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Facile synthetic route toward poly(vinyl benzyl amine) and its versatile intermediates

Wei-Ho Ting [a], Shenghong A. Dai [a], Yeng-Fong Shih [b], I-Kuan Yang [c], Wen-Chiung Su [d], Ru-Jong Jeng [a,*]

[a] Department of Chemical Engineering, National Chung Hsing University, 250 Kuo-Kuang Road, Taichung 402, Taiwan
[b] Department of Applied Chemistry, Chaoyang University of Technology, Taichung County 41319, Taiwan
[c] Department of Chemical Engineering, Tunghai University, Taichung 40704, Taiwan
[d] Chung-Shan Institute of Science and Technology, Lungtan, Taoyuan 325, Taiwan

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Abstract

Poly(vinyl benzyl amine) (PVBAm) has been synthesized by modifying poly(vinyl benzyl chloride) (PVBC) via an unique synthetic route. According to the literature, most polyamines are synthesized from PVBC through the Gabriel reaction. In this investigation, we adopt Staudinger synthesis to avoid drastic decomposition which occurs in the Gabriel reaction during synthesis. Three types of polyamine polymers – homopolymer, block copolymer and random copolymer, were synthesized without incurring any crosslinking reaction. The amine-containing polymers can further undergo ring-opening addition reaction with *N*-phenyl-3,3-dimethyl-azetidine-2,4-dione. Notably, the intermediates, phosphine imine and azide functionalities can be easily converted into various functionalities such as carbodiimide, imine, amine, triazo, aziridine, etc. by adding suitable reagents.

Keywords: Poly(vinyl benzyl amine); Living free radical polymerization; TEMPO

1. Introduction

Poly(vinyl benzyl amine) (PVBAm, polyamine) not only exhibits similar physical properties to those of polystyrene, but also comprises highly active primary amine groups. Therefore, PVBAm can be adopted as a curing agent for commercial epoxy resins or polyurethanes. Mitchell [1] and Adams et al. [2] found that PVBAms are indispensable platforms for the attachment of handles and linkers that facilitate solid phase-mediated organic transformations (such as in peptide, DNA, and combinatorial synthesis applications). Longo et al. [3] utilized block copolymer (*b*-polystyrene–PVBAm) to produce vesicles for use in drug delivery techniques. Mitchell [1] synthesized PVBAm via free radical polymerization of vinyl benzyl chloride (VBC) with azoisobutyronitrile (AIBN), followed by undergoing Gabriel reaction [2–6].

In recent years, many researchers have developed well-defined homopolymers and block copolymers through stable free radical polymerization. There are various forms of living free radical polymerizations, including atom transfer radical polymerization (ATRP) [7–9], reversible addition–fragmentation chain transfer (RAFT) [10–12], and nitroxide-mediated controlled radical polymerization (NMCRP) [13–18]. All have been heavily studied for the production of polymers with specifically designed structures. The above systems provide a narrow polydispersity under 1.4 and a stepwise growth from low molecular weight to high molecular weight.

Since the VBC monomer is highly reactive, the polydispersity and self-polymerization at high temperatures during living free radical polymerization are higher than those of styrene monomer in bulk polymerization. Marinai et al. [4] and Ohno et al. [6] used the VBC monomer to make a vinyl benzyl

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* Corresponding author. Tel.: +886 4 22852581; fax: +886 4 22854734.
E-mail address: rjjeng@nchu.edu.tw (R.-J. Jeng).

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phthalimide monomer which in turn synthesized di-block copolymer via the NMCRP route with controllable polydispersity. Subsequently, the phthalimide groups were reduced to amino groups via the Gabriel reaction. Longo et al. [3] applied the same concept in vesicle research using an ATRP system. Based on the above, the Gabriel reaction is a direct technique for synthesizing polyamines. However, the conversion of the phthalimide groups to amino groups and the details of the physical properties have not been fully investigated.

In this work, styrene and VBC monomers were polymerized via NMCRP [13–18] to obtain polyvinyl benzyl chloride (PVBC) homopolymer, di-block and random-type copolymers with narrow polydispersity. Subsequent azidation, phosphine imination [19–22], acidification and alkalization were performed to synthesize three types of polyamines – homopolymer, di-block and random-type copolymers, without incurring subsequent crosslinking.

During these processes, the intermediates including functional groups such as azide and phosphine imine are highly versatile in various reactions, as displayed in Scheme 1. For instance, the azide group can be applied in Click chemistry [23–26] to react with alkyne or carbon nanotubes [27–29], whereas the phosphine imine [19] groups can be treated with water to produce amine groups, or react with isocyanate or aldehyde to yield carbodiimide groups or imine groups, respectively.

2. Experimental

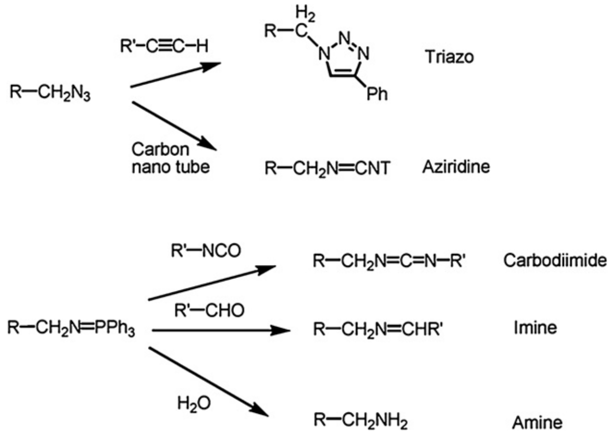
2.1. Materials and reagents

Benzoyl peroxide, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), sodium azide (NaN_3), triphenylphosphine (TPP), styrene, VBC, tetrahydrofuran (THF) and dimethylsulphoxide (DMSO) were purchased from Aldrich Co. Prior to use, styrene and VBC were freshly distilled under reduced pressure.

2.2. Synthesis of polymers

2.2.1. Preparation of homo-polystyrene (h-PS)

Bulk polymerization was carried out on the purified commercial grade sample of styrene monomer. Typically, the purified styrene (30 ml), benzoyl peroxide (56 mg) and TEMPO (47.7 mg) were added in 50 ml, three-necked flask. The orange reactant solution was heated at 95 °C for 3.5 h and then at 125 °C for several hours to obtain the h-PS sample. The h-PS sample was purified by repeated precipitations from dichloromethane into methanol ($T_g = 95$ °C, $M_n = 16\,557$, polydispersity = 1.13).



Scheme 1. Versatility of azide and phosphine imine functional groups.

2.2.2. Preparation of homopolymer PVBC (h-PVBC)

Bulk polymerization was carried out on the purified commercial grade sample of VBC monomer. Typically, the purified VBC (9.16 g), benzoyl peroxide (56 mg) and TEMPO (47.7 mg) were added in 50 ml, three-necked flask. The mixture was heated at reflux temperature (125 °C) for several hours in nitrogen. The polymer, h-PVBC was purified by repeated precipitations from dichloromethane into methanol ($T_g = 95$ °C, $M_n = 12\,140$, polydispersity = 1.46).

2.2.3. Preparation of di-block copolymer (b-PS–PVBC)

Bulk polymerization was carried out on macroinitiator h-PS (100 mg) and VBC monomer (10 ml) at 125 °C for several hours. The di-block copolymer, *b*-PS–PVBC, was purified by repeated precipitations from dichloromethane into methanol. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.10–2.22 (br, 6H), 4.30–4.50 (br, 2H, $-CH_2-Cl$), 6.10–7.20 (br, 9H). FT-IR spectrum (ν, cm^{-1}): 1266 (CH_2-Cl) (PS/PVBC = 7, $M_n = 18\,830$, PVBC repeat unit = 22, polydispersity = 1.28, $T_g = 87$ °C). The *b*-PS–PVBC copolymer with low PS/PVBC ratio (PS/PVBC = 2.1) was prepared in the same manner as *b*-PS–PVBC with high PS/PVBC ratio (PS/PVBC = 7). Similar spectroscopic characteristics of ^{1}H NMR and FT-IR were obtained for all of the block copolymers (PS/PVBC = 2.1, $M_n = 145\,048$, PVBC repeat unit = 391, polydispersity = 1.81, $T_g = 106$ °C).

2.2.4. Preparation of random copolymer (r-PS–PVBC)

Bulk polymerization was carried out on styrene monomer (10 ml) and VBC monomer (10 ml) at 125 °C for several hours. Subsequently, the random copolymer, r-PS–PVBC was purified by repeated precipitations from dichloromethane into methanol. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.10–2.22 (br, 6H), 4.30–4.50 (br, 2H, $-CH_2-Cl$), 6.10–7.20 (br, 9H). FT-IR spectrum (ν, cm^{-1}): 1266 (CH_2-Cl) ($T_g = 100$ °C, $M_n = 22\,797$, polydispersity = 1.31).

2.3. Azidation

2.3.1. Preparation of poly(vinyl benzyl azide)s: homopolymer (h-PVBAz), block copolymer (b-PS–PVBAz) and random copolymer (r-PS–PVBAz)

The homopolymer, h-PVBC (100 mg) and excessive molar equivalent of sodium azide were stirred at 60 °C in THF and DMSO co-solvent system for 4 h. Subsequently, 200 ml of de-ionized (DI) water was added to the solution. The solution was then extracted with 400 ml of ethyl acetate for three times. Precipitation was performed by adding the ethyl acetate solution into methanol. Finally, the solvent was removed under vacuum for 3 h at 50 °C to obtain solid compound, h-PVBAz. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.10–2.22 (br, 6H), 4.00–4.30 (br, 2H, $-CH_2-N_3$), 6.10–7.20 (br, 9H). FT-IR spectrum (ν, cm^{-1}): 2100 (CH_2-N_3). The copolymers, *b*-PS–PVBAz and r-PS–PVBAz were, respectively, prepared in the same manner as h-PVBAz. Similar spectroscopic characteristics of ^{1}H NMR and FT-IR were obtained for all of the azide-functionalized polymers.

2.4. Acidification

2.4.1. Preparation of poly(vinyl benzyl amine salt)s: homopolymer (h-PVBAS), block copolymer (b-PS–PVBAS) and random copolymer (r-PS–PVBAS)

The homopolymer h-PVBAz (100 mg) and excessive molar equivalent of TPP were mixed and stirred at room temperature in THF for 8 h. After the nitrogen was released from the reactant, the azide functional group transformed into triphenylphosphine imine functional groups. The phosphine imine functionalized polymer solution was added to the hydrochloride solution to obtain the amine-salt-containing homopolymer (h-PVBAS). Extraction (EA/water) was used to separate triphenylphosphine, triphenylphosphine oxide and h-PVBAS. ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.10–2.22 (br, 6H), 3.65–4.20 (br, 2H, $-CH_2-$), 6.10–7.50 (br, 9H), 8.20–9.00 ($-^+NH_3Cl^-$). The copolymers, *b*-PS–PVBAS and r-PS–PVBAS were, respectively, prepared in the same manner as h-PVBAS. Similar spectroscopic characteristics of ^{1}H NMR and FT-IR were obtained for all of the amine-salt-containing polymers.

2.5. Alkalization

2.5.1. Preparation of poly(vinyl benzyl amine)s: homopolymer (h-PVBAm), block copolymer (b-PS–PVBAm) and random copolymer (r-PS–PVBAm)

The homopolymer h-PVBAS (100 mg) was dissolved in methanol and treated with sodium hydroxide solution. An excessive amount of water was added to obtain the precipitate of the alkalized polymer, PVBAm. ^{1}H NMR (200 MHz, DMSO-d_6, δ, ppm): 1.10–2.22 (br, 6H), 3.40–3.80 (br, 2H, $-CH_2-$), 6.10–7.20 (br, 9H). FT-IR spectrum (ν, cm^{-1}): 3370 and 3460 ($-NH_2$). The copolymers, *b*-PS–PVBAm and r-PS–PVBAm were prepared in the same manner as h-PVBAm. Similar spectroscopic characteristics of ^{1}H NMR and FT-IR were obtained for all of the amine-containing polymers.

2.6. Synthesis of N-phenyl-3,3-dimethyl-azetidine-2,4-dione (mono-dione)

The synthetic details have been reported by our laboratory previously [33]. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.41 (s, 6H, $-CH_3$), 7.25 (m, 2H, ArH), 7.34 (d, 1H, ArH), 7.78 (d, 2H, ArH). FT-IR spectrum (ν, cm^{-1}): 1740 and 1855 (dione peak).

2.7. Grafting mono-dione onto r-PS–PVBAm

2.7.1. Preparation of r-polystyrene-co-poly(2,2-dimethyl-N-phenyl-N-(4-vinylbenzyl) malonamide) (r-PS–PVBAM)

Random copolymer, r-PS–PVBAm (500 mg) and mono-dione (0.1250 g) were dissolved in 30 ml of DMSO and kept at 70 °C for 4 h. Primary amines of r-PS–PVBAm reacted with the dione ring at 70 °C in ring-opening addition manner. After the ring-opening reaction, the solution was added to methanol and the precipitate (r-PS–PVBAM) was obtained as a result. ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.10–2.22 (br, 6H), 4.1–4.4 (br, 2H, $-CH_2-$), 6.10–7.60 (br, 14H), 8.8–9.3 (br, 2H). FT-IR spectrum (ν, cm^{-1}): 1678 ($-NH-C{=}O$).

2.8. Measurements

^{1}H NMR spectra were taken on a Varian Gemini-200 FT-NMR spectrometer. IR measurements were performed on a Perkin–Elmer Spectrum One FT-IR spectrometer. Thermal analysis was performed in N_2 on a TA Instruments DSC2010 at a heating rate of 10 °C min^{-1}. Thermogravimetric analysis (TGA) was performed using a Seiko SSC-5200 thermogravimetric analyzer at a heating rate of 10 °C min^{-1} under nitrogen. Thermal degradation temperature (T_d) was taken at 5% weight loss. Gel permeation chromatography (GPC) was performed in THF using a Waters Apparatus equipped with Waters Styragel columns and a refractive index detector with a polystyrene calibration.

3. Results and discussion

3.1. Synthesis and characterization of polymers

In the bulk living free radical polymerization, 1% benzoic acid was added to inhibit the thermal polymerization which is caused by high reactivity of the VBC monomer at high temperatures [30–32]. The chemical structures of all synthesized compounds were verified by ^{1}H NMR, FT-IR, and GPC. Table 1 presents the characteristics and polydispersities of polymers. The polydispersities of three types of polymers and their derivatives were less than 1.46. The segment ratios (PS/PVBC) of *b*-PS–PVBC and r-PS–PVBC, based on ^{1}H NMR, were 7:1 (157:22) and 6:1 (175:28), respectively.

^{1}H NMR and FT-IR characterizations reveal no significant difference among h-PVBC, *b*-PS–PVBC and r-PS–PVBC. As presented in Figs. 1A and 2A, the chloromethyl ($-CH_2-Cl$)

Table 1
Molecular weights for polymers

Type	Code	M_n[a]	PDI[a]	Repeat unit[b]
Homopolymer	h-PS	16 557	1.13	157
Block copolymer	*b*-PS–PVBC	18 830	1.28	157:22
Homopolymer	h-PVBC	12 140	1.46	78
Random copolymer	r-PS–PVBC	22 797	1.31	175:28

[a] Determined by GPC analysis in THF (calibration with polystyrene standards).

[b] Calculated by ^{1}H NMR.

functional group IR absorption peaks are found at 1266 cm^{-1} in the FT-IR spectrum and NMR chemical shifts are found at 4.44 ppm in the ^1H NMR spectrum for r-PS–PVBC. Similar IR absorption peaks and NMR chemical shifts for the chloromethyl groups were also found for h-PVBC and *b*-PS–PVBC.

Scheme 2 displays the synthetic route toward acquiring the polyamines. Complete conversion was achieved in the azidation process. According to the FT-IR and ^1H NMR spectra, the chloromethyl ($-CH_2-Cl$) functional group at 1266 cm^{-1} was replaced with an azide ($-CH_2-N_3$) functional group at 2100 cm^{-1} (Fig. 1A), and the chemical shift at 4.44 ppm (Fig. 2A) was shifted to 4.14 ppm (Fig. 2B) after azidation.

It is reported that phosphine imination of azide is a mild and effective process to obtain amine-containing compounds [34–36]. However, crosslinking reactions are prone to occur in the polymer system if drying solvent is absent or if excessive TPP is not provided [20]. After phosphine imination, the unstable intermediate product must immediately undergo amination because of the high reactivity of phosphine imine functional groups. In a small molecular system, the addition of DI water to the solution of phosphine imine-containing compound to yield an amine derivative is straightforward. However, this approach was not effective in the polymer system. Cohen [19] and Cimecioglu et al. [20] utilized the same route to synthesize homo-polyamine. However, undesirable crosslinking reaction occurs when using the addition of DI water to synthesize homo-polyamine. Cohen assumed that the lack of dryness in the polyamine salts induced the crosslinking reaction, whereas Cimecioglu utilized a highly polar solvent system to prevent the unwanted crosslinking reaction. To clarify this issue, three different types of polymers were

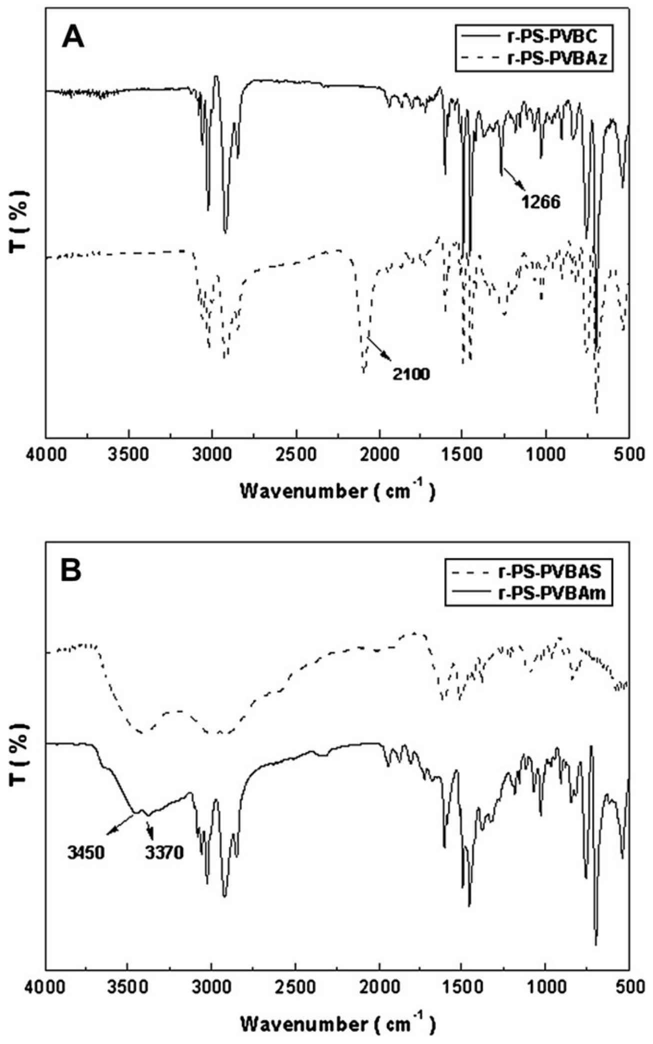


Fig. 1. IR spectra of (A) r-PS–PVBC and r-PS–PVBAz (B) r-PS–PVBAS and r-PS–PVBAm.

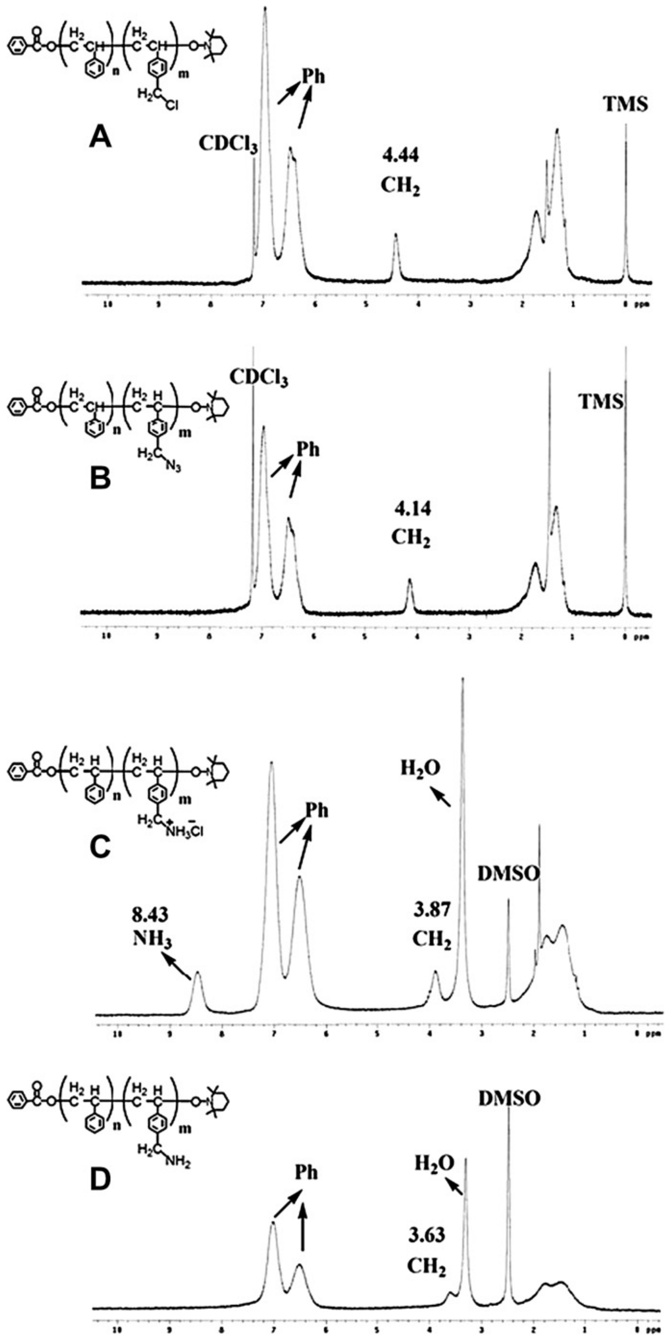
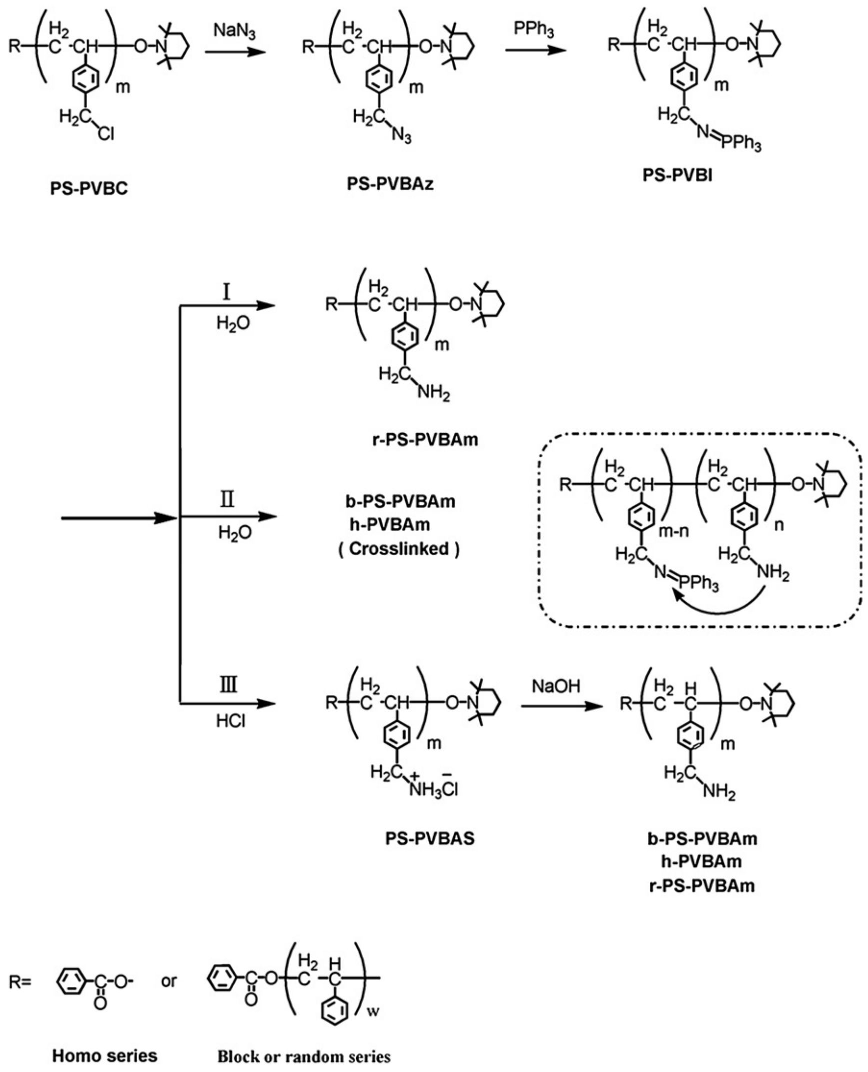


Fig. 2. ^1H NMR spectra of (A) r-PS–PVBC, (B) r-PS–PVBAz, (C) r-PS–PVBAS and (D) r-PS–PVBAm.



Scheme 2. Synthesis of poly(vinyl benzyl amine).

introduced in this amination process. As shown in Scheme 2, only random-type copolymer could follow the above route without incurring crosslinking (route I). Regardless of the solvent base, homopolymer and block copolymer eventually led to crosslinked structures after amination (route II).

Unlike earlier researches [19,20], Abraham and Ha [22] employed a star-shaped polymer with only one functional group on its exterior. No crosslinking reaction occurred during amination. This is attributed to the dilution of adjacent phosphine imine groups by PS segments. Therefore, this investigation indicates that the crowded phosphine imine groups would lead to the crosslinking reaction during amination. In the random copolymer system, the PS segments would protect the formed amine groups from the attack by the nearby phosphine imine groups. On the other hand, the block copolymer system would undergo crosslinking without the isolation of PS segments of the formed amine groups. Hence, only the isolated phosphine imine groups in the polymer can be transformed into amine functional groups by direct addition of DI water, without the occurrence of crosslinking.

In order to obtain amine-containing homopolymer and block copolymer without incurring the crosslinking reaction, another approach was adopted. First the phosphine imine functional groups were acidified, and subsequently alkalized to produce amine functional groups, as displayed in route III of Scheme 2. The phosphine imine groups were first neutralized with hydrochloride to form more stable amine-salt functional groups. Fig. 2C shows that the chemical shift of CH_2 was found at 3.87 ppm with the appearance of $^{+}NH_3Cl^{-}$ at 8.47 ppm for the amine-salt containing random copolymer. Moreover, the ratio of integrated areas was 2:3 (CH_2/$^{+}NH_3Cl^{-}$). The presence of more amine-salt functional groups in the polymer chains would result in a proton chemical shift of amine-salt functional groups moving downfield further, as presented in Fig. 3. However, the chemical shifts of methyl groups for these amine-salt containing polymers are similar. The polyamine salt was not identified in the FT-IR spectrum due to the absorption of moisture by the amine salt (Fig. 1B).

In amination, the acidified homopolymer and random copolymer, amine-salt containing polymers were, respectively,

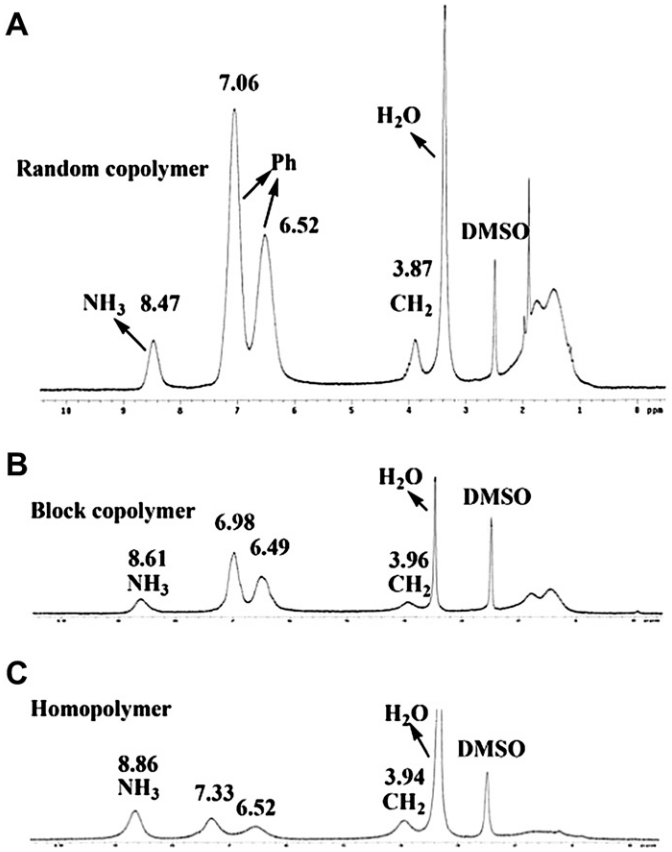


Fig. 3. ^{1}H NMR spectra of (A) r-PS–PVBAS, (B) *b*-PS–PVBAS and (C) h-PVBAS (in DMSO-d_6).

dissolved in methanol and treated with sodium hydroxide solution to yield amine-containing h-PVBAm and r-PS–PVBAm. This approach could not be employed for the *b*-PS–PVBAS system, due to its lack of solubility. Therefore, a co-solvent system, methanol/THF was utilized to increase the solubility. Fig. 1B shows the absorption peak of the primary amine located at 3200–3300 cm^{-1} for the r-PS–PVBAm sample. This corroborates the result of the ^{1}H NMR study (Fig. 2D). A chemical shift at 3.63 ppm in DMSO-d_6 appeared after alkalization. Table 2 presents the absorption characteristics of FT-IR and ^{1}H NMR for the random copolymer system.

Since the solubility of *b*-PS–PVBAm is poor in DMSO-d_6 or $CDCl_3$, a co-solvent such as acetic acid-*d*/DMSO-d_6 is chosen for ^{1}H NMR analysis. Intermolecular attraction between the primary amine of r-PS–PVBAm and acetic acid caused the absorption shifting from 3.63 ppm to 4.04 ppm, as shown in Fig. 4A. Similar results were obtained for homopolymer and block copolymer (Fig. 4B and C). This is confirmed by analyzing the model compound 4-aminobenzyl amine in acetic acid-*d* (Fig. 4D).

To prove that the primary amines of the polymers are sufficiently stable and able to exhibit reactivity, mono-dione is introduced to react with the r-PS–PVBAm sample, as shown in Scheme 3. As mentioned in Section 1, only the primary amine can undergo ring-opening addition reaction. When monitored by FT-IR analysis, disappearance of the 1855 cm^{-1} and 1740 cm^{-1} peaks were accompanied concurrently by the emergence of a new absorption peak at 1650 cm^{-1} corresponding to the carbonyl group of the malonamide linkage (Fig. 5). In the ^{1}H NMR spectrum ($CDCl_3$), a chemical shift at 3.63 ppm corresponding to methylene of benzyl group was shifted to 4.22 ppm indicating the formation of

Table 2
Absorption characteristics of FT-IR and ^{1}H NMR for the random copolymer system

	IR (cm^{-1})	NMR (ppm)
r-PS–PVBC	1266	4.44[a]
r-PS–PVBAz	2100	4.14[a]
r-PS–PVBAS	–[c]	3.87[b]
r-PS–PVBAm	3370, 3460	3.63[b]
r-PS–PVBAM	1678	4.22[a]

[a] In $CDCl_3$.
[b] In DMSO-d_6.
[c] Not clear.

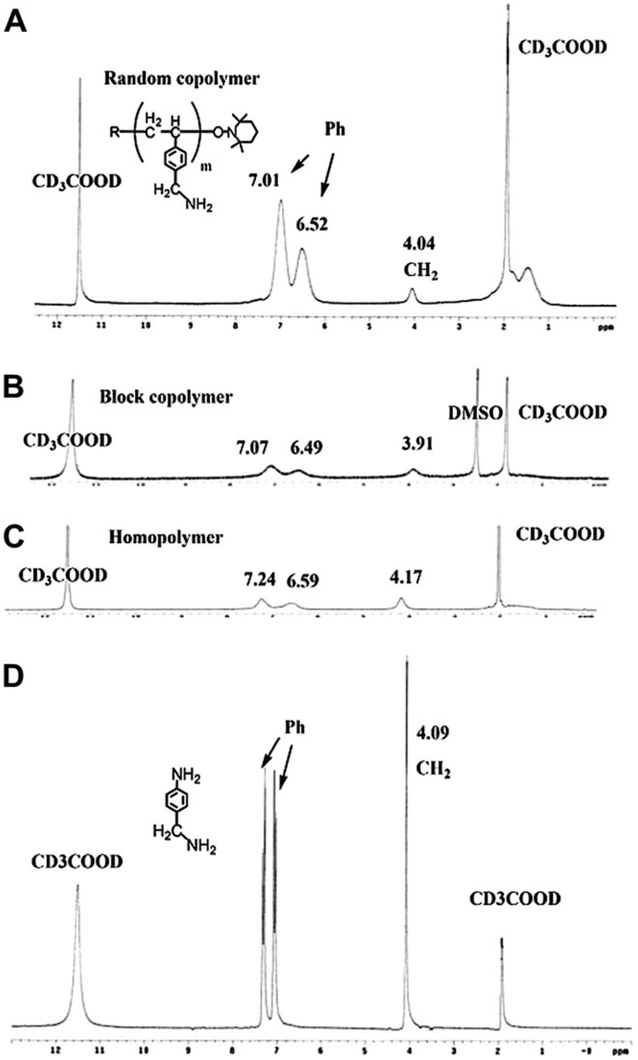
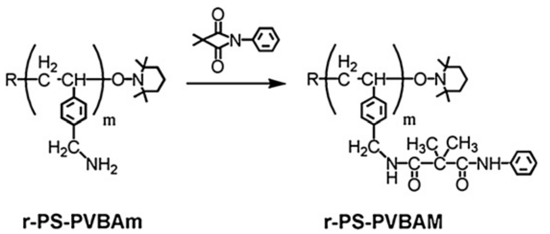


Fig. 4. ^{1}H NMR spectra of (A) r-PS–PVBAm, (B) *b*-PS–PVBAm, (C) h-PVBAm and (D) 4-aminobenzyl amine.



Scheme 3. Synthesis of r-polystyrene-*co*-poly(2,2-dimethyl-*N*-phenyl-*N*-(4-vinyl benzyl)malonamide) (r-PS–PVBAM).

malonamide (Fig. 6). The results reveal that these polyamines are capable of proceeding to a ring-opening addition reaction.

3.2. Thermal properties

Table 3 presents thermal properties of the polymers. For the homopolymer system (h-PVBC; the number of repeating units: 78), the T_g is 95 °C. After azidation of the homopolymer, the T_g of h-PVBAz decreased to 52 °C. According to literature [34], the azide functional groups are not thermally stable, and at high temperatures readily decompose and release nitrogen. Once the azide functional groups are functionalized in the polymer, the T_g of azide-containing polymer was low [37–39]. As the polymer was acidified, strong ionic bonds in the h-PVBAS restricted the segmental motions and further decreased the free volume among polymer chains. Hence, the T_g of h-PVBAS elevated to 164 °C. Upon reaching higher temperatures, the ionic bonds are found to be destroyed with the release of hydrogen chloride. Therefore, the T_g of h-PVBAS is relatively high, whereas the T_d is relatively low compared to that of the h-PVBC system. In addition, the T_g of the amine-containing h-PVBAm sample was approximately 116 °C. The T_g of the amine-containing h-PVBAm sample is higher than that of the h-PVBC system because of the presence of highly polar amino groups. Moreover, the T_d of h-PVBAm was higher than that of h-PVBAS because of the more stable nature of h-PVBAm at elevated temperatures.

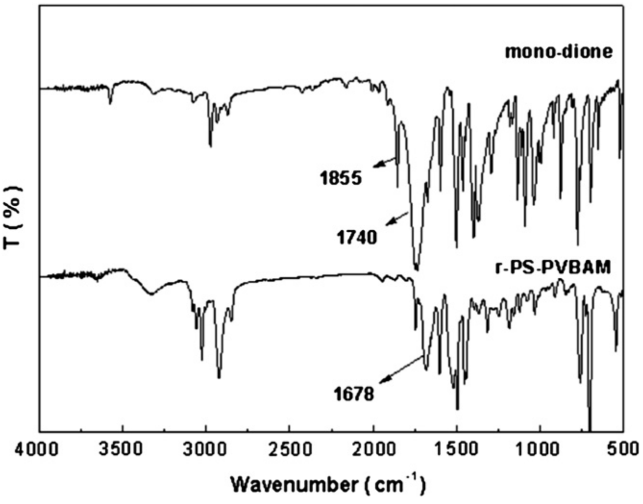


Fig. 5. IR spectra of mono-dione and r-PS–PVBAM.

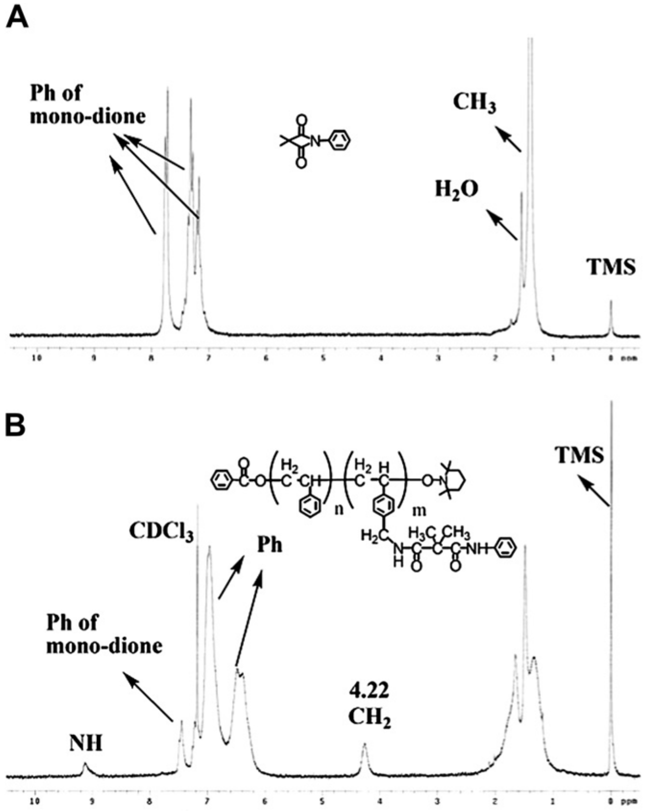


Fig. 6. ^{1}H NMR spectra of (A) mono-dione and (B) r-PS–PVBAM.

In general, random copolymers possess only one T_g even though they are composed of different segments, as shown in Table 3. In the random copolymer system, the T_g of r-PS–PVBAz was 90 °C, which is higher than that of h-PVBAz (52 °C), suggesting the notion that the r-PS–PVBAz was composed of h-PS and h-PVBAz. In general, the T_g of r-PS–PVBAz would appear between those of h-PS and h-PVBAz [40]. Due to the major presence of styrene segments in the r-PS–PVBAz, the thermal properties of r-PS–PVBAz were

Table 3
Thermal properties for polymers

Type	Code	Repeat unit	T_g[a] (°C)	T_d[b] (°C)
Homopolymer	h-PS	157	95	313
Block copolymer	*b*-PS–PVBC	157:22	87	307
	b-PS–PVBAz		87	250
	b-PS–PVBAm		102	366
	b-PS–PVBAS		104	286
Homopolymer	h-PVBC	78	95	282
	h-PVBAz		52	231
	h-PVBAm		116	311
	h-PVBAS		164	274
Random copolymer	r-PS–PVBC	175:28	100	302
	r-PS–PVBAz		90	257
	r-PS–PVBAm		108	378
	r-PS–PVBAS		154	265

[a] Data were taken from DSC second heating trace, with a heating rate of 10 °C min^{-1}.

[b] Data were taken from TGA trace, 5% weight loss.

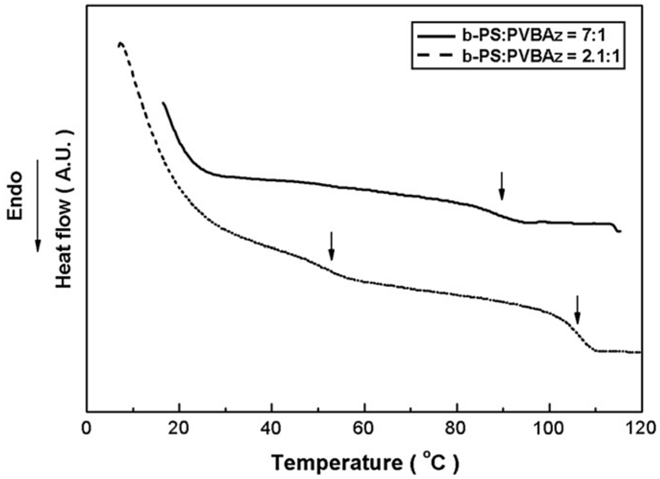


Fig. 7. DSC thermograms of *b*-PS−PVBAz with different molar ratios.

dominated by the PS segments. The T_g of r-PS−PVBAz can be predicted using Fox's equation: $1/T_g = M_1/T_{g1} + M_2/T_{g2}$ [40]. The predicted value was 86 °C while the experimental value was 90 °C. The deviation of 4.4% indicates an accurate prediction. This prediction was not fitted for the r-PS−PVBAS and r-PS−PVBAm systems. This is because the presence of these high polar functional groups would result in high T_gs in spite of low concentrations of amine and amine salt in the random polymers. In particular, strong ionic bonds would further restrict the polymer chain motions.

Di-block copolymers would normally exhibit two T_gs because of the presence of two different types of segments in polymer chain. The measurements from DSC revealed that the T_g values of all the block copolymers were almost around 90 °C, indicating a large presence of styrene segments. The undetectable second T_gs were attributed to the low concentration of VBC segments in the copolymer (PS/PVBC = 7, PVBC repeat unit = 22). Notably, the second T_gs were still not available while amine and amine-salt functional groups were introduced into the block copolymers. Nevertheless, the second T_g might be able to appear if the content of VBC in the block copolymer increases to a certain degree. Because of this, the PS/PVBC ratio was declined from 7 to 2.1 in the *b*-PS−PVBC system, i.e. increasing the content of VBC. The second T_g was still not detectable for the *b*-PS−PVBC with a high VBC content. This is due to the likeness between the VBC and styrene monomers. After the azidation of this high VBC-containing *b*-PSPVBC, the synthesized *b*-PS−PVBAz exhibited two T_gs of the PS and PVBAz segments at 106 °C and 52 °C, respectively (Fig. 7).

4. Conclusion

Through living free radical polymerization, h-PVBC, *b*-PS−PVBC and r-PS−PVBC have been synthesized. These polymers can be functionalized via azidation, phosphine imination, acidification and alkalization in sequence. As a result, one is able to obtain polyamines such as h-PVBAm, *b*-PS−PVBAm and r-PS−PVBAm. The characteristic and thermal properties of each polymer are clearly specified. In a homopolymer system, the presence of ionic bonds increases the T_g of the polymer from 52 °C to 164 °C. Currently we are investigating the utilities of these homopolymer, block copolymer and random copolymer in the aspects of biochemistry, membrane, and self-assembly.

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