Synthesis of Poly(Vinyl Alcohol-Graft-Hyperbranched Glycerol)

This manuscript is dedicated to the 75th birthday of Professor Bob Grubbs for his life-long extraordinary achievement in research and education.

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ABSTRACT: We report the first example of grafting hyperbranched polyglycerol onto poly(vinyl alcohol) via ring-opening polymerisation of glycidol to prepare poly(vinyl alcohol-graft-hyperbranched glycerol) (P[(VA)-g-(hPG)]). The effects of catalyst, molecular weight of PVA, reaction temperature, water content, moles of reagent, and addition time of reagent were also investigated. P[(VA)-g-(hPG)] with various mole fractions of hPG were prepared and the degrees of substitution and branching were determined. P[(VA)-g-(hPG)] displayed decreased degree of crystallinity and also increased solubility in water, compared to PVA. P[(VA)-g-(hPG)] was shown to be a superior hair styling polymer with a curl retention value of 85% after 4 h. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. 2017, 55, 3041–3047

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INTRODUCTION Poly(vinyl alcohol) (PVA), a known biodegradable and biocompatible water soluble polymer, has a multitude of applications ranging from packaging to adhesives.1,2 The modification of PVA through the hydroxyl functionalities has been accomplished using epoxides,3 isocyanates,4 acyl chlorides,5 and anhydrides6 broadening the number of possible applications. However, yields have been low mainly due to the presence of less reactive secondary alcohols in PVA and the presence of less reactive secondary alcohols in PVA.

The ring-opening polymerization (ROP) of glycidol, a latent AB2 monomer, affords hyperbranched polymeric chains.7 The structure of these branched chains can be established by the degree of branching (%DB); ranging from linear (%DB = 0) to dendrimers (%DB = 1), and hyperbranched materials (%DB = 0–1). Sunder et al. have synthesised hyperbranched polyglycerol (hPG) using 1,1,1-tris(hydroxymethyl)propane as an initiator, and shown that the %DB of hPG can be determined from the ratio between the terminal, dendritic and two linear structural units.7 The hyperbranched structure results in increased hydroxyl functionality and therefore polymers with greater %DB will have greater hydroxyl content. Harth and coworkers polymerized glycidol using isooamy alcohol as the initiator and tin octoate as the catalyst and have shown that temperature can affect the %DB of hPG, as the %DB decreased from 24% at 40 °C to 15% at −15 °C.8

The grafting of glycidol onto linear polymers to synthesise hyperbranched graft copolymers has been carried out via “grafting from” and “grafting to” methodologies. The “grafting from” methods have used ring-opening polymerisation of glycidol on hydroxyl group containing polymers, such as poly(4-hydroxystyrene) and hydroxylated butadiene.9,10 Poly[(4-hydroxystyrene)-graft-(hPG)] was quoted as having increased solubility in polar solvents as well as a lower glass transition temperature (Tg) than the original polymer backbone. A “grafting-from” method where hPG is initially synthesised using N,N-dibenzyl tris(hydroxymethyl) aminomethane as an initiator has been reported.11 After deprotection of the initiator, hPG is “grafted to” poly(pentafluorophenol methacrylate), via the ester linkages to form the graft copolymer. Surface modification by ROP of glycidol has been carried out on activated glass and silicon substrates, which produced ultralow-fouling polymer coatings.12 As hPG has a large number of hydroxyl groups, it has been used as a macroinitiator for further ROP. ε-Caprolactone was grafted onto hPG in bulk conditions to prepare an amphiphilic block copolymer.13 Furthermore, hPG modified with 2-bromoisobutyryl bromide14 has also been used as the basis for a “grafting from” macroinitiator for controlled radical polymerization of vinyl monomers.15,16 However, the conversion of the polymerization reactions in some cases were limited to <35% to prevent gelation.

Copolymers containing acrylates and acrylamides, are used in styling gels as they are adsorbed to hair fibres increasing the stiffness and maintaining the targeted hairstyle.17,18 The dendronized architecture of graft copolymers with hPG side chains results in polymers with high functional group
densities, which increases the number of possible interaction sites.

In this paper, the use of PVA macroinitiator for ROP of Glycidol to synthesize P[(VA)-g-(hPG)] is described. The effects of the reaction conditions on the structure of the graft copolymer as well as the effect of chemically bound hPG on the physical properties of the graft copolymer compared to PVA are investigated. Grafting hPG onto PVA will incorporate primary hydroxyl functionalities into the structure, which is anticipated to increase reactivity towards functionalization as well increasing solubility of the polymer in water. Moreover, the hyperbranched graft copolymer is anticipated to result in superior hair fixation and therefore superior hairstyle retention. To the best of our knowledge this is the first example of P[(VA)-g-(hPG)].

**EXPERIMENTAL**

**Materials**

Poly(vinyl alcohol) (M_w = 1.3 × 10^6 (LMW) and 18.6 × 10^6 g mol^-1 (HMW), 99% hydrolyzed), 1,1,1-tris(hydroxymethyl) propane and sodium methoxide solution (25 wt% methanol) purchased from Sigma Aldrich and were used without purification. Glycidol was purified by vacuum distillation and was purchased from Sigma Aldrich. Acetone, methanol, isopropanol and sodium hydroxide were purchased from Fischer Scientific and used without further purification. Carbomer™ 980 (1.5 wt%), and 2-amino-2-methyl-1-propanol (0.25 wt%) were prepared by sequential addition. The polymer component, P[(VA)-g-(hPG)] (a and c). The coalesced resonances for all hPG, were all recorded in D_2O on a Bruker Avance-400 operating at 400 MHz or VNMR-700 at 700 MHz. 13C NMR and Inverse gated 13C NMR spectra were carried out in D_2O on a VNMR-700 at 176 MHz. Fourier transform infra-red (FTIR) spectroscopy was performed using a Perkin Elmer 1600 Series FTIR. Thermogravimetric analysis (TGA) measurements were made using a Perkin Elmer Pyris 1 in a nitrogen (N_2) atmosphere. Samples were heated at a rate of 10 °C min^-1 to 500 °C. Differential scanning calorimetry (DSC) measurements were carried out using a TA Instruments DSC Q1000. Samples were heated at a rate of 10 °C min^-1 between 28 and 300 °C.

**Synthesis of Poly(Vinyl Alcohol-Graft-Hyperbranched Glycerol)**

PVA (1–20 g, 22.7 × 10^-3–45.4 mol) was dissolved in water (8–160 mL) at 80 °C. The reaction mixture was then acclimated to the reaction temperature (0–100 °C). NaOH_{aq} (0–2.3 mL, 0–50 mol%, 5 M, 0–22 mmol) was added followed by glycolid (0.75–68.7 mL, 50–350 mol%) at an addition rate of 6–0.075 ml h^-1 and stirred for 4–44 h. The reaction mixture was then neutralised with HCl_{aq} (5 M) and was added into acetone. The resulting white solid was purified by Soxhlet extraction using isopropanol to remove the hPG contaminant. The purified solid was precipitated from water into acetone and dried under reduced pressure for 16 h at 40 °C, to afford P[(VA)-g-(hPG)].

Yield = 22.8 g (89%). 1H NMR (700 MHz, D_2O): δ (ppm): 1.66 (m, 2H, CH_2), 3.62 (m, 5H, CH_2CHOH)CH_3), 4.04 (m, 1H, CH). 13C NMR (176 MHz, D_2O): δ (ppm): 41.3 (CH_2), 44.2 (CH_2), 61.0 (CH_2CHOH)CH_2), 62.8 (CH_2CHOH)CH_2), 64.9 (CH), 66.38 (CH), 68.0 (CH), 69.3 (CH_2CHOH)CH_2), 70.7 (CH_2CHOH)CH_2), 72.3 (CH_2CHOH)CH_2), 75.2 (CH), 76.8 (CH_2CHOH)CH_2), 80.0 (CH_2CHOH)CH_2). FT-IR ν (cm^-1): 3290 (ν -OH), 2902(ν -CH), 1052 (ν -O-). T_m = 219–200 °C; T_g = 42.59 °C.

**Preparation of Blend of PVA and hPG**

A polymer blend was prepared to mimic P[(VA)-g-(hPG)] with x_{hPG} = 25%. An aqueous solution of PVA (0.1 g, 2.2 mmol, 2.2 mol L^-1) was prepared and hPG (0.04 g, 5.68 mmol) was added. The mixture was stirred using a magnetic flea for a period of 2 h. The solvent was then removed under reduced pressure producing a translucent film.

**Evaluation Methods for Curl Retention**

Gels containing P[(VA)-g-(hPG)] or PVA (2.5 wt%), Carbo-mer™ 980 (1.5 wt%), and 2-amino-2-methyl-1-propanol (0.25 wt%) were prepared by sequential addition. The polymer comprising gels was tested for hair curl retention at 27 °C and 90% relative humidity by manual application onto Dark Brown virgin hair tresses (6.5 g, 3.5 g) which were then set on rollers. After drying and equilibration at low humidity, tresses were removed and hung upright. The length of tresses was then quantified at 27 °C and 90% relative humidity at 0.25, 0.5, 0.75, 1, 1.5, 2, 3, and 4 h. Testing was performed on four tresses to ensure statistical rigour.

**Qualitative Ranking of Treated Hair Tresses**

Dark Brown virgin hair tresses (6.5 g, 3.5 g) were treated with aqueous solutions of P[(VA)-g-(hPG)] or PVA (5 wt%). The hair tresses were then rolled, dried, and evaluated in a temperature and humidity controlled environment. Two judges from Ashland Inc. then subjectively assessed the hair tresses on a scale from 0 to 10, for shine or lustre, stiffness, crunch, curl snap, smooth comb through, lack of residue on comb, lack of residue on hair, manageability, and lack of static.

**RESULTS AND DISCUSSION**

**Characterization**

P[(VA)-g-(hPG)] was successfully synthesized at high yield (>90%) using a base catalyst in water as a solvent and fully characterized, Scheme 1. Pure hPG was also produced as a side product, which was removed by Soxhlet extraction using isopropanol. In the 1H NMR spectrum (Fig. 1), the broad resonance at 1.5–1.9 ppm is attributed to the methylene protons on the backbone of P[(VA)-g-(hPG)] (b and d) and at 3.9–4.1 ppm to the methine protons on the backbone of P[(VA)-g-(hPG)] (a and c).
three proton environments (methylene protons e and g and methine proton f) in hPG graft are assigned to 3.5–3.8 ppm.

In the \(^{13}\text{C}\) NMR spectrum of P[(VA)-g-(hPG)] (Fig. 2), the resonance at 44.10 and 41.17 ppm correspond to the methylene carbon atoms of (b) and (d), respectively. The three resonances at 67.64, 66.18, and 64.64 ppm correspond to the methine carbon atom \(a\). These triad of resonances are characteristics of PVA and are due to the tacticity.\(^{20}\) The resonances at 74.94 and 76.44 ppm are attributed to the methine carbon atom \(c\). In the grafted hPG chains, the multiple resonances corresponding to the carbon atom neighbouring the secondary hydroxyl/ether group in each structural unit are observed at 77.82 ppm \(f\), \(70.34\) ppm \(i\), \(69.29\) ppm \(l\), \(70.34\) ppm \(q\), \(62.73\) ppm \(j\), \(72.02\) ppm \(m\), \(60.68\) ppm \(q\), \(70.34\) ppm \(g\), \(70.34\) ppm \(h\), \(72.02\) ppm \(k\), \(69.29\) ppm \(n\), \(70.34\) ppm \(e\), \(72.02\) ppm \(k\), and \(69.29\) ppm \(n\).

The mole fractions of hPG \(x_{\text{hPG}}\) in P[(VA)-g-(hPG)] which was determined using eq 1 and the integrations in \(^1\text{H}\) NMR spectra. Where, \(\int X\) is the integral of the signals between 3.5 and 4.2 ppm due to methine protons \((a)\) and \((c)\) of PVA segment of the backbone and methylene protons \((e)\) and \((g)\), and methine proton \((f)\) in hPG segment (labeled X, in Fig. 1).

\[
x_{\text{hPG}} = \frac{\int X - 0.5 \int Y}{\int X + \int Y} \quad (1)
\]

The grafted efficiency, \(\%GE\), of the is determined by comparing the \(x_{\text{hPG}}\) with the molar quantity of glycidol used, where \(n_{\text{gly}}\) is the moles of added glycidol:

\[
\%GE = \frac{x_{\text{hPG}}}{n_{\text{gly}}} \quad (2)
\]

The degree of substitution \(\%DS\) corresponding to the number of functionalized hydroxyl atoms in PVA, was determined from the \(^{13}\text{C}\) NMR spectrum (Fig. 2) and eq 3. This is calculated from the ratio of the integration of the two methylene carbon environments in at 44 ppm \(b\) and \(41\) ppm \(d\) on the backbone chain corresponding to unsubstituted and substituted hydroxyl functionalities, respectively:

\[
\%DS = \frac{\int d}{\int b + \int d} \quad (3)
\]

The \%DB was calculated using the method outlined by Sunder et al. for hPG.\(^7\) However, it was not possible to determine the \%DB for samples with \(x_{\text{hPG}} < 15\%\) due to the low signal to noise ratio in their \(^{13}\text{C}\) NMR spectra.

**Effects of Reaction Conditions**

The effect of hPG grafting on the molecular weight of the PVA macroinitiator was monitored by using \(1.3 \times 10^4\) g mol\(^{-1}\) (LMW) and \(18.6 \times 10^5\) g mol\(^{-1}\) (HMW) PVA. The \(x_{\text{hPG}}\) of 14% for P[(VA)-g-(hPG)] synthesized from HMW PVA was lower...
than 17% found when LMW PVA is used, under the same conditions. This can be attributed to the decreased solubility of the HMW polymer in water. The $x_{\text{HPG}}$ of HMW P[VA]-g-(hPG) was increased by a subsequent reaction with glycidol, attaining a polymer with a $x_{\text{HPG}}$ of 25%.

The effect of water on the efficacy of the synthesis of P[VA]-g-(hPG) was investigated by varying the concentration of PVA macroinitiator in water. When the concentration of PVA was halved the $x_{\text{HPG}}$ decreased from 26 to 17%, possibly due to the increased likelihood of the side reaction between water and glycidol resulting in the formation of polyglycerol. The effect of reaction time on $x_{\text{HPG}}$ of P[VA]-g-(hPG) was investigated using parallel reactions (Table S1). The reaction proceeds to an $x_{\text{HPG}}$ of 23% after 4 h, and then to a plateau at 26% up to 24 h. This indicates the rapid consumption of glycidol.

Investigation of the effect of varying molar equivalences of the base catalyst showed a slight decrease for $x_{\text{HPG}}$ from 27 to 18%, for 5–50 mol% of NaOH (Fig. 3 and Table S2). This is believed to be caused by a slight increase in water content, as previously mentioned in the preparation of HMW P[VA]-g-(hPG) and LMW P[VA]-g-(hPG). The higher water content promotes the hydrolysis of glycidol, as the result of the addition of increasing amounts of NaOH at equal concentrations.

An increase in molar quantity of glycidol resulted in an increase in $x_{\text{HPG}}$ (Fig. 4, •) and %DS (Fig. 4, ▲); this is expected as more glycidol will be available for the reaction (Table S3). A maximum is observed for the $x_{\text{HPG}}$ at 225% molar equivalences. This increase beyond the expected value is also observed for 200 and 250% molar equivalences.
However, this unexpected increase is not observed for the %DS. This suggests that the %DS depends on the amount of glycidol added, whereas the $x_{hPG}$ could also be potentially affected by changes in steric hindrance induced by ratio of primary and secondary hydroxyl groups in the randomly branched structure of the grafted hPG. The correlation between $x_{hPG}$ and %DB was not possible due to the poor resolution in the $^{13}$C NMR spectra of the graft copolymers with low $x_{hPG}$. Furthermore, the %GE decreases with increasing molar equivalents of glycidol from 26 to 6% for 50 and 350% molar equivalences, respectively (Fig. 4, $/$H17004). This is potentially due to the increase, to a greater extent, in rate of the formation of the side products (hPG and thermally ring-opened glycidol) compared to the rate of the formation of P[(VA)-g-(hPG)].

Reducing the rate of glycidol addition to the reaction from 6 to 0.08 mL h$^{-1}$ resulted in an increase in $x_{hPG}$ from 26 to 42% (Fig. 6, •) and %DS from 14 to 20% (Fig. 6, $/$H17039). This could be explained by a decreased concentration of glycidol in the reaction mixture retarding the homopolymerization side reaction producing hPG.

Initially, an increase in %DB (Fig. 6, $/$H17039) was observed with an increase in $x_{hPG}$. However, at higher $x_{hPG}$ (30%), %DB begins to decrease. However, it should be taken into account that the data is only semiquantitative due to the large signal to noise ratio in the quantitative $^{13}$C NMR spectrum and therefore accurate conclusions may not be drawn.

Physical Properties

DSC thermograms were recorded for LMW PVA and the corresponding P[(VA)-g-(hPG)] (Fig. 7). Upon heating, P[(VA)-g-(hPG)] shows a melting endotherm ($T_m$) at 209 °C [Fig. 7(b)] which is lower than the $T_m$ of PVA at 219 °C [Fig. 7(a)]. Moreover, the glass transition temperature ($T_g$) of P[(VA)-g-(hPG)] at 49 °C is lower than the $T_g$ of PVA at 79 °C, due to the addition of flexible hPG side chains. However, both PVA and P[(VA)-g-(hPG)] display a crystallisation temperature ($T_c$) of 180 °C.

Furthermore, P[(VA)-g-(hPG)] shows superior aqueous solubility compared with PVA, as it readily dissolves at ambient
The ability of P[(VA)g-(hPG)] to act as a styling agent was compared with linear PVA. Hair tresses were treated with polymer gels containing 2.5 wt% of PVA or P[(VA)g-(hPG)] and crosslinkers. The hair tresses were then kept in a room of 90% relative humidity at 32 °C. Preliminary tests have shown that hair tresses coated with P[(VA)g-(hPG)] retain their curl better than hair tresses coated with PVA (Fig. 9). This can be attributed to the increase in hydroxyl group density in P[(VA)g-(hPG)] compared with PVA, therefore increasing potential interaction sites.

Furthermore, qualitative tests were carried out at Ashland Laboratories in a temperature and humidity controlled room on curled hair tresses treated with polymer solutions (5 wt%) of PVA and P[(VA)g-(hPG)]. The hair tresses were subjectively compared on a numeric scale between 0 and 10 for shine/lustre, stiffness, crunch, curl snap, manageability, residual polymer and static. P[(VA)g-(hPG)] showed superior manageability, lack of static as well as lack of residue on hair and comb compared with PVA (Fig. S2). However, despite showing superior curl retention, hair tresses treated with P[(VA)g-(hPG)] are less stiff than hair tresses treated with PVA. This could be due to lower Tg of 49 °C for P[(VA)g-(hPG)] compared to 79 °C for PVA.

**CONCLUSION**

PVA of different molecular weights were successfully used as macroinitiators for ROP of glycidol to synthesise the novel polymer P[(VA)g-(hPG)] with varying x(hPG). P[(VA)g-(hPG)] was synthesised using water as a solvent with a maximum x(hPG) of 42%, %DS of 20%, and %DB of 20%. The x(hPG) was increased by increasing the reaction temperature from 0 to 100 °C and the reaction time from 4 to 24 h. Furthermore, an increase was observed by increasing molar equivalents of glycidol from 50 to 225% and addition time of glycidol from single addition to over a time period of 40 h. An increase in %DS coincided with an increase in the x(hPG). No change in %DB was observed with increasing temperature. However, a maximum in %DB was observed with increasing reagent addition time (31% after 12 h). The average %DB of P[(VA)g-(hPG)] was 25%, indicating a slightly branched structure.

The x_c of P[(VA)g-(hPG)] decreased greatly in comparison with PVA. The Tm of P[(VA)g-(hPG)] decreased with increasing x(hPG). Furthermore, the change in degradation temperature of P[(VA)g-(hPG)] compared with PVA was negligible. PVA/hPG blends did not show the improved solubility of the change in Tm or the magnitude of change in x_c.

In contrast to PVA, P[(VA)g-(hPG)] is readily soluble in water at ambient temperature.

Hair tresses with a solution containing P[(VA)g-(hPG)] showed superior curl retention compared with hair tresses treated with a PVA solution, potentially due to the increase in interaction site density on the graft copolymer. Moreover, P[(VA)g-(hPG)] also showed superior manageability, lack of static as well as lack of residue on hair and comb compared with PVA.
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REFERENCES