular sieves (2 × 1 m) and was finally bubbled through a toluene solution of oligostyryllithium anion. 1,1-Diphenylethylene (DPE, Aldrich) was distilling over a small amount of nBuLi under high vacuum. p-Chloromethylstyrene (Aldrich) was distilled over CaH_2 under vacuum, and methacrylic acid (Aldrich) was used as received. $LiClO_4$ (Aldrich) was dried under dynamic high vacuum overnight at 100 °C and then dissolved in a known amount of dry THF. Triphenylmethane (Aldrich) was dried under high vacuum for 2 days at room temperature. Triphenylmethylpotassium was prepared by reacting potassium mirrors and triphenylmethane in THF at room temperature under vacuum. The excess metal was filtered off, and the initiator solution was stored under pure nitrogen. DPHLi initiator was prepared by reacting nBuLi with an equimolar amount of DPE in THF at −40 °C and stored under a pure nitrogen atmosphere in a refrigerator.

4-Vinylbenzyl methacrylate (VBMA) was synthesized following Pugh and Percec[9] reported procedure using p-chloromethylstyrene and potassium methacrylate in THF and dimethyl sulfoxide as a mixed solvent in the presence of tetrabutylammonium hydrogen sulfate. VBMA was obtained in 70% yield. The obtained VBMA was stirred over a small amount of CaH_2 for 4−6 h under vacuum at 0 °C. Subsequently, it was distilled under dynamic vacuum at 60 °C just prior to the polymerization. It was noticed ~10% of monomer underwent thermal polymerization during distillation. Attempts to purify this monomer using trialkylaluminum treatment failed due to excessive thermal polymerization during distillation.

Methyl methacrylate (MMA, Aldrich) was first distilled under vacuum from CaH_2 after stirring for 12 h at room temperature and then stored under a nitrogen atmosphere at −10 °C. The required

amount of the distilled MMA was taken into a flask to which triisobutylaluminum or 10 wt % $AlEt_3$ solution in hexane was added drop by drop until a persistent yellowish-green color was observed. MMA was redistilled under reduced pressure, just prior to polymerization experiments.

Polymerization. The polymerizations were carried out in a flamed glass reactor under a pure nitrogen atmosphere. Solvent, initiator, $LiClO_4$ solution in THF, and monomer were transferred by capillary technique or syringe. The required amount of a solution of $LiClO_4$ in THF was added into a single-neck round-bottom flask containing 100 mL of THF. DPHLi solution was added drop by drop until a persistent red color was observed. Subsequently, the required amount of the initiator was added and the reactor was brought to a desired temperature (−78, or −40, or −20 °C). The purified neat VBMA was added to the initiator solution using a stainless steel cannula under N_2 pressure. The reaction was terminated after 15 min with degassed methanol. In case of block copolymerization, a small amount of sample was withdrawn for analysis, and MMA was added into the reactor and terminated after 30 min with degassed methanol. Poly(4-vinylbenzyl methacrylate) (PVBMA) and poly(4-vinylbenzyl methacrylate-b-methyl methacrylate) were recovered by stripping off the solvent, dissolving the residue in a small amount of benzene (10 mL), and freeze-drying at 0 °C. The polymer was not dried in the vacuum as it was noticed in a few early experiments that the polymer underwent thermal cross-linking at 80 °C during drying.

Measurements. Characterization of polymers was carried out using size exclusion chromatography (SEC) consisting of a ThermoSeparation's Spectra System P100 pump, an AS 300 autosampler, a UV-100 detector, and a RI-150 refractive index detector with either $10^2−10^5$ linear Å 60 cm and 100 Å 60 cm 5 μm PSS-SDV gel columns or with series of 10^6, 10^4, 10^3, 500, and 100 Å 30 cm 5 μm PSS-SDV gel columns. The data were processed using Polymer Standards Service software (PSS WinGPC). THF was used as the mobile phase at a flow rate of 1 mL min^{-1} at 30 °C. Standard monodisperse poly(styrene)s (PL, UK) were used for calibration. ^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker 300 MHz spectrometer. A TA Instruments Q10 differential scanning calorimeter (DSC) was used at a heating rate of 10 °C/min. The glass transition temperature (T_g) was measured in first heating scan from 0 to 250 °C. The second heating cycle did not show any endothermic peak due to cross-linking reaction during first heating to 250 °C. The midpoint of endothermic transition was considered as T_g. DSC was calibrated using indium as standard for temperature and enthalpy. A TA Instruments TGA Q5000IR was used to determine thermal degradation of PVBMA in air at a heating rate of 10 °C/min.

■ RESULTS AND DISCUSSION

Attenuation of DPHLi Reactivity at −78 °C. To find a most suitable reaction condition for selective initiation of VBMA, the reactivity of DPHLi with styrene was first examined in THF at −78 °C. Accordingly, purified styrene (3 mL) was added under nitrogen into THF (100 mL) containing DPHLi (3.7×10^{-4} mol) at −78 °C. It was found that the red color of the initiator remained unchanged after addition of styrene. As the colors of DPHLi and styryl anions are similar, it is difficult to ascertain the initiation process visually. Nevertheless, the

reaction after termination did not produce any polymer when precipitated in excess methanol. The analysis of the crude reaction mixture by SEC confirmed the absence of polystyrene and established the inability of DPHLi to initiate styrene polymerization in THF at −78 °C.

Selective Anionic Polymerization of VBMA. Based on this observation, selective anionic initiation of VBMA was attempted using DPHLi and TritylK as initiators in THF at −78 °C (Table 1). Polymerizations were performed in the

Table 1. Anionic Polymerization of 4-Vinylbenzyl Methacrylate (M) Using DPHLi and TritylK as Initiators (I) in the Presence of LiClO$_4$ ([LiClO$_4$]$_0$/[I]$_0$ = 10) in THF at −78 °C^a

run	[I] × 10^3 (mol/L)	[M] (mol/L)	T (°C)	$M_{n,th}{}^b$ (g/mol)	$M_{n,SEC}{}^c$ (g/mol)	M_w/M_n	f^d
1	1.24	0.115	−78	18 700	19 300	1.19	0.97
2	5.72	0.216	−78	7 640	8 300	1.18	0.92
3^e	5.07	0.091	−78	3 600	5 100	1.15	0.70
4^f	1.75	0.189	−78	21 800	25 100	1.20	0.87
5^f	2.54	0.189	−78	15 000	16 600	1.17	0.90
6	1.83	0.096	−40	10 570	20 800	1.21	0.51
7	1.83	0.096	−20	10 570	89 000	1.82	0.12

^{a}Polymer was freeze-dried from benzene for 10 h. $^b M_{n,th}$ = grams of monomer/mole of initiator. ^{c}Apparent molecular weight obtained using SEC calibrated with standard PMMA. ^{d}Initiator efficiency, f = $M_{n,th}/M_{n,SEC}$. ^{e}In the absence of LiClO$_4$ additive. ^{f}TritylK was used as initiator.

presence of excess LiClO$_4$ to control the equilibrium dynamics of propagating enolate anions.[32] Upon addition of VBMA into the DPHLi solution in THF (Scheme 1), the red color of the

initiator disappeared, immediately indicating a fast initiation at the methacrylate functionality. The viscosity of the homogeneous polymerization solution slightly increased during the polymerization. After termination, poly(4-vinylbenzyl methacrylate) (PVBMA) was recovered by precipitation in excess methanol; the gravimetric yield indicated that the conversion was nearly 100%.

The ^{1}H NMR of the synthesized PVBMA showed an absence of signals at 5.6 and 6.18 ppm (b) corresponding to methacrylate vinyl protons and an appearance of new signals for the backbone aliphatic protons at ∼1 ppm (a) and 1.5 ppm (b). The signals corresponding to the styrene moiety at 5.2, 5.7 ppm (doublets, f) and 6.6 ppm (multiplet, e) are intact in the PVBMAs indicating the styrene pendants were not involved in the polymerization. Furthermore, the proton intensity of the methyl group matched with the vinyl protons of the styrene pendants (Figure 1). Several batch polymerizations were performed. The results are given in Table 1. The obtained PVBMA was completely soluble in solvents such as THF, chloroform, toluene, and benzene, indicating an absence of cross-linking.

The number-average molecular weights (M_n) of PVBMAs were determined using size exclusion chromatography (SEC) with respect to poly(methyl methacrylate) standards, and hence they are apparent ones. However, they agreed well with the molecular weight calculated ($M_{n,th}$) on the basis of the concentration of monomer to the initiator in the feed, indicating the PVBMA has a similar hydrodynamic volume compared to PMMA. As shown in the Table 1, the (PVBMA)s exhibited narrow molecular weight distribution (MWD) ($M_w/M_n < 1.2$) without high molecular weight fraction, indicating the absence of cross-linking during the polymerization at −78 °C
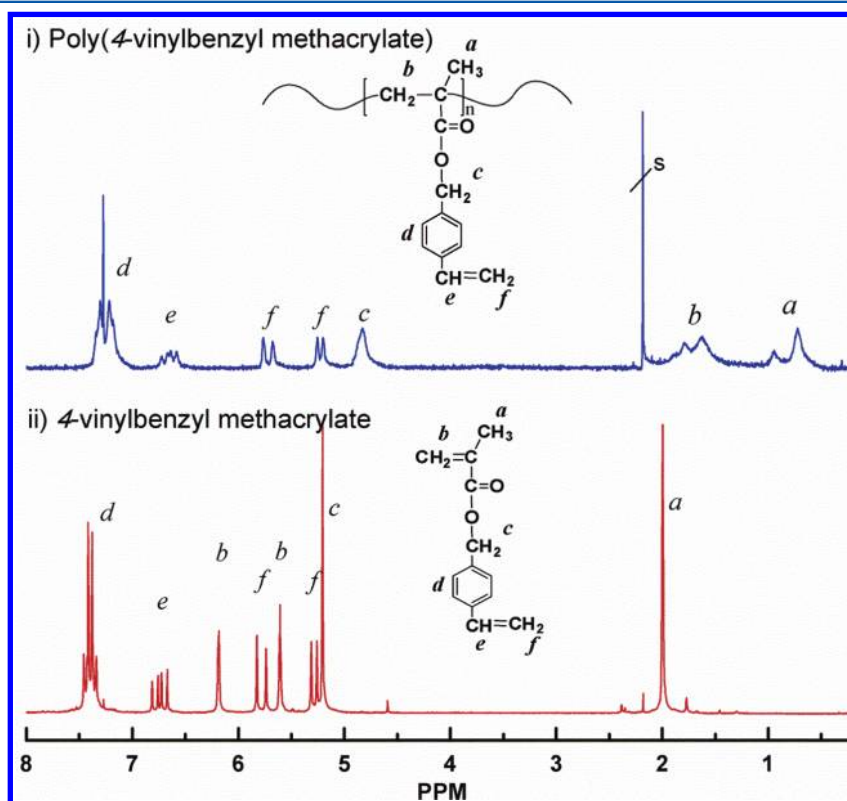

Figure 1. ^{1}H NMR of monomer before and after anionic polymerization using DPHLi as initiator in the presence of LiClO$_4$ as additive in THF at −78 °C: (i) PVBMA and (ii) VBMA ("s" indicates residual solvent).
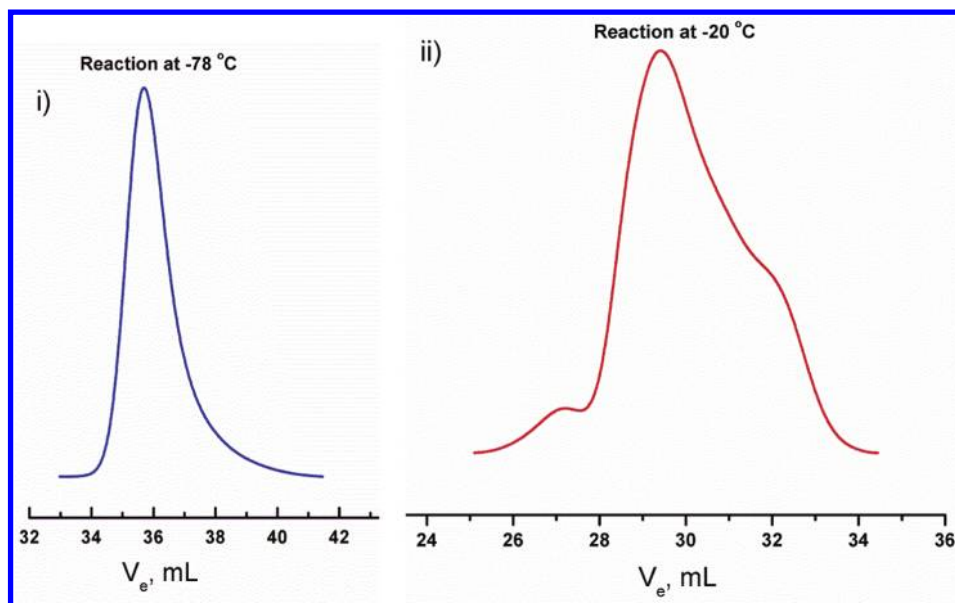
Figure 2. SEC traces of poly(4-vinylbenzyl methacrylate) (PVBMA) using DPHLi as initiator in the presence of LiClO$_4$ as additive in THF. (i) Reaction performed at −78 °C; $M_{n,SEC}$ = 19 260 g/mol, M_w/M_n = 1.19. (ii) Reaction performed at −20 °C in THF; $M_{n,SEC}$ = 89 000 g/mol, M_w/M_n = 1.82.

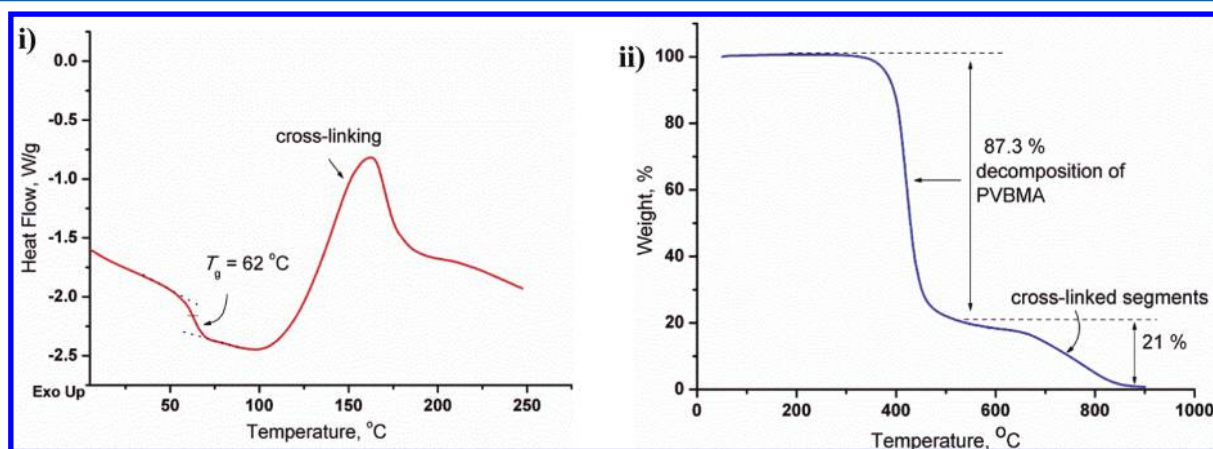**Figure 3.** Thermal characterization of PVBMA. (i) DSC at first heating cycle showing T_g at 62 °C and a broad exotherm for cross-linking. (ii) TGA of PVBMA performed in the presence of air showing cross-linking during decomposition at the heating rate of 10 °C/min.

(Figure 2i). However, the precipitated polymer which exhibited narrow MWD (M_w/M_n = 1.19) when dried at 80 °C under vacuum showed a high molecular weight hump in SEC with M_w/M_n > 1.80 (Supporting Information, Tables S1 and S2). This is consistent with the results obtained by Pugh and Percec.[9] Thus, the vinyl pendant in close proximity with ester linkage is highly reactive even in the solid state. Therefore, in subsequent reactions, the polymer was recovered by freeze-drying in benzene at −10 °C and stored in the refrigerator. Polymerization performed in the absence of additive also produced PVBMA with narrow MWD (Table 1, run 3). It appears that the presence of LiClO$_4$ does not have a significant effect in modulating the aggregation dynamics of the enolate anion derived from VBMA. The reason for such a behavior is not clearly understood, a steric factor associated with styrene pendants may be attributed to an ineffective salt complexation.

Similarly, the polymerization initiated using TritylK produced PVBMAs with narrow MWD through selective initiation at methacrylate functionality at −78 °C (Table 1, runs 4 and 5). On the other hand, the polymerization of VBMA

carried out using commercial anionic initiators such as *sec*-butyllithium or *n*-butyllithium in THF at −78 °C produced insoluble gel with low yields, indicating the occurrence of cross-linking due to the participation of both the vinyl groups in the monomer. The results confirm that the resonance-stabilized carbanions with an optimum pK_a (30 ≤ pK_a ≤ 32) of their conjugate acids such as DPHLi and TritylK[33] do not react with styrene functionality at −78 °C. It should be mentioned that DPHLi anion has been used as an initiator for styrene to create a wide variety of architectures at room temperature in nonpolar solvents.[31] The temperature-dependent selective initiation can be attributed to the higher electronegativity of the methacrylate group as compared to vinyl group of styrene. The formation of linear PVBMA with styrene pendants at −78 °C in THF indicates the rate of initiation at the vinyl functionality with these initiators is strongly dependent on the temperature. No evidence of cross-linking was observed even when the reaction was performed at −40 °C as evident from the obtained narrow MWD of PVBMA (Table 1, run 6).

Table 2. Anionic Diblock Copolymerization of MMA with VBMA Using DPHLi in the Presence of LiClO$_4$ Additive ([LiClO$_4$]$_0$/[DPHLi]$_0$ = 10) in THF at −78 °C^a

| run	[DPHLi] × 10^3 (mol/L)	first block					PMMA-b-PVBMA				
		[MMA] (mol/L)	$M_{n,calcd}$^{b} (g/mol)	$M_{n,SEC}$^{c} (g/mol)	M_w/M_n	f^{d}	[VBMA] (mol/L)	$M_{n,calcd}$^{b} (g/mol)	$M_{n,SEC}$^{c} (g/mol)	M_w/M_n	f^{d}
1	1.87	0.343	18 300	23 300	1.09	0.80	0.013	19 700	24 300	1.09	0.81
2	1.87	0.487	26 000	28 500	1.09	0.91	0.052	27 600	30 300	1.10	0.91
3^c	2.84	0.295	10 400	11 500	1.07	0.90	0.105	17 900	19 700	1.11	0.91

^{a}Polymer was precipitated from methanol and dried in air at room temperature for 4 h. ^{b}$M_{n,cal}$ = grams of monomer/mole of initiator. ^{c}Obtained using SEC calibrated with PMMA standards. ^{d}Initiator efficiency, $f = M_{n,calcd}/M_{n,SEC}$. ^{e}VBMA was first polymerized followed by MMA to obtain PVBMA-b-PMMA.

However, polymerization carried out at −20 °C gave PVBMA, which exhibited uncontrolled molecular weight with low and high molecular weight humps in SEC, indicating the occurrence of cross-linking through the styrene pendants (Figure 2ii). It should be noted that the homopolymerization of VBMA via GTP using silylketen acetal as the initiator did not proceed to 100% conversion. The synthesized PVBMA exhibited a broad and bimodal distribution.^{9} Although the primary fraction showed a narrow molecular weight distribution, the overall polydispersity index was high (M_w/M_n = 8.3). The high molecular weight hump was attributed to an uncontrolled cross-propagation at room temperature due to thermal polymerization of the styrene groups. Nevertheless, in the present study, clearly such cross-propagation does occur even at −20 °C in the anionic polymerization. Although the reaction mixture did not show any indication of the development of a typical red color of styryl anion, the SEC result suggests that the cross propagation of enolate ion pairs occurs with styrene at −20 °C. A multimodal distribution was obtained (Figure 2ii), confirming the local exotherm resulting from the enolate propagating centers complicated the process via thermal initiation of styrene pendants.

The differential scanning calorimetry (DSC) analysis of the PVBMA showed two transitions in the first scan. The midpoint endothermic transition at 62 °C is a glass transition temperature which is in accordance with the reported value^9 and a substantial exothermic broad peak in the region between ∼110 and 180 °C is arising from the thermal cross-linking via styrene pendants (Figure 3). Thermogravimetric analysis (TGA) showed two distinct decomposition peaks: a sharp one at T_{max} ∼ 445 °C and a broad one at T_{max} ∼ 700 °C. The latter is attributed to the decomposition of the segments that had undergone thermal cross-linking while heating the sample at the rate of 10 °C/min.

Synthesis of Block Copolymer with MMA. The living nature of the polymerization of VBMA could be used for the preparation of diblock copolymer through sequential block copolymerization with MMA. The block copolymerization of VBMA with MMA was carried out in the presence of LiClO$_4$ in THF at −78 °C. Well-defined block copolymers with short segments of PVBMA were obtained regardless of the monomer addition sequence (Table 2). The SEC traces of the diblock copolymers showed controlled molecular weight with narrow MWD supporting a noninterfering nature of the styrene pendants during the diblock formation (Figure 4).

High Reactivity of Pendant Styrene Units. Interestingly, the THF solution of PVBMA ($M_{n,SEC}$ = 8300 g/mol, M_w/M_n = 1.18, Table 1, run 2) kept at 35 °C had a slow cross-linking even without an initiator and produced higher molecular weight polymer. The SEC of the aged polymer showed appearance of
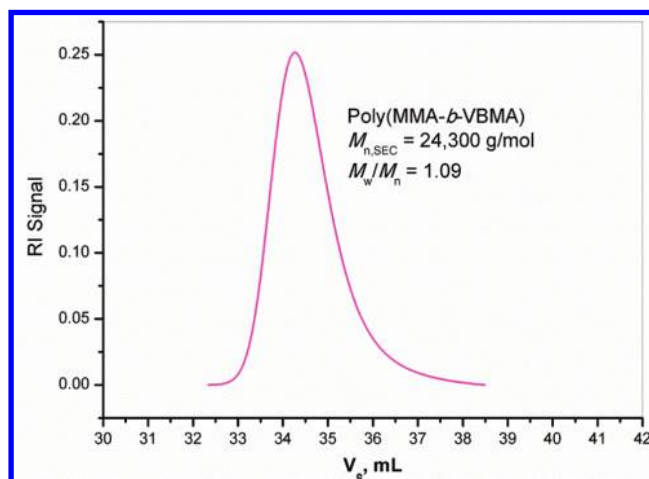
Figure 4. SEC trace of Poly(MMA-b-VBMA) via sequential monomer addition in THF at −78 °C; $M_{n,SEC}$ = 24 300 g/mol, M_w/M_n = 1.09 (PMMA block, $M_{n,SEC}$ = 23 300 g/mol, M_w/M_n = 1.09).

high molecular weight fractions in the eluogram with broader MWD (Figure 5). The soluble nature of the cross-linked
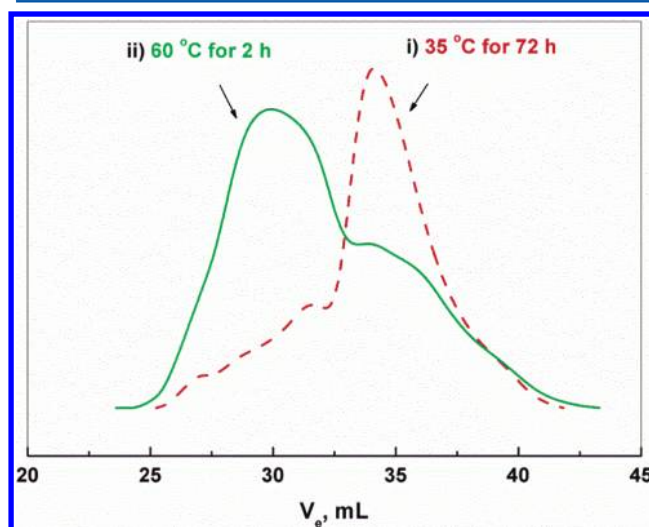
Figure 5. SEC traces of PVBMA (Table 1, run 2) kept at 35 °C for 72 h in THF, $M_{w,SEC}$ = 168 800 g/mol, M_w/M_n = 8.20 and at 60 °C for 2 h, $M_{w,SEC}$ = 411 100 g/mol, M_w/M_n = 15.22 in the absence of radical initiator showing substantial radical cross-linking of pendant styrene units.

polymer indicates that the extent of cross-linking is very low. The SEC eluogram of PVBMA obtained from an aged sample solution at 60 °C for 2 h shows a multimodal distribution with

an increased higher molecular weight fraction ($M_{w,SEC}$ = 411 100 g/mol, M_w/M_n = 15.22). Thus, PVBMA can be readily cross-linked thermally in the solution with or without a radical initiator and could be photo-cross-linked. However, the polymers can be stored in refrigerator without undergoing cross-linking. The results indicate that the reactivity of the pendant styrene in PVBMA is higher in solution than in the solid state. Thus, the pendant styrene units can serve as a replacement for other cross-linkable segments like polybutadiene, poly(allyl methacrylate), or poly(cinnamoyl methacrylate).

As the styrene pendants are very reactive in the polymer both in solid and in solution, a short PVBMA segment containing PMMA-*b*-PVBMA diblock copolymer was cross-linked using benzyl peroxide as radical initiator in toluene at 80 °C to obtain a cross-linked polystyrene core with starlike PMMA arms emanating from it (Supporting Information, Figure S1). Although the reaction was not complete, the SEC showed a peak at substantially high elution volume, indicating the formation of starlike PMMA with cross-linked PS polymer. The high reactivity of styrene pendants can find usage in many applications such as synthesis of polymer nanoparticles, core cross-linked micelles, and also freezing microphase-separated morphologies of block copolymers containing PVBMA segments via cross-linking at low temperature using solvent swollen (wet) condition.

CONCLUSIONS

Polymers bearing reactive styrene pendants as repeat units have been synthesized through selective anionic initiation of 4-vinylbenzyl methacrylate (VBMA) using resonance stabilized carbanions, 1,1-diphenylhexyllithium (DPHLi) and trityl potassium (TritylK), in THF at −78 °C. We have shown that the nucleophilicity of the stabilized carbanions can be attenuated at −78 °C, for selective anionic initiation of VBMA at its more polar methacrylate site in the presence of styrene functionality. The successful selective polymerization of VBMA through methacrylate group is attributed to a higher activation energy associated with the initiation of styrene using stabilized DPHLi or TritylK initiators. Highly reactive poly(4-vinylbenzyl methacrylate)s and poly(4-vinylbenzyl methacrylate-*b*-methyl methacrylate)s have been synthesized and characterized. The PVBMAs are thermally reactive in solid as well as in solution and will find applications in reactive cross-linking and network formation.

ASSOCIATED CONTENT

ⓢ Supporting Information
SEC data on cross-linking in solid and in solution (Tables S1 and S2); SEC of star polymer synthesis from PMMA-*b*-PVBMA copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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