Preparation and Characterization of Ultra-Low Molecular Weight Poly(vinyl alcohol) Graft Copolymer

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ABSTRACT: Graft reaction of acrylamide (AM) and 4-vinyl pyridine (4-VP) onto ultra-low molecular weight poly(vinyl alcohol) by ceric (IV) ion initiation had been systematically investigated; and the graft conditions were optimized by studying the effect of monomer/initiator concentration, solvents composition, reaction time and temperature. At optimized conditions, the maximum grafting efficiency and grafting ratio was $\sim$ 50% and 51%, respectively with the presence of AM, whereas they decreased to 19% and 23%, respectively, without the presence of AM. Thermogravimetric analysis showed that as-resulted graft copolymer had a lower thermal stability than homopolymer PVA. FTIR and ^{1}H-NMR confirmed chemical structure of as-synthesized graft copolymer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3954–3962, 2009

Key words: degree of polymerization; poly(vinyl alcohol); graft copolymers; 4-vinyl pyridine

INTRODUCTION

Poly(vinyl alcohol) (PVA) is one of the important water-soluble polymers and useful for industrial,[1,2] commercial,[3] medical,[4–6] and food[7] applications. Owing to its innocuousness, excellent biocompatibility, and water-solubility, PVA has attracted lots of interests for the production of environmentally friendly plastic materials[8,9] and biocompatible materials[10–13]; and PVA has been also approved for use in several medical applications like controlled release of oral drugs and ophthalmic solutions.[14–16]

It is well known that molecular weight of conventional PVA products differ from 20,000 to 400,000, which rely on the length of the initial vinyl acetate polymer and the degree of hydrolysis (DH). Meanwhile, the properties of PVA, such as solubility, flexibility, tensile strength, and adhesiveness are based on degree of polymerization (DP) and the DH.[17] High molecular weight (HMW) PVA, usually DP >1500, has been mainly used as raw materials of synthetic fiber, adhesive, suspension agent; and low-molecular weight (LMW) PVA has been widely used in such fields like cosmetics, foods, medicine, and so on. Ultra-low molecular weight (ULMW) PVA (DP $<$ 500) is obtained through the methods of semicontinuous aqueous indirect operation or adding molecular chain transfer agent in industry. This kind of ULMW PVA mainly is used as fiber treatment agent, paper intensifier, and emulsion protecting colloid.

Specially, LMW PVA, as polymeric stabilizer, is widely used industrially in combination with LMW surfactants for the emulsion polymerization of vinyl acetate and vinyl acetate/ethylene comonomer systems. PVA (DH = 87–89%, DP = 500) and its grafting polymer were used in miniemulsion approach to determine the feasibility of preparing stable acrylic latexes.[18] PVA is the only carbon-carbon backbone polymer that is biodegradable under both aerobic and anaerobic conditions. PVA-degrading (DH = 98%, DP = 500) enzyme and the degradation mechanism were studied by Matsumura et al.[19] There are some ways to develop biodegradable polymer-related PVA, including incorporation of vinyl alcohol block into a nonbiodegradable functional polymer chain and grafting functional oligomers into the LMW PVA chain. Ossipovand Hilborn[20] introduced azide and alkyne pendant groups onto ULMW PVA (DP = 360) to investigate the possibility of hydrogel formation by "click chemistry." With consideration

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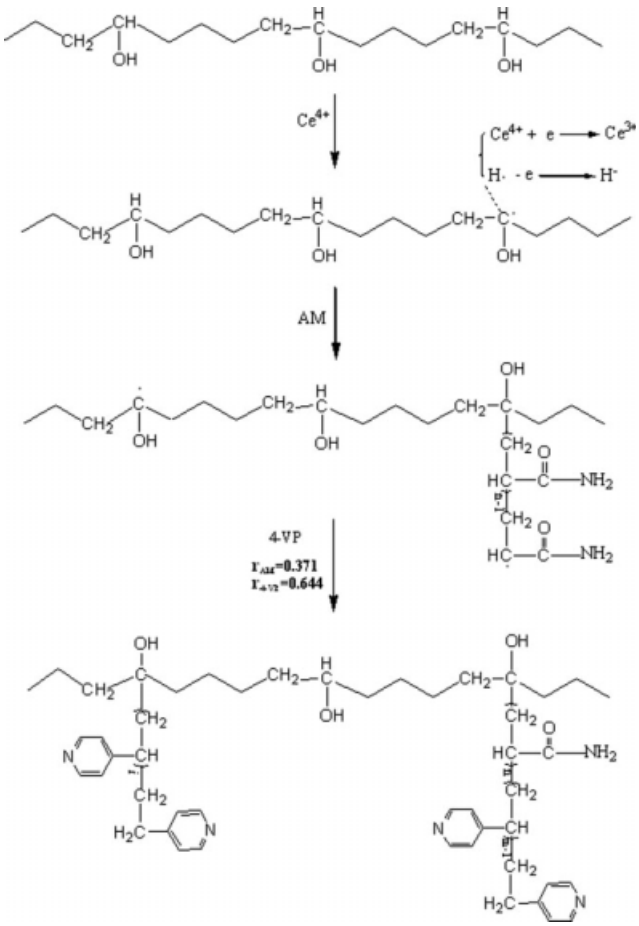

Scheme 1 Synthesis route of PVA graft copolymer

of its biocompatibility and elimination from the body by renal excretion, ULMW PVA with DP = 340 were also applied in gene delivery.[21] ULMW PVA, DP = 300–500, was patterned into a hexagonal porous render which was a self-assembly-based means to fabricate ordered polymeric arrays for the spatial localization of proteins. The cross-linked framework of PVA features good optical transparency and protein resistance.[22]

PVA, water-soluble polymer, has been used as protein imprinting investigation.[23,24] Molecularly imprinted polymers are artificial, template-made receptors with the ability to recognize and to specially rebind the target molecule and can be applied for separation,[25] drug delivery,[21,26] biosensors,[27,28] etc. PVA (DH = 80%, DP = 136), as a nonionic cosurfactant, was introduced the protein imprinting system and PVA had proved to effectively preserve the template protein structural integrity.[29] But the numerous hydroxyl groups on PVA chains limit its application in conventional molecular imprinting because hydroxyls will disrupt any hydrogen-bonding sites on the template and monomers.[30] So in our previous work, we have reported a new protein imprinting method with assistant recognition polymer chains for imprinting and LMW PVA being used as backbone.[31]

PVA is relatively insoluble in organic solvents, but soluble in aqueous solutions. However, intra- and intermolecular hydrogen bonds limits its applicable temperature in aqueous solution because of its dehydration at high temperature. Graft copolymerization is a valid approach to modify the PVA with lowing the intra- and intermolecular hydrogen bonds. In this work, we reported the modifying of the backbone of low polymerization degree PVA by using acrylamide (AM) and 4-vinyl pyridine (4-VP) through graft polymerization. Graft reaction has been shown in Scheme 1. This modification would produce many short AM side chains and 4-VP side chains, and increase water solubility at high temperature due to the decrease of the intramolecular and intermolecular hydrogen bonds; and such similar LMW polymer attaching diverse groups, such as carboxyl group, had been succeeded in molecular imprinting of protein in our previous work.[32] To optimize the grafting conditions of AM and 4-VP onto PVA backbone, the effect of monomer concentration, initiator concentration, solvents composition, reaction time and temperature on the grafting ratio (GR), and the grafting efficiency (GE) was thoroughly studied.

EXPERIMENTAL

Materials

4-vinyl pyridine (4-VP) was purchased from Aldrich (Milwaukee, WI). Vinyl acetate (VAc) and 2,2′-Azobisisobutyronitrile (AIBN) were supplied by Special Chemical Reagent Factory of Nankai University. Acrylamide (AM) (analytical grade) was purchased from Research Institute of Chemical Reagent in Tianjin. Ammonium cerium (IV) nitrate (CAN) was obtained form Damao Chemical Apparatus Ltd. of Tianjin. Methanol, *N*,*N*-dimethylformamide (DMF), ethanol, and ether from Chemical Reagent Ltd. of Tianjin were analytical grade. VAc and 4-VP were vacuum distilled before use. AIBN and AM were purified by recrystallizing in methanol and water, respectively. All other chemicals and solvents were obtained from commercial sources and were used as received.

Synthesis of PVA graft copolymer (PVAVP)

Graft copolymerization was carried out in a three-necked flask equipped with condenser, nitrogen gas inlet, and was kept in water bath. Purified PVA, DP was about 30, DH was above 99%, synthesized with free-radical polymerization of vinyl acetate, was dissolved in hot DMF-water solution and the mixture was stirred by an electromagnetic mixer for half an

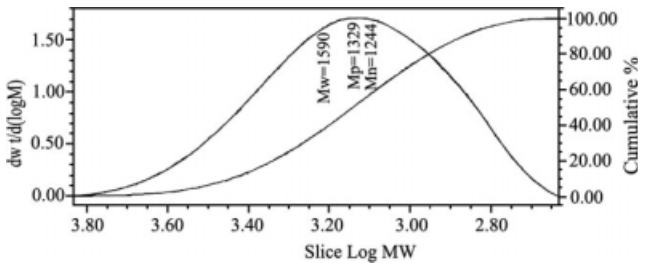

Figure 1 G.P.C. chart of purified PVA.

hour with ventilated N_2 for removing O_2. After adding CAN the mixture was stirred for 15 min under above-mentioned condition for initiation. Then AM would be added and then 4-VP was added, and the reaction would continue under constant flow of nitrogen for several hours. The accurate amounts of various reagents were listed in the corresponding tables. After precipitated with ethanol, the samples were extracted with ether-water mixture (80/20) in a soxhlet apparatus for 6 h. The product was dried in a vacuum oven at room temperature until it reached a constant weight.

Molecular weights determination of PVA and PVAVP

The molecular weight and molecular weight distributions of the synthesized PVA and PVAVP were determined with a Waters 410 G.P.C. with 0.25M sodium nitrate ($NaNO_3$) aqueous as eluent, with standard polyethylene oxide as calibrating agent, and the flow rate was 1.0 m L min^{-1}: the parameters of PVA is: $Mp = 1329$, $M_W/M_n = 1.28$ (Fig. 1).

The intrinsic viscosity ([η]) of the polymer solutions was measured with Ubbelodhe capillary viscosimeter at 25 ± 0.1°C in the methanol aqueous ($v_{methanol}/v_{water} = 20/80$).

Characterization of graft copolymer (PVAVP)

In this experiment, the weight of PVA would be decreased when the PVA dissolved in water and precipitated with solvent (such as methanol, ethanol, ether, acetone, etc.). Maybe the LMW PVA could be partially dissolved in organic solvent (ethanol was used in this experiment).

The yield of graft product was calculated by the following equation:

$$\text{yield } (\%) = \frac{\text{weight of purified PVAVP}}{\text{the total weight of (PVA + AM + 4 - VP)}} \times 100 \quad (1)$$

GR expresses a weight percentage of the polyvinyl pyridine (PVP) and poly acrylamide (PAM) in graft product to PVA substrate. GR was calculated by the following equation:

$$\text{GR } (\%) = \frac{\text{weight of purified PVAVP} - \text{weight of PVA}}{\text{weight of PVA}} \times 100 \quad (2)$$

Considering the amount losing of PVA during precipitating, we used the contents of pyridine for calculating the conversion of monomer (CM) and the GE. The photometric adsorption of the pyridine ring in the graft polymer was measured by UV-vis spectrophotometer (Purkinje General instrument, TU-1900) at 242 nm with the methanol aqueous as reference sample.

CM denotes a weight percentage of the original PVP formed to the VP monomer charged. CM was determined for measuring the pyridine contents of raw product precipitated with ethanol after grafting polymerization.

$$\text{CM } (\%) = \frac{\text{pyridine contents of raw product}}{\text{pyridine contents of VP monomer}} \times 100 \quad (3)$$

GE indicates a weight percentage of PVP in purified grafts to the raw product. The purified PVAVPis extracted with ether-water mixture (80/20) in a soxhlet apparatus for 6 h. GE was determined by using the following equation:

$$\text{GE } (\%) = \frac{\text{pyridine contents of purified PVAVP grafted}}{\text{pyridine contents of raw product}} \times 100 \quad (4)$$

In this investigation, we described the molecular weight of polymer with the intrinsic viscosity because we found that the copolymer molecular weight characterized by GPC had great deviation from which calculated by the Mark and Houwink equation, which values of constants k and α were equal to 2.7×10^{-4} and 0.71 at 25°C, respectively.[33] We believe the deviation is caused by the LMW of PVAVP.

Evidence of graft

The photometric adsorption of the pyridine ring in the graft polymer was measured by UV-vis spectrophotometer (Purkinje General instrument, TU-1900) at 242 nm with the 4-VP monomer as reference sample.

The FTIR spectra were recorded with Bio-Rad FTS 6000 spectrometer in the range of 4000–400 cm^{-1}. KBr pellets of the products were used for FTIR analysis.

TABLE I
Effect of Initiator Concentration on Grafting Efficiency: [HNO_3] = 1.0 mol/L, Time = 12 h, Temperature = 40°C

			Monomer		Solvent					
Code	[CAN] × 10^3 mol/L	PVA (g)	AM (g)	VP (g)	H_2O (mL)	DMF (mL)	[η], mL/g	GR (%)	CM (%)	GE (%)
G17-1	2.84	2	0.97	1.43	18.0	2.0	–	31.20	42.36	21.53
G17-2	5.95	2	0.97	1.43	18.0	2.0	18.20	36.46	45.86	26.78
G17-3	10.20	2	0.97	1.43	18.0	2.0	23.52	46.74	54.28	40.88
G17-4	15.73	2	0.97	1.43	18.0	2.0	–	41.68	58.32	33.01
G17-0	10.20	2	0.00	1.43	18.0	2.0	16.37	21.55	43.19	18.39
G15-1	2.84	2.5	1.94	2.86	24.0	2.7	–	25.17	44.52	20.98
G15-2	5.95	2.5	1.94	2.86	24.0	2.7	19.26	39.06	48.46	31.73
G15-3	10.20	2.5	1.94	2.86	24.0	2.7	27.28	51.10	56.12	50.36
G15-4	15.73	2.5	1.94	2.86	24.0	2.7	–	48.98	59.01	40.45
G15-0	10.20	2.5	0.00	2.86	24.0	2.7	17.00	23.14	49.18	19.35

The ^{1}H-NMR spectra were measured with VARIAN Unity-plus-400 spectrometer in DMSO-d6 and D_2O for PVAVP and PVA, respectively.

TGA thermograms were recorded by using a Netzsch Sta 409 PC/PG thermal analyzer. The analysis was carried out at a constant heating rate of 10°C /min in the temperature range 30–600°C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Optimization of graft condition

Table I lists the data of the parameters of GE, GR, and CM with different initiator concentration during graft copolymerization. The three parameters show the same tendency. They first increase with increasing concentration of CAN initially up to 10.20 × 10^{-3} mol/L and then decrease with further increase in initiator. The initial increase could be associated with increase of the number of active free radicals on the PVA backbone. The decrease in parameters after a certain concentration of CAN (>10.20 × 10^{-3} mol/L) may be due to the decrease of ratio of nitric acid to ceric (IV) ions concentration.[34] The excess Ce^{4+} acts as terminator, and the chains termination rate is faster besides the tendency of monomer homopolymerization is upward.

The effect of monomer concentration on the three parameters is shown in Table II. From Table II, the parameters of GE, GR, and CM increase with increase of AM concentration initially and then decreases with the further increase of AM. Similar trends were also observed during the graft of acrylamide onto cellulose in the presence of methylacrylate as comonomers.[35] The increase in GE is attributed to the transportation of a higher number of free radicals to branch chain. The previous work had demonstrated the monomer reactivity ratios of 4-VP and AM is 0.644 ($r_{4\text{-vp}}$) and 0.371 (r_{AM}), respectively, when copolymerization of 4-vinyl pyridine with acrylamide.[36] A further increase in AM monomer concentration caused a slight decrease in the GE because higher amounts of monomer resulted in homopolymer formation which competed with the grafting reaction.

The data given in Table III showed the effect of reaction time on the graft polymerization. The initial increase in GE is remarkable at a wide range of time. The initial remarkable increase in GE is due to increase of the contact time of monomer molecules with the PVA macromolecular radicals, then

TABLE II
Effect of Monomer Concentration on Grafting Efficiency: [HNO_3] = 1.0 mol/L, Time = 12h, Temperature = 40°C, [CAN] = 10.20 × 10^{-3} mol/L

	Monomer			Solvent					
Code	AM (g)	VP (g)	PVA (g)	H_2O (mL)	DMF (mL)	[η], mL/g	GR (%)	CM (%)	GE (%)
G27-1	0.48	1.43	2	18.0	2.0	–	28.13	36.58	19.87
G17-3	0.97	1.43	2	18.0	2.0	23.52	46.74	54.28	40.88
G27-2	1.94	1.43	2	18.0	2.0	–	46.46	58.70	38.70
G17-0	0.00	1.43	2	18.0	2.0	16.37	21.55	43.19	18.39
G25-1	0.97	2.86	2.5	24.0	2.7	–	46.12	56.21	44.37
G15-3	1.94	2.86	2.5	24.0	2.7	27.28	51.10	56.12	50.36
G25-2	3.88	2.86	2.5	24.0	2.7	–	38.13	49.36	35.65
G15-0	0.00	2.86	2.5	24.0	2.7	17.00	23.14	43.76	19.35

TABLE III
Effect of Reaction Time on Grafting Efficiency: [PVA] = 0.1 g/mL, [HNO_3] = 1.0 mol/L, Temperature = 40°C, [CAN] = 8.95 × 10^{-3} mol/L, V_{water}/V_{DMF} = 80/20

Code	Time (h)	Monomer		Yield (wt %)	[η], mL/g	GR (%)	CM (%)	GE (%)
		AM (g)	VP (g)					
G9-1	4	0.97	1.43	17.15	14.01	16.37	26.49	11.88
G9-2	6	0.97	1.43	35.34	17.85	30.19	40.12	23.34
G9-3	12	0.97	1.43	45.27	23.68	48.55	55.46	40.96
G9-4	24	0.97	1.43	51.79	25.17	49.57	56.98	43.18
G9-5	30	0.97	1.43	55.80	26.00	50.00	57.13	45.34
G9-6	48	0.97	1.43	48.77	26.34	51.00	58.01	46.02

decrease in GE after certain time is due to depletion of initiator and monomer with the progress of reaction. Generally, the grafting parameters increase rapidly with time up to several hours in most graft copolymerization,[37,38] but the trends of grafting parameters in our experiments are almost smoothly until 12 h. But the yield of graft product is increased at first and then decreased. The possible reason is that the LMW PVA copolymer with more pyridine groups is methanol-soluble when the products undergo precipitation.

The effect of reaction temperature on the grafting level is shown in Table IV. With increase of temperature, GE increases due to increase of decomposition rate of initiator. On the other hand, the diffusion rate of monomer onto the PVA backbone is also faster. As a result, GE has shown an increasing trend up to 40°C. Further increase of temperature decreased the GE; the trend is the same as the graft copolymerization of acrylonitrile onto PVA.[39] From Table IV, the trend of CM is not identical with GE. The different trend between CM and GE may be attributed to the increased tendency of homopolymerization of 4-vinyl pyridine at higher temperature and less acrylamide monomer undergoes copolymerization, and GE is described with the weight percentage of PVP in purified grafts to the raw product in this experiment.

On the basis of the above results, we chose the appropriate conditions as the next grafting conditions: time = 12 h, temperature = 40°C.

Among components of graft copolymerization, 4-VP is an oil-soluble monomer. Because of both PVA and AM are water-soluble monomer, 4-VP could be induced hydrophilicity to some extent. So the solvents systems with high solubility parameter (δ) were adopted in our experiments. The preliminary experimental results (Table V) show that the GE increases initially and then decreases with the volume of H_2O increases. This effect of solvents mixture on graft reaction would be explained as follows: the medium solution where graft copolymerization happen is not uniform phase, it is obvious that the solubility parameter (δ) of solvents increases with the increase of volume of H_2O, and an optimum solubility parameter is suitable for the reaction system, especially suitable for both PVA and 4-VP. With the further increase in volume of water, the contact chance between 4-vinyl pyridine (hydrophobic monomer) and the macromolecular radical (hydrophilic backbone) would be reduced, so the GE decreases as the results display.

At optimized conditions, the maximum GE and GR were ~ 50% and 51%, respectively, with the presence of AM, whereas, they decreased to 19% and 23%, respectively, without the presence of AM; and the conversion of monomer increases from 32% up to ~ 50% with increase in AM and 4-VP concentration to a certain concentration.

To assess the graft polymerization of AM and 4-VP onto the PVA, the intrinsic viscosity and the molecular weights of PVAVP were determined. The

TABLE IV
Effect of Temperature on Grafting Efficiency: [PVA] = 0.1 g/mL, [HNO_3] = 1.0 mol/L, [CAN] = 10.20 × 10^{-3} mol/L, V_{water}/V_{DMF} = 80/20, Time = 12h

Code	Temperature (°C)	Monomer		Yield (wt %)	[η], mL/g	GR (%)	CM (%)	GE (%)
		AM (g)	VP (g)					
G21-1	35	0.97	1.43	17.15	–	18.23	25.18	11.88
G21-2	40	0.97	1.43	46.34	25.12	49.00	56.13	42.34
G21-3	45	0.97	1.43	45.27	22.98	45.69	58.47	39.72
G23-1	35	1.94	1.43	21.23	–	23.55	38.16	19.35
G23-2	40	1.94	1.43	49.19	27.00	50.23	58.72	46.71
G23-3	45	1.94	1.43	47.64	25.86	49.13	59.30	44.11

TABLE V
Effect of Solvents on Grafting Efficiency: [PVA] = 0.05 g/mL, [HNO_3] = 1.0 mol/L, Temperature = 40°C, [CAN] = 10.20 × 10^{-3} mol/L, Time = 12 h

	Monomer		Solvent						
Code	AM (g)	VP (g)	H_2O (mL)	DMF (mL)	δ $(J/cm^3)^{1/2}$	[η], mL/g	GR (%)	CM (%)	GE (%)
G30-1	0.97	1.43	18.0	12.0	31.25	–	34.24	45.46	26.47
G30-2	0.97	1.43	21.0	9.0	33.48	–	39.94	50.07	31.43
G30-3	0.97	1.43	24.0	6.0	36.57	23.13	45.57	55.38	38.05
G30-4	0.97	1.43	27.0	3.0	41.10	22.77	51.44	58.96	44.56
G30-5	0.97	1.43	30.0	0.0	48.40	–	36.04	46.12	30.82
G31-1	1.40	2.14	18.0	12.0	31.25	–	38.76	48.64	30.19
G31-2	1.40	2.14	21.0	9.0	33.48	–	41.59	52.49	32.07
G31-3	1.40	2.14	24.0	6.0	36.57	24.00	49.00	58.76	41.01
G31-4	1.40	2.14	27.0	3.0	41.10	27.37	55.49	59.00	47.89
G31-5	1.40	2.14	30.0	0.0	48.40	–	38.74	48.90	31.49

parameters of PVAVP are showed in Table VI and curves are showed in Figure 2. With the molecular weight of PVAVP, we could calculate the total number of pyridine unit and AM unit of the graft side chains, which was ∼ 14–27; and this value was described as the average number of function groups of the graft side chains.

FTIR analysis of graft copolymers

FTIR spectra showed the chemical structures of grafting copolymer. The FTIR spectra of PVA and graft copolymer are shown in Figure 3(a,b), respectively. The hydroxyl stretching vibration, the methylene stretching vibration, and the C—H stretching vibration of PVA are observed at 3332 cm^{-1}, 2942 cm^{-1} and 2907 cm^{-1}, respectively. The C—H and O—H bending vibrations appear in the 1460–1200 cm^{-1} region and the alcoholic C—O stretching is observed at 1091 cm^{-1}. In the spectrum of the extracted graft copolymer, two new bands appear at 1603 cm^{-1} and 1558 cm^{-1} that may be attributed to stretching vibrations of C=N in pyridine ring, which indicate the 4-vinyl pyridine monomer was grafted onto the PVA backbone successfully. The O—H and the N—H stretching vibrations overlap at 3348 cm^{-1} and the stretching vibration band of C=O of amide group appears at 1675 cm^{-1}. These peaks of PVAVP confirmed the grafting of AM and 4-VP onto PVA backbone.

^{1}H-NMR spectra analysis of graft copolymers

^{1}H-NMR analysis provided evidence of a successful graft reaction further. Figure 4 shows ^{1}H-NMR spectrums of the PVA (a) and PVAVP (b). The absorption peaks are assigned as shown in the figure, and the spectrum confirmed the chemical structure of PVAVP. In the spectrum of PVA, the chemical shifts at 4.69 ppm (numbered 6), 4.49 ppm (numbered 5) and 4.24 ppm (numbered 4) belong to hydroxyl hydrogen; the signal at ∼ 3.82 ppm (numbered 3) belong to hydrogen in the —CH— group attached to hydroxyl and the signals at about 1.34 ppm (numbered 1) represent the —CH_2 group hydrogen in the polymer backbone. It is evident by comparing the

TABLE VI
G.P.C. Parameters of Purified Partial PVAVP

Curve number	Code	[η], mL/g	GE (%)	PY (%)[a]	Parameters					No. PY[c]	No. AM[d]	Total Number[e]
					Mp	*Mw*	*Mn*	*Mw/Mn*	*Mps*[b]			
a	G23-2	27.00	50.23	37.31	3907	4125	2946	1.40	2578	19	8	27
b	G9-6	26.34	46.02	34.19	3485	3789	2746	1.38	2156	15	8	23
c	G21-2	25.12	42.34	31.45	3010	3213	2472	1.30	1681	12	6	18
d	G9-3	23.68	40.96	30.43	2887	3037	2250	1.35	1558	11	6	17
e	G30-4	22.77	44.56	33.10	2659	2870	2065	1.39	1330	11	3	14

[a] Pyridine contents of purified PVAVPgrafted.
[b] The molecular weight of side chains of PVAVP, $Mps = Mp - M_{PVA}$, the value of M_{PVA} is 1329.
[c] The number of pyridine unit of the graft side chains in the PVAVP, which is calculated by the equation of (PY × *Mp*/78), here 78 is the molecular weight of pyridine.
[d] The number of AM unit of the graft side chains in the PVAVP, which is calculated by the equation of (Mps-numbers of PY × 105/71), here 105 is the molecular weight of 4-VP and 71 is the molecular weight of the AM.
[e] The total number is the sum of the numbers of pyridine unit and the numbers of AM unit of the graft side chains.

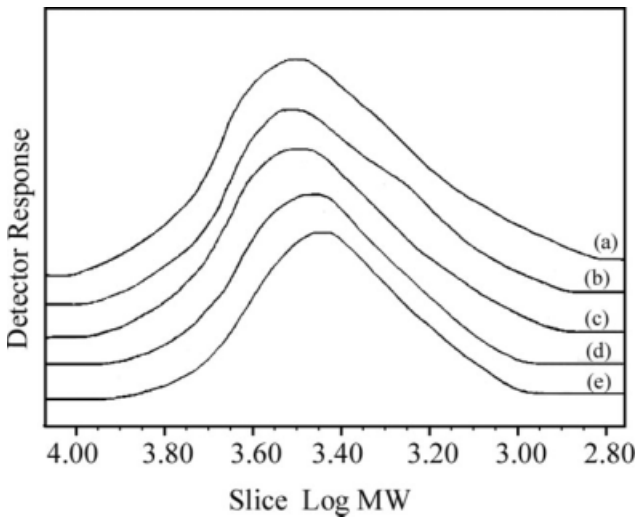

Figure 2 G.P.C. chart of purified partial PVAVP: (a) G23-2, (b) G9-6, (c) G21-2, (d) G9-3, and (e) G30-4.

^{1}H-NMR spectrum in curve (a) and curve (b) that the pyridine ring was grafted onto the PVA. The new peak at 2.08 ppm represents the adsorption of hydrogen in methylene adjoined the pyridine ring in the grafting side chain, the peaks near 7.22 ppm and 8.43 ppm represent the adsorption of hydrogen atoms in pyridine ring. The PVAVP having a pyridine ring was thus successfully obtained. However, the ^{1}H-NMR characters of the PAM parts in the graft copolymer are not evidently owing to their similar structure to the polymer chain, so their chemical shifts are consistently to the other similar units in the copolymer.

From the ^{1}H-NMR measurement in curve (a), the degree of hydrolysis, Dh, was calculated using the following equation.

$$D_h = [\text{area of (6)} + \text{area of (5)} + \text{area of (4)}]/[\text{area of (6)} + \text{area of (5)} + \text{area of (4)} + \text{area of (7)}] \quad (5)$$

It is an interesting thing that the absorption peaks of hydroxyl group are obvious different when the purified PVA for ^{1}H-NMR analysis in D_2O and DMSO-d6 medium. The absorption peaks of hydroxyl group in DMSO-d6 are broken into three-division peaks whereas only one peak in D_2O medium [seen in Fig. 4(a,c)]. The results maybe due to the difference of the linked pattern of PVA repeat units and as results the peak displacement are approached each other.

Thermal characterization of graft copolymers

The TGA diagram of PVA and PVAVP copolymer are shown in Figure 5. The TGA curve of PVAVP (G15-3) shows three inflexions around 230, 330, and 410°C and weight loss are 2%, 50, and 22%, respectively. Whereas the TGA curve of PVA only has one inflexion and PVA begins to decompose until 300°C. The three inflexions observed in the TGA curve of PVAVP indicated that the graft copolymer had different structures considering to the destruction of the crystallization region of PVA polymer. The TGA curves also indicated that the thermal stability of the graft copolymer was inferior to that of PVA. The facts maybe attribute to the follows: after graft

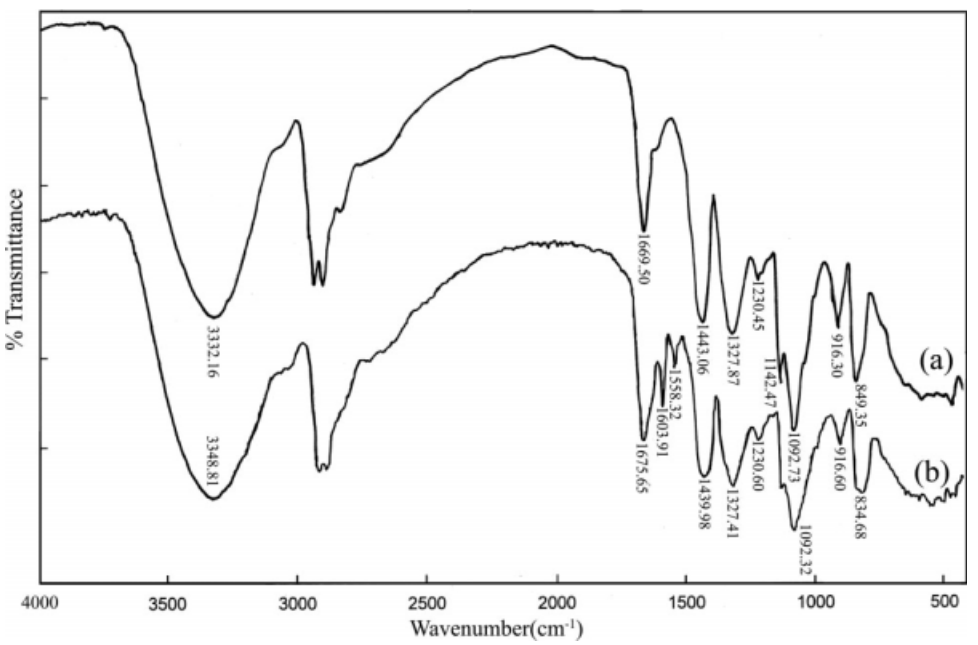

Figure 3 FTIR spectra of PVA (a) and PVAVP, G15-3 (b).

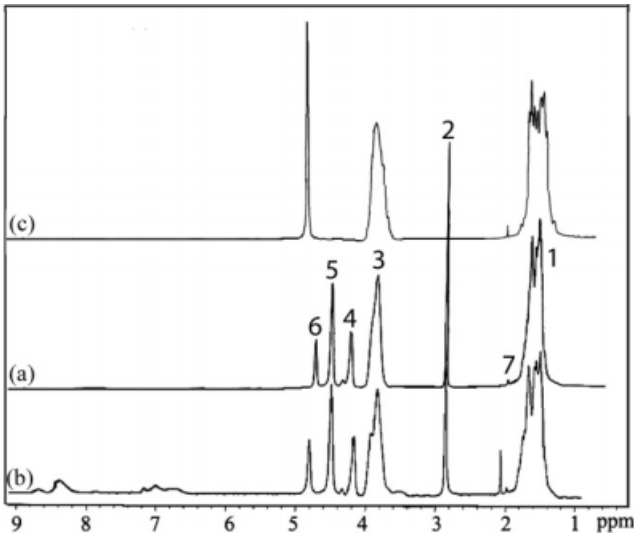

Figure 4 ^{1}H-NMR spectrum of (a) PVA in DMSO medium; (b) PVAVP, G15-3 in DMSO medium; and (c) PVA in D_2O medium.

copolymerization, the graft units in the side chains of the copolymer destroy the regular arrangement of PVA; the degree of crystallization of the graft copolymer is decreased. So the arrangements of the copolymer molecular chains tend to be random and their intermolecular force is weaker than the PVA intermolecular force. As a result, the thermal stability of the graft copolymer is inferior to that of PVA. Figure 6 show TGA thermograms and DTG thermograms of graft copolymers. Thermal analysis results were summarized at Table VII. TGA thermograms of PVAVP graft copolymers exhibit three decomposition temperatures. TGA analyses demonstrated the graft copolymers had the decreases of thermal stability in comparison with homopolymer PVA.

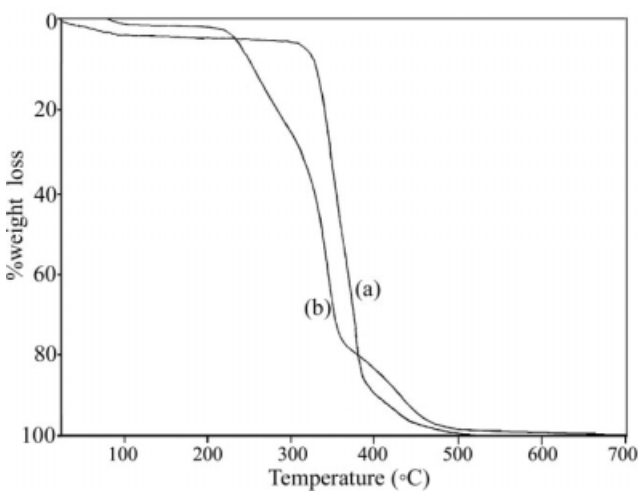

Figure 5 TGA thermograms of (a) PVA and (b) PVAVP, G15-3.

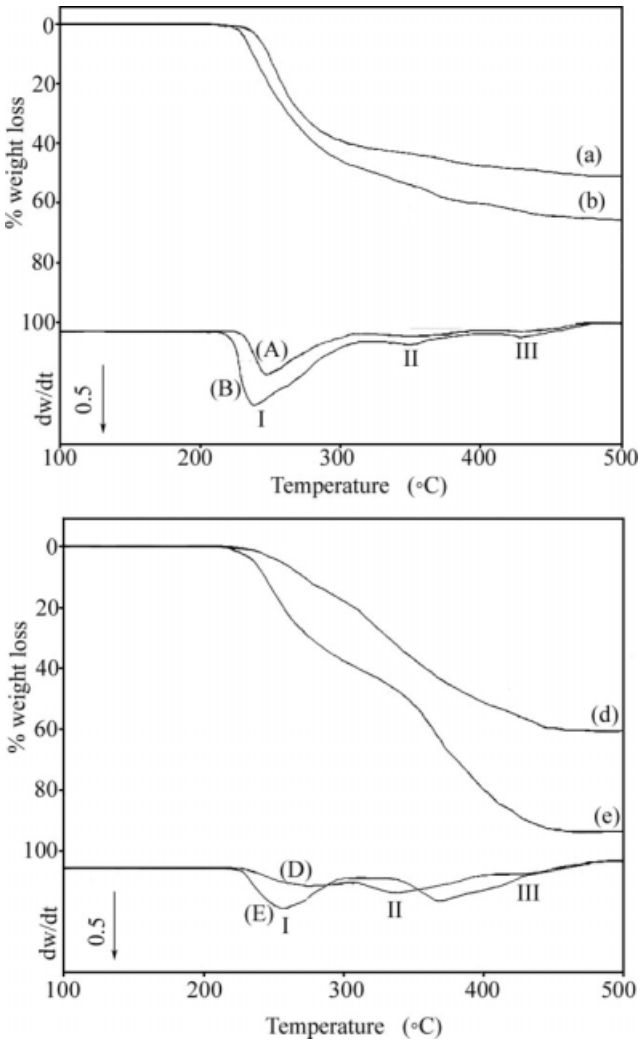

Figure 6 TGA and DTG thermograms of (a) G21-2, (b) G 23-2, (d) G9-3, (e) G9-6.

CONCLUSIONS

4-vinyl pyridine (4-VP) could be easily grafted onto LMW PVA with the presence of acrylamide in the mixed solvents of H_2O and DMF. AM monomer acted as medium for the formation and transportation of free radicals to branch chains. The effect of the reaction conditions on graft copolymerization was carried out, and the results showed that monomer concentration had more noticeable effect on graft polymerization than the others reaction conditions like reaction time, temperature, solvents composition, and initiator concentration. The maximum GE and GR were obtained as 50 and 51%, respectively, at a reaction time of 12 h. CAN concentration of 0.01 mol/L, at a reaction temperature of 40°C and $n_{AM} : n_{VP} = 1 : 1$.

On the basis of ^{1}H-NMR and FTIR analyses, it was safely said that AM and 4-VP were grafted onto the PVA backbone. According to the TGA

TABLE VII
Thermal Analysis Parameters of Graft Copolymers

Curve number	Code	Parameters						
		T_{onset} (°C)	T_{peakI} (°C)	T_{peakII} (°C)	$T_{peakIII}$ (°C)	A_I (%)	A_{II} (%)	A_{III} (%)
A	G21-2	222	245	345	438	32	11	9
B	G23-2	208	238	350	430	42	16	11
D	G9-3	224	270	338	440	24	30	8
E	G9-6	218	255	365	420	48	40	5

T_{onset} is the temperature of the peak onset. T_{peak} is the temperature of the peak top. A is the peak area of the three peaks.

thermogram, the thermal stability of the graft products was lower than that of PVA homopolymer, which indicated that disruption of hydrogen bond happened during graft reaction.

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