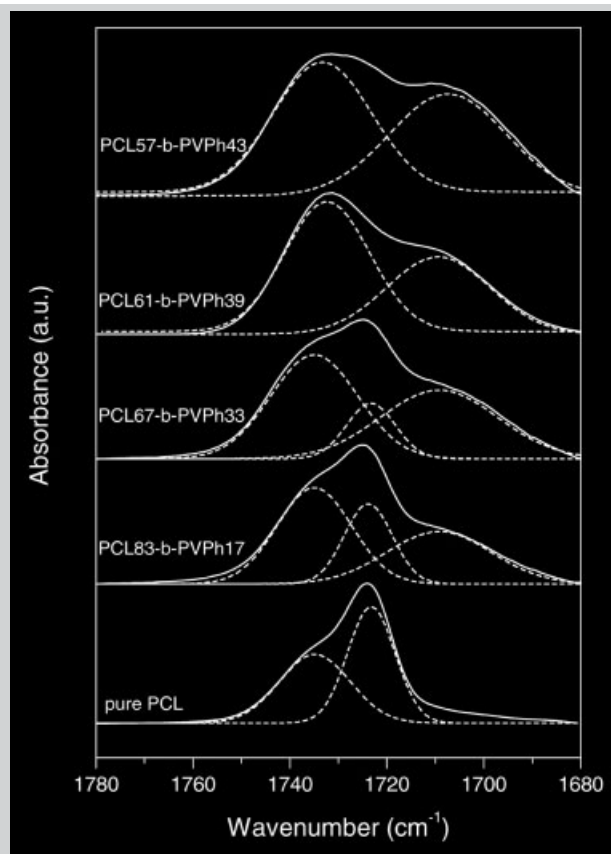


Summary: A series of PCL-*b*-PVPh diblock copolymers were prepared through combinations of ring-opening and atom-transfer radical polymerizations of ϵ -caprolactone and 4-acetoxystyrene, and subsequent selective hydrolysis of the acetyl protective group. This PCL-*b*-PVPh diblock copolymer shows a single glass transition temperature over the entire composition range, indicating that this copolymer is able to form a miscible amorphous phase due to the formation of intermolecular hydrogen bonding between the hydroxyl of PVPh and the carbonyl of PCL. In addition, DSC analyses also indicated that the PCL-*b*-PVPh diblock copolymers have higher glass transition temperatures than their corresponding PCL/PVPh blends. FT-IR was used to study the hydrogen-bonding interaction between the PVPh hydroxyl group and the PCL carbonyl group at various compositions.

FT-IR spectra in the 1680–1780 cm^{-1} for PCL-*b*-PVPh copolymers with various PVPh contents.



Syntheses and Specific Interactions of Poly(ϵ -caprolactone)-*block*-poly(vinyl phenol) Copolymers Obtained via a Combination of Ring-Opening and Atom-Transfer Radical Polymerizations

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Introduction

The study of new living/controlled polymerizations has been one of the most interesting topics in polymer chemistry for many years. Today, many "living" systems are known to encompass polymerization mechanisms such as anionic, cationic, radical, ring-opening and coordinative.^[1,2] Controlled polymerizations have provided new materials with precise control over the macromolecular parameters, in particular, molecular weight, polydispersity, architecture, and composition. Among them, controlled radical polymerizations have received a great deal of attention over the last few years because various monomers, including functional ones, can be radically polymerized. Controlled or living free radical polymerization has several forms including atom-transfer radical polymerization (ATRP),^[3–6] reversible addition-fragmentation chain transfer (RAFT),^[7] and nitroxide-mediated polymerization (NMP),^[8–11] which have been heavily investigated to produce polymers with controlled and often novel architecture. Among these controlled systems, ATRP is probably the most versatile providing a variety of adjustable options such as varied choice of monomers, catalysts, solvents, and reaction temperatures.^[12–15] Similarly, the living ring-opening polymerization of lactones has also received intensive attention leading to the discovery of different living/controlled systems. The desire to control polymer properties through the syntheses of block copolymers and complex macromolecular architectures is a continuing theme throughout polymer chemistry.

Miscible binary polymer blends with strong interaction have also attracted great interest in polymer science.^[16–18] Based on the crystallizability of the constituents, binary crystalline polymer blends can be categorized into crystalline/amorphous and crystalline/crystalline systems.^[19,20] Crystalline/amorphous binary polymer blends are more widely studied because of their simpler crystalline phase relative to crystalline/crystalline ones.^[21–25] A commonly employed component in most crystalline miscible blends is a polyester, such as poly(ϵ -caprolactone) (PCL). PCL is a highly crystalline polymer miscible with several amorphous polymers through specific interactions that were discussed in Eastmond's review.^[26] In our previous studies,^[27–30] we also studied the PCL blending with various amorphous hydrogen bond-donating polymers, such as poly(vinyl phenol) (PVPh), phenolic resin, and phenoxy resin. However, to the best of our knowledge, the crystalline-amorphous diblock copolymer through hydrogen bonding interaction has never been reported.

PVPh is an interesting monomer with ring-substituted styrene derivatives that has been reported to form miscible blends with several polymers containing accessible "proton-acceptor" or "proton-donor" groups, such as acrylate, ester, ether, pyridine, and hydroxyl groups through the formation of hydrogen bond interactions.^[30–34] According

to the literature,^[35–37] most of the immiscible block copolymers with self-regular morphologies have primarily emerged from the investigation of diblock copolymers with macrophase or microphase separation as a function of composition, temperature, and interaction parameter. However, we intend to synthesize the miscible poly(ϵ -caprolactone)-*block*-poly(vinyl phenol) (PCL-*b*-PVPh) block copolymers by a combination of ring-opening and ATRPs to compare with the corresponding PCL/PVPh blends which are known as miscible in the amorphous region due to strong hydrogen bonding between the PCL carbonyl and the PVPh hydroxyl groups.^[30,38] To the best of our knowledge, block copolymers of PVPh with biodegradable polymers PCL have not been reported so far.^[39–43] In this paper, we first come up with a strategy to combine two dissimilar chemistries in sequence to prepare a series of block copolymers, poly(ϵ -caprolactone)-*block*-poly(4-acetoxystyrene) (PCL-*b*-PAS), and then convert to PCL-*b*-PVPh block copolymers through base-catalyzed hydrolysis. The chemical structure, molecular weight, variation of glass transition behavior, and specific interaction in these block copolymers are characterized and investigated by using ¹H NMR, gel permeation chromatography (GPC), DSC, and FT-IR spectroscopy analyses.

Experimental Part

Materials

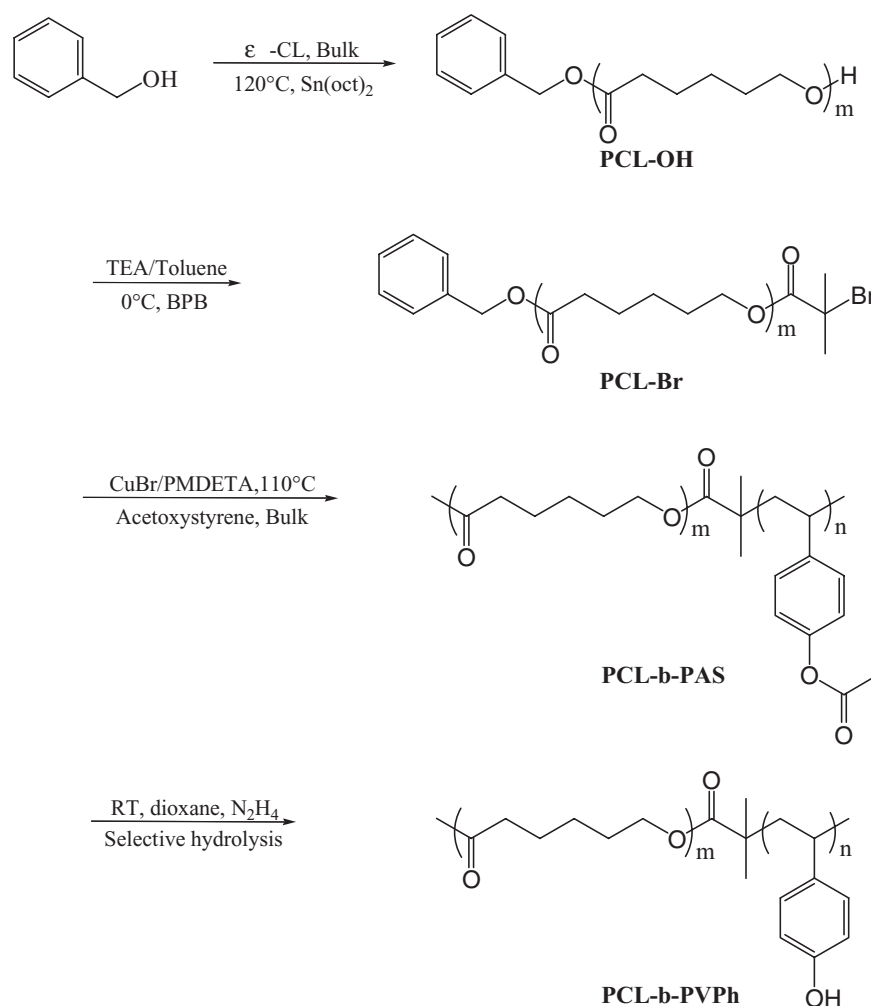
4-Acetoxystyrene (AS) was purified by column chromatography and the ϵ -caprolactone (ϵ -CL) was distilled from calcium hydride before use. Following purification, all monomers were stored in a freezer. All solvents were distilled prior to use. Triethylamine was stirred over magnesium sulfate and filtered prior to use. Copper(I) bromide (CuBr) was stirred in glacial acetic acid overnight, filtered, and then rinsed with absolute ethanol under a blanket of argon and dried under vacuum at 60 °C overnight. Amberlite IR-120 (H form) cation exchange resin, *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA) (99% Acros), benzyl alcohol (99% Acros), stannous octoate [Sn(oct)₂] (99% Aldrich), 2-bromopropionyl bromide (99% TCI), and 4,4'-dinonyl-2,2'-dipyridyl (dNBipy) were used as received (97% Aldrich).

Procedure for Ring-Opening Polymerization

The polymerization of ϵ -CL was initiated with benzyl alcohol by using a catalytic amount of Sn(oct)₂. The polymerization was carried out in the melt at 120 °C (20 h). The polymer was then dissolved in tetrahydrofuran (THF) and precipitated from cold methanol and purified by repeating its precipitation three times from MeOH. The resulting polymer was filtered and dried overnight at 40 °C under vacuum to obtain a white powder.

Preparation of Macroinitiator

Under argon, 2-bromoisobutyl bromide (5.37 mL, 43.4 mmol) was added dropwise to a stirring mixture of PCL-OH



Scheme 1. The synthetic routes of PCL-b-PVPh by combinations of ring-opening and atom transfer radical polymerizations.

(17.3 mmol) and triethylamine (6.02 mL, 42.8 mmol) in 50 mL of toluene in an ice bath for 1 h. After complete addition of the acid bromide, the reaction was stirred at room temperature for 24 h. The reaction mixture was washed with water (3×150 mL) and then dried with MgSO_4 . After filtration, the mixture was precipitated with ten-fold methanol for purification. The resulting polymer was filtered and dried overnight at 40°C under vacuum to obtain a white powder.

General Procedure for Synthesis of PCL-b-PAS Block Copolymers

Block copolymers are easily prepared by ATRP of AS and PCL-Br in the presence of CuBr/PMDETA as a catalyst system. In a typical experiment, a 100-mL round-bottom flask was charged with appropriate amounts of CuBr , macroinitiator. O_2 was removed by repeated vacuum-nitrogen cycles.

Table 1. Summary of the ring-opening polymerization of PCL-OH.

Samples	CL ^{a)}	BA ^{a)}	Yield	$\bar{M}_{n,\text{th}}$	$\bar{M}_{n,\text{GPC}}^{\text{b)}$	$\bar{M}_{n,\text{NMR}}$	PDI
	g	g					
PCL-1	6.3	0.1	81	6 900	3 200	6 400	1.18
PCL-2	9.2	0.1	87	9 300	4 800	9 400	1.19
PCL-3	9.4	0.1	88	10 000	7 700	10 400	1.22
PCL-4	27.3	0.1	71	30 000	15 800	21 600	1.17

^{a)} CL: ϵ -caprolactone, BA: benzyl alcohol.

^{b)} Ref.^[58]: $\bar{M}_{\text{PCL}} = 0.259 \bar{M}_{\text{PS}}^{1.073}$.

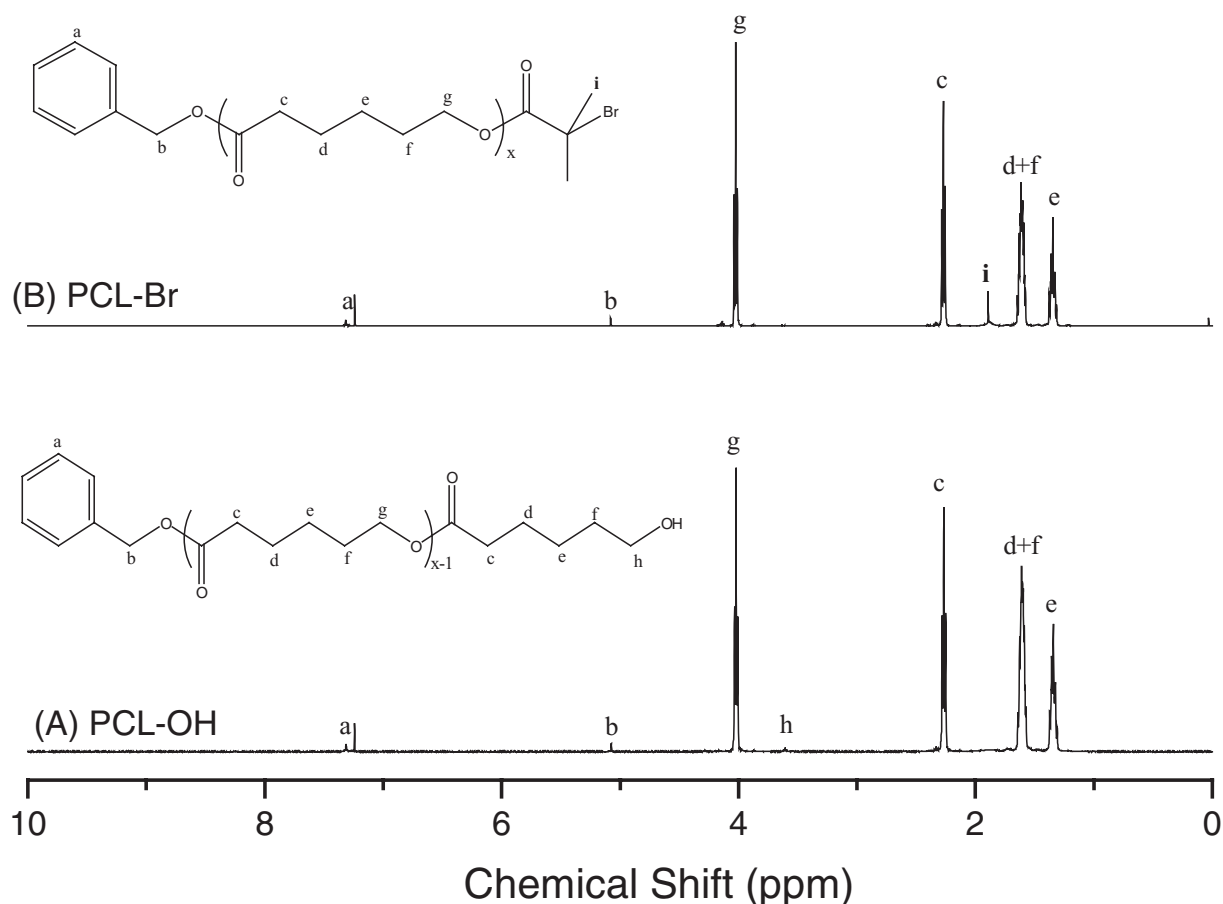


Figure 1. ^1H NMR spectra of (A) PCL-OH and (B) PCL-Br.

Once filled with N_2 , deoxygenated acetoxystyrene and ligand were added and the solution was stirred for 30 min at room temperature to promote the formation of the Cu complex. All processes were undertaken in a N_2 -filled dry box. The polymerization was then performed in an oil bath at an appropriate temperature. The reaction mixture immediately became dark-green and more viscous as it progressed. After a specific time, the mixture was cooled and diluted with five-fold THF and stirred with Amberlite IR-120 (H form) cation-exchange resin (3–5 g) for 30–60 min to remove the catalyst. The mixture was then passed through an alumina column and precipitated into MeOH. The product was dissolved in THF and purified by three times repeated precipitations from MeOH and ether. The resulting PCL-*b*-PAS block copolymer was filtered and dried overnight at 50°C under vacuum to obtain a white powder.

Selective Hydrolysis

PCL-*b*-PVPh was prepared from the selective hydrolysis of the PCL-*b*-PAS. Removal of the acetyl protecting groups from the AS polymers was carried out in 1,4-dioxane by treating it with hydrazine hydrate at room temperature. Typically, a block copolymer PCL-*b*-PAS (7.2 mmol of AS) was added in a flask and solubilized with 1,4-dioxane (30 mL). Then, hydra-

zine hydrate (3 mL) was added via a syringe and the ratio of hydrazine hydrate to 1,4-dioxane was 1:9 by volume. The reaction was allowed to proceed at room temperature under nitrogen for approximately 10 h. The solution was concentrated by evaporation of the solvent and washed with deion-

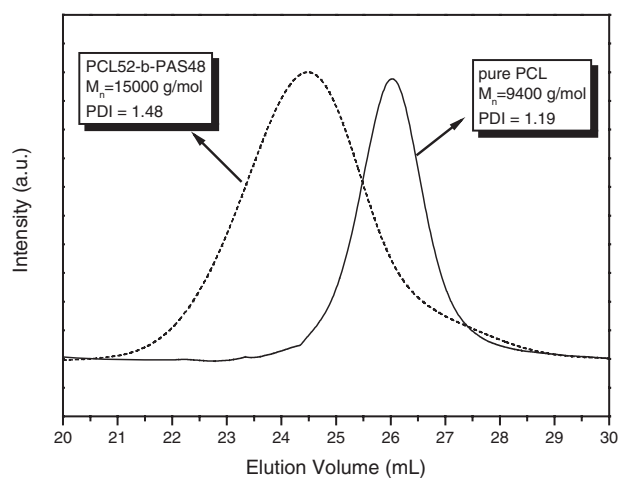


Figure 2. GPC traces of PCL-OH and PCL-*b*-PAS copolymer.

ized water several times, followed by drying in a vacuum oven at room temperature for 2 d.

Measurements

^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 on a Bruker AM 500 (500 MHz) spectrometer and the solvent signal was used as an internal standard. Molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) using a Waters 510 HPLC equipped with a 410 Differential Refractometer, a UV detector, and three Ultrastaygel columns (100, 500, and 10^3 \AA) connected in series. The THF was used as an eluent at a flow rate of $0.4 \text{ mL} \cdot \text{min}^{-1}$. The molecular weight calibration curve was obtained using polystyrene standards. FT-IR measurement was made using a Nicolet Avatar 320 FT-IR Spectrometer, 32 scans at a resolution of 1 cm^{-1} were collected with a NaCl disk. The THF solution-containing the sample was cast onto a NaCl disk and then dried at 50°C . The sample chamber was purged with nitrogen in order to maintain the film

dryness. Thermal analysis was carried out on a DSC instrument from DuPont (model 910 DSC-9000 controller) with a scan rate of $20^\circ\text{C} \cdot \text{min}^{-1}$ and a temperature range of $30\text{--}170^\circ\text{C}$ in nitrogen atmosphere. Approximately 5–10 mg of sample was weighed and sealed in an aluminum pan. The sample was then quickly cooled to room temperature from the first scan and then scanned between -100 and 200°C at a scan rate of $20^\circ\text{C} \cdot \text{min}^{-1}$. The glass transition temperature is taken as the midpoint of the heat capacity transition between the upper and lower points of deviation from the extrapolated glass and liquid lines.

Results and Discussion

Syntheses of PCL-Based Block Copolymers

The strategy for the synthesis of PCL based block copolymers was modified from Matyjaszewski^[41] and is outlined in Scheme 1. The ring-opening polymerization of $\epsilon\text{-CL}$, initiated by benzyl alcohol using $\text{Sn}(\text{oct})_2$ as a catalyst, produced PCL containing one hydroxyl chain end.

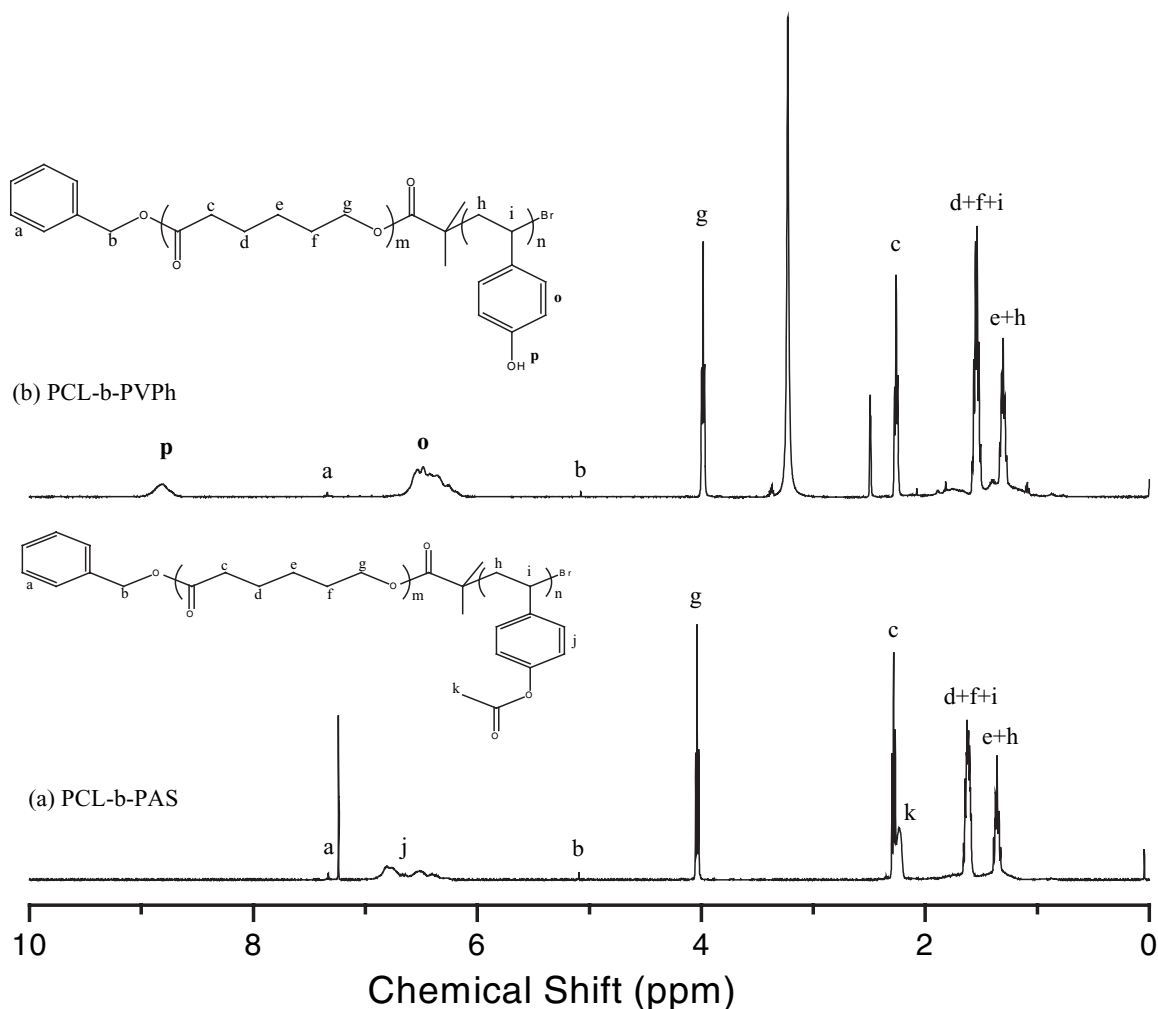


Figure 3. ^1H NMR spectra (a) before hydrolysis, PCL-*b*-PAS, and (b) after hydrolysis, PCL-*b*-PVPh.

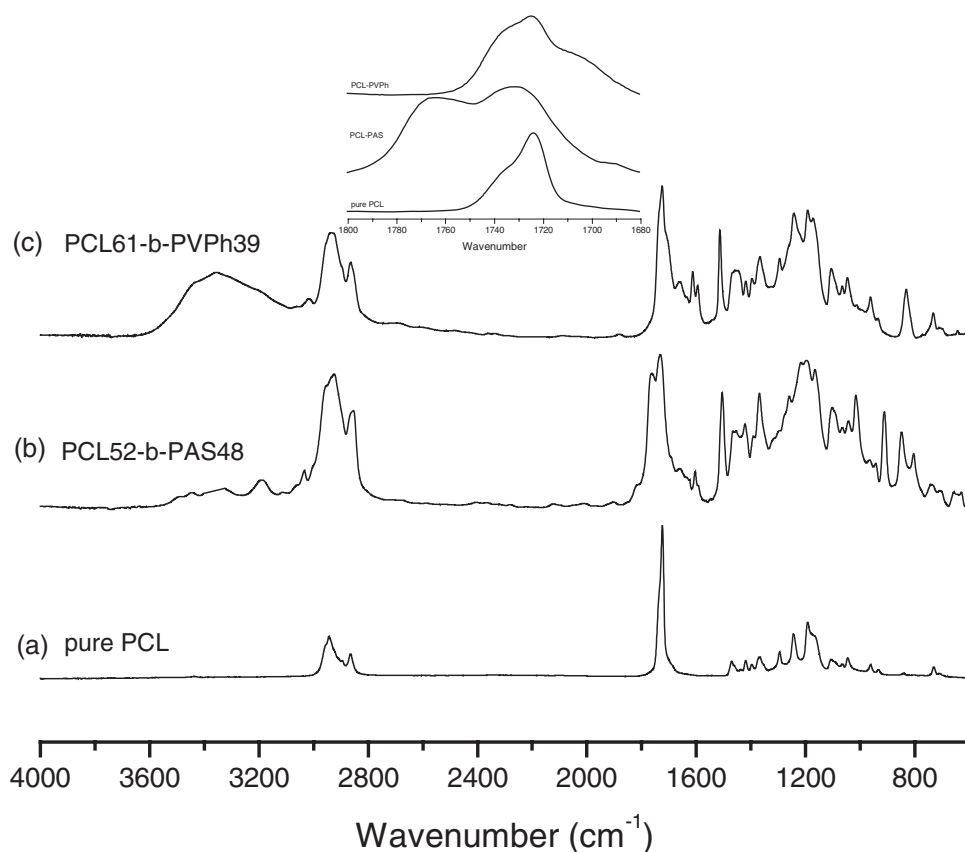


Figure 4. IR spectra of (a) pure PCL, (b) PCL-*b*-PAS, and (c) PCL-*b*-PVPh at room temperature ranging from 600 to 4000 cm^{-1} .

The ring-opening polymerization of ϵ -CL is summarized in Table 1, indicating the low polydispersity (<1.2) of this series of PCL-OH homopolymers. The hydroxyl chain end was modified to form an α -haloester, PCL-Br, an effective initiator for ATRP. The macroinitiator PCL-Br was then employed as the initiating species for the ATRP of AS in the presence of CuBr/PMDETA complex to produce

PCL-*b*-PAS diblock copolymers. Eventually, PCL-*b*-PAS diblock copolymers were converted into PCL-*b*-PVPh diblock copolymers by selective hydrolyses. According to the literature,^[44–46] a number of methods have been employed to convert the AS polymer into the corresponding polymer containing a phenolic group. It is difficult to proceed with the hydrolysis of PAS to PVPh in the presence

Table 2. Characterizations of PCL-*b*-X (X = PAS or PVPh) copolymers prepared by ring-opening and atom transfer radical polymerizations.

Copolymer	$\bar{M}_{n,\text{PCL}}^{\text{a)}}$	$\bar{M}_{n,\text{X}}^{\text{a)}}$	Total $\bar{M}_n^{\text{a)}}$	Total $\bar{M}_n^{\text{b)}}$	X ^{a)}	$\bar{M}_w/\bar{M}_n^{\text{b)}}$
					wt.-%	
PCL48- <i>b</i> -PAS52	6 400	6 800	13 200	13 000	52	1.42
PCL52- <i>b</i> -PAS48	9 400	8 600	18 000	15 000	48	1.48
PCL58- <i>b</i> -PAS42	10 400	7 600	18 000	19 500	42	1.32
PCL77- <i>b</i> -PAS23	21 600	6 500	28 100	32 000	23	1.24
PCL57- <i>b</i> -PVPh43	6 400	4 800	11 200	11 300	43	1.42
PCL61- <i>b</i> -PVPh39	9 400	6 000	15 400	13 600	39	1.48
PCL67- <i>b</i> -PVPh33	10 400	5 300	15 700	17 100	33	1.32
PCL83- <i>b</i> -PVPh17	21 600	4 600	26 200	30 000	17	1.24

^{a)} Obtained from ^1H NMR measurement.

^{b)} Obtained from GPC analysis.

of PCL due to its unstable behavior against hydrolysis conditions. To address this problem, selective hydrolysis between PAS and PCL is necessary to produce a desirable diblock copolymer by reacting with hydrazine hydrate. An optimal hydrolysis condition was chosen to convert the PCL-*b*-PAS into PCL-*b*-PVPh diblock copolymers (see *Experimental Part*).

Figure 1 illustrates ^1H NMR of PCL-OH homopolymer and PCL-Br macroinitiator, showing the methyl group (*i* hydrogen) of the 2-bromopropionyl bromide unit in the PCL-Br. This result indicates that the PCL-Br macroinitiator was indeed synthesized successfully. The GPC trace of the PCL-*b*-PAS block copolymer was obtained after ATRP as shown in Figure 2. Block copolymers prepared from the PCL macroinitiator resulted in products with narrow polydispersity and high symmetry, with monomodal GPC traces. The absence of the PCL macroinitiator peak supports the formation of PCL-*b*-PAS diblock copolymers.

Complete elimination of the protective groups and the generation of the phenolic hydroxyl groups were demonstrated by ^1H NMR spectroscopy. Figure 3 shows typical ^1H NMR spectra of the diblock copolymer recorded before (bottom) and after (top) deprotection. A chemical shift at 2.2 ppm corresponds to the acetyl group of the PCL-*b*-PAS

copolymer (in $\text{DMSO-}d_6$). These peaks corresponding to the acetyl group disappeared essentially from the spectrum of the hydrolyzed block copolymer, and only the polymer backbone protons appear in the chemical shift region of 1–2 ppm. In addition, a peak (8.0 ppm) corresponding to the proton of the hydroxyl group appears after hydrolysis reaction. Although this diblock copolymer system has not been investigated previously, ATRP of the protected 4-vinyl phenol monomer^[47–49] and the ring-opening polymerization of caprolactone monomer^[50] have been documented. To obtain a PVPh block, it is necessary to protect the hydroxyl group prior to polymerization to avoid the termination of the living chain end. Various protecting groups, including acetyl,^[47] *tert*-butyl ether,^[51] and *tert*-butyldimethylsilyl^[52] groups, have been used for hydroxyl group protection during polymerization.

As mentioned above, the acetyl group was deliberately chosen as a protective group in this study because it was expected to be more selective and readily removed from the parent copolymer without hydrolyzing the ester groups.^[53] The FT-IR spectra of pure PCL, PCL-*b*-PAS, and PCL-*b*-PVPh are shown in Figure 4. The characteristic carbonyl stretching of the PCL-*b*-PAS is split into two bands, due to absorption by PCL and PAS at 1724 and 1760 cm^{-1} , respectively. The absorption at 1760 cm^{-1}

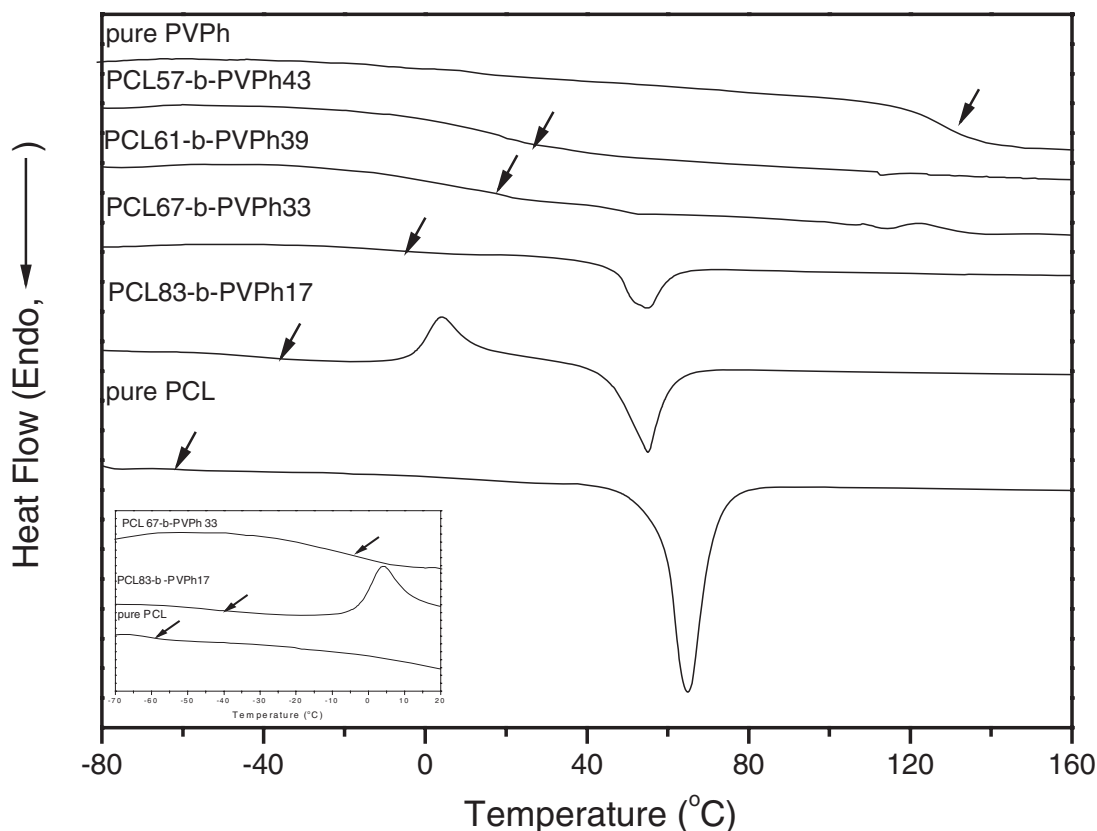


Figure 5. DSC traces of PCL-*b*-PVPh copolymers with various PVPh contents.

corresponding to the acetyl group of the PCL-*b*-PAS disappeared essentially and it shifted to 1708 cm^{-1} corresponding to the hydrogen bonded carbonyl group between the carbonyl group of PCL and the hydroxyl group of PVPh after hydrolysis. The broad peak at 3350 cm^{-1} in Figure 4(c) also indicates the presence of the hydroxyl groups. The molecular weight fraction of the PCL-*b*-PVPh block copolymer was measured by ^1H NMR spectroscopy and GPC, by analyzing the relative signal intensities of the protons of the PCL and PVPh segments. The calculation was performed by comparing the signals of the aromatic protons of the PVPh segment (6.4–6.8 ppm) and the signal of the methylene groups of the PCL segment (3.6 ppm). Table 2 lists these calculated molecular weight fractions and the total molecular weights determined by GPC; the number “*n*” beside the descriptor “PCL-*b*-PAS” and “PCL-*b*-PVPh” reflects the molecular weight percent. Table 1 and 2 demonstrate a common problem in GPC measurement due to the use of PS as the standard, which has a dissimilar solution behavior in the resulting polymers (here, PCL and PCL-based block copolymers). We believe that there is a systematic deviation in measuring the values of \bar{M}_n and \bar{M}_w in our GPC system, whereas the polydispersity values provided us a relative molecular weight distribution at the stage of macroinitiator and block copolymer preparations. Later, our quantitative represen-

tation of chain length was based on the ^1H NMR measurements for the resulting polymers.

Thermal Analyses

Figure 5 shows DSC thermograms for PVPh, PCL, and PCL-*b*-PVPh copolymers, indicating that the T_g of the pure PVPh is 120°C ($\bar{M}_n = 1500\text{--}7000\text{ g}\cdot\text{mol}^{-1}$), and the melting temperature of the pure PCL is 60°C . The T_g of PVPh shifts to lower temperature as the PCL content in the diblock copolymer is increased. Meanwhile, the melting temperature of the PCL component in the copolymer decreased with increase in the PVPh content. A melting depression is characteristic of the miscible diblock copolymer in the melting state. Although the immiscible diblock copolymer also has similar phenomena,^[54] we believe that this is characteristic of miscible diblock copolymers since all PCL-*b*-PVPh copolymers show only one single glass transition temperature (T_g) with an overall blend composition. A single T_g strongly suggests that these two components are fully miscible diblock copolymers in the amorphous phase. The dependence of T_g on the composition of the miscible PCL-*b*-PVPh is shown in Figure 6. Over the years, a number of equations have been proposed to predict the variation of the glass transition temperature

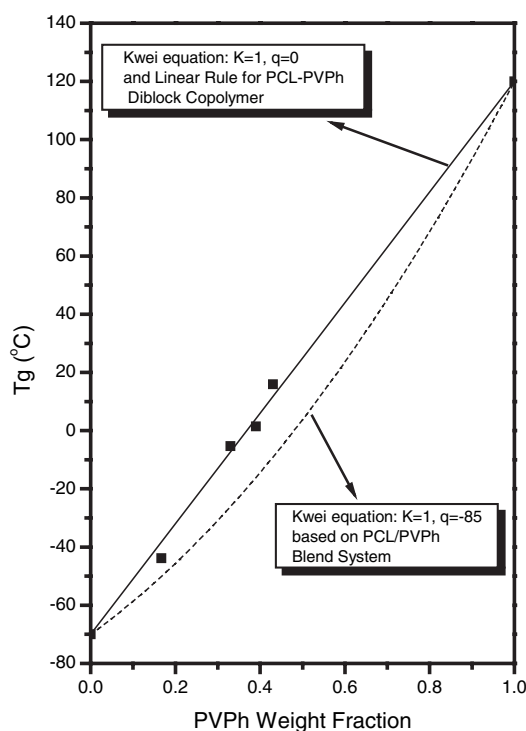


Figure 6. Plots of T_g versus composition based on (■) experimental data and Kwei equation.

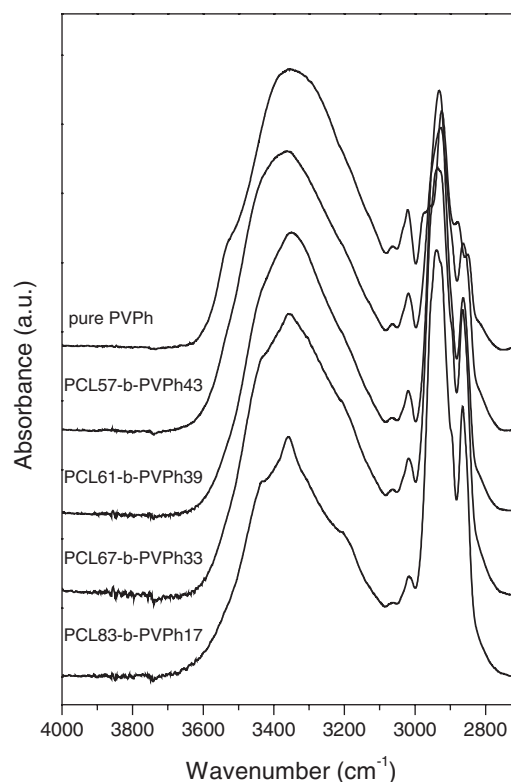


Figure 7. FT-IR spectra in the $2700\text{--}4000\text{ cm}^{-1}$ region for PCL-*b*-PVPh copolymers with various PVPh contents.

of a miscible blend as a function of composition. The most popular equation is the Kwei equation:^[55]

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + qW_1 W_2 \quad (1)$$

where W_1 and W_2 are component weight fractions of the copolymer, T_{g1} and T_{g2} represent the corresponding glass transition temperatures, and k and q are fitting constants. The parameter q corresponds to the strength of the specific interaction in a copolymer or polymer blend. The Kwei equation can apply to polymer blends with specific interaction, such as hydrogen bonding in polymer blend, and copolymer system. In this study, we use the Kwei equation from binary blend in order to predict the miscible diblock copolymer. $k=1$ and $q=0$ are obtained from the non-linear least squares “best fit” values, which is similar to the linear rule. Compared with the previous PCL/PVPh blend ($k=1$, $q=-85$), the difference in q observed between the two systems can be interpreted as it indicates that the strength of the specific interactions within the PCL-*b*-PVPh diblock copolymers is greater than the corresponding PCL/PVPh blends, which is consistent with our previous studies.^[33,56]

FT-IR Analyses

Infrared spectroscopy has proven to be a powerful tool for investigating specific interactions between polymers and the mechanism of interpolymer miscibility through the formation of hydrogen bonds both qualitatively and quantitatively. Several regions within the infrared spectra of PCL-*b*-PVPh copolymers are influenced by a hydrogen-bonding interaction. Figure 7 shows the infrared spectra in the 2700–4000 cm^{-1} of pure PVPh, and various PCL-*b*-PVPh copolymers measured at room temperature. The pure PVPh polymer is composed of two components in this spectrum; a very broad band centered at 3350 cm^{-1} is attributed to the wide distribution of the hydrogen bonded hydroxyl groups, while a relatively narrow band at 3525 cm^{-1} is caused by the free hydroxyl group. Figure 7 indicates that the intensity of free hydroxyl group (3525 cm^{-1}) decreases gradually with the increase in PCL content. However, the broad hydrogen bonded hydroxyl band of the PVPh does not shift significantly at around 3350 to 3360 cm^{-1} . Compared with the PCL/PVPh blend system,^[30] the broad hydrogen bonded hydroxyl band of the PCL-*b*-PVPh shifts into a higher frequency region with increasing PCL content at 3430 cm^{-1} . This shift is due to the switch from the hydroxyl-hydroxyl bond to the hydroxyl-carbonyl bond, indicating the existence of an hydrogen bonding interaction between the PCL carbonyl group and the hydroxyl group of PVPh. The average strength of the intermolecular interaction can be obtained by the frequency

difference ($\Delta\nu$) between the hydrogen bonding hydroxyl absorption and free hydroxyl absorption.^[57] This observation reveals that the average strength of the hydrogen bond between the PVPh hydroxyl and the PCL carbonyl in the blend system ($\Delta\nu=95 \text{ cm}^{-1}$) is weaker than that of the self-associated hydroxyl of the PVPh ($\Delta\nu=175 \text{ cm}^{-1}$), which is responsible for the observed negative q value in the Kwei equation in this blend system. However, in a PCL-*b*-PVPh diblock copolymer system, $\Delta\nu \approx 165\text{--}175 \text{ cm}^{-1}$ between the hydroxyl and carbonyl groups is close to the hydroxyl-hydroxyl, and thus results in $q=0$ in the Kwei equation.

Figure 8 shows the infrared spectra of the carbonyl stretching at room temperature ranging from 1680 to 1780 cm^{-1} for PCL-*b*-PVPh copolymers. The carbonyl stretching for the pure PCL is split into two bands, absorption by amorphous and crystalline conformations at 1734 and 1724 cm^{-1} , respectively. Another contribution at approximately 1708 cm^{-1} is assigned to the PCL carbonyl group, and hydrogen bonded to the PVPh hydroxyl group. These absorptions can be well fitted in the Gaussian function as shown in Figure 8. The fraction of the hydrogen bonded carbonyl group of PCL can be

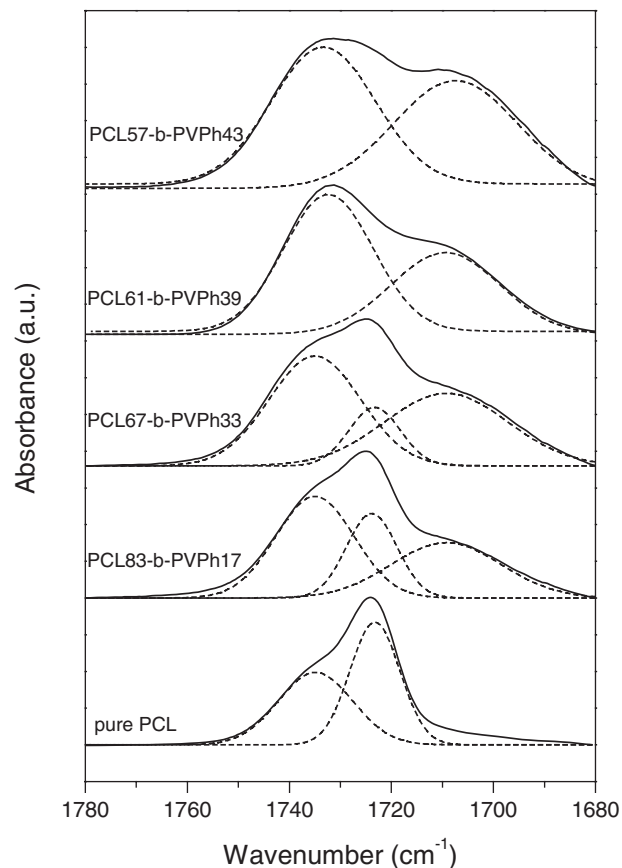


Figure 8. FT-IR spectra in the 1680–1780 cm^{-1} for PCL-*b*-PVPh copolymers with various PVPh contents.

Table 3. Curve fitting results of the PCL-*b*-PVPh block copolymer at room temperature [ν : wavenumber (cm^{-1}), $W_{1/2}$: half-width (cm^{-1}), A_f : area fraction, f_b : fraction of hydrogen bonded carbonyl group].

Copolymers	Amorphous C=O			Crystalline C=O			H-bonded C=O			f_b
	ν	$W_{1/2}$	A_f	ν	$W_{1/2}$	A_c	ν	$W_{1/2}$	A_b	
	cm^{-1}		%	cm^{-1}		%	cm^{-1}		%	
Pure PCL	1734	17	47	1723	12	53	–	–	–	–
PCL83- <i>b</i> -PVPh17	1734	18	44	1723	12	23	1709	26	33	24.8
PCL67- <i>b</i> -PVPh33	1734	20	46	1723	11	14	1709	27	40	31.0
PCL61- <i>b</i> -PVPh39	1733	20	58	–	–	–	1709	25	42	32.5
PCL57- <i>b</i> -PVPh43	1733	22	52	–	–	–	1708	27	48	38.1

calculated by using an appropriate absorptivity ratio ($a_R = a_{\text{HB}}/a_{\text{F}} = 1.5$) which has been discussed in our previous study.^[27] The results from curve fitting are summarized in Table 3, indicating that the hydrogen bonded fraction of the carbonyl group increases with the PVPh content. In addition, the crystallinity of PCL decreases with the increase in the PVPh content. It is consistent with the DSC analyses that the crystallinity disappeared for PVPh at 39 wt.-% in PCL-*b*-PVPh copolymer as shown in Figure 5.

Conclusion

¹H NMR, FT-IR spectroscopy, and GPC analyses give evidence that the PCL-*b*-PVPh diblock copolymers are prepared successfully through a combination of ring-opening and atom transfer radical polymerizations. DSC results show that the PCL-*b*-PVPh diblock copolymer has a single glass transition temperature over the entire composition range, and also has higher glass transition temperatures compared to the corresponding PCL/PVPh blends. FT-IR analysis confirms the hydrogen-bonding interaction between the PVPh hydroxyl group and the PCL carbonyl group. The crystallization and microstructure behavior of this miscible diblock copolymer will be studied in the near future.

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