Polyvinyl Alcohol Modification with Sustainable Ketones

Yu-Kai Su, Caroline M. Coxwell, Steven Shen, and Stephen A. Miller* The George and Josephine Butler Polymer Laboratory Department of Chemistry, University of Florida Gainesville, Florida 32611-7200, USA

Electronic Supplementary Information (ESI)

Supplementary Information Available: Synthetic methods, hydrolysis study protocols, and complete polymer characterization data.

Table of Contents

Polyvinyl ketal synthesis	S2
Optimization studies	S6
Summary of GPC results	S7
Effect of ketalization degree on glass transition temperature	S8
Thermogravimetric analysis (TGA)	S9
Differential scanning calorimetry (DSC)	S17
Gel permeation chromatography (GPC) analysis	S23
2D NMR spectra and analysis	S27
¹ H NMR spectra	S31
¹³ C NMR spectra	S41
Room temperature hydrolysis study	S47
Heated hydrolysis study	S50



Water-degradable polyvinyl ketals with high glass transition temperatures (78–127 °C) were made via ketalization of polyvinyl alcohol (PVA) with sustainable ketones.

Polyvinyl ketal synthesis

Synthesis of polyvinyl butanone ketal PV-B-K (Table 1, Entry 2)

PV-B-K was synthesized using a procedure similar to that for **PV-A-K**. First, 0.50 g pre-ground PVA (11 mmol), 0.040 g *p*-TSA (0.2 mmol), 10 mL DMSO, and a stir bar were added to a RBF, which was attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was lowered into a hot oil bath and at 60°C, PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 10.24 mL butanone (114 mmol) and the temperature was lowered to 40 °C. For 24 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 0.433 g of product, obtained as white solid chunks. The product was sufficiently pure, and therefore additional purification was not necessary. The calculated isolated yield was 49.3%, according to the theoretical value set by a ketalization degree of 54.8%. ¹H NMR (DMSO-*d*₆) δ ppm 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 2.11 H), and 0.5-1.9 (m, 9.60 H). ¹³C NMR δ ppm 100.0, 99.0, 65.3, 63.8, 63.1, 46.2, 45.0, 42.3, 37.4, 23.9, 17.8, and 8.4.

Synthesis of polyvinyl 3-pentanone ketal PV-P-K (Table 1, Entry 3)

PV-P-K was synthesized using a procedure similar to that for **PV-A-K**. 0.50 g pre-ground PVA (11 mmol), 0.040 g *p*-TSA (0.23 mmol), 10 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was lowered into a hot oil bath and at 60°C, PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 6.16 mL 3-pentanone (58 mmol) and the temperature was lowered to 40 °C. For 8 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 0.362 g of product, obtained as white solid chunks. The product was sufficiently pure, and therefore additional purification was not necessary. The calculated isolated yield was 37.9%, according to the theoretical value set by a ketalization degree of 21.9%. ¹H NMR (DMSO-*d*₆) δ ppm 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 1.28 H), and 0.5-1.9 (m, 4.21 H). ¹³C NMR δ ppm 100.8, 67.8, 65.8, 63.8, 45.8, 45.3, 37.3, 30.8, 21.6, 8.1, and 7.2.

Synthesis of polyvinyl raspberry ketone ketal PV-RK-K (Table 1, Entry 4)

PV-RK-K was synthesized using a procedure similar to that for **PV-A-K**. 0.40 g pre-ground PVA (9.1 mmol), 0.03 g *p*-TSA (0.17 mmol), 10 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was lowered into a hot oil bath and at 60°C, PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 7.46 g raspberry ketone (45 mmol) and the temperature was lowered to 40 °C. For 8 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 0.691 g of product. The purified product was obtained following a procedure similar to that for **PV-TM-K** described in the Experimental section. In this case, 0.250 g were purified to yield 0.130 g of final product, collected as white solid chunks. The calculated isolated yield was 62.3%, according to the theoretical value set by a ketalization degree of 41.5%. ¹H NMR (DMSO-*d*₆) δ ppm 8.98-9.18 (m, 0.36 H), 6.5-7.1 (m, 1.49 H), 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 2.66 H) and 0.8-2.0 (m, 5.24 H). ¹³C NMR δ ppm 155.2, 132.3, 129.0, 115.0, 99.3, 97.4, 65.5, 63.8, 63.2, 46.1, 45.9, 45.0, 44.6, 34.3, 29.1, 27.9, 27.3, and 17.7.

Synthesis of polyvinyl zingerone ketal PV-ZG-K (Table 1, Entry 5)

PV-ZG-K was synthesized using the similar procedure as for **PV-A-K**. 0.50 g pre-ground PVA (11 mmol), 0.04 g *p*-TSA (0.23 mmol), 10 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 11.04 g zingerone (57 mmol) and the temperature was lowered to 40 °C. For 24 hours, the system remained homogeneous. Next, the reaction was cooled

and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 3.34 g of product. The purified product was obtained following a procedure similar to that for **PV-TM-K** described in the Experimental section. In this case, 2.60 g were purified to yield 0.323 g of final product, collected as white solid chunks. The calculated isolated yield was 46.2%, according to the theoretical value set by a ketalization degree of 39.0%. ¹H NMR (DMSO-*d*₆) δ ppm 8.56-8.69 (m, 0.34 H), 6.4-6.85 (m, 1.03 H), 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 1.71 H), and 0.8-1.9 (m, 4.95 H). ¹³C NMR δ ppm 148.5, 145.7, 135.1, 120.2, 115.2, 111.9, 110.1, 99.3, 67.1, 64.4, 55.9, 47.1, 45.8, 44.9, 29.3, and 28.8.

Synthesis of polyvinyl levulinic acid ketal PV-LA-K (Table 1, Entry 6)

PV-LA-K was synthesized using a procedure similar to that for **PV-A-K**. 1.00 g pre-ground PVA (22 mmol), 0.08 g *p*-TSA (0.46 mmol), 20 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 13.8 g levulinic acid (118 mmol) and maintained at 60 °C. For 24 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 0.707 g of product. The purified product was obtained following a procedure similar to that for **PV-TM-K** described in the Experimental section. In this case, 0.174 g were purified to yield 0.069 g of final product, collected as transparent films. The calculated isolated yield was 12.8%, according to the theoretical value set by a ketalization degree of 15.3%. ¹H NMR (DMSO-*d*₆) δ ppm 3.7-4.1 (m, 7.60 H), 2.2-2.32 (m, 1.00 H), and 0.5-1.9 (m, 15.61 H). ¹³C NMR δ ppm 175.4, 99.3, 98.2, 68.3, 66.0, 63.9, 47.0, 45.8, 45.3, 44.0, 37.6, 38.6, and 26.4.

Synthesis of polyvinyl cyclopentanone ketal PV-CP-K (Table 1, Entry 7)

PV-CP-K was synthesized using a procedure similar to that for **PV-A-K**. 0.8 g pre-ground PVA (18 mmol), 0.06 g *p*-TSA (0.35 mmol), 16 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 16.00 mL cyclopentanone (181 mmol) and the temperature was lowered to 40 °C. For 12 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 0.601 g of product as white solid chunks. The product was pure enough, and therefore purification was not necessary. The calculated isolated yield was 42.9%, according to the theoretical value set by a ketalization degree of 62.7%. ¹H NMR (DMSO-*d*₆) δ ppm 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 2.68 H), and 0.8-1.9 (m, 11.89 H). ¹³C NMR δ ppm 109.9, 67.8, 66.2, 63.5, 47.1, 45.2, 42.6, 37.6, 31.9, 24.4, and 22.0.

Synthesis of polyvinyl cyclohexanone ketal PV-CH-K (Table 1, Entry 8)

PV-CH-K was synthesized using a procedure similar to that for **PV-A-K**. 1.0 g pre-ground PVA (22 mmol), 0.08 g *p*-TSA (0.46 mmol), 20 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 4.46 mL cyclohexanone (43 mmol) and the temperature was lowered to 40 °C. For 12 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 1.15 g of product as white solid chunks. The product was pure enough, and therefore purification was not necessary. The calculated isolated yield was 60.8%, according to the theoretical value set by a ketalization degree of 62.4%. ¹H NMR (DMSO-*d*₆) δ ppm 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 2.66 H), and 0.8-1.9 (m, 12.81 H). ¹³C NMR δ ppm 99.2, 97.7, 65.6, 64.5, 63.7, 45.0, 38.6, 33.7, 28.2, 25.5, and 22.1.

Synthesis of polyvinyl dihydrocarvone ketal PV-DC-K (Table 1, Entry 9)

PV-DC-K was synthesized using a procedure similar to that for **PV-A-K**. 0.50 g pre-ground PVA (11 mmol), 0.04 mL 36% hydrochloric acid solution (0.47 mmol), 10 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 10.03 g D-dihydrocarvone (66 mmol) and maintained at 60 °C. For 4 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 1.84 g of product. The purified product was obtained following a procedure similar to that for **PV-TM-K** described in the Experimental section. In this case, 0.500 g were purified to yield 0.134 g of final product, collected as white solid chunks. The calculated isolated yield was 38.7%, according to the theoretical value set by a ketalization degree of 55.2%. ¹H NMR (DMSO-*d*₆) δ ppm 4.55-4.76 (m, 1.15 H), 4.18-4.55 (m, 1.00 H), 3.5-4.18 (m, 2.23 H), and 0.7-2.25 (m, 12.59 H). ¹³C NMR δ ppm 149.2, 108.1, 98.5, 65.8, 65.2, 63.9, 45.4, 44.8, 44.3, 40.6, 37.2, 33.8, 30.4, 20.8, and 13.6.

Synthesis of polyvinyl 3,3,5-trimethylcyclohexanone ketal PV-TM-K (Table 1, Entry 10)

PV-TM-K was synthesized using a procedure similar to that for **PV-A-K**. 1.0 g pre-ground PVA (22 mmol), 0.08 mL 36% hydrochloric acid solution (93 mmol), 30 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 17.9 mL 3,3,5-trimethylcyclohexanone (113 mmol) and maintained at 60 °C. For 24 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 3.11 g of product. The purified product was obtained following a procedure similar to that for **PV-TM-K** described in the Experimental section. In this case, 0.500 g were purified to yield 0.172 g of final product, collected as white solid chunks. The calculated isolated yield was 62.4%, according to the theoretical value set by a ketalization degree of 51.7%. ¹H NMR (DMSO-*d*₆) δ ppm 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 2.07 H), and 0.5-1.9 (m, 11.35 H). ¹³C NMR δ ppm 99.3, 98.8, 65.9, 64.7, 63.8, 49.8, 48.3, 47.1, 46.2, 45.8, 45., 44.7, 36.9, 33.8, 31.5, 27.1, 25.5, 24.6, and 22.1.

Synthesis of polyvinyl furfural acetal PV-F-A (Table 1, Entry 11)

PV-F-A was synthesized using a procedure similar to that for **PV-A-K**. 1.0 g pre-ground PVA (22 mmol), 0.08 g *p*-TSA (0.46 mmol), 20 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 19.0 mL furfural (229 mmol) and the temperature was lowered to 40 °C. For 3 hours, the system remained homogeneous. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 2.42 g of product. The purified product was obtained following a procedure similar to that for **PV-TM-K** described in the Experimental section. In this case, 0.500 g were purified to yield 0.333 g of final product, collected as white solid chunks. The calculated isolated yield was 66.1%, according to the theoretical value set by an acetalization degree of 83.2%. ¹H NMR (DMSO-*d*₆) δ ppm 7.41-7.70 (m, 1.04 H), 6.20-6.58 (m, 2.08 H), 5.45-6.10 (m, 1.00 H), 3.5-4.7 (m, 2.92 H), and 0.8-1.9 (m, 4.81 H). ¹³C NMR δ ppm 151.7, 151.3, 142.5, 110.2, 107.4, 94.7, 88.5, 73.8, 73.1, 72.3, 68.2, 62.3, 44.1, 42.1, 37.0, 35.7, and 34.5.

Synthesis of polyvinyl acetone ketal PV-A-K* (Table 1, Entry 17)

PV-A-K* was synthesized using a procedure similar to that for **PV-A-K**. 2.0 g pre-ground **high** molecular weight PVA (45 mmol), 0.15 g *p*-TSA (0.87 mmol), 40 mL DMSO, and a stir bar were added to a RBF attached to a condenser. Then, 0.5 g anhydrous magnesium sulfate was wrapped in

filter paper and placed at the neck of the condenser. The RBF was heated to 60 °C until PVA and *p*-TSA completely dissolved in the DMSO. The RBF was charged with 120 mL acetone (1620 mmol) and the temperature was lowered to 40 °C. Next, the reaction was cooled and terminated through neutralization with 1 M NaOH. Precipitation in water followed by filtration afforded 2.31 g of product as white solid chunks. The product was pure enough, and therefore purification was not necessary. The calculated isolated yield was 70.6%, according to the theoretical value set by a ketalization degree of 68.1%. ¹H NMR (DMSO-*d*₆) δ ppm 4.15-4.7 (m, 1.00 H), 3.5-4.15 (m, 3.13 H), and 0.8-1.9 (m, 12.81 H). ¹³C NMR δ ppm 99.7, 97.84, 97.78, 85.9, 84.2, 83.6, 81.5, 47.3, 45.0, 44.2, 43,1, 36.5, 30.2, 24.6, 24.3, and 19.9.

Optimization studies

Table S1. Optimization study: **catalyst**. Ketalization reactions of **PV-DC-K** and **PV-TM-K** were performed using HCI and *p*-TSA as catalysts. The procedures of Entry 38 and 39 were the same as Entry 9 and 10, but the catalyst was switched to *p*-TSA instead of HCI.

Entry		Catalyst	Ketalization (%)
9		HCI	55.2
38	FV-DC-N	p-TSA	0.0
10		HCI	51.7
39		p-TSA	0.0

Table S2. Optimization study: **ketone equivalents**. Ketalization reactions of **PV-A-K**, **PV-RK-K** and **PV-F-A** were performed using various ketone equivalents, defined as the number of ketones added per main-chain hydroxy group of PVA. The procedures of Entry 19, 20 and 21 were the same as Entry 1, but the added acetone amounts reduced to 200, 167 and 33 mL. The procedure of Entry 22 was same as Entry 4, but the added raspberry ketone amount reduced to 2.98 g. The procedure of Entry 23 was same as Entry 11, but the added furfural amount reduced to 3.8 mL.

Entry		Ketone equivalents	Ketalization (%)	T _g (°C)
1		36	69.2	100
19		30	63.1	91
20	FV-A-N	25	60.8	83
21		5	43.5	N/A
4		5	41.5	109
22		2	35.9	94
11		10	83.2	138
23	F V-F-A	2	67.7	134

Table S3. Optimization study: **drying agent**. Ketalization reactions of **PV-A-K** were performed with and without a drying agent. The procedure of Entry 18 was the same as Entry 1, but the magnesium sulfate bag was not employed.

Entry	Ketone equivalents	Drying agent	Ketalization (%)	$T_g(^{\circ}C)$
1	36	MgSO ₄ anhydrous (bag)	69.2	100
18	36	none	65.0	96

Entry	Time (minutes)	Ketalization (%)
0	0	0
22	15	38.7
23	30	49.0
24	45	50.0
25	60	53.1
26	75	57.4
27	90	59.8
28	105	60.3
29	120	60.9
30	135	62.1
31	150	62.8
32	165	64.0
33	180	65.2
34	240	67.4
35	360	67.7
36	480	67.7
37	1440	68.2

Table S4. Kinetic study data for the synthesis of PV-A-K in DMSO with *p*-TSA catalyst at 40 °C.

Table S5. Temperature effects on the synthesis **PV-P-K**. The temperature effects on ketalization were studied for 3-pentanone instead of acetone since 3-pentanone has a higher boiling point (102 vs. 56 $^{\circ}$ C).

Entry	Reaction Temperature (°C)	Ketalization (%)	Product color
³ ру-р-к	40	21.9	white
40	100	13.8	yellow

Summary of GPC results

Table S6. The molecular weight of polymers measured by GPC in THF and calculated by ¹H NMR.

Entry Calculated <i>M</i> _n (Da)		Calculated M_n (Da)	GPC <i>M</i> _n ^a (Da)	PDI
Entry 0	PVA	-	22,300 ^{<i>b</i>}	2.05
Entry 1	PV-A-K	29,300	27,400	1.90
Entry 7	PV-CP-K	32,800	31,900	2.32
Entry 8	PV-CH-K	35,400	30,200	1.88
Entry 16	PVA*	-	146,000-186,000 ^c	-
Entry 17	′ PV-A-K *	191,000-244,000	-	-

^aDetermined by GPC in tetrahydrofuran. ^bDetermined by GPC in hexafluoroisopropanol. ^c High molecular weight PVA; molecular weight reported by vendor.



Effect of ketalization degree on glass transition temperature

Figure S1. The glass transition temperature (T_g) of modified PVA is proportional to the degree of ketalization or acetalization, which depends on the ketone/aldehyde equivalents employed (Table S2: **PV-A-K**, **PV-RK-K**, and **PV-F-A**) or the use of a drying agent (Table S3: **PV-A-K**).

Thermogravimetric analysis (TGA)



Figure S2. TGA thermogram of PV-A-K (Table 1, Entry 1).



Figure S3. TGA thermogram of PV-B-K (Table 1, Entry 2).



Figure S4. TGA thermogram of PV-P-K (Table 1, Entry 3).



Figure S5. TGA thermogram of PV-RK-K (Table 1, Entry 4).



Figure S6. TGA thermogram of PV-ZG-K (Table 1, Entry 5).



Figure S7. TGA thermogram of PV-LA-K (Table 1, Entry 6).



Figure S8. TGA thermogram of PV-CP-K (Table 1, Entry 7).



Figure S9. TGA thermogram of PV-CH-K (Table 1, Entry 8).



Figure S10. TGA thermogram of PV-DC-K (Table 1, Entry 9).



Figure S11. TGA thermogram of PV-TM-K (Table 1, Entry 10).



Figure S12. TGA thermogram of PV-F-A (Table 1, Entry 11).



Figure S13. TGA thermogram of PV-A-K (Table 1, Entry 17).



Figure S14. TGA thermogram of PV-A-K (Table S3, Entry 18).



Figure S15. TGA thermogram of PV-A-K (Table S2, Entry 19).



Figure S16. TGA thermogram of PV-A-K (Table S2, Entry 20).



Differential scanning calorimetry (DSC)

Figure S17. DSC thermogram of PV-A-K (Table 1, Entry 1).



Figure S18. DSC thermogram of PV-B-K (Table 1, Entry 2).



Figure S19. DSC thermogram of PV-P-K (Table 1, Entry 3).



Figure S20. DSC thermogram of PV-RK-K (Table 1, Entry 4).



Figure S21. DSC thermogram of PV-ZG-K (Table 1, Entry 5).



Figure S22. DSC thermogram of PV-LA-K (Table 1, Entry 6).



Figure S23. DSC thermogram of PV-CP-K (Table 1, Entry 7).



Figure S24. DSC thermogram of PV-CH-K (Table 1, Entry 8).



Figure S25. DSC thermogram of PV-DC-K (Table 1, Entry 9).



Figure S26. DSC thermogram of PV-TM-K (Table 1, Entry 10).



Figure S27. DSC thermogram of PV-F-A (Table 1, Entry 11).



Figure S28. DSC thermogram of PV-A-K (Table 1, Entry 17).

Gel permeation chromatography (GPC) analysis



Figure S29. GPC chromatogram of PVA (Table 1, Entry 0) in HFIP.

Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Μv	PD
Peak 1	217004	310161	345404	389547	437651	382531	1.114
Peak 2	50187	27382	52020	82598	111151	78271	1.9

Peak information

	Start (mins)	End (mins)
Baseline region 1	6.34	9.25
Baseline region 2	27.70	29.48
Peak 1	9.77	11.18
Peak 2	11.18	16.10

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	11.18	97736.409	4250.946
Peak 2	RI	12.69	4543314.234	32226.629

Chromatogram



Figure S30. GPC chromatogram of PV-A-K (Table 1, Entry 1) in THF.



Figure S31. GPC chromatogram of PV-CP-K (Table 1, Entry 7) in THF.

Molecular Wei	ght Averages						
Peak	Мр	Mn	Mw	Mz	Mz+1	Μv	PD
Peak 1	56185	30189	56860	95534	139998	89471	1.883

Peak information

	Start (mins)	End (mins)	
Baseline region 1	5.40	9.34	
Baseline region 2	23.85	25.63	
Peak 1	10.71	15.21	
Book	Traco Book	Max PT (mine) Book Ar	001

Peak	Trace	Peak Max RT (mins)	Peak Area (mV.s)	Peak Height (mV)
Peak 1	RI	12.57	3382958.149	24149.792

Chromatogram



Figure S32. GPC chromatogram of PV-CH-K (Table 1, Entry 8) in THF.

2D NMR spectra and analysis



Figure S33. Complete NMR assignment of PV-A-K (Table 1, Entry 1).

Because of overlapping ¹H NMR peaks, ¹³C and 2D NMR were needed for conclusive ¹H NMR peak assignment for **PV-A-K**. The peaks at 97.78, 99.59 and 106.99 ppm in the ¹³C NMR spectrum were assigned as ketal carbons. The peak at 97.78 ppm was flanked by at least one PVA-OH unit, and the peaks at 99.59 and 106.99 were flanked by other ketals. In the gHMBC spectrum, the ketal carbons coupled to ketal methyl protons. With this information, the ketal methyl carbon chemical shifts were located by the gHSQC spectrum. The main-chain methine carbon chemical shifts were tracked by the gHSQC spectrum with four major methine proton peaks at 4.02, 3.95, 3.82, and 3.67 ppm which were separated into two groups. The main-chain methylene protons were separated into three groups depending on the nature of their neighbors: S1 - a methylene in an acetal ring; S2 - a methylene between an acetal and a PVA unit; and S3 - a methylene between PVA-OH units. The methylene protons (S1, S2, S3) correlated to the methine protons in the ¹H-¹H COSY spectrum. For the assignment, S1 protons displayed cross-peaks with methine protons proximal to a ketal group, S2 protons displayed cross-peaks with both kinds of methine protons, and S3 protons displayed crosspeaks only with methine protons proximal to PVA-OH. The alcoholic proton peaks were assigned to 4.44, 4.30 and 4.22 ppm. The unhydrolyzed acetyl proton and carbon chemical shifts were identified via ¹H and ¹³C NMR directly.



Figure S34. ¹H NMR spectrum of **PV-A-K** (Table 1, Entry 1). Ketalization degree = (3.25 - 1)/3.25 = 69.2%.



Figure S35. ¹³C NMR spectrum of PV-A-K (Table 1, Entry 1).



Figure S36. PV-A-K gHSQC spectrum (Table 1, Entry 1).



Figure S37. PV-A-K gHMBC spectrum (Table 1, Entry 1).



Figure S38. PV-A-K ¹H-¹H COSY spectrum (Table 1, Entry 1).

¹H NMR spectra



Figure S39. ¹H NMR spectrum of **PVA** (Table 1, Entry 0).



Figure S40. ¹H NMR spectrum of **PV-B-K** (Table 1, Entry 2). Ketalization Degree = (2.21 - 1)/(2.21 = 54.8%).



Figure S41. ¹H NMR spectrum of **PV-P-K** (Table 1, Entry 3). Ketalization Degree = (1.28 – 1)/1.28 = 21.9%.



Figure S42. ¹H NMR spectrum of **PV-RK-K** (Table 1, Entry 4). Ketalization Degree = (1.71 - 1)/1.71 = 41.5%.



Figure S43. ¹H NMR spectrum of **PV-ZG-K** (Table 1, Entry 5). Ketalization Degree = $\{2.66 - (3 \times 0.34)\}$ = 39.0%. For the **PV-ZG-K** ketalization degree calculation, the methoxy hydrogens shown in orange overlapped with methine hydrogens shown in blue. Therefore, the ketalization degree could not be directly determined by the method described in the *Polymer characterization by NMR* section in the main article. To modify the method to **PV-ZG-K**, the methine hydrogen (3.50–4.15 ppm, blue) integration was reduced by the methoxy hydrogen integration (3.71–3.75 ppm, orange). The methoxy hydrogen integration equates to three times the phenolic hydrogen integration (8.56–8.68 ppm) since they are attached to the same aromatic ring. The ketalization degree is equal to $\{([-CH(OR)] + ArOCH_3) - 3[ArOH] - [-CH(OH)]\} / \{([-CH(OR)] + ArOCH_3) - 3[ArOH]] - [-CH(OH)]\} / \{(3 \times 0.34)\} = 39.0\%$. Note that a very similar result (38.6%) is obtained if the methoxy hydrogen correction is determined by the three Ar-H hydrogens since $3 \times 0.34 \sim 1.03$.



Figure S44. ¹H NMR spectrum of **PV-LA-K** (Table 1, Entry 6). Ketalization Degree = 15.3%. For the **PV-LA-K** ketalization degree calculation, the PVA alcoholic hydrogens shown in blue overlapped with the methine hydrogens shown in green. Therefore, the ketalization degree could not be directly determined by the method described in the section *Polymer characterization by NMR* in the main article. Alternatively, the ketalization degree is determined by the quotient, $\alpha/(\alpha+\beta)$, where α represents hydrogen on ketalized PVA and β represents hydrogen on unreacted PVA. Since the side-chain methylene (-CH₂-) hydrogen integration shown in red is 1.00 and that shown in orange is 1.00, two α hydrogens are represented by an integration value of 1.00 ($2\alpha = 1.00$ and hence, $\alpha = 0.50$). The broad peaks shown in purple from 0.5–1.9 ppm include all of the main-chain methylene hydrogens ($4\alpha + 4\beta$), the side-chain methyl hydrogens (3α), and the methylene hydrogens proximal to the carboxylic acid (2α). Therefore, $9\alpha + 4\beta = 15.61$. Since $\alpha = 0.50$, $\beta = 2.78$. And, the ketalization degree = $\alpha/(\alpha+\beta) = 0.5/(0.5 + 2.78) = 15.3\%$.



Figure S45. ¹H NMR spectrum of **PV-CP-K** (Table 1, Entry 7). Ketalization Degree = (2.68 – 1)/2.68 = 62.7%.



Figure S46. ¹H NMR spectrum of **PV-CH-K** (Table 1, Entry 8). Ketalization Degree = (2.66 - 1)/2.66 = 62.4%.



Figure S47. ¹H NMR spectrum of **PV-DC-K** (Table 1, Entry 9). Ketalization Degree = (2.23 - 1)/2.23 = 55.2%.



Figure S48. ¹H NMR spectrum of **PV-TM-K** (Table 1, Entry 10). Ketalization Degree = (2.07 - 1)/2.07 = 51.7%.



Figure S49. ¹H NMR spectrum of **PV-F-A** (Table 1, Entry 11). Acetalization Degree = (4×1.00)/4.81 = 83.2%.



Figure S50. ¹H NMR spectrum of **PV-A-K** (High M_n) (Table 1, Entry 17). Ketalization Degree = (3.13 - 1)/3.13 = 68.1%.



Figure S51. ¹H NMR spectrum of **PV-A-K** (Table S3, Entry 18). Ketalization Degree = (2.86 - 1)/2.86 = 65.0%.



Figure S52. ¹H NMR spectrum of **PV-A-K** (Table S2, Entry 19). Ketalization Degree = (2.71 - 1)/2.71 = 63.1%.



Figure S53. ¹H NMR spectrum of **PV-A-K** (Table S2, Entry 20). Ketalization Degree = (2.55 - 1)/2.55 = 60.8%.



Figure S54. ¹H NMR spectrum of **PV-A-K** (Table S2, Entry 21). Ketalization Degree = (1.77 - 1)/1.77 = 43.5%.



Figure S55. ¹H NMR spectrum of **PV-RK-K** (Table S2, Entry 22). Ketalization Degree = (1.56 - 1)/1.56 = 35.9%.



Figure S56. ¹H NMR spectrum of **PV-F-A** (Table S2, Entry 23). Acetalization Degree = (4×1.00)/5.91 = 67.7%.

¹³C NMR spectra



Figure S57. ¹³C NMR spectrum of PVA (Table 1, Entry 0).



Figure S58. ¹³C NMR spectrum of PV-B-K (Table 1, Entry 2).



Figure S59. ¹³C NMR spectrum of PV-P-K (Table 1, Entry 3).



Figure S60. ¹³C NMR spectrum of PV-RK-K (Table 1, Entry 4).



Figure S61. ¹³C NMR spectrum of PV-ZG-K (Table 1, Entry 5).



Figure S62. ¹³C NMR spectrum of PV-LA-K (Table 1, Entry 6).



Figure S63. ¹³C NMR spectrum of PV-CP-K (Table 1, Entry 7).



Figure S64. ¹³C NMR spectrum of PV-CH-K (Table 1, Entry 8).



Figure S65. ¹³C NMR spectrum of PV-DC-K (Table 1, Entry 9).



Figure S66. ¹³C NMR spectrum of PV-TM-K (Table 1, Entry 10).



Figure S67. ¹³C NMR spectrum of PV-F-A (Table 1, Entry 11).



Room temperature hydrolysis study

PV-A-K with a 69.2% ketalization degree (Table 1, Entry 1) was subjected to aqueous buffers having pH = 2, pH = 3, and pH = 5, in addition to deionized (DI) water, and seawater. The photographs were taken periodically: time = 0, 24 hours, 1 week, 1 month, 2 months, 3 months, and 1 year.



Figure S69. Photograph of PV-A-K immediately after addition to aqueous media.



Figure S70. Photograph of **PV-A-K** 24 hours after addition to aqueous media. The samples in pH 2 and pH 3 dissolved completely.



Figure S71. Photograph of **PV-A-K** 1 week after addition to aqueous media. These samples remained visually unchanged.



Figure S72. Photograph of **PV-A-K** 1 month after addition to aqueous media. The sample in the pH 5 buffer swelled slightly.



Figure S73. Photograph of **PV-A-K** 2 months after addition to aqueous media. The sample in the pH 5 buffer swelled and became transparent.



Figure S74. Photograph of **PV-A-K** 3 months after addition to aqueous media. The sample in the pH 5 buffer dissolved thoroughly.



Figure S75. Photograph of **PV-A-K** 1 year after addition to aqueous media. These samples remained visually unchanged.



Figure S76. Photograph of **PV-A-K** 2 years after addition to aqueous media. These samples remained visually unchanged.

Table S7. Room temperature hydrolysis study of **PV-A-K** in buffers (pH = 2, 3, and 5), deionized water, and seawater. Ketalization degree (%) data versus time.

Room temperature hydrolysis study							
Medium	pH 2	рН 3	pH 5	DI water	seawater		
Time	Ketalization degree (%)						
0	69.2	69.2	69.2	69.2	69.2		
3H	12.3	55.6	69.2	69.2	69.2		
1D	1.0	2.0	69.0	69.0	68.9		
1W	-	-	64.4	69.2	68.8		
2W	-	-	53.3	69.4	69.7		
1M	-	-	49.5	69.0	69.6		
2M	-	-	24.8	69.7	69.1		
3M	-	-	0	68.5	68.8		
6M	-	-	-	67.1	69.3		
1Y	-	-	-	64.2	68.2		
2Y				66.2	65.9		



Figure S77. Room temperature hydrolysis study of **PV-A-K** in buffers (pH = 2, 3, and 5), deionized water, and seawater. Ketalization degree (%) data graphed versus time.

Heated hydrolysis study

PV-A-K with a 69.2% ketalization degree was subjected to deionized water and sea water at 80 °C. The photographs were taken at 1 week, 1 month, and 3 months.



Figure S78. Photograph of **PV-A-K** 1 week after addition to seawater and deionized water at 80 °C. Both samples swelled slightly.



Figure S79. Photograph of **PV-A-K** 1 month after addition to seawater and deionized water at 80 °C. Both samples swelled and fell apart.



Figure S80. Photograph of **PV-A-K** 3 months after addition to seawater and deionized water at 80 °C. Both samples dissolved thoroughly.

Heated (80 °C) hydrolysis study						
Medium	DI water	seawater				
Time	ketalization degree (%)					
0	69.2	69.2				
1W	50.5	61.5				
1M	49.0	58.3				
3M	4.8	1.0				

Table S8. High temperature (80°C) hydrolysis study of **PV-A-K** in deionized water and seawater. Ketalization degree (%) data versus time.



Figure S81. High temperature (80°C) hydrolysis study of **PV-A-K** in deionized water and seawater. Ketalization degree (%) data graphed versus time.