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Poly(vinyl alcohol) Functionalization with Aldehydes in Organic Solvents: Shining Properties of Poly(vinyl acetals)

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ABSTRACT: Poly(vinyl alcohol) has been functionalized with aldehydes in tetrahydrofuran (THF) with a good control of the grafting. A wide library of poly(vinyl acetals) could be obtained in order to study some structure/property correlations. The influence of the aldehyde nature on the functionalization rates has been studied, in particular for optical properties by measurement of the shininess for further applications in the cosmetic field. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40677.

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INTRODUCTION

Poly(vinyl alcohol) (PVA) is a nontoxic biocompatible polymer synthesized for the first time from poly(vinyl acetate) in 1927. PVA is a water-soluble, film-forming, and odorless polymer and its properties may depend on its hydrolysis and polymerization degrees. A large number of applications of PVA and its derivatives can be found in several fields, in particular for the development of biomedical, cosmetic, textiles, paper, and adhesives.[1]

PVA functionalizations have been reported through esterifications,[2–20] etherifications,[21–26] silylations,[27,28] carbamoylations, borylations, or others.[29–44] Thus, PVA acetalization with aldehydes has also been reported[45] and some of the resulting poly(vinyl acetals) are commercially available.[1] Poly(vinyl butyral) is used in particular for its coating and adhesive properties.[46–49] Several other aldehydes have been grafted on PVA[49–65] and poly(vinyl acetals) have been utilized, among others, to obtain Langmuir–Boldgett films,[50,51] membranes for ultrafiltration,[66] fluorescent polymers for biomedical uses,[67] or anti-corrosions agents for material science.[68] Concerning the cosmetic field, only few applications of poly(vinyl acetals) have been reported and concern the formation of cosmetic sponges[69,70] and their use in masks[71] or in nail polishing, by improving their resistance and their thermal stability.

An important aspect within cosmetic applications, in particular for applications in lipsticks, gloss, and nail polish, is the shininess of the compounds. Cosmetic ingredients with shining properties are reported, for example, for long chain aliphatic compounds[72–74] and for some polymeric derivatives.[75,76]

Herein, we present a general and convenient method to functionalize PVA with aldehydes in easy-to-remove organic solvents. The shininess of the resulting polymers has been measured for further cosmetic applications.

EXPERIMENTAL

Materials

PVA 1 (Mw = 9000–10,000 g mol^{-1}, nominal degree of hydrolysis = 80%), **PVA 3** (Mowiol® 4–98; Mw = 27,000 g mol^{-1}, nominal degree of hydrolysis = 98%) and **PVA 5** (Mw = 31,000–50,000 g mol^{-1}, nominal degree of hydrolysis = 98–99%) were purchased from Sigma–Aldrich. **PVA 4** (SELVOL™ E 203; Mw = 27,000 g mol^{-1}, nominal degree of hydrolysis = 88%) was kindly provided by Sekisui, **PVA 2** (Mowiol® 3–85; Mw = 22,200 g mol^{-1}, nominal degree of hydrolysis = 85%), **PVA 6** (Mowiol® 4–88; Mw = 31,000 g mol^{-1}, nominal degree of hydrolysis = 88%), **PVA 7** (Mowiol® 10–98; Mw = 61,000 g mol^{-1}, nominal degree of hydrolysis = 98%), **PVA 8** (Mowiol® 8–88; Mw = 67,000 g mol^{-1}, nominal degree of hydrolysis = 88%), **PVA 9** (Mowiol® 18–88; Mw = 130,000 g mol^{-1}, nominal degree of hydrolysis = 88%), and **PVA 10** (Mowiol® 30–92; Mw = 175,000 g mol^{-1}, nominal degree of hydrolysis = 92%), were kindly provided by Kuraray. If not specified, most of commercially available aldehydes and solvents were used as received.

Instruments

^{1}H NMR (200 MHz) spectra were recorded on a BRUCKER AC 200 spectrometer at 21°C in chloroform-*d* ($CDCl_3$) or

DMSO-d_6 (CD_3SOCD_3) and chemical shifts (δ, ppm) were calibrated according to the residual peak of solvent. FT IR spectra were recorded on a Spectrum 100 spectrometer with UATR modulus by Perkin Elmer. Gas chromatography (GC) were performed with an HP 6890 series apparatus with a capillary column (WCOT fused silica, 25 m × 0.25 mm i.d. film thickness: 0.25 μm). Thermogravimetric analyses were performed on a TG/ATD Diamond apparatus from 25 to 560°C at a heating rate of 10°C/min under nitrogen flow (30 mL/min).

General Procedure for the Poly(Vinyl Acetals) Synthesis

PVA 1 (200 mg, 3.82 mmol) was added to a flask containing 3 mL of tetrahydrofuran (THF). The mixture was heated at 60°C before adding the aldehyde (0.6 eq.) and *p*-toluenesulfonic acid (PTSA) (69 mg, 0.46 mmol, 0.1 eq.). The mixture was stirred at 60°C for 1 h for aldehydes containing aromatic groups or for 12 h for aliphatic aldehydes. The obtained poly(vinyl acetal) was precipitated by adding 10 mL of pentane (for aromatic aldehydes) or water (for aliphatic aldehydes) to the reaction mixture at room temperature. The solid was filtered off and washed with pentane (for aromatic aldehydes) or with water (for aliphatic aldehydes). The polymer was dissolved in THF and reprecipitated twice. The poly(vinyl acetal) was then dried under *vacuum*.

Synthesis of 1. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), benzaldehyde (241 mg, 2.28 mmol) to obtain **1** as a white solid (299 mg, 96% yield).

IR (cm^{-1}): 3455, 3063, 3038, 2953, 2917, 2865, 1733, 1600, 1500, 1452, 1432, 1372, 1239, 1112, 1055, 1010, 939, 906, 827, 753–698–649. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.34 (m, 5 H), 5.60–5.35 (m, 1 H), 5.29–3.80 (m, 4.29 H), 2.08–0.85 (m, 8 H). PVA functionalization with aldehyde = 65%.

Synthesis of 2. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-nitrobenzaldehyde (345 mg, 2.28 mmol) to obtain **2** as a white solid (364 mg, 91% yield).

IR (cm^{-1}): 3454, 3028, 2920, 2857, 1732, 1608, 1518, 1432, 1341, 1295, 1241, 1105, 1065, 1011, 921, 856, 832, 701, 682. ^{1}H NMR (200 MHz, d6-DMSO) δ 8.15 (bs, 2.21 H), 7.66 (bs, 2 H), 6.10–5.54 (m, 0.88 H), 4.71–3.75 (m, 4.56 H), 2.19–1.18 (m, 6.5 H). PVA functionalization with aldehyde = 78%.

Synthesis of 3. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-cyanobenzaldehyde (299 mg, 2.28 mmol) to obtain **3** as a white solid (336 mg, 94% yield).

IR (cm^{-1}): 3501, 2960, 2917, 2861, 2228, 1735, 1610, 1443, 1388, 1341, 1241, 1114, 1065, 1007, 918, 885, 816–679. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.81 (bs, 2 H), 7.59 (bs, 2.06 H), 5.96–5.64 (m, 0.72 H), 5.64–4.73 (m, 0.76 H), 4.61–3.77 (m, 2.38 H), 2.10–1.20 (m, 6.5 H). PVA functionalization with aldehyde = 72%.

Synthesis of 4. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-trifluoromethylbenzaldehyde (397 mg, 2.28 mmol) to obtain **4** as a white solid (387 mg, 89% yield).

IR (cm^{-1}): 3517, 3009, 2942, 2909, 2825, 1736, 1614, 1586, 1504, 1465, 1321, 1243, 1206, 1157, 1107, 1065, 921, 824, 764, 687, 668, 635.

^{1}H NMR (200 MHz, d6-DMSO) δ 7.62 (d, 4 H), 6,0–5.5 (m, 0.64 H), 4.5–3.75 (m, 1.74 H), 2–1 (m, 6.70 H). PVA functionalization with aldehyde = 78%.

Synthesis of 5. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-bromobenzaldehyde (422 mg, 2.28 mmol) to obtain **5** as a white solid (383 mg, 90% yield).

IR (cm^{-1}): 3454, 2943, 2916, 2864, 1734, 1596, 1491, 1372, 1341, 1299, 1237, 1112, 1066, 1010, 946, 915, 808, 718, 693, 666, 628, 605. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.51 (s, 2 H), 7.33 (s, 2 H), 5.50 (s, 0.78 H), 5.25–4.5 (m, 0.56 H), 4.25–3.75 (m, 2.58 H), 2.00–1.00 (m, 7.46 H). PVA functionalization with aldehyde = 70%.

Synthesis of 6. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-phenylbenzaldehyde (415 mg, 2.28 mmol) to obtain **6** as a white solid (365 mg, 86% yield).

IR (cm^{-1}): 3398, 3056, 3027, 2956, 2913, 2863, 1733, 1559, 1516, 1488, 1376, 1340, 1290, 1241, 1212, 1108, 1065, 1006, 913, 842, 762, 742, 728, 696. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.49 (m, 9 H), 5.57 (bs, 1 H), 5.27–3.76 (m, 3.24 H), 2.09–0.99 (m, 7.52 H). PVA functionalization with aldehyde = 71%.

Synthesis of 7. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-butylbenzaldehyde (370 mg, 2.28 mmol) to obtain **7** as a white solid (315 mg, 96% yield).

IR (cm^{-1}): 3381, 2917, 2859, 2359, 2323, 1732, 1571, 1434, 1374, 1341, 1313, 1241, 1178, 1143, 1106, 1014, 950, 820, 702, 684, 606, 556. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.29 (bs, 2 H), 7.17 (bs, 2 H), 5.46 (s, 1.01 H), 5.25–3.50 (m, 5.82 H), 2.00–1.00 (m, 17.46 H), 0.88 (t, J = 7.0 Hz, 3 H). PVA functionalization with aldehyde = 46%.

Synthesis of 8. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-methoxybenzaldehyde (310 mg, 2.28 mmol) to obtain **8** as a white solid (246 mg, 82% yield).

IR (cm^{-1}): 3462, 3004, 2939, 2912, 2872, 1733, 1615, 1373, 1243, 1022, 938, 824, 776. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.31 (s, 2.07 H), 6.87 (s, 2.00 H), 5.45 (s, 0.82 H), 5.20–3.65 (m, 11 H), 3.73 (s, 3 H), 2.00–1.00 (m, 11.74 H). PVA functionalization with aldehyde = 44%.

Synthesis of 9. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 4-dimethylaminobenzaldehyde (340 mg, 2.28 mmol) to obtain **9** as a white solid (209 mg, 85% yield).

IR (cm^{-1}): 3420, 2956, 2918, 2862, 1733, 1657, 1596, 1496, 1434, 1345, 1373, 1222, 1164, 1119, 1031, 1007, 902, 817, 681. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.41 (s, 2 H), 7.12 (s, 2 H), 5.47 (s, 1 H), 5.21–3.65 (m, 17.98 H), 3.06 (s, 6 H), 2.04–1.01 (m, 28.86 H). PVA functionalization with aldehyde = 18%.

Synthesis of 10. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 1-naphthaldehyde (356 mg, 2.28 mmol) to obtain **10** as a white solid (400 mg, 97% yield).

IR (cm^{-1}): 3371, 3184, 3064, 2956, 2921, 2858, 1735, 1703, 1635, 1595, 1512, 1431, 1371, 1336, 1215, 1183, 1118, 1035, 1010, 863, 814, 798, 776, 685, 648. ^{1}H NMR (200 MHz, d6-DMSO) δ 8.13 (bs, 1 H), 7.76 (bs, 3 H), 7.46 (bs, 3 H), 6.04 (s, 1 H), 5.29–3.72 (m, 2.15 H), 2.12–0.94 (m, 6.5 H). PVA functionalization with aldehyde = 80%.

Synthesis of 11. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 2-naphthaldehyde (356 mg, 2.28 mmol) to obtain **11** as a white solid (316 mg, 83% yield).

IR (cm^{-1}): 3366, 2940, 2915, 1708, 1507, 1435, 1377, 1207, 1167, 1142, 1122, 1093, 1033, 1008, 815, 749, 683, 614, 565. ^{1}H NMR (200 MHz, d6-DMSO) δ 9.78 (bs, 1 H), 8.42 (bs, 1 H), 7.69 (bs, 2 H), 7.32 (bs, 2 H), 7.08 (bs, 1 H), 6.30 (m, 1 H), 5.18–3.05 (m, 6 H), 2.02–0.93 (m, 11.52 H). PVA functionalization with aldehyde = 68%.

Synthesis of 12. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), phenylacetaldehyde (274 mg, 2.28 mmol) to obtain **12** as a white solid (311 mg, 87% yield).

IR (cm^{-1}): 3498, 3029, 2918, 2858, 1734, 1604, 1580, 1496, 1432, 1372, 1300, 1238, 1126, 1078, 1011, 940, 892, 752, 698. ^{1}H NMR (200 MHz, d6-DMSO) δ 7.24 (m, 5 H), 5.18–4.41 (m, 1.5 H), 4.02–3.29 (m, 2.0 H), 2.79 (m, 2 H), 1.95–1.85 (m, 1.5 H), 1.85–0.93 (m, 5.0 H). PVA functionalization with aldehyde = 80%.

Synthesis of 13. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), decanal (356 mg, 2.28 mmol) to obtain **13** as a white solid (409 mg, 99% yield).

IR (cm^{-1}): 3391, 2921, 2853, 1733, 1410, 1433, 1439, 1378, 1347, 1240, 1009, 948, 888, 832, 721, 685. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.11–3.13 (m, 3.15 H), 2.00–0.91 (m, 22.50 H), 0.93–0.74 (m, 3 H). PVA functionalization with aldehyde = 80%.

Synthesis of 14. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), undecanal (388 mg, 2.28 mmol) to obtain **14** as a white solid (407 mg, 97% yield).

IR (cm^{-1}): 3527, 2921, 2852, 2731, 1740, 1648, 1466, 1434, 1414, 1375, 1239, 1132, 1017, 961, 874, 822, 798, 721, 605. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.11–3.13 (m, 3.80 H), 2.15–1.12 (m, 24.96 H), 0.97–0.75 (m, 3.00 H). PVA functionalization with aldehyde = 75%.

Synthesis of 15. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 2-methylundecanal (420 mg, 2.28 mmol) to obtain **15** as a white solid (442 mg, 97% yield).

IR (cm^{-1}): 3529, 2921, 2853, 1740, 1647, 1466, 1437, 1374, 1315, 1239, 1121, 1018, 982, 887, 823, 722, 606. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.11–3.13 (m, 3,15 H), 2.12–1.00 (m, 23.50 H), 0.97–0.75 (m, 6.00 H). PVA functionalization with aldehyde = 80%.

Synthesis of 16. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 2-octyldodecanal (678 mg, 2.28 mmol) to obtain **16** as a white solid (572 mg, 96% yield).

IR (cm^{-1}): 3365, 2951, 2923, 2868, 1740, 1652, 1545, 1463, 1436, 1412, 1378, 1366, 1239, 1123, 1012, 889, 800, 734, 685, 605, 568. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.11–3.13 (m, 3.86 H), 2.16 (m, 1 H), 1.98 (m, 0.60 H), 2.12–0.95 (m, 40.02 H), 0.85 (m, 6 H). PVA functionalization with aldehyde = 74%.

Synthesis of 17. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), 3,7-dimethyloctanal (356 mg, 2.28 mmol) to obtain **17** as a white solid (297 mg, 78% yield).

IR (cm^{-1}): 3365, 2951, 2923, 2868, 1740, 1652, 1545, 1463, 1436, 1412, 1378, 1366, 1239, 1123, 1012, 889, 800, 734, 685, 605, 568. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.11–3.13 (m, 4.40 H), 2.50–1.01 (m, 17.62 H), 0.88 (m, 6 H), 0.95–0.75 (m, 3 H). PVA functionalization with aldehyde = 68%.

Synthesis of 18. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), campholenic aldehyde (347 mg, 2.28 mmol) to obtain **18** as a white solid (230 mg, 71% yield).

IR (cm^{-1}): 3374, 2950, 2912, 2865, 1739, 1433, 1360, 1239, 1125, 1014, 998, 856, 883, 795. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.18 (bs, 1 H), 5.15–3.15 (m, 5.52 H), 2.00–1.00 (m, 15.88 H), 0.96–0.80 (m, 9 H). PVA functionalization with aldehyde = 48%.

Synthesis of 19. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), olealdehyde (746 mg, 2.28 mmol) to obtain **19** as a white solid (352 mg, 89% yield).

IR (cm^{-1}): 3543, 2953, 2930, 2872, 1743, 1468, 1437, 1427, 1382, 1381, 1243, 1129, 1073, 1020, 1011, 932, 894, 803, 738, 692, 611, 450. ^{1}H NMR (200 MHz, d6-DMSO) δ 5.34 (t, J = 4.7 Hz, 2 H), 4.44 (m, 0.65 H), 4.25–3.25 (m, 6.78 H), 2.02–1.00 (m, 42.70 H), 0.88 (t, J = 6.2 Hz, 3.00 H). PVA functionalization with aldehyde = 41%.

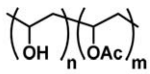
Synthesis of 20. The general procedure was applied to **PVA 1** (200 mg, 3.82 mmol), PTSA (69 mg, 0.46 mmol), adoxal® (480 mg, 2.28 mmol) to obtain **20** as a white solid (278 mg, 67% yield).

^{1}H NMR (200 MHz, d6-DMSO) δ 5.09 (t, J = 6.7 Hz, 1 H, H_4), 4.24 (bs, 0.85 H), 4.20–3.25 (m, 4.20 H), 2.02–1.00 (m, 26.92 H), 0.88 (t, J = 6.0 Hz, 6.00 H). PVA functionalization with aldehyde = 58%.

Synthesis of 21. The general procedure was applied to **PVA 2** (200 mg, 3.96 mmol), PTSA (69 mg, 0.46 mmol), 4-nitrobenzaldehyde (360 mg, 2.38 mmol) to obtain **21** as a white solid (404 mg, 95% yield).

^{1}H NMR (200 MHz, d6-DMSO) δ 8.21 (bs, 2 H), 7.69 (s, 2 H), 6.17–5.53 (m, 0.94 H), 4.68–3.25 (m, 3.64 H), 2.16–1.04 (m, 7.08 H). PVA functionalization with aldehyde = 85%.

Synthesis of 22. The general procedure was applied to **PVA 4** (200 mg, 4.07 mmol), PTSA (69 mg, 0.46 mmol), 4-



PVA 1 (n:m = 80:20; Mw = 9000-10000 g.mol^{-1})

Figure 1. Poly(vinyl alcohol) used (**PVA 1**).

nitrobenzaldehyde (369 mg, 2.44 mmol) to obtain **22** as a white solid (352 mg, 98% yield).

^{1}H NMR (200 MHz, d6-DMSO) δ 8.21 (bs, 2 H), 7.69 (s, 2 H), 6.17–5.53 (m, 1 H), 4.68–3.25 (m, 2.34 H), 2.16–1.04 (m, 5.70 H). PVA functionalization with aldehyde = 65%.

Synthesis of 23. The general procedure was applied to **PVA 6** (200 mg, 4.07 mmol), PTSA (69 mg, 0.46 mmol), 4-nitrobenzaldehyde (369 mg, 2.44 mmol) to obtain **23** as a white solid (396 mg, 96% yield).

^{1}H NMR (200 MHz, d6-DMSO) δ 8.21 (bs, 2 H), 7.69 (s, 2 H), 6.17–5.53 (m, 1 H), 4.68–3.25 (m, 2.82 H), 2.16–1.04 (m, 6.02 H). PVA functionalization with aldehyde = 78%.

Synthesis of 24. The general procedure was applied to **PVA 8** (200 mg, 4.07 mmol), PTSA (69 mg, 0.46 mmol), 4-nitrobenzaldehyde (369 mg, 2.44 mmol) to obtain **24** as a white solid (370 mg, 92% yield).

^{1}H NMR (200 MHz, d6-DMSO) δ 8.21 (bs, 2 H), 7.69 (s, 2 H), 6.17–5.53 (m, 1 H), 4.68–3.25 (m, 3.08 H), 2.16–1.04 (m, 6.36 H). PVA functionalization with aldehyde = 74%.

Synthesis of 25. The general procedure was applied to **PVA 9** (200 mg, 4.07 mmol), PTSA (69 mg, 0.46 mmol), 4-nitrobenzaldehyde (369 mg, 2.44 mmol) to obtain **25** as a white solid (338 mg, 97% yield).

^{1}H NMR (200 MHz, d6-DMSO) δ 8.21 (bs, 2 H), 7.69 (s, 2 H), 6.17–5.53 (m, 1 H), 4.68–3.25 (m, 3.92 H), 2.16–1.04 (m, 7.88 H). PVA functionalization with aldehyde = 65%.

Shininess Measurements

Shininess measurements were recorded with a SAMBA apparatus from BossaNova Technologies® equipped with a CCD camera. Samples were applied with a pneumatic applicator on varnish coated BYK Gardner contrast cards. Solutions of polymers in THF (10 %w) were applied. After 30 min, a second layer was added. Measurements were carried out 30 min after the second application. A polarized vertically beam of light is directed towards the sample. A part of this light is reflected to a detector with the initial polarization. A parameter called specular maximum is measured by this detector. The higher this value is, the better is the shininess of the sample. The unit of this measure is a normalized value in function of light intensity. For instance, one of the oils used in a gloss known to be very shining, a phenyl siloxysilicate resin **A**, has a specular maximum of 414.[77,78]

RESULTS AND DISCUSSION

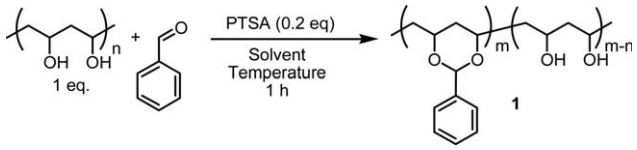
(**PVA 1** (Mw = 9000–10,000 g.mol^{-1}) with a hydrolysis rate of about 80% was first used (Figure 1).

Upon reaction of **PVA 1** with aldehydes, the highest functionalization attainable will be of 80%. In the following schemes, the acetate groups of **PVA 1** are voluntary not represented for simplicity.

Synthesis of Poly(Vinyl Acetals)

Poly(vinyl acetals) are generally synthesized through an acid-catalyzed coupling of PVA in the presence of an aldehyde, in water or dimethyl sulfoxide (DMSO).[29–44] We were interested in developing a convenient and efficient method to perform this reaction in more volatile organic solvents, in order to facilitate the isolation of the functionalized polymers. PTSA has been used as the organic acid catalyst. The PVA functionalization was optimized with benzaldehyde as the model aldehyde. DMSO, acetonitrile, a mixture of DMSO and acetonitrile in a 1 : 1 ratio and THF were tested as the reaction solvents and similar functionalization rates were obtained (Table I, entries 1–3, 6). We found out that the acetalization reaction occurred efficiently in THF, although the starting hydrophilic **PVA 1** was not only slightly soluble in the reaction medium. However, the solubility

Table I. Optimization of the Reaction Conditions



Entry	Solvent	Temperature	eq. of PhCHO	Functionalization of 1 (%)
1	DMSO	60°C	1.2	71%
2	DMSO/MeCN	60°C	1.2	72%
3	MeCN	60°C	1.2	73%
4	MeCN	30°C	1.2	37%
5	MeCN	80°C	1.2	60%
6	THF	60°C	1.2	65%
7	THF	60°C	1.00	43%
8	THF	60°C	2.40	65%

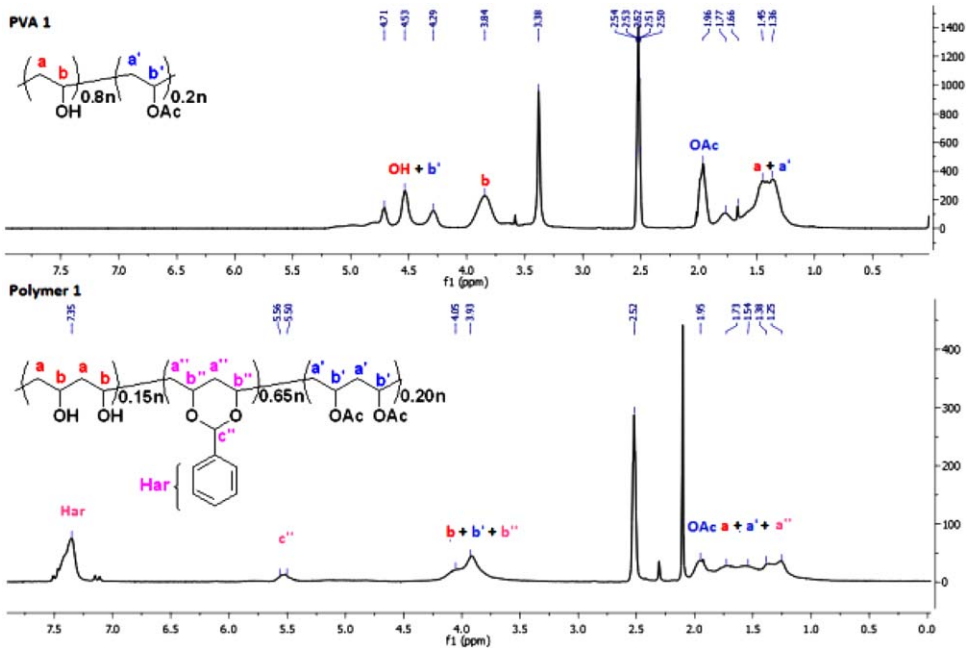


Figure 2. Comparison between ^{1}H NMR spectra of polymer **1** and **PVA 1** (Table I, entry 6). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the polymer increased upon its functionalization. All the poly(vinyl acetals) were generally soluble in THF.

Even if the results of the functionalization of **1** are somehow lower in THF than in DMSO, THF was preferred as the reaction solvent because of its higher volatility and for the ease of isolation of the polymers. Polymers prepared in DMSO media were more difficult to obtain in a pure form, this solvent remaining coordinated to the polymer even after washing for several times.

A temperature of 60°C seemed to be the most appropriated to achieve the best results. At a lower temperature (30°C, entry 4), the grafting ratio was low and at higher temperature (80°C, entry 5) we observed some aldehyde degradation. In THF, a maximum functionalization of 65% (80% being the theoretical maximum) could be reproducibly reached with a slight excess of benzaldehyde (1.2 equivalents). The functionalization could not be improved even with an excess of aldehyde (Table I, entry 8). The conditions of entry 6 were applied for further experiments.

The grafting rates were determined by ^{1}H NMR. The spectra obtained for **PVA 1** and polymer **1** are depicted in Figure 2.

The integration of the proton of the acetal group of the former aldehyde (in Figure 2 the aldehyde user is benzaldehyde **1**) is compared to the integration of the CH and CH_2 protons of the polymer chain. The ratio between these integrations allows to determine the relative amount of aldehyde grafted into the polymer, and thus its functionalization.

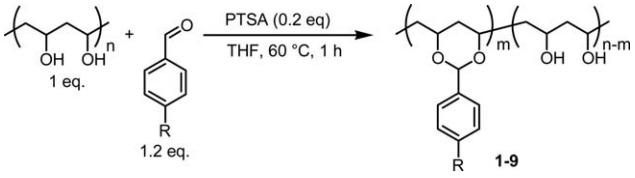
Influence of the Aldehyde Structure on the PVA Functionalization

Aromatic Aldehydes. *Benzaldehyde derivatives.* Several differently substituted benzaldehyde derivatives have been grafted on the **PVA 1** using the optimized conditions defined above. Results are summarized in Table II. Electronic effects of the *p*-substituents had an important influence on the grafting. High functionalizations were attained for polymers derived from aldehydes bearing an electron-withdrawing groups (Table II, entries 1–6). However, the presence of an electron-donating group slowed down the acetalization process and led to a modest functionalization (Table II, entries 7–9).

Attempts were done to correlate these functionalization data with the electronic nature of the aryl substituents, via the Hammet constants, generally used for analyzing kinetic data.[79,80]

The results of the functionalization of **PVA-1** with aromatic aldehydes bearing different functional groups R at the *para* position were thus correlated with the Hammet constants for

Table II. Poly(Vinyl Acetal) Syntheses with Benzaldehyde Derivatives



Entry	R	Polymer	Functionalization (%)
1	H	**1**	65
2	NO_2	**2**	78
3	CN	**3**	72
4	CF_3	**4**	78
5	Br	**5**	70
6	Ph	**6**	71
7	*n*-Bu	**7**	46
8	OMe	**8**	44
9	NMe_2	**9**	18

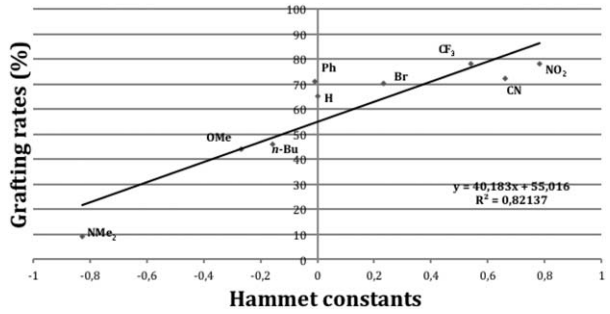


Figure 3. Grafting rates as a function of Hammett constants.

these R substituents. Figure 3 presents a plot of the correlation between the functionalization and the Hammett constants for the different functional groups.

The good correlation obtained indicates that for the process examined, the aldehydes with electron-withdrawing substituents such as NO_2 or CF_3 were the most reactive in the acetalization process, whereas the electron-attracting substituents such an *n*-butyl, methoxy and in particular *N*-dimethylamino were less suitable for the coupling reaction.

Naphthyl derivatives and phenylacetaldehyde. 1-Naphtaldehyde and 2-naphtaldehyde were also efficiently grafted on the **PVA 1** (Table III). A good grafting of 68% was obtained with the 1-naphthaldehyde (Table III, entry 1) and fully functionalized polymers **11** and **12** were obtained with 2-naphthaldehyde and phenylacetaldehyde, respectively.

Aliphatic Aldehydes. The results of the functionalization of **PVA 1** with aliphatic aldehydes are summarized in Table IV. Very good grafting was obtained for polymers **13–17** with fully saturated linear and branched aliphatic aldehydes such as decanal, undecanal, 2-methylundecanal, octyldodecanal, and 3,7-dimethyloctanal (Table IV, entries 1–5). In the case of unsaturated aliphatic aldehydes, the presence of a double bond in the aldehyde chain decreased the functionalization, with the presence of side-reactions in acidic media (e.g. for polymer **18**, entry 6).

Table III. PVA Acetalization with Naphthyl Aldehydes and Phenylacetaldehyde

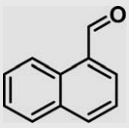
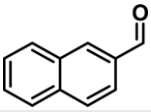
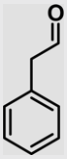
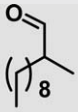
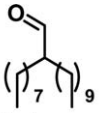
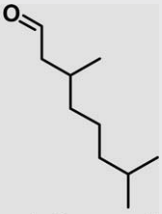
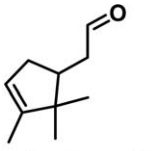
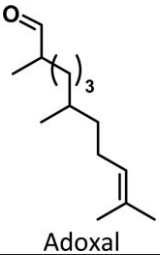
Entry	Aldehyde	Polymer	Grafting rate (%)
1		10	68
2		11	80
3		12	80

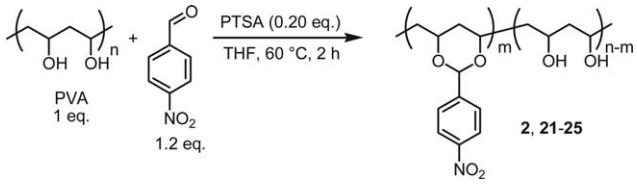
Table IV. PVA Acetalization with Aliphatic Aldehydes

Entry	Aldehyde	Polymer	Functionalization
1	 decanal	**13**	80%
2	 undecanal	**14**	75%
3	 2-methyl-undecanal	**15**	80%
4	 Octyl-dodecanal	**16**	74%
5	 3,7-dimethyl-octanal	**17**	68%
6	 Campholenic aldehyde	**18**	48%
7	 Olealdehyde	**19**	41%
8	 Adoxal	**20**	58%

Influence of the PVA

The reaction with aldehydes was run with other PVAs, featuring different lengths and hydrolysis ratios (see Table V). A model reaction with 4-nitrobenzaldehyde was chosen because of its excellent functionalization. The reaction time was adjusted to 2

Table V. Functionalization of Various PVAs with 4-Nitrobenzaldehyde



PVA	Mw (g/mol)	[Hydrolysis ratio]	Polymer	Functionalization (%)
PVA 1	9000–10,000	[80%]	2	80
PVA 2	22,200	[85%]	21	85
PVA 3	27,000	[98%]	–	0
PVA 4	27,000	[88%]	22	65
PVA 5	31,000–50,000	[98–99%]	–	0
PVA 6	31,000	[88%]	23	78
PVA 7	61,000	[98.5%]	–	0
PVA 8	67,000	[88%]	24	74
PVA 9	130,000	[88%]	25	65
PVA 10	175,000	[92%]	–	0

h to allow the functionalization with high molecular weight PVAs.

Interesting observations could be made from this set of experiments. In the first hand, the size of the PVA was not a limiting factor for the success of the reaction. Indeed, **PVA 9**, with a molecular weight of 130 kDa could be efficiently transformed into polymer **25**. The most important factor was the hydrolysis ratio of the PVA. Full functionalizations were possible with PVAs containing 20% and 15% of acetate groups (**PVA 1** and **PVA 2**, respectively). Reactions were still efficient with **PVA 4**, **PVA 6**, **PVA 8**, and **PVA 9**, displaying 12% of acetate groups. However, it turned out that no functionalization was observed for PVAs with higher hydrolysis ratio (from 92% to 99%) (**PVA 3**, **PVA 5**, **PVA 7**, **PVA 10**). The presence of the acetate groups might strongly influence the solubility of the starting PVA in THF.

Shininess Measurements

In the cosmetic field, more specifically for lipstick and nail polish applications, the shininess may constitute an important parameter. Although this property is highly sought after in this field, only a few compounds are available to induce shininess in the cosmetic formulations. Cosmetic ingredients with shining properties include, among others, octyldodecanol[72,73] or glyceryl behenate,[74] long chain aliphatic compounds. Polymeric derivatives such as polybutene[75] or polydecene[76] have also been reported in this field.

The measurement of shininess of the different poly(vinyl acetals) containing aromatic groups was carried out and the results are reported in Figure 4. Except for polymer **4**, obtained from 4-trifluoromethylbenzaldehyde, all the prepared poly(vinyl acetals) presented a better shininess than starting **PVA 1**. Moreover, the specular maxima was higher than that of polyglyceryl tri-*i*-stearate oil **B**, a classical base used in lipstick formulations. Poly(vinyl acetals) **10** and **11** containing naphthyl groups were the most shiny with a specular maxima values of around 500. It is worth to note that a shininess differences can be visually noticed within a gap of 20 units. The values corresponding to polymers **6** and **9** were not measured because of their low solubility in THF.

The values corresponding to the shininess of poly(vinyl acetals) containing aliphatic groups were also measured and are summarized in Figure 5.

These poly(vinyl acetals) do not display high shininess and the obtained values were slightly lower than that of the starting **PVA 1**.

The results allow concluding that unlike aliphatic groups, aromatic groups can enhance the shininess to **PVA 1**, naphthyl aromatic nuclei being the most efficient groups to enhance this property.

Influence of the Grafting Ratios on the Polymers Shininess

The correlation between the functionalization ratios and the shininess of the polymers was carried out with poly(vinyl acetals) **5** (Figure 6). For this polymer, the shininess was dependent on the

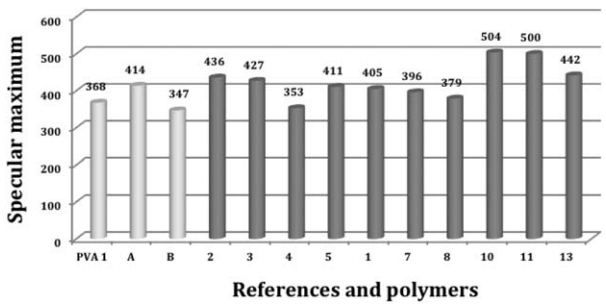


Figure 4. Shininess of poly(vinyl acetals) containing aromatic groups.

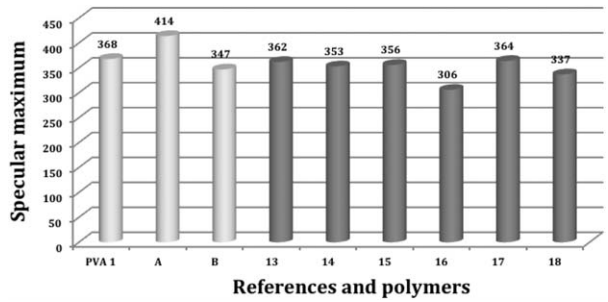


Figure 5. Shining measurements of poly(vinyl acetals) containing aliphatic groups.

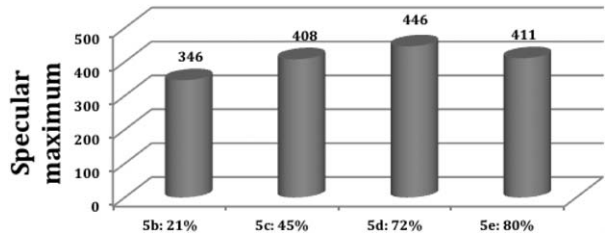


Figure 6. Grafting rates influence on shining values.

grafting ratio. The best shininess was obtained for **5d**, with a relatively high grafting rate of 72%. A fully functionalized PVA such as **5e** did not present the highest shining value.

Thermal Stability

Thermal stability for some representative polymers was examined with TGA measurements. The thermal stability of the new polymeric compounds was of interest, because of the needs of some cosmetic formulation procedures. Thus for example, the polymers needed to be stable up to 90°C for lipstick formulations. The thermal stability of **PVA 1** and some derivatives is presented in Figure 7.

Poly(vinyl acetal) **1** was stable until a temperature of about 150°C and **PVA 1** until about 220°C. The functionalized polymers generally presented a slightly lower thermal stability as compared to the starting **PVA 1**. This effect was particularly important for R═H and R═Br. In contrast, polymer **4**, grafted with *p*-trifluoromethyl benzaldehyde, presented a higher thermal stability as compared to **PVA 1**. Explanations for this thermal behavior is not very well understood.

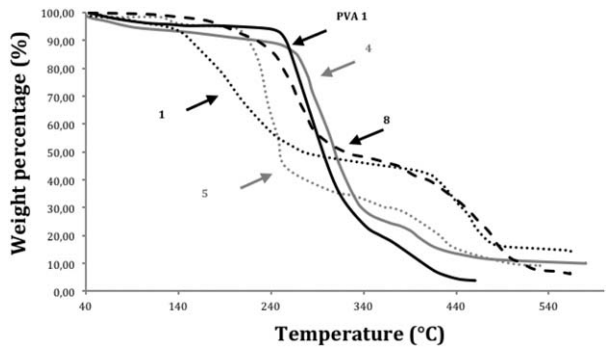


Figure 7. TGA analyses of the starting **PVA 1** and derived polymers.

CONCLUSIONS

PVA of different molecular weights and with a minimum acetate rate of 12% have been functionalized with aromatic and aliphatic aldehydes in THF with high grafting rates. A series of new polymers with different functionalization ratios have been obtained. PVAs functionalized with aromatic aldehydes present high shining values as compared to the starting non-grafted PVA. In contrast, the functionalization of PVA with aliphatic aldehydes does not enhance the shininess of the polymers. The thermal stability of the tested polymers allows for the desired cosmetic application. Some of these new polymers could be used in the cosmetic field.

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