Effect of Vinyl Pivalate/Vinyl Acetate Comonomer Composition on the Self-Assembled Morphology of Poly(vinyl alcohol) Prepared by *In Situ* Fibrillation: Preparation of PVA with a Spherical Morphology

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ABSTRACT: The photoinitiated copolymerization of vinyl pivalate (VPi) and vinyl acetate (VAc) was carried out in bulk. Varying monomer feed ratios of VPi/VAc (mol %/mol %) of 100/0, 90/10, 60/40, 50/50, and 30/70 were used. Polyvinyl alcohol (PVA) with s-diad contents ranging from 61.8% to 55.7% was obtained. The morphology and thermal properties of the different PVA samples were investigated. PVA prepared from PVPi homopolymer resulted in PVA with a well-aligned microfibrillar structure. With a decrease in the VPi content in the precursor polymer, the fibrous morphology was gradually lost, resulting in PVA with mixtures of fibrillar and spherical structures. When the PVPi content was 38.5 mol %, only spherical particles were observed. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3460–3465, 2010

Key words: block copolymers; fibers; self-assembly; syndiotactic; morphology

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a highly crystalline polymer, with excellent mechanical and thermal properties; oxygen barrier properties; oil, grease, and organic solvent resistance; low moisture permeability; high heat resistance; and high UV and IR stability; more importantly, it is biodegradable and nontoxic. Due to these unparalleled properties, PVA finds widespread application in many areas: in suspension, dispersion, and emulsion polymerization as colloids,[1,2] in films,[3–5] fibers,[6–9] membranes,[10,11] drug delivery systems in medicines, cancer-cell-killing embolic material,[6,8,12–14] and in textile and paper sizing.[1,13] PVA spun into fibers can be used in a range of applications such as reinforcement material, replacement material for the carcinogenic asbestos fiber in building applications, embolic fiber for cancer-cell killing, and binders for calcium carbonate in the paper industry. Lyoo et al. reported the synthesis of well oriented PVA fibers via the saponification of PVPi under shear (with stirring).[6,8,15–19] For a successful *in situ* fibrillation of PVA, the PVPi precursor polymer must have a molecular weight of $P_n > 1140$,[17] the PVA a molecular weight of $P_n > 800$,[17] syndiotacticity (s-diad content) >56%,[6] and degree of saponification 85.0–99.9%.[6]

In this work, PVA fibers were also prepared by *in situ* fibrillation. VPi and VAc were copolymerized in varying molar ratios and the resultant PVPi-co-PVAc hydrolyzed. The PVA self assembled to form various morphologies ranging from fibrillar to spherical structures. This report therefore presents a novel route for the synthesis of spherical PVA particles composed entirely of PVA. These can potentially be used in biomedical applications as cancer-cell killing embolic material.

EXPERIMENTAL

Reagents

Vinyl pivalate (VPi) and vinyl acetate (VAc) were purchased from Sigma-Aldrich (Sigma-Aldrich Chemie, Steinheim, Germany). The monomers were washed successively with aqueous potassium hydroxide (KOH) and distilled water; dried over anhydrous magnesium sulphate ($MgSO_4$) and then purified by passing through a column packed with inhibitor remover obtained from Sigma-Aldrich

Additional Supporting Information may be found in the online version of this article.

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TABLE I
Conditions for VPi and VPi/Vac Photoinitiated Bulk Polymerization

Sample	[AIBN]/mol VPi[a]	VPi (mol %) in feed	VPi (mol %) in copolymer[b]	M_n (g/mol)[c]	DP[d]
1	5.72×10^{-4}	100	100	460,430	3592
2	5.76×10^{-4}	90	98.8	494,260	3871
3	4.20×10^{-4}	60	76.9	537,900	4541
4	5.20×10^{-4}	50	58.8	322,698	2912
5	5.40×10^{-4}	30	38.5	218,794	2139

[a] mol AIBN/mol VPi.
[b] VPi content in copolymer determined by ^{1}H NMR.
[c] Obtained from SEC.
[d] Degree of polymerization obtained using eqs. (1) and (2) [see Supporting Information, S2].

(Sigma-Aldrich Chemie, Steinheim, Germany). KOH, $MgSO_4$ were supplied by Merck Chemicals (Wadeville, Gauteng, South Africa). 2,2′-azobis(isobutyronitrile) (AIBN) obtained from Riedel de Haën (Sigma-Aldrich Chemie, Steinheim, Germany) was recrystallized from methanol and dried under vacuum. Tetrahydrofuran (THF) and methanol were supplied by were Merck Chemicals (Wadeville, Gauteng, South Africa) and used as received.

The synthesis of PVPi and PVPi-co-PVAc and subsequent saponification are summarized in Supporting Information Schemes 1 and 2.

Polymerization procedure

The following typical procedure was used for the photoinitiated polymerization of VPi and VAc: A dry Schlenk flask was charged with VPi and VAc of varying mole ratios (as tabulated in Table I) and the initiator and a magnetic stirrer added. The mixture was thoroughly degassed by three successive freeze-pump-thaw cycles, backfilled with nitrogen, sealed, and irradiated with a high pressure 400 watt mercury lamp. As the polymerization proceeded, the reaction mixture became very viscous, and the reaction was stopped when the magnetic follower could no longer effect stirring. The polymer was dissolved in THF and precipitated from a methanol/water mixture. The polymer was filtered and then dried under vacuum at 60°C. The conversions were determined gravimetrically. The molecular weight and molecular weight distributions were determined by size exclusion chromatography (SEC). The PVPi/PVAc copolymer compositions were determined by ^{1}H NMR spectroscopy.

Saponification

For the saponification of PVPi homopolymer: PVPi (3 g) was dissolved in THF (300 mL) and placed in a three-neck round-bottom flask equipped with a reflux condenser, dropping funnel [containing 60 mL of a 6% alkali solution of KOH/methanol/water (90/10, v/v)], a nitrogen inlet, and a magnetic stirrer. The PVPi solution was degassed using nitrogen before the temperature of the oil bath was raised to 65°C. Degassing was continued for a further 20 min. The alkali solution was then added drop wise with stirring at 100 revolutions/min, and then the mixture left to react overnight under a nitrogen atmosphere. The resultant fibers were treated with an ultrasonic generator, filtered, washed several times with methanol, and dried in a vacuum oven.

For the saponification of VPi/VAc copolymers: PVPi-co-PVAc (2 g) was dissolved in THF (100 mL) and the solution placed in a three-neck round-bottom flask equipped with a reflux condenser, dropping funnel [containing 20 mL of a 5% alkali solution of KOH/methanol/water (90/10 v/v)], a nitrogen inlet, and a magnetic stirrer. The PVPi-co-PVAc solution was flushed with nitrogen for 20 min before the temperature of the oil bath was raised to 65°C. Degassing was continued for a further 20 min. The alkali solution was added drop wise, with stirring at 100 revolution/min, and then the mixture was stirred overnight under a nitrogen atmosphere. The product was filtered, washed several times with methanol, and dried in a vacuum oven.

Analysis methods

SEC

The molecular weight and molecular weight distributions of PVPi and PVPi-co-PVAc were determined using SEC. The SEC instrument consisted of a Waters 717 plus Autosampler, Waters 600E system controller, and a Waters 610 fluid unit. The detector used was a Waters 410 differential refractometer (at 35°C). Two PLgel 5 μm Mixed-C columns and a

PLgel 5 μm guard column were used. The column injection volume was 60 μL, and the column oven was kept at a temperature of 30°C. The eluent was THF (HPLC grade, BHT stabilized); used at a flow rate of 1 mL/min. Calibration was carried out using narrow poly(styrene) standards with a molecular weight range of 800–2× 10^6 g/mol. All SEC data obtained is reported as poly(styrene) equivalents.

NMR

The PVPi-co-PVAc copolymer compositions were determined using ^{1}H NMR spectroscopy. Deuterated $CDCl_3$ was used as the solvent and TMS as a reference. The degree of saponification and the stereoregularity (diads, triads, and tetrads) of the PVA samples were also determined using ^{1}H NMR and ^{13}C NMR spectroscopy. Deuterated DMSO-*d6* was used as the solvent and TMS as the reference. All NMR spectra were acquired using a 600-MHz Varian ^{Unity}Inova spectrometer.

SEM

Imaging of the PVA samples was accomplished using a Leo® 1430VP and a Cambridge S200 scanning electron microscopes. The conditions used for the former were an accelerating voltage of 7 kV and a probe current of 150 pico amperes (pA), whilst for the latter an accelerating voltage of 10 kV and a probe current of 50 pA were used.

Thermal analyzes

The crystalline melting temperatures (T_m) were determined using a TA Instruments Q100 Differential Scanning Calorimeter. Samples of 8–10 mg were weighed and analyzed at a heating rate of 10°C/min, under a nitrogen atmosphere. Non isothermal thermogravimetry was carried out using a TA Instruments Q500 Thermogravimetric Analyzer. The samples were heated from 25°C to 900°C at a heating rate of 15°C/min, under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Microstructural analysis

The quantities of VPi (mol %) in the monomer feed and in the final copolymer are tabulated in Table I. The PVPi-co-PVAc copolymer compositions were determined using ^{1}H NMR spectroscopy. Figure 1 shows the typical spectrum for PVPi-co-PVAc. The signals at 4.8 and 1.8 ppm (labeled a and b, respectively) are attributed to the methine (—CH—) and methylene (—CH_2—) protons of the copolymer.[6,7,20,21] The signal at 1.2 ppm (labeled d) is attributed to the pivaloyl protons, while that at 2.2 ppm (labeled c) is ascribed to the methyl protons of the PVAc. The signals at 3.75 and 1.56 are likely to be ethanol and water solvent contaminants, respectively.

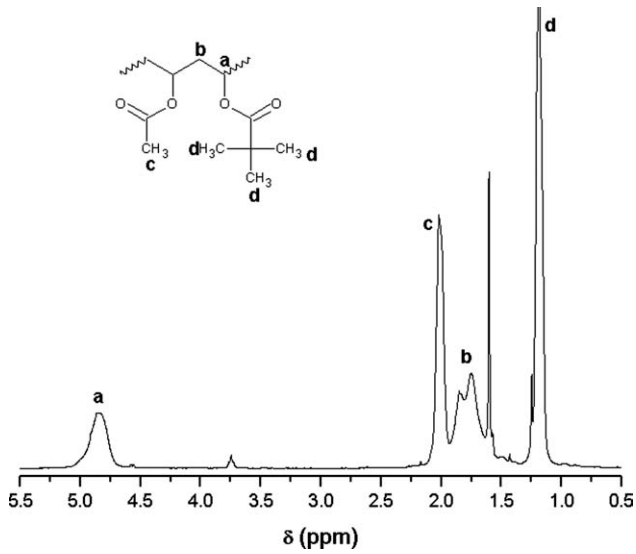

Figure 1 Typical ^{1}H NMR spectrum of poly(vinyl pivalate)-co-poly(vinyl acetate) in $CDCl_3$.

The results obtained show that the amount of VPi in the copolymer was higher than the amount in the feed; and was in agreement with the reactivity ratios of 3.1 and 1.6 for VPi and VAc, respectively.[15] Table I also tabulates the DP values of polymer Samples 1–5. It can be deduced from the results that the PVA samples were of sufficiently high molecular weight for *in situ* fibrillation (the required DP for fiber formation ought to be greater than 800). The samples also had a degree of saponification (>98%), thus they would be expected to form fibers upon saponification, provided they are sufficiently syndiotactic.

The diad, triad (shown in Table II), and tetrad tacticities were determined and the results obtained were in agreement with literature, i.e., when the amount of VPi in the copolymer was decreased, the syndiotacticity also decreased.[15]

Morphology

The differences in the syndiotacticity were rather small to attribute the changes observed in the morphology of the fibers to the stereoregularity. However, it is known that an increase in syndiotacticity leads to an increase in crystallinity because of the more regular packing of the crystallites.[16] When PVPi homopolymer (Sample 1) was saponified, PVA fibers with an s-diad content of 61.8% was obtained. The fibers [Fig. 2(A)] were composed of well-aligned microfibrils with dimensions of 0.4–1.2 μm in

TABLE II
Syndiotacticity and Degree of Saponification

Sample	Triad tacticity[a]			s-diad content		Degree of saponification (%)
	mm	*mr*	*rr*	*m*	*r*	
1	0.164	0.478	0.358	0.382	0.618	100
2	0.057	0.589	0.356	0.397	0.603	100
3	0.153	0.492	0.354	0.420	0.580	99
4	0.179	0.518	0.304	0.429	0.571	100
5	0.192	0.519	0.288	0.443	0.557	100

[a] Observed from the hydroxyl proton triad, *mm*-isotactic, *mr*-heterotactic, *rr*-syndiotactic.

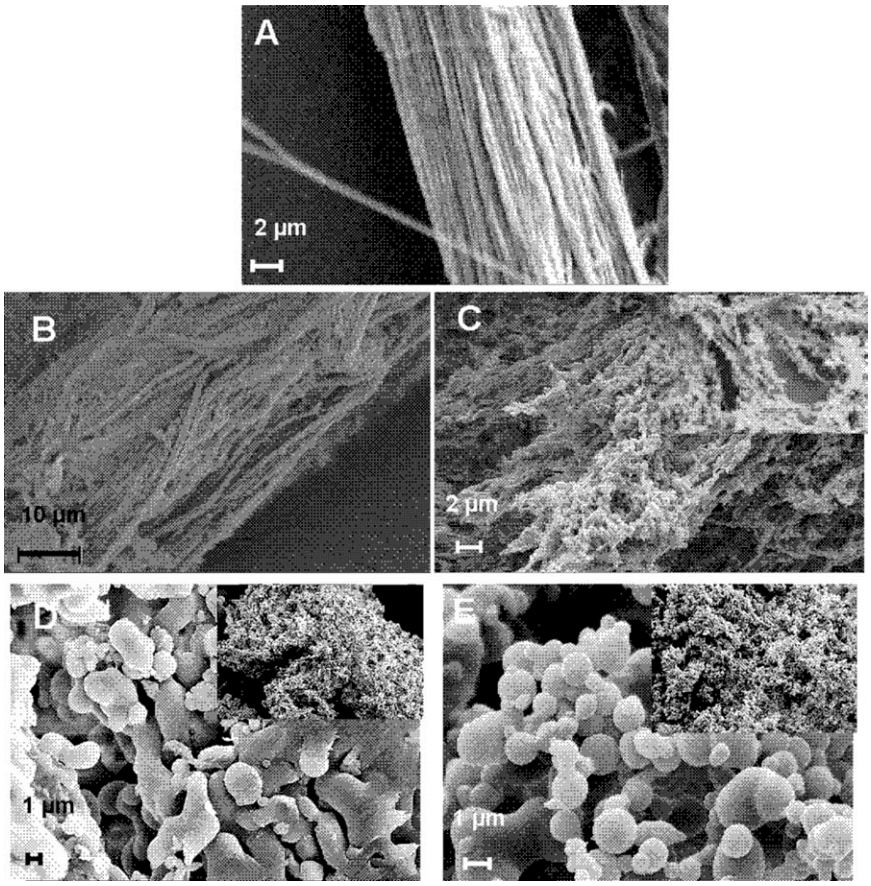

Figure 2 SEM images of PVAs with different s-diad contents: (A) 61.8%, (B) 60.3%, (C) 58.0%(insert magnification: ×1000 and main picture magnification: ×2500), (D) 57.1% (insert magnification: ×1660 and main picture magnification: ×3000), and (E) 55.7% (insert magnification: ×3470 and main picture magnification: ×25,000).

diameter. A VPi content of 98.8% (s-diad content 60.3%) lead to PVA fibers with fairly well-aligned microfibrils Fig. 2(B)]. Figure 2(C) shows the SEM images of PVA prepared from PVPi-co-PVAc with a VPi content of 76.9%. The PVA sample was not composed of bundles of microfibrils like Samples 1 and 2 but instead was composed of individual microfibrils with spherical particles on their surfaces

Figure 2(D) shows PVA Sample 4 with VPi content in the precursor polymer of 58.8% and an s-diad content of 57.1%. PVA with an s-diad content of 57.1% is expected to self assemble to form microfibrillar PVA fibers, however this was not observed for the sample. This was probably because of the high amount of PVAc, 41.2% in the precursor polymer, which leaves the polymer with high amounts of amorphous regions. A high level of crystallinity is required to stabilize the fibers, lack of this results in the loss of fibrous morphology hence the sample consists of poorly formed spherical particles and very few fibrous regions. The fibers were short and had diameters of 3.8–6.3 μm, whilst the particles

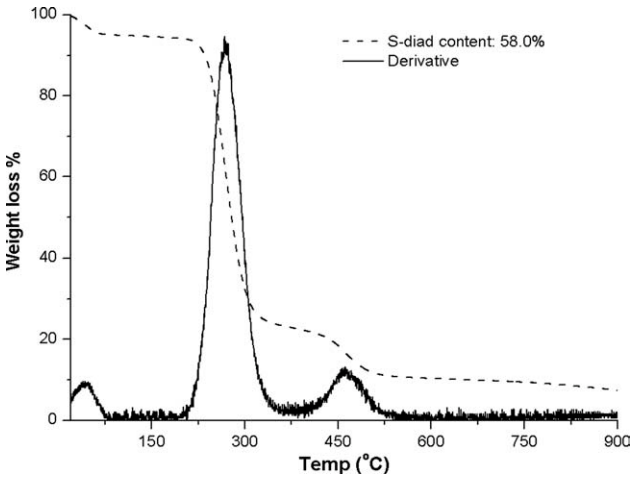

Figure 3 TG and DTGA thermograms of PVA.

were 2.5–3.8 μm in diameter. These results were in agreement with those predicted by Ghim et al.[22] When the comonomer composition of VPi : VAc is about 50 : 50 (mol %) the copolymer comprises very short blocks of PVPi and PVAc. Upon saponification of a copolymer with an almost similar composition, it is thus expected that poorly formed fibrous material would result.

The loss of fibrous morphology with a decline in the VPi content in the precursor polymer was attributed to a decrease in crystallinity. The highly crystalline regions (brought about by the PVPi) self assembled to form the fibrillar structures, whilst the amorphous regions are responsible for the spherical structures formed. A certain level of crystallinity is required to stabilize the fibers.[16] The SEM images for Sample 5 (VPi content in precursor polymer 38.5 mol %, s-diad content of 55.7%) are shown in Figure 2(E). The fibrous morphology of the syndiotactic PVA was completely lost, and the sample was composed entirely of spherical particles which had diameters of 3–12.1 μm. These results were also in agreement with those of Ghim et al.[22] When the VPi content is less than 40 mol %, the VPi/Vac copolymer comprised VAc blocks subdivided by an almost single VPi unit. This is insufficient to bring about chain orientation that is necessary for fibrillation, hence no fibers were observed. However, the formation of PVA particles in this manner was unprecedented.

This finding is unique in that the PVA particles comprise entirely of PVA—a feature lacked by particles prepared by the traditional methods of emulsion/suspension[23,24] polymerization followed by hydrolysis.

Thermal analysis

The accepted mechanism for thermal decomposition of PVA involves two steps (illustrated in Fig. 3). The first involves the elimination of water, and the second involves pyrolysis via main chain scission.[25,26] In atactic PVA, the first degradation step occurs at 220–275°C and the second step at 300–350°C.[27] Table III tabulates the T_{onset} and mass loss data (DTGA) for syndiotactic PVA (s-diad content of 55.7–61.8%). The slight weight loss below 100°C occurring in all the samples was attributed to

TABLE III
TGA Analysis of PVA with Varying Syndiotacticity

Sample	s-diad (%)[a]	D.S (%)[b]	T_{onset} (°C)[c]	DTGA peak (°C)[d]	Weight loss (%)[e]	Residue at 900°C[f]
1	61.8	100	275	50	5.9	5.9
				306	73.9	
				465	12.4	
2	60.3	100	255	43	5.4	4.1
				303	79.1	
				462	7.4	
3	58.0	99	236	41	5.5	7.3
				268	71.1	
				466	12.3	
4	57.1	100	249	60	4.3	5.6
				283	77.1	
				464	11.1	
5	55.7	100	264	53	3.7	3.1
				285	83.3	
				454	6.8	

[a] Diad syndiotacticity obtained from ^{1}H NMR.
[b] Degree of saponification obtained using ^{1}H NMR.
[c] Onset temperature for thermal decomposition.
[d] Differential mass loss peak maxima.
[e] Weight loss at DTGA peak maximum.
[f] Carbon residue at 900°C.

moisture loss. Water elimination occurs at 268–306°C and pyrolysis at 454–466°C. These results clearly show an enhancement in thermal stability with an increase in syndiotacticity. This was attributed to higher chain compactness owing to the tight intermolecular hydrogen bonding and higher stereoregularity.[7] The glass transition temperature (T_g) could not be observed in any of the samples analyzed in this work. However, the crystalline melting temperature (T_m) was observed at temperatures greater than 210°C. Generally an increase in T_m was observed with an increase in syndiotacticity. This is because, with an increase in syndiotacticity, the intermolecular hydrogen bonding also increases and the polymer becomes highly crystalline.

CONCLUSIONS

VPi/VAc copolymers of varying comonomer contents were prepared by photoinitiated free radical polymerization (FRP) in bulk. Upon saponification, PVA fibers of varying s-diad contents were obtained. A decrease in VPi content led to a decrease in syndiotacticity as a result of the dependence of syndiotacticity on the bulkiness of the side group of the poly(vinyl ester) precursor. The effect of VPi/VAc comonomer composition on the morphology of PVA microfibrils was also investigated. As the VPi content decreased, the fibrous morphology of the PVA was gradually lost as a result of the decrease in crystallinity. When the copolymer composition was 38.5/61.5 (VPi/VAc, mol %), spherical particles were obtained. These particles have potential applications in the medical industry as embolic material, owing to their biocompatibility and good binding properties.[24] They also have potential application in the paper industry, whereby if added in the paper making process they can impart properties such as oil, grease, and organic solvent resistance.

Studies are underway in our labs to extend the full potential of these PVA particles.

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