

Synthesis and Characterization of Poly(vinyl chloride-*co*-vinyl acetate)-graft-Poly[(meth)acrylates] by Atom Transfer Radical Polymerization

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ABSTRACT: The graft polymerization of methyl methacrylate and butyl acrylate onto poly(vinyl chloride-*co*-vinyl acetate) with atom transfer radical polymerization (ATRP) was successfully carried out with copper(I) thiocyanate/*N,N,N',N',N''*-pentamethyldiethylenetriamine and copper(I) chloride/2,2'-bipyridine as catalysts in the solvent *N,N*-dimethylformamide. For methyl methacrylate, a kinetic plot of $\ln([M]_0/[M])$ (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration) versus time for the graft polymerization was almost linear, and the molecular weight of the graft copolymer increased with increasing

conversion, this being typical for ATRP. The formation of the graft polymer was confirmed with gel permeation chromatography, $^1\text{H-NMR}$, and Fourier transform infrared spectroscopy. The glass-transition temperature of the copolymer increased with the concentration of methyl methacrylate. The graft copolymer was hydrolyzed, and its swelling capacity was measured. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 183–189, 2005

Key words: atom transfer radical polymerization (ATRP); hydrogels; poly(vinyl chloride) (PVC)

INTRODUCTION

Graft copolymers derived from commercial polymers offer an effective approach for incorporating specific properties into a material while retaining desirable properties of the parent polymer. Poly(vinyl chloride) (PVC) is one of the most widely used vinyl polymers in the world.^{1,2} Replacing chlorine atoms of PVC with other atoms or groups would yield new polymer properties (or effects), such as thermal stability, polymer-solvent interactions, and dielectric response. Much research has been conducted on the graft copolymerization of PVC since the 1960s.^{3–6}

Metal-catalyzed living radical polymerization (LRP) initiated by allylic halides, also called atom transfer radical polymerization (ATRP), has recently been used to prepare well-defined polymers^{7,8} and provides another approach to the preparation of graft copolymers. Any compounds, including macromolecular species, can potentially be used to initiate ATRP as long as they contain activated halogen atoms. Matyjaszewski

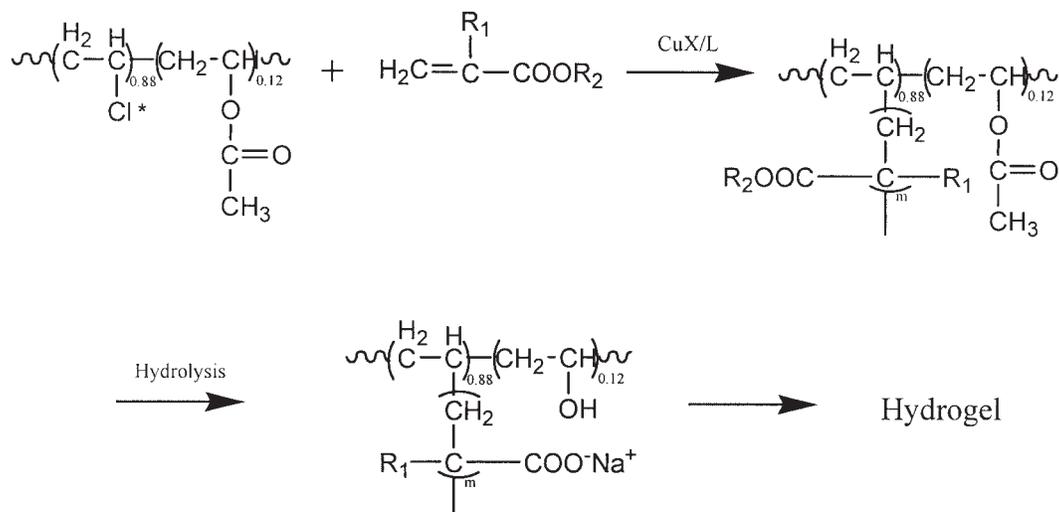
et al.⁹ polymerized styrene and various acrylates onto PVC by ATRP with the chloroacetyl groups as the initiating sites. Percec and Asgarzadeh¹⁰ carried out the metal-catalyzed LRP of PVC with the active chloride groups from structural defects of PVC. Also, with the active (labile) chloride atoms in commercial PVC, the graft copolymerization of butyl acrylate (BA) and 2-ethyl hexylacrylate onto PVC was reported by Bicak and Ozlem.¹¹

Here we present the preparation of grafted poly(vinyl chloride-*co*-vinyl acetate) (PVCAc) with methyl methacrylate (MMA) and BA by ATRP, with the active chlorides in commercial PVCAct acting as the initiating sites (Scheme 1). Furthermore, the graft copolymer was hydrolyzed, and the hydrolyzed copolymer showed some swelling capacity in water. This type of hydrogel is physically crosslinked by hydrogen bonds between the carboxyl groups and hydroxyl groups in the hydrolyzed graft copolymer. Hydrophobic interactions may also play a role.¹² Because of their hydrophilic character and potential to be biocompatible, hydrogels have been very interesting to biomaterial scientists for many years. The greatest advantage of physically crosslinked gels is that they avoid the adverse effects caused by crosslinking agents, which are often toxic compounds.

In this study, after graft polymerization with ATRP, we hydrolyzed graft copolymers. The swelling capac-

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Scheme 1 Graft polymerization of MMA or BA onto PVCAc and hydrolysis of the copolymer (CuX/L = CuSCN/PMDETA or CuCl/bpy; R₁ = CH₃ or H; R₂ = CH₃ or C₄H₉; Cl* = active chloride atoms in PVCAc).

ity of the hydrolyzed copolymers and the influence of the pH on the swelling capacity were studied.

EXPERIMENTAL

Materials

MMA and BA (chemically pure; Shanghai Chemical Reagent Co., Ltd., Shanghai, China) were purified by extraction with a 5% sodium hydroxide aqueous solution, followed by washing with water, were dried with anhydrous sodium sulfate overnight, and finally were distilled *in vacuo*. Copper(I) chloride (CuCl; analytical reagent; Shanghai Zhenxin Chemical Reagent Factory, Shanghai, China) was dissolved in hydrochloric acid, precipitated into a large amount of deionized water, filtered, washed with absolute ethanol, and dried *in vacuo*. Copper(I) thiocyanate (CuSCN; 98.04%; Yixing Liaoyuan Chemical Co., Ltd., Yixing, China) was purified by washing with acetic acid and acetone and then dried *in vacuo*. *N,N,N',N',N''*-Pentamethyldiethylenetriamine (PMDETA) was dried with a 4-Å molecular sieve and distilled *in vacuo*. 2,2'-Bipyridine (bpy; analytical reagent; Shanghai Chemical Reagent Co., Ltd., Shanghai, China), *N,N*-dimethylformamide (DMF; analytical reagent; Shanghai No. 1 Chemical Reagent Factory), tetrahydrofuran (THF; analytical reagent; Shanghai Chemical Reagent), and toluene (analytical-reagent; Shanghai Chemical Reagent) were used as received. PVCAc was provided by Nantong Resin Co. A ¹H-NMR study showed that 12 mol % vinyl acetate with respect to vinyl chloride (VC) was incorporated into PVCAc [gel permeation chromatography (GPC) determined number-average molecular weight ($M_{n,\text{GPC}}$) = 43,800, weight-average molecular

weight (M_w)/number-average molecular weight (M_n) = 1.81].

Copolymerization and hydrolysis

A dry glass tube was filled with MMA (or BA), PVCAc, CuSCN, PMDETA, and DMF. Three freeze-pump-thaw cycles were performed, and the tube was sealed *in vacuo* and placed in an oil bath held by a thermostat at the desired temperature for polymerization. The polymerization was stopped at a desired time by the cooling of the tube in ice water. Afterwards, the tube was opened, and its contents were dissolved in THF and precipitated into a large amount of methanol. The polymer was purified by redissolution in THF and reprecipitation in methanol three times.

The copolymers were hydrolyzed at 100°C with an NaOH solution in THF for 12 h and then were cooled, filtered, washed, and dried *in vacuo*.

Swelling procedure

A dried copolymer of a known weight was placed in clean glass containers. Different solvents were added to the containers, and the containers were sealed. The swelling process was carried out at room temperature overnight for maximum absorption, and the swelling gel was then filtered with an 80-mesh sieve and weighed. The swelling capacity was calculated as follows:

$$\text{Swelling capacity} = (W - W_0)/W_0 \text{ (g/g)}$$

TABLE I
Results of the Graft Copolymerization of BA and MMA onto PVCAc

No.	Monomer	[M]/[VC]/ [CuX]/[L]	Time (h)	Temperature (°C)	Conversion (%)	$M_{n,GPC}$	$M_{n,Gravimeter}$	M_w/M_n
1	BA	200:40:1:3	7	110	43.0	46,000	128,000	2.56
2	BA	200:10:1:3	42		52.9	57,000	491,000	2.93
3	MMA	200:40:1:3	0.5	80	20.5	47,000	109,000	1.84
4	MMA	200:40:1:3	4.0		57.2	78,000	225,000	2.29
5	MMA	200:44:1:3	47	110	60.8	78,000	236,000	2.56
6	MMA	200:44:1:3	57		67.8	86,000	258,000	2.60

V = Volume, L = Ligand; W = weight of polymer. Experimental conditions: $[MMA]_0 = 4.7M$; $[BA]_0 = 3.51M$; $V(DMF):V(Monomer) = 1:1$; $CuX/L = CuSCN/PMDETA$ (nos 1–4) and $CuCl/bpy$ (nos 5–6); $M_{n,Gravimeter} = M_{n,PVCAC} \times (W_{copolymer}/W_{PVCAC})$.

where W_0 and W are the weights of the polymer before and after swelling.

Characterization

The monomer conversion was determined by gravimetry. The molecular weight and its distribution were measured with a Waters 1515 gel permeation chromatograph with THF as a mobile phase at a column temperature of 30°C. Polystyrene standards were used to calibrate the columns. ¹H-NMR spectra are recorded in CDCl₃ with an Inova 400-MHz spectrometer (Palo Alto, CA) at the ambient temperature. Fourier transform infrared (FTIR) was measured with a Nicolet Avatar 360 spectrometer (San Jose, CA). Differential scanning calorimetry (DSC) data were obtained with a PerkinElmer DSC 7 (New Castle, DE) at a scanning rate of 20°C/min.

RESULTS AND DISCUSSION

Synthesis of PVCAc-g-PMMA and PVCAc-g-pba [pmma = poly(methyl methacrylate) and pba = poly(butyl acrylate)]

The graft polymerization was performed with MMA and BA. The GPC curves showed that the molecular weight of the copolymer increased after the polymerization. The results are summarized in Table I. The polymerization rate with the CuSCN/PMDETA system was much faster than that with the CuCl/bpy system. A similar phenomenon was reported by Singha and Klumperman.¹³

A kinetic plot of $\ln([M]_0/[M])$ (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration) versus time for the graft polymerization of MMA onto PVCAc is shown in Figure 1. The slope indicates that the polymerization proceeded with an approximately constant number of active species for the duration of the reaction, although there are deviations from linearity because of the variable num-

ber of active chloride atoms in the starting macroinitiator.

Figure 2 shows M_n and the molecular weight distribution (M_w/M_n) as a function of conversion. $M_{n,GPC}$ of PVCAc-g-PMMA increased with increasing conversion; the polydispersity index (PDI) varied from 1.84 to 2.29 and increased a little with increasing conversion. The polydispersities of the resulting graft copolymers were relatively high because of the high polydispersities (1.81) of the starting macroinitiator and may also have been due to the variable number of active chloride atoms in the macroinitiator. The deviation of $M_{n,GPC}$ from the gravimeter-determined number-average molecular weight ($M_{n,gravimeter}$) may be due to the difference in the hydrodynamic volumes between the graft copolymer and linear polystyrene standards. On the other hand, M_n determined by ¹H-NMR was close to that to $M_{n,gravimeter}$.

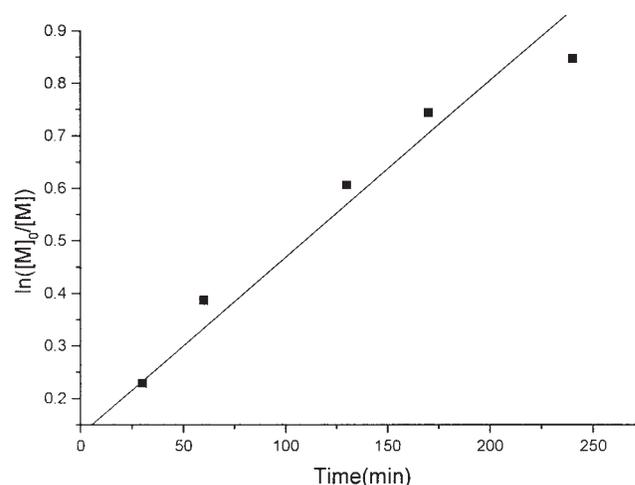


Figure 1 Kinetics of the graft polymerization of MMA onto PVCAc with ATRP [temperature = 80°C; $[MMA]_0 = 4.7M$; $[MMA]_0/[VC]_0/[CuSCN]_0/[PMDETA]_0 = 20:40:1:3$; $V(DMF)/V(MMA) = 1:1$].

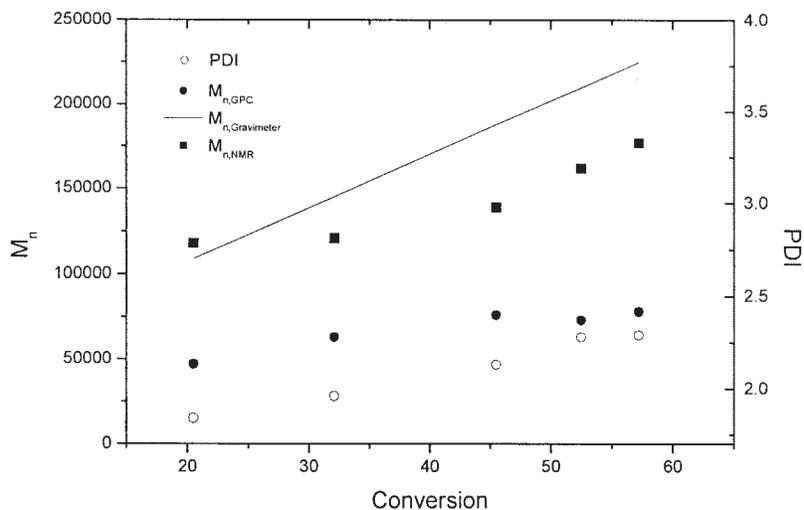


Figure 2 Dependence of M_n and M_w/M_n on the conversion in the graft polymerization of MMA onto PVCAc with ATRP {temperature = 80°C; $[MMA]_0 = 4.7M$; $[MMA]_0/[VC]_0/[CuSCN]_0/[PMDETA]_0 = 20:40:1:3$; Volume ratio: (DMF)/V(MMA) = 1:1}.

Analysis of the PVCAc graft copolymer

The formation of the graft copolymer was also supported by FTIR analysis (Fig. 3). The spectra of the PVCAc macroinitiator showed C—Cl stretching ($\nu = 608 \text{ cm}^{-1}$ and $\nu = 692 \text{ cm}^{-1}$) in the VC groups [Fig.

3(A)]. These two peaks became smaller after the graft polymerization, and this indicated a successful incorporation of MMA and BA initiated by the active chloride atoms in PVCAc. The strong carbonyl peak at $\nu = 1732 \text{ cm}^{-1}$ and $\nu = 1734 \text{ cm}^{-1}$ corresponded to the

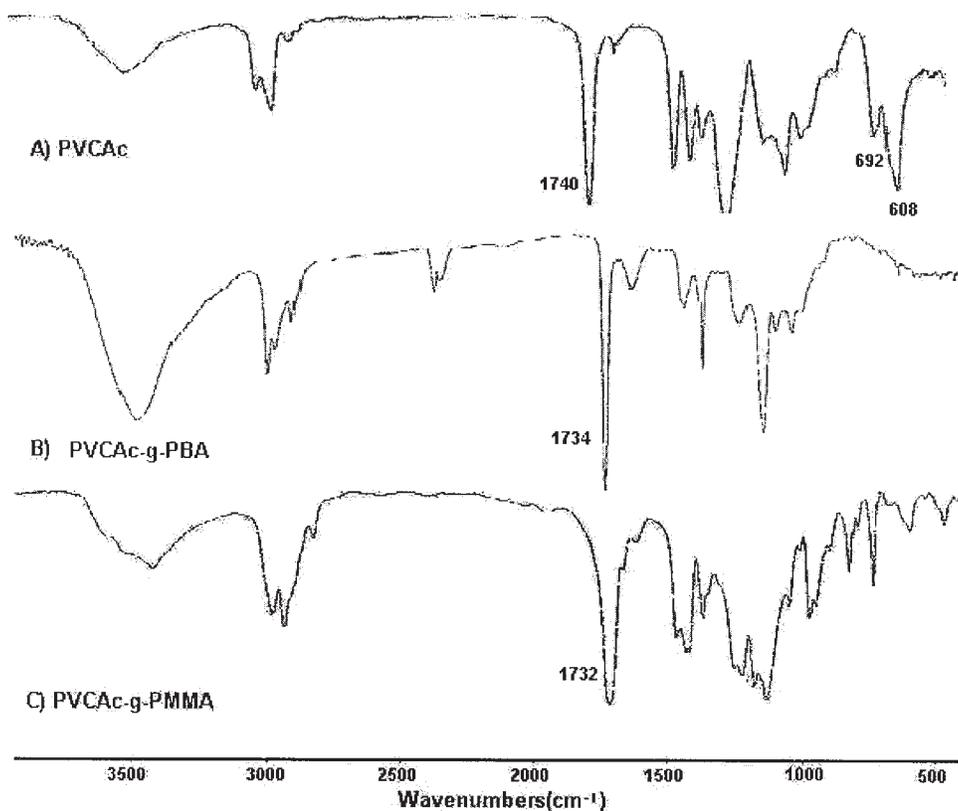


Figure 3 FTIR spectra of PVCAc and grafted copolymers.

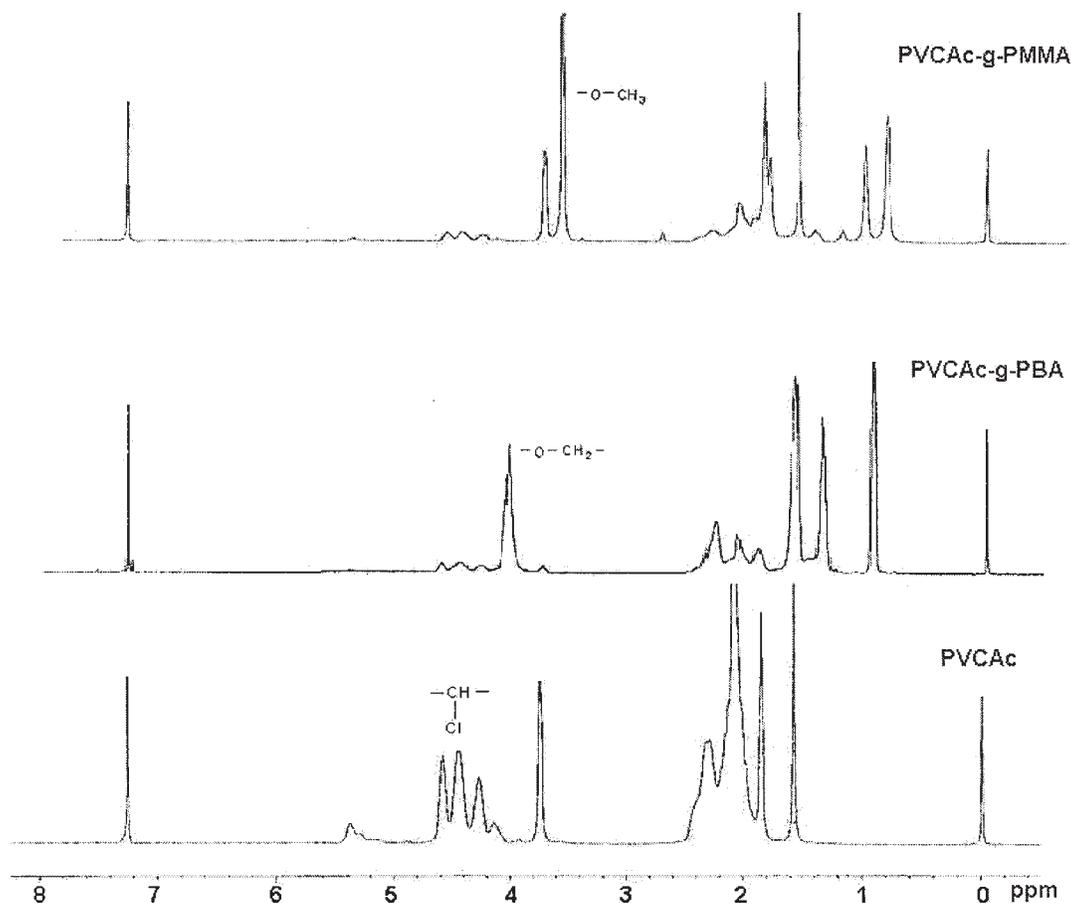


Figure 4 $^1\text{H-NMR}$ spectra of PVCAc and grafted copolymers.

carbonyl stretching from the acrylate groups [Fig. 3(B,C)].

Figure 4 presents the $^1\text{H-NMR}$ spectra of pure PVCAc and the resulting graft copolymers. All the spectra show the characteristic resonances corresponding to both PVCAc and the graft copolymer; for the BA-grafted copolymer, the signal (3.75) of the ether group in vinyl acetate became weaker after

graft polymerization, and only a small peak could be observed. This may have been due to the hydrolysis of acetate at a higher temperature with PM-DETA. The $^1\text{H-NMR}$ spectra also allowed for the determination of the VC/graft monomer molar ratio and the number-average molecular weight of the graft copolymer ($M_{n,\text{graft}}$), as presented in Table II. The molecular weights measured by GPC, gravim-

TABLE II
Characterization of Selected Graft Copolymerizations of BA and MMA onto PVCAc by GPC, $^1\text{H-NMR}$, DSC, and Gravimetric Measurements

No.	Monomer	Conversion	Incorporated	$M_{n,\text{GPC}}$	$M_{n,\text{Gravimeter}}^b$	$M_{n,\text{NMR}}^c$	T_g ($^\circ\text{C}$)
1	—	0	0	43,800	—	—	77.9
2	BA	43.0	58	46,000	128,000	154,000	8.9
3	MMA	20.5	54	46,500	109,000	118,000	106.1
4	MMA	45.5	60	76,000	188,000	139,000	113.5
5	MMA	57.2	68	78,300	225,000	177,000	119.8

W = weight of polymer.

^a Composition of monomer by $^1\text{H-NMR}$.

^b Calculated on the basis of the weight of the graft copolymer with $M_{n,\text{Gravimeter}} = M_{n,\text{PVCAc}} \times (W_{\text{copolymer}}/W_{\text{PVCAc}})$.

^c Calculated from $^1\text{H-NMR}$ analysis with $M_{n,\text{Graft}} = M_{n,\text{PVCAc}} \times [1 + (M_{w,\text{Monomer}}/69.5) \times [\text{Mole}_{\text{Grafted}}/(\text{Mole}_{\text{VC}}/0.88)]]$.

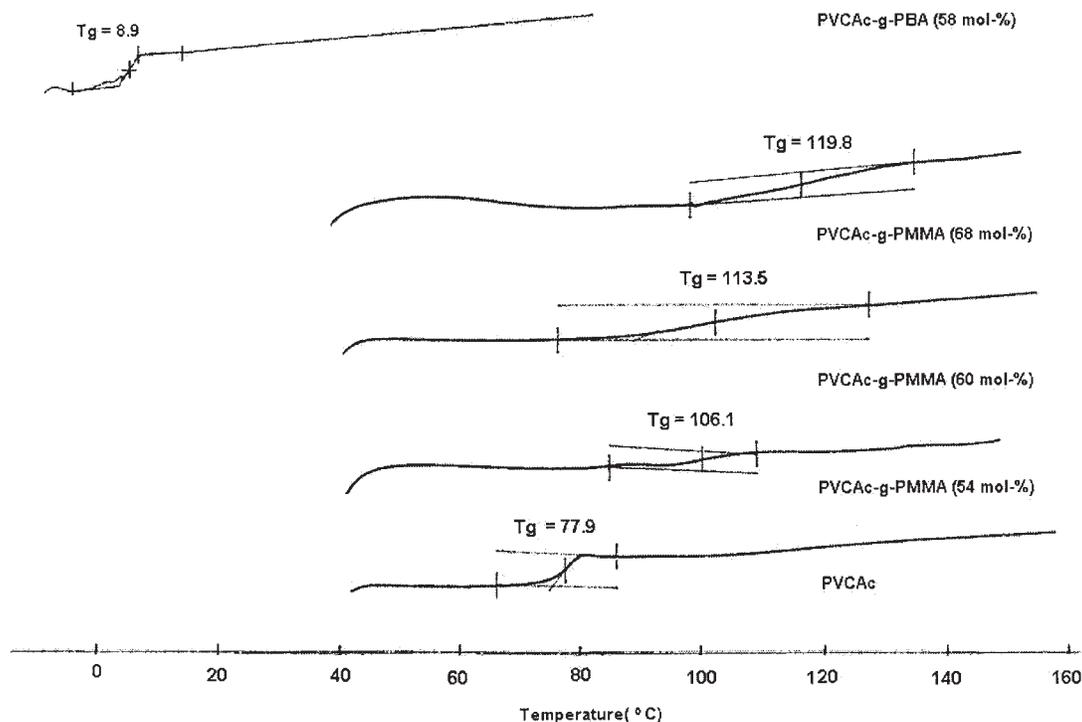


Figure 5 DSC curves of PVCAc and grafted copolymers.

etry, and $^1\text{H-NMR}$ all increased with increasing polymerization time.

Thermal analysis (DSC) revealed only one glass-transition temperature (T_g) for all the copolymers. It increased with the MMA concentration in the copolymer (Fig. 5). The results are summarized in Table II.

Swelling capacity of the copolymer after hydrolysis

After the graft copolymerization with ATRP, the graft copolymer was hydrolyzed. The swelling capacity of the hydrolyzed graft copolymer of PVCAc and PMMA (HP(PVCAc-g-PMMA)) in water was disappointing, although it had a swelling capacity of 7.2 g/g in DMF. This was possibly because the backbone of PVC was hydrophobic and the average length of PMMA in the copolymer was small. For example, the average length of PMMA (sample 4 in Table II) was 1.7 according to $^1\text{H-NMR}$, with every chloride group assumed to be connected to PMMA. In addition, the methyl group of PMMA played a negative role during swelling in water.

However, after PVCAc-g-PBA (sample 2 in Table II) was hydrolyzed, the swelling capacity of the hydrolyzed copolymer was promising, as shown in Figure 6. HP(PVCAc-g-PBA) not only swelled in organic solvents such as DMF but also swelled in water. This was

due to the hydrogen bond between the carboxylic groups and hydroxyl groups, which led to a physically crosslinked network. In addition, the hydrolyzed copolymer showed some pH sensitivity; the swelling capacity (8.6 g/g) of water at pH 7 was higher than that (4.6 g/g) at pH 3. This may be attributed to the different free water contents under various conditions. At pH 3, poly(acrylic acid) existed in a hydrated state and formed strong hydrogen bonds with water and

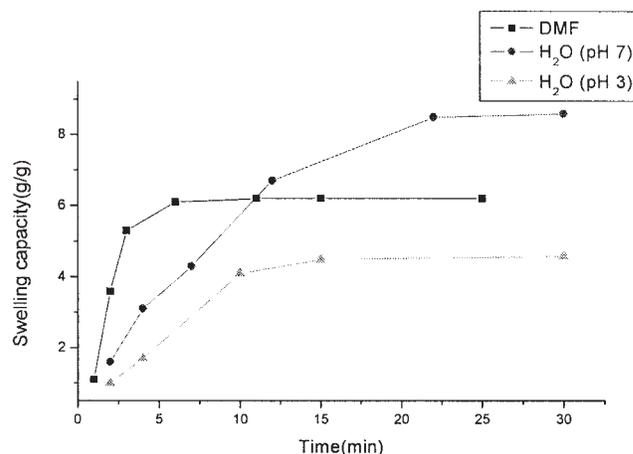


Figure 6 Swelling capacity of the copolymer (PVCAc-g-PBA) hydrolyzed in DMF and pH water solutions.

hydroxyl groups of poly(vinyl alcohol), and the free water contents were lower than those at pH 7.^{14,15}

CONCLUSIONS

The graft polymerization of MMA and BA onto PV-CAC was successfully carried out with ATRP catalyzed by CuSCN/PMDETA and CuCl/bpy in the solvent DMF. A kinetic plot of $\ln([M]_0/[M])$ versus time for the graft polymerization of MMA was almost linear, and the molecular weight increased with increasing conversion. The formation of the graft polymer was confirmed with GPC, ¹H-NMR, and FTIR spectroscopy. The swelling behavior of HP(PVCac-g-PBA) in different solvents was studied and showed pH sensitivity in water.

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