Amino Acids (2012) 42:1287–1295
DOI 10.1007/s00726-010-0823-9

ORIGINAL ARTICLE

Preparation and characterization of novel optically active poly(vinyl alcohol-co-vinyl ester) in nonaqueous medium using L-phenylalanine as a chiral material

Shadpour Mallakpour · Abdolvahid Barati

Received: 16 October 2010 / Accepted: 4 December 2010 / Published online: 4 January 2011

Abstract In this investigation, poly(vinyl alcohol) was chemically modified by the introduction of different amounts of *N*-phthaloyl-L-phenylalanine. The modification was carried out by the reaction of PVA hydroxyl groups with (2S)-3-phenyl-2-phthalimidylpropanoyl chloride using *N*,*N*-dimethyl acetamide/lithium chloride as a reaction media. The novel copolymers obtained were characterized by spectroscopic techniques, elemental analysis, X-ray diffraction and thermal methods. Optical rotation and viscosities were also measured. The degree of esterification was determined by ^{1}H-NMR. The influence of reagent molar ratio on the degree of modification was also evaluated. The vinyl(3-phenyl-2-phthalimidopropanoate) content in the copolymer was attained up to 52%. Thermal stability of the copolymers was checked by thermogravimetric analysis and differential thermogravimetric analysis. All copolymers displayed improved thermal stability compared to the parent polymer.

Keywords L-Phenylalanine · Poly(vinyl alcohol) · Optically active polymers · Copolymer · Biologically active polymer · Thermal stability

S. Mallakpour (✉)
Organic Polymer Chemistry Research Laboratory,
Department of Chemistry, Isfahan University of Technology,
84156-83111 Esfahān, Islamic Republic of Iran
e-mail: mallak@cc.iut.ac.ir; mallak777@yahoo.com;
mallakpour84@alumni.ufl.edu

S. Mallakpour · A. Barati
Nanotechnology and Advanced Materials Institute,
Isfahan University of Technology, 84156-83111
Esfahān, Islamic Republic of Iran

Introduction

In recent years, the need of polymers and copolymers with more complex architecture for specific applications in industry and science led to the development of chemical modification of some commercially available synthetic polymers. This modification is an important technique for obtaining new polymers with improved properties and therefore increases the scope of their applications. Poly(vinyl alcohol) (PVA) is especially suitable for that purpose because it can be easily modified through its hydroxyl groups. PVA, a nontoxic, semicrystalline, polyhydroxy polymer, is the largest volume, synthetic water-soluble plastic in use (Goodship and Jacobs 2005). It has been widely used in different fields such as textile sizing and has been utilized as a finishing agent, an emulsifier, a photosensitive coating, and as an adhesive for paper, wood, textiles, and leather (Goodship and Jacobs 2005; Utracki 2004). Besides, it has good membrane forming properties, good chemical stability and most importantly it is cheap, which is the prerequisite condition for commercial applications. Most recently, due to its degradable and nontoxic properties PVA has been used in pharmaceutical and biomedical applications such as wound dressings (Saha et al. 2005; Sedlarik et al. 2006, 2007), artificial skin, coatings, transdermal patches, cardiovascular devices (Thomas et al. 2009) and drug delivery systems (Orienti et al. 2001).

The most common PVA modification reactions are esterification and etherification of the hydroxyl groups. The esterification of PVA in order to prepare poly(vinyl alcohol-co-vinyl ester) have been carried out by reacting the polymer with an acyl chloride (Cimenez et al. 1996; Sahmetlioglu et al. 2004) and anhydrides (Baudrion et al. 1998; Bruzaud and Levesque 2000; Martensa et al. 2002). Yagci and coworkers reported partial modification of the

PVA hydroxyl groups via ''click'' chemistry (Gacal et al. 2009). Because of the stronger intermolecular and intramolecular hydrogen bonding water is the only known solvent for PVA (Goodship and Jacobs 2005). It is not possible to synthesize an ester by homogeneous esterification of PVA with the corresponding acid in aqueous medium. To solve this problem, many dipolar aprotic solvent and catalyst system such as *N*-methyl-2-pyrrolidone (NMP) (Gimenez et al. 1999), *N*,*N*-dimethylpropylene urea (DMPU) (Fernandez and Fernandez 2008), dimethyl sulfoxide (DMSO) (Ciminez et al. 1996), ethyl nitrate dimethyl sulfoxide (DMSO) (Chetri et al. 2006), *N*,*N*-dimethyl acetamide/lithium chloride (DMAc–LiCl) (Tosh et al. 1999) have been improved for modification of PVA.

Over the past decades, interest in green chemistry has lead to a renewed interest in novel polymeric materials containing amino acids (Mallakpour and Dinari 2009; Mallakpour and Khani 2010; Mallakpour and Mirkarimi 2010; Mallakpour and Rafiee 2009). On the other hand, PVA is the only vinyl-type synthetic polymer which has been confirmed to be biodegradable, but its biodegradation rate under natural environmental conditions is too slow that cannot be applied as an industrial degradable polymer (Chiellini et al. 2003; Corti et al. 2002). Therefore, exploring new chemical modifications with biologically active groups (Aoi et al. 2000; Takasu et al. 2003) as well as building up miscible blends of PVA with other biodegradable polymers such as starch (Jayasekara et al. 2004; Zhai et al. 2002), cellulose (Ibrahim et al. 2010; Nishiot and John Manley 1988) and chitin (Aoi et al. 1997; Takasu et al. 1999) are the most interesting approaches to improve the poor biodegradability of PVA.

Optically active polymers are potentially suitable for applications in biology, biomedicine, chiral media for asymmetric synthesis, chromatographic methods for enantiomer separation and optical devices. α-Amino acids are natural chiral materials that have been widely used to synthesize optically active compounds (Ghorai et al. 2007; Luo et al. 2007; Mallakpour and Rafiee 2008a). Among them, L-phenylalanine is an aromatic α-amino acid that exists in two isomeric forms; D-phenylalanine and L-phenylalanine. Due to the different biological natures and pharmacological activities of both enantiomers, it is important to use them in their pure forms for specific therapeutic uses. Recently, we have synthesized optically active polymers containing α-amino acids by different methods such as modification of polybutadiene with an optically active substituted urazole group, (Mallakpour et al. 1998, 1999a, b) and polycondensation reactions of an optically active monomer with different diamines (Mallakpour and Rafiee 2008b), diols (Mallakpour and Asadi 2010) and diisocyanates (Mallakpour and Taghavi 2008). These synthetic polymers based on α-amino acids are expected to be biodegradable (Mallakpour et al. 2010a, b, c).

So far, no study has been reported in the literature related to the synthesis of optically active copolymer based on PVA. Although modification of PVA with biologically active compound containing chiral center was performed (Dumitriu et al. 2006), use of dicyclohexyl carbodiimide/*N*,*N*-dimethyl amino pyridine caused racemization and optical rotation was not observed (Dhaon et al. 1982; Dumitriu et al. 2006). In the present study, attempts were made to synthesize and characterize a novel, optically active poly(vinyl alcohol-co-vinyl-3-phenyl-2-phthalimidopropanoate) (VA-VPP) by the modification of virgin PVA with *N*-phthaloyl-L-phenylalanine (P-phe) as a chiral and bioactive reagent. These copolymers have been prepared using DMAc-LiCl as a solvent system.

Experimental

Materials

All chemicals were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), Riedel–deHaen AG (Seelze, Germany) and Merck. L-phenylalanine (Phe) ($C_9H_{11}NO_2$, 165.19 g mol^{-1}, ≥99%) and PVA (molecular weight M_w = 72,000 g mol^{-1}, degree of hydrolysis 99%) were obtained from Merck Chemical Co. PVA was rigorously dried at 80°C in vacuo for 3 h until a constant weight was obtained. *N*,*N*-Dimethylacetamide (DMAc) was dried over barium oxide and purified by distillation under reduced pressure. LiCl was dried at 100°C overnight and stored in a desiccator until used.

Instrument and measurement

FT-IR spectra of the hybrid films were recorded with a Jasco-680 (Japan) spectrometer at a resolution of 4 cm^{-1}. The spectra of solids were obtained using KBr pellets. The pressed disk containing 2 mg of the sample and 200 mg of fine grade KBr was scanned at wavenumber range of 400–4000 cm^{-1}. Proton nuclear magnetic resonance (^{1}H-NMR, 500 MHz) spectra were recorded in DMSO-d_6 solution using a Bruker (Germany) Avance 500 instrument. Inherent viscosities (η_{inh}) were measured by a standard procedure using a Cannon–Fenske Routine Viscometer (Cannon, Mainz, Germany) at a concentration of 0.5 g dL^{-1} at 25°C. Specific rotations were measured by a JASCO Polarimeter to confirm incorporation of chiral biologically active structure in PVA backbone. Quantitative solubility of copolymers in various polar and non-polar solvents was determined using 5 mg of the polymer in 1 mL of solvent. Elemental analyses were performed by

Leco, CHNS-932 in Isfahan University (Isfahan, Islamic Republic of Iran). Thermogravimetric analysis (TGA) data for PVA and copolymers were taken on Perkin Elmer in nitrogen atmosphere at a heating rate of 10°C min^{-1} from room temperature to 800°C. The X-ray diffraction (XRD) patterns were recorded by employing a Philips X'PERT MPD diffractometer (Cu $K\alpha$ radiation: $\lambda = 0.154056$ nm at 40 kV and 30 mA) over the 2θ range of 10–100° at a scan rate of 0.05° min^{-1}.

N-phthaloylation of L-phenylalanine

(2S)-3-Phenyl-2-phthalimidylpropanoic acid (**4**) was prepared and characterized by a reported procedure (Bose et al. 1958; Zeng et al. 2004). Briefly, 1 g (6.75 mmol) of phthalic anhydride (**1**) and 1.12 g (6.75 mmol) of L-phenylalanine (**2**) were heated in 10 mL of refluxing dimethylformamide for 45 min (Scheme 1). The product, isolated by pouring the reaction mixture into 30 mL of ice and water, a white precipitate was formed, filtered off and dried, to give 1.83 g (92%) of imide acid (**4**) m.p. 180–182°C.

Synthesis of optically active compound **5**

(2S)-3-phenyl-2-phthalimidylpropanoyl chloride (**5**) was prepared according to our previous report (Mallakpour and Sepehri 2008). Briefly, into a 25 mL round-bottomed flask, 1 g (3.4 mmol) of compound **4**, 5 mL of thionyl chloride, 5 mL of dichloromethane and a stirring bar were placed. The stirrer was started and the mixture was refluxed for 4 h at 45°C (Scheme 1). The solvent was removed via distillation and 3 mL of *n*-hexane was added and stirred for 30 min. *n*-Hexane was distilled off, and the product was collected and dried in vacuum to give 0.98 g (94%) of white solid $[\alpha]_D^{25} = -120$ (0.05 g in 10 mL of DMF) m.p. = 82°C.

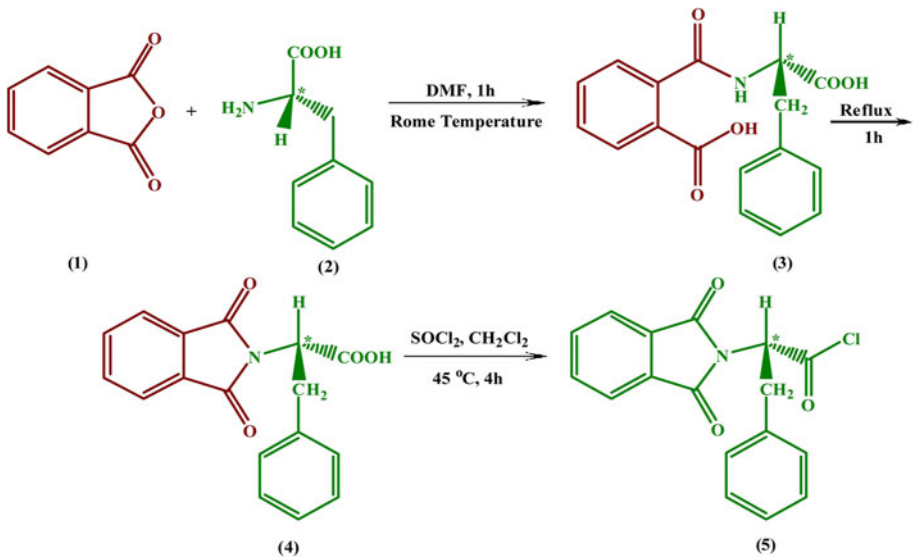
Synthesis of optically active VA-VPP copolymers

A typical experimental procedure is as follows: The DMAc-LiCl solvent system was prepared by dissolving 0.28 g (7.1 mmol) of LiCl in 6 mL of DMAc at 40°C in a 25 mL round-bottom flask equipped with a magnetic stirrer. The concentration of LiCl in the solvent system was maintained at equivalent to OH group of PVA, according to the literature (Tosh et al. 1999). Then 0.30 g (6.81 mmol equivalent to OH group of repeating unit) of PVA was added and the mixture was heated at 50°C for 1 h, after which a clear solution was obtained. The PVA solution was cooled to 0°C in an ice bath, then esterification of PVA was conducted by adding different molar ratios of optically active compound (**5**/OH group of repeating unit 0.25/1, 0.50/1, and 1/1 (mol/mol)) at 0°C for 1 h and the solution was stirred for 16 h at room temperature. The viscous reaction mixture was poured into 30 mL of cooled distillated water to remove DMAc and LiCl, resulting in the precipitation of VA-VPP copolymer. The white precipitate was washed with methanol for three times to obtain purified VA-VPP copolymer. The final product was then dried under vacuum at 70°C for 8 h, ground in a mortar, and submitted to analyses.

Result and discussion

Modification of PVA with *N*-phthaloyl-L-phenylalanine (P-phe)

The most common way to esterify polymers containing functional hydroxyl groups is the reaction of these groups



Scheme 1 synthesis of (2S)-3-phenyl-2-phthalimidylpropanoyl chloride **(5)**

Scheme 2 Synthesis of VA-VPP copolymers by the esterification reaction of PVA with (**5**)

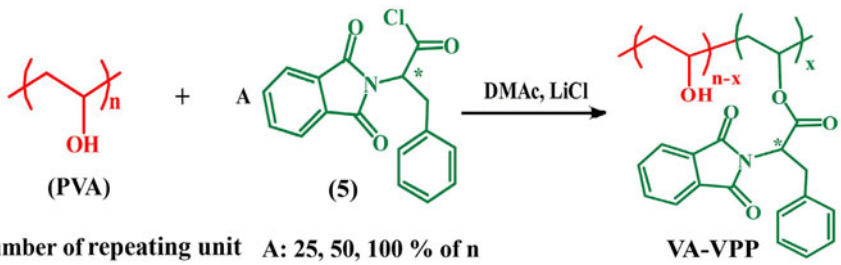


Table 1 Synthesis and some physical properties of optically active VA-VPP copolymers

Polymer	5/OH (%)[a]	VPPC (%)[b]	Yield (%)	Yield of modification (%)	$[\alpha]_D^{25c}$	η_{inh} (dL g^{-1})[c]
VA-VPP18	25	18	68	72	−106	1.60
VA-VPP42	50	42	73	84	−158	1.18
VA-VPP52	100	52	81	52	−135	1.06

[a] Feed molar ratio of **5** to hydroxyl groups in PVA (mol/mol)

[b] Obtained from ^{1}H-NMR

[c] Measured at a concentration of 0.5 dL g^{-1} in DMSO at 25°C

with acyl chlorides using an appropriate solvent in homogeneous medium. In the case of PVA these solvents must be very polar solvents with high dipole moment such as DMAc and DMSO. According to Scheme 2, PVA was esterified with different amounts of (2S)-3-phenyl-2-phthalimidylpropanoyl chloride (**5**) by a homogeneous process using DMAc-LiCl as solvent system. The experimental results are presented in Table 1. Since only a partial modification was desired, a considerable number of hydroxyl groups of PVA remained in the final copolymer which interacted with the DMAc and making their complete elimination difficult, therefore giving a low yield of pure product. The results showed that yields increased with the degree of modification, probably because it makes them more insoluble in the precipitation mixture making more efficient the isolation of the product. Using the ratios specified in the experimental part, copolymers with a modification degree of 18 P-phe units (VA-VPP18), 42 P-phe units (VA-VPP42) and 52 P-phe units (VA-VPP52) per 100 total units were obtained. The vinyl(3-phenyl-2-phthalimidopropanoate) content (VPPC) values are plotted in Fig. 1 as a function of the feed molar ratio of **5** to hydroxyl group of PVA (mol/mol). The VPPC value is increased up to 52% with an increase of **5**/OH. The degrees of modification did not coincide with the ratio of the reagents in the feed. Yields of the modification were calculated on the basis of amounts of the substituted PVA and acyl chloride (**5**). In order to get the maximum degree of modification different **5**/OH (mol/mol) ratios (0.25/1, 0.50/1, and 1/1) were used, but increasing the amount of **5** did not increase the degree of esterification very much. Likewise, different reaction times were also tested (1, 4, 16, and

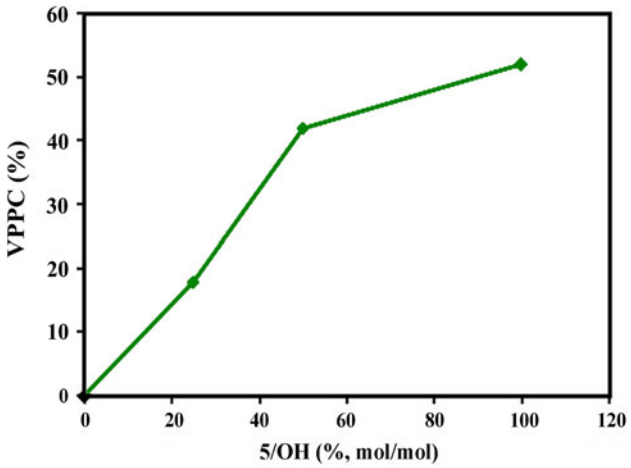


Fig. 1 VPPC (%) as a function of feed molar ratio of **5** to hydroxyl group of PVA (mol/mol)

24 h) but longer reaction times did not improve the degree of esterification and a maximum modification was reached at 16 h. Because the incorporated bulk optically active group prevents the proximity of other P-phe and –OH groups, therefore, increase in reaction time has no significant effect in VPPC. The resulting copolymers show optical rotations (Table 1), which indicate that during the reaction process the chiral centers do not change, and therefore the chirality is introduced into the backbone of the polymers. The resulting copolymers showed white colors and exhibited inherent viscosities of 1.06–1.60 dL g^{-1} in DMSO at 25°C (Table 1). With increase in VPPC the viscosity of copolymers decreases, because of decrease in the intra and intermolecular hydrogen bonding between copolymer chains.

Characterization of the molecular structure of VA-VPP copolymers

PVA was converted to VA-VPP copolymers by esterification with compound **5**, the copolymers obtained were characterized by FT-IR and ^{1}H-NMR. Figure 2 presents the FT-IR spectrum of PVA and of the corresponding VA-VPP copolymers. The spectrum of the optically active compound **5** was also included for comparison. The partial modification of PVA was confirmed by FT-IR spectroscopy (Fig. 2), since in all cases the characteristic band at 3,450 cm^{-1} (OH group) was observed even when the stoichiometric ratio of optically active compound and PVA was used (VA-VPP52). The absorption at 2,900–3,000 cm^{-1} is associated with the C–H stretching mode. In addition, the C=O stretching absorption of ester group at 1,715 cm^{-1} was observed in all copolymers. The peak at 1,386 and 730 cm^{-1} shows the existence of the imide heterocycle in these copolymers. Detailed information on the molecular structure of VA-VPP was obtained from the ^{1}H-NMR spectrum. Figure 3 shows the ^{1}H-NMR spectrum of a sample of VA-VPP42 with the assignment of signals in the copolymer. The copolymer provides not only the signals due to the feature of the original PVA backbone structure (Ohgi and Sato 2002; Wu and Ovenal 1973) but also shows the signals due to VPP group. The broad multiplet at 1.4–1.9 ppm corresponds to the main chain methylene resonance (a, a′) in copolymer. The resonance at 2.1 ppm corresponds to the methyl of residue acetate group from poly(vinyl acetate). The signals at 3.3 ppm and 3.8 ppm in the spectrum of the copolymer are attributable

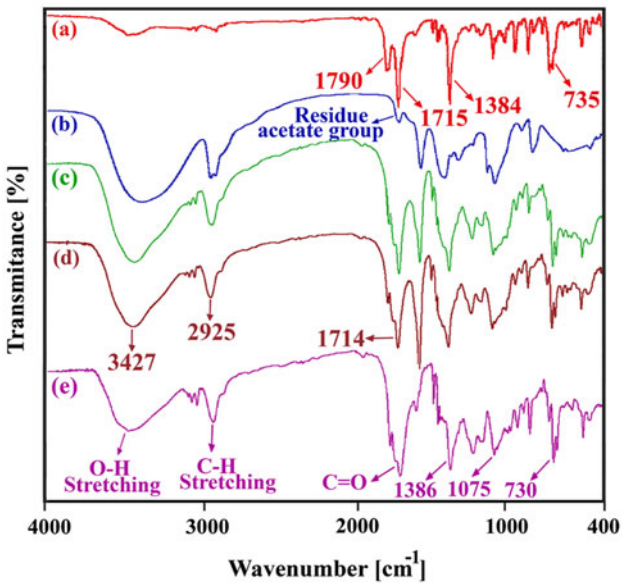


Fig. 2 FT-IR spectra of **5** (*a*), unmodified PVA (*b*), VA-VPP18 (*c*), VA-VPP42 (*d*) and VA-VPP52 (*e*) copolymers

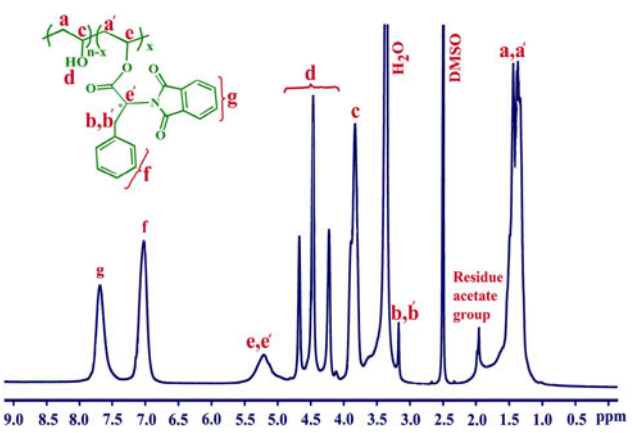


Fig. 3 ^{1}H-NMR spectra (500 MHz) of VA-VPP42 copolymer recorded in DMSO-d_6

Table 2 Elemental analysis of VA-VPP copolymers

Polymer	^{1}H-NMR[a]			Elemental analysis[b]		
	%C	%H	%N	%C	%N	%H
VA-VPP18	64.69	6.37	2.68	62.34	6.14	2.67
VA-VPP42	68.40	5.37	3.66	65.6	5.41	3.53
VA-VPP52	69.18	5.20	3.87	67.13	5.52	3.46

[a] Calculated value from ^{1}H-NMR

[b] Calculated value in elemental analysis

to the methylene (b, b′) group of phe and methine (c) protons of PVA units, respectively. The hydroxyl protons of unmodified PVA unit (d) are separated into triads between 4.1 and 4.7 ppm. The signal centered at 5.2 ppm (e, e′) is assignable to methine proton of the esterified units and chiral center of L-phenylalanine. The resonance of aromatic protons (f, g) of P-phe group appears at 7.1 and 7.7 ppm. The modification of PVA also confirmed via elemental analysis (Table 2) and found to agree satisfactorily with the ^{1}H-NMR data. These findings clearly demonstrate that the novel optically active VA-VPP copolymers were successfully formed by the homogeneous esterification.

Determination of VPPC

The vinyl(3-phenyl-2-phthalimidopropanoate) content (VPPC) was calculated by ^{1}H-NMR from the signal area intensity ratio between the protons due to VPP groups and those due to the polymer backbone. When each integral value will be expressed by putting I in front of the corresponding signal, e.g. $I_{C_6H_4(g)}$and $I_{CH_2(a+a')}$ which are the integral values of peak area of C_6H_4(g) proton signal and of the CH_2(a) and CH_2(a′) signals, VPPC may be calculated by the following equations:

$$\text{VPPC} = \frac{I_{C_6H_4\,(g)}}{2I_{CH_2(a+a')}} \quad (1a)$$

$$\text{VPPC} = \frac{I_{C_6H_5\,(f)}}{5I_{CH_2(a+a')}} \quad (1b)$$

$$\text{VPPC} = \frac{I_{C_6H_4\,(g)}}{4I_{OH\,(d)} + I_{C_6H_4\,(g)}} \quad (1c)$$

$$\text{VPPC} = \frac{I_{C_6H_5\,(f)}}{5I_{OH\,(d)} + I_{C_6H_5\,(f)}} \quad (1d)$$

where a, a′, d, f and g are signals assigned in Fig. 3. Mean VPPC values obtained from these equations mentioned in Table 1.

Solubility of VA-VPP copolymers

The water resistance is a very important property for PVA-based materials used in industrial applications such as food packaging films. Studies on the water resistance of PVA and VA-VPP copolymers were carried out according to solubility measurements. Quantitative solubility of polymers is listed in Table 3. PVA is soluble in water and DMSO, but insoluble in other organic solvents. Solubility of PVA in organic solvents was improved by the modification because the esterification decreases the number of hydroxyl groups contributing to strong intra and intermolecular hydrogen bonding. These results indicate that the chemical modification of PVA by the P-phe is an effective method for the improvement of water resistance compared to virgin PVA. Moreover, VA-VPP copolymers were not swollen or sticky when immersed in water.

Thermal analysis of VA-VPP copolymers

It is well known that thermal stability is the most crucial property for melt processing of PVA (Goodship and Jacobs 2005). It should, therefore, be desirable that the chemical modification of PVA can provide an improved melt processing ability. Thermal stability of the VA-VPP copolymers were investigated by TGA/DTG and compared with virgin PVA. The TGA curves are presented in Fig. 4 and weight loss behaviors of the species are given in Table 4. Three weight loss stages were observed in the TGA curve for PVA film, as shown in the literature (Goiti et al. 2007; Peng and Kong 2007). The first weight loss takes place at 50–170°C due to the evaporation of the trapped water; the second stage at 200–350°C involves the elimination reactions of water. The degradation step at 400–550°C is more complex and includes the further degradation of polyene

Table 3 Quantitative solubility of PVA and VA-VPP copolymers

Solvent	PVA[a]	VA-VPP18	VA-VPP42	VA-VPP52
Water	+	–	–	–
DMSO	+	+	+	+
DMF	–	–	–	–
DMAc	–	+	+	+
Methanol	–	–	–	–
Chloroform	–	–	–	–
n-Hexane	–	–	–	–
Tetrahydrofuran	–	–	–	–

5 mg of polymer in 1 mL of solvent at room temperature, solubility observed after 2 h

+, soluble; –, insoluble

[a] Degree of hydrolysis 99% as reported by supplier

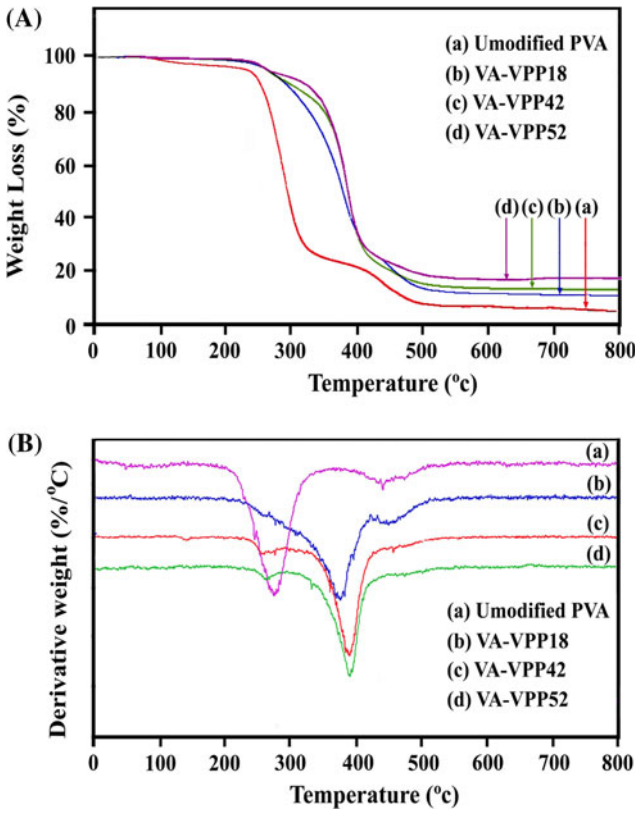


Fig. 4 TGA (**a**) and DTG (**b**) curves of unmodified PVA and VA-VPP copolymers with different VPPC

Table 4 The data obtained from TGA/DTG curves of PVA and VA-VPP copolymers-residual mass at different temperature

Polymer	% Residual mass						
	200°C	300°C	400°C	500°C	600°C	700°C	800°C
PVA	98.20	46.10	23.30	9.84	8.50	7.94	7.05
VA-VPP18	98.48	86.69	33.52	15.11	13.73	13.11	12.53
VA-VPP42	99.24	89.06	29.66	14.55	13.08	12.88	12.49
VA-VPP52	99.43	92.30	27.37	15.98	15.13	14.49	14.06

residues to yield the carbon and hydrocarbons. TGA data showed that the degradation for the VA-VPP18 is similar to unmodified PVA and take place in three steps, but thermal stability improved about 75°C. From DTG curves, it was observed that the thermal decomposition of VA-VPP42 and VA-VPP52 take place in two stages. The first stage degradation is due to the elimination of water from neighboring pairs of unmodified hydroxyl groups and the second stage may attributable to the cleavage of the main chain and side chain of copolymer. On the other hand, the thermal data also reveals that the char yield of the VA-VPP52 is enhanced approximately two folds compared to pristine PVA because of the presence of more rigid and bulky VPP groups. From these results, it can be expected that the P-phe side chains may serve as an effective internal plasticizer and improved melt processing property of PVA.

XRD studies of copolymers

Based on the principle of polymer physics, the polymer with higher crystallinity would have higher melting point (Yang et al. 2008). The effect of modification on the structure of PVA was further characterized with XRD and shown in Fig. 5. Due to the high hydrogen bond of hydroxyl groups in the PVA chain, the crystalline area of pure PVA was formed. Two peaks for the PVA were found, one peak with high intensity appears at about $2\theta = 19.5^{o}$ and another peak with low intensity appears at about $2\theta = 41^{o}$. The degree of crystallinity decreased with the increase of VPPC in the VA-VPP copolymers. The reason is that the hydrogen bonding effect between PVA molecules weakens as a result of esterification. Thus from this XRD data it is understood that the modification disrupts the crystalline phase of PVA which decreases melting point and caused increase the difference between melting point and decomposition temperature.

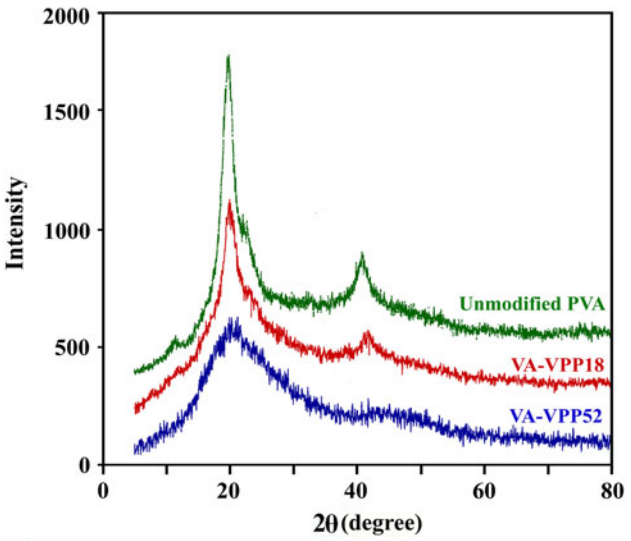


Fig. 5 XRD patterns of unmodified PVA, VA-VPP18 and VA-VPP52 copolymers

Conclusions

In this study, novel optically active VA-VPP copolymers containing P-phe as biologically active moieties were successfully synthesized through esterification reaction of PVA with acyl chloride (**5**) using DMAc/LiCl as reaction medium. Different feed molar ratios of compound **5** to PVA have obvious effects on VPPC and properties of the obtained copolymers. Because of the existence of amino acids in the copolymer side chain these copolymers are expected to be potentially more biodegradable. In addition, the resulting copolymers are optically active and can be used as a chiral support in asymmetric synthesis and chiral stationary phase in chromatographic technique for the separation of enantiomeric mixtures. Studies on thermal degradation of polymers are a matter of major interest for determining the thermal stability of the polymers. Thermogravimetry has been extensively used for such studies. The results presented herein also clearly demonstrate that incorporation of the phthalimide group into the copolymer side chain enhanced the thermal stability of the new copolymers. Due to partial esterification, remaining hydroxyl group in this copolymer can be used for synthesis of optically active three-dimensional networks by reaction with different difunctional compounds in a further step.

Acknowledgments We wish to express our gratitude to the Research Affairs Division Isfahan University of Technology (IUT), Isfahan, for partial financial support. Further financial support from National Elite Foundation (NEF) and Center of Excellency in Sensors and Green Chemistry Research (IUT) is gratefully acknowledged. We also like to thank Mr. M. Hatami and Mr. M. Dinari for their valuable help.

References

Aoi K, Takasu A, Okada M (1997) New chitin-based polymer hybrids. 2. improved miscibility of chitin derivatives having monodisperse poly(2-methyl-2-oxazoline) side chains with poly(vinyl chloride) and poly(vinyl alcohol). Macromolecules 30:6134–6138

Aoi K, Takasu A, Okada M (2000) DNA-based polymer hybrids Part 1. Compatibility and physical properties of poly(vinyl alcohol)/DNA sodium salt blend. Polymer 41:2847–2853

Baudrion F, Perichaud A, Coen S (1998) Chemical modification of hydroxyl functions: introduction of hydrolyzable ester function and bactericidal quaternary ammonium groups. J Appl Polym Sci 70:2657–2666

Bose AK, Greer F, Price CC (1958) A procedure for phthaloylation under mild conditions. J Org Chem 23:1335–1338

Bruzaud S, Levesque G (2000) Synthesis and characterization of new functional polymers by polymer-analog reactions on EVOH copolymer. Macromol Chem Phys 201:1758–1764

Chetri P, Dass NN, Sarma NS (2006) Synthesis of poly(vinyl propionate) from poly(vinyl alcohol) in nonaqueous medium using ethyl nitrate dimethyl sulfoxide as a catalyst. J Appl Polym Sci 102:5675–5679

Chiellini E, Corti A, Antone SD, Solaro R (2003) Biodegradation of poly (vinyl alcohol) based materials. Prog Polym Sci 28:963–1014

Cimenez V, Mantecon A, Cadiz V (1996) Modification of poly(vinyl alcohol) with acid chlorides and crosslinking with difunctional hardeners. J Polym Sci A Polym Chem 34:925–934

Ciminez V, Mantecon A, Cadiz V (1996) Crosslinking of poly(viny1 alcohol) using dianhydrides as hardeners. J Appl Polym Sci 59:425–431

Corti A, Roberto S, Chiellini E (2002) Biodegradation of poly(vinyl alcohol) in selected mixed microbial culture and relevant culture filtrate. Polym Degrad Stab 75:447–458

Dhaon MK, Olsen RK, Ramasamy K (1982) Esterification of *N*-protected α-amino acids with alcohol/carbodiimide/4-(dimethylamino)-pyridine. Racemization of aspartic and glutamic acid derivatives. J Org Chem 47:1962–1965

Dumitriu CL, Popa M, Savin A, Sunel V, Pintilie O, Craciun R, Popa AA (2006) Polymer-biologically active principle conjugates obtained by esterification of poly(vinyl alcohol). Polym Plast Technol Eng 45:481–486

Fernandez MD, Fernandez MJ (2008) Cyclic ureas as solvents for esterification of poly(vinyl alcohol) and vinyl acetate-vinyl alcohol copolymers with acid chlorides. J Appl Polym Sci 107:2509–2519

Gacal BN, Koz B, Gacal B, Kiskan B, Erdogan M, Yagci Y (2009) Pyrene functional poly(vinyl alcohol) by ''Click'' chemistry. J Polym Sci A Polym Chem 47:1317–1326

Ghorai MK, Das K, Kumar A (2007) A convenient synthetic route to enantiopure *N*-tosylazetidines from α-amino acids. Tetrahedron Lett 48:2471–2475

Gimenez V, Reina JA, Mantecon A, Cadiz V (1999) Unsaturated modified poly(vinyl alcohol) crosslinking through double bonds. Polymer 40:2759–2767

Goiti E, Salinas MM, Arias G, Puglia D, Kenny JM, Mijangos C (2007) Effect of magnetic nanoparticles on the thermal properties of some hydrogels. Polym Degrad Stab 92:2198–2205

Goodship V, Jacobs D (2005) Polyvinyl alcohol: materials processing and applications. Smithers rapra technology, UK

Ibrahim MM, El-Zawawy WK, Nassar MA (2010) Synthesis and characterization of polyvinyl alcohol/nanospherical cellulose particle films. Carbohydr Polym 79:694–699

Jayasekara R, Harding I, Bowater I, Christie GBY, Lonergan GT (2004) Preparation, surface modification and characterisation of solution cast starch PVA blended films. Polym Test 23:17–27

Luo Z, Li B, Fang X, Hu K, Wu X, Fu E (2007) Novel chiral solvating agents derived from natural amino acid: enantiodiscrimination for chiral α-arylalkylamines. Tetrahedron Lett 48:1753–1756

Mallakpour S, Asadi P (2010) Novel chiral poly(ester-imide)s with different natural amino acids in the main chain as well as in the side chain: synthesis and characterization. Colloid Polym Sci 288:1341–1349

Mallakpour S, Dinari M (2009) Soluble new optically active polyamides derived from 5-(4-methyl-2-phthalimidylpentanoylamino)isophthalic acid and different diisocyanates onder microwave irradiation in molten ionic liquid. J Appl Polym Sci 112:244–253

Mallakpour S, Khani M (2010) Construction of chiral polyesters from polycondensation of multifunctional monomer containing both flexible amino acid and rigid pendant groups with aromatic diols. Amino Acids 39:841–848

Mallakpour S, Mirkarimi F (2010) Synthesis and characterization of novel, optically active polyamides derived from *S*-valine natural amino acid and bulky anthracenic side chain. Amino Acids. doi:10.1007/s00726-010-0560-0

Mallakpour S, Rafiee Z (2008a) Use of ionic liquid and microwave irradiation as a convenient, rapid and eco-friendly method for synthesis of novel optically active and thermally stable aromatic polyamides containing *N*-phthaloyl-L-alanine pendent group. Polym Degrad Stab 93:753–759

Mallakpour S, Rafiee Z (2008b) Safe and fast polyamidation of 5-[4-(2-phthalimidiylpropanoylamino)-benzoylamino]isophthalic acid with aromatic diamines in ionic liquid under microwave irradiation. Polymer 49:3007–3013

Mallakpour S, Rafiee Z (2009) Microwave-induced synthesis of new optically active and soluble polyamides containing pendent 4-(2-phthalimidiylpropanoylamino)benzoylamino-groups. Amino Acids 37:665–672

Mallakpour S, Sepehri S (2008) Polycondensation of new optically active diacid with diisocyanates in the presence of tetrabutylammonium bromide as a green media under microwave heating. React Funct Polym 68:1459–1466

Mallakpour S, Taghavi M (2008) A facile, microwave-assisted synthesis of novel optically active polyamides derived from 5-(3-methyl-2-phthalimidylpentanoylamino) isophthalic acid and different diisocyanates. Eur Polym J 44:87–97

Mallakpour SE, Hajipour AR, Khoee S, Sheikholeslami B (1998) A new method for producing optically active polybutadiene. Polym Int 47:193–197

Mallakpour SE, Hajipour AR, Mahdavian AR, Khoee S (1999a) Asymmetric polymerization via cycloaddition reactions. J Polym Sci A Polym Chem 37:1211–1219

Mallakpour SE, Hajipour AR, Mahdavian AR, Rafiemanzelat F (1999b) Highly diastereoselective synthesis of novel polymers via tandem Diels-Alder-ene reactions. Polym Int 48:109.116

Mallakpour S, Tirgir F, Sabzalian MR (2010a) Synthesis and structural characterization of novel biologically active and thermally stable poly(ester-imide)s containing different natural amino acids linkages. J Polym Res. doi:10.1007/s10965-010-9427-z

Mallakpour S, Tirgir F, Sabzalian MR (2010b) Novel biobased polyurethanes synthesized from nontoxic phenolic diol containing L-tyrosine moiety under green media. J Polym Environ 18:685–695

Mallakpour S, Tirgir F, Sabzalian MR (2010c) Synthesis, characterization and in vitro antimicrobial and biodegradability study of pseudo-poly(amino acid)s derived from *N,N*-(pyromellitoyl)-bis-L-tyrosine dimethyl ester as a chiral bioactive diphenolic monomer. Amino Acids. doi:10.1007/s00726-010-0686-0

Martensa P, Hollandb T, Anseth KS (2002) Synthesis and characterization of degradable hydrogels formed from acrylate modified poly(vinyl alcohol) macromers. Polymer 43:6093–6100

Nishiot Y, John Manley RS (1988) Cellulose/poly(vinyl alcohol) blends prepared from solutions in *N,N*-dimethylacetamide-lithium chloride. Macromolecules 21:1270–1277

Ohgi H, Sato T (2002) Highly isotactic poly(vinyl alcohol). III: hetrogenous cationic polymerization of tert-butyl vinyl ether. Polym commun 43:3829–3836

Orienti I, Bigucci F, Gentilomi G, Zecchi V (2001) Self-assembling poly(vinyl alcohol) derivatives, interactions with drugs and control of release. J Pharm Sci 90:1435–1444

Peng Z, Kong LX (2007) A thermal degradation mechanism of polyvinyl alcohol/silica nanocomposites. Polym Degrad Stab 92:1061–1071

Saha N, Sedlarik V, Saha P (2005) Electromagnetic properties of aluminosilicate-filled polymer composites of poly(vinyl alcohol)-poly(vinyl pyrrolidone). Polym Compos 26:739–744

Sahmetlioglu E, Yuruk H, Toppare L, Cianga I, Yagci Y (2004) Synthesis and characterization of conducting copolymers of

poly(vinyl alcohol) with thiophene side-groups and pyrrole. Polym Int 53:2138–2144

Sedlarik V, Saha N, Kuritka I, Saha P (2006) Characterization of polymeric biocomposite based on poly(vinyl alcohol) and poly(vinyl pyrrolidone). Polym Compos 27:147–152

Sedlarık V, Saha N, Kuritka I, Saha P (2007) Environmentally friendly biocomposites based on waste of the dairy industry and poly(vinyl alcohol). J Appl Polym Sci 106:1869–1879

Takasu A, Aoi K, Tsuchiya M, Okada M (1999) New chitin-based polymer hybrids, 4: soil burial degradation behavior of poly(vinyl alcohol)/chitin derivative miscible blends. J Appl Polym Sci 73:1171–1179

Takasu A, Itou H, Takada M (2003) Accelerated biodegradation of poly(vinyl alcohol) by a glycosidation of hydroxyl groups. Polymer 43:227–231

Thomas LV, Arun U, Remya S, Nair PD (2009) A biodegradable and biocompatible PVA- itric acid polyester with potential applications as matrix for vascular tissue engineering. J Mater Sci Mater Med 20:259–269

Tosh B, Saikai CN, Dass NN (1999) Development of a nonaqueous solvent system for poly(vinyl alcohol) and its characterization. J Appl Polym Sci 74:663–669

Utracki LA (2004) Clay-containing polymeric nanocomposites. Rapra technology limited, UK

Wu TK, Ovenal DW (1973) Proton and carbon-13 nuclear magnetic resonance studies of poly(viny1 alcohol). Macromolecules 6:582–584

Yang JM, Wang HZ, Yang CC (2008) Modification and characterization of semi-crystalline poly(vinyl alcohol) with interpenetrating poly(acrylic acid) by UV radiation method for alkaline solid polymer electrolytes membrane. J Membr Sci 322:74–80

Zeng Q, Liu Z, Li B, Wang F (2004) Mild and effective *N*-phthaloylation of amino acids. Amino Acids 27:183–186

Zhai M, Yoshii F, Kume T, Hashim K (2002) Synthesis of PVA/starch grafted hydrogels by irradiation. Carbohydr Polym 50:295–303