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Synthesis and Characterization of Hydroxyl-Functionalized Poly(propylene carbonate)

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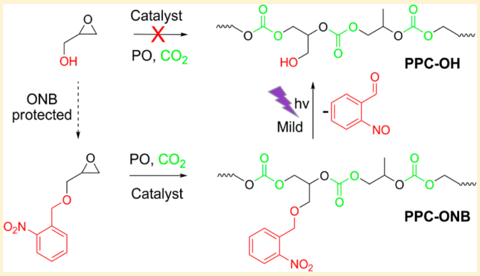
Supporting Information

ABSTRACT: Hydroxyl-functionalized poly(propylene carbonate) (PPC) was synthesized by a zinc glutarate catalyst mediated terpolymerization of carbon dioxide (CO_2), propylene oxide (PO), and 2-[[(2-nitrophenyl)methoxy]-methyl]oxirane (monomer **A**). PPC with varying monomer **A** contents (0–10.6 mol %) were obtained and could be transformed into hydroxyl-functionalized PPC by ultraviolet (UV) light irradiation without backbone degradation. The process of removing *o*-nitrobenzyl (ONB) protecting groups was monitored by UV–vis spectrometry to proceed within minutes. Thermal properties and contact angles of the functionalized PPCs were measured, showing the expected increase in hydrophilicity and glass transition temperature with increasing content of hydroxyl entities.



INTRODUCTION

Aliphatic poly(carbonate)s (APCs) are known biodegradable polymers and have been introduced as integral components of e.g. engineered tissues, medical devices, and drug delivery systems.[1−9] Tuning the hydrophilic properties of APCs in that regard is important and has been challenging for the fact that the relatively hydrophobic APCs are not easily modified in a post polymerization process, i.e., functional groups are not easily introduced to the backbone that contains only saturated CH and carbonate entities. There are two established polymerization methods for obtaining functionalized and more reactive APCs: (i) by ring-opening polymerization (ROP) of designated cyclic carbonates[1,3,10−20] and (ii) by copolymerization of carbon dioxide with functional epoxide comonomers.[8,21−26] Both routes rely on catalysts, which tolerate only a limited number of types of functionalities and usually only those that are comparable in coordination strength to epoxides and carbonates and thus are not particularly polar. A post polymerization functionalization of the thus-prepared functionalized APCs is therefore an efficient route to attain derived polymers with very hydrophilic groups (OH, COOH).[8,21,27,28] This process would allow tailoring the physical and chemical properties of the products for specific applications.

Hydroxyl-functionalized APCs with three or more carbon atoms between the carbonate entities were thus accessible by a sequence of copolymerization of functionalized cyclic carbonates with caprolactone, mediated by stannous octoate and subsequent modification.[29−31] Catalysts for preparing APCs with two carbons between the carbonate units from epoxides (majorly propylene oxide) and carbon dioxide have been improved in activity and tolerance of functional groups ever since the first report on poly(propylene carbonate) (PPC) from the alternate copolymerization of carbon dioxide and propylene oxide in 1969 with a catalyst prepared from diethyl zinc and water.[8,21,32] Homogeneous catalysts having metal centers including Cr(III), Co(III), rare earth metal, and zinc atoms[7,21,33] are known for their "relatively" high activity and to yield polymer with high carbonate linkage content.[8,21,33−39] Also, catalysts for stereoselective copolymerization have been reported.[7,40] Some of these catalysts give also access to polycarbonates with functional groups if starting from mixtures of (modified) epoxides.[8,27,38,41]

PPC has been a polymer of continuous interest and newly aroused more interest from chemical industry as well as environmentalists due to its utilization of CO_2 as carbon resource.[7,42,43] Large scale PPC production capacities have recently been reported, while their application fields remain still comparatively limited.[44] The latter is mainly related to the material properties: benchmarking these to commodity market requirements reveals challenges, in particular the unusual glass transition temperature of about 40 °C, which leads to cold flow at ambient temperatures.[42,45] Introduction of cross-links would improve the dimensional stability of PPC, for example by the formation of urethanes after reaction with diisocyanates of backbone bound functionalities.[46−49] Therefore, we set out to develop a facile route to synthesize hydroxyl-functionalized PPC without the danger of loss in molecular weight. We considered the ultraviolet light (UV light) cleavable *o*-nitrobenzyl (ONB) protecting group as an effective option for that purpose.[50−54] As shown in Figure 1, a series of functionalized PPCs were thus synthesized by terpolymerization of CO_2-, PO-, and ONB-protected glycidol. Cleavage

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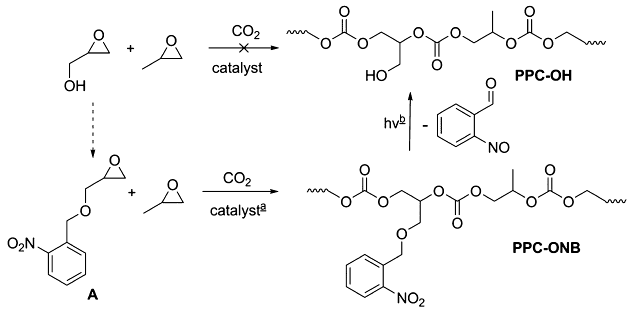


Figure 1. Synthesis of hydroxyl-functionalized poly(propylene carbonate): (a) zinc glutarate catalyst; (b) UV light irradiation with 313 nm UV light.

imposed by UV light irradiation leads to hydroxyl-functionalized PPCs without backbone degradation.

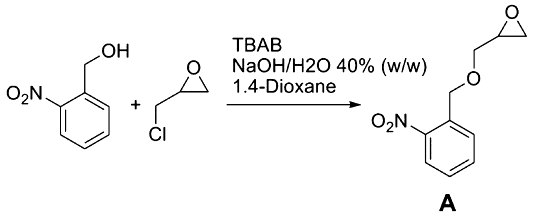
EXPERIMENTAL SECTION

Materials and Methods. All chemical products were obtained from Alfa Aesar, Aldrich, or Merck and used as received unless stated differently; polymerizations were performed with dry and purified solvents.

^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded on a Bruker 300 MHz FT-NMR spectrometer in chloroform-d_1. The chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS). Gel permeation chromatography (GPC, Agilent: Intelligent pump AI12, RI detector RI 101, set of two columns 2 × 5 μm Polypore from Varian) was used to determine the molecular weights distribution of the polymer samples relative to polystyrene standards in tetrahydrofuran as solvent. Differential scanning calorimetry (DSC, Mettler instruments) was used to determine the glass transition temperature of the polymer samples. UV spectra obtained on a Jasco V-630 were used in the ONB group cleavage process. An Oriel LSH3023 500 W UV-lamp equipped with a 313 nm filter was used to generate UV-radiation. Static water contact angle measurements were performed with contact angle system OCA 15plus (Dataphysics Instrument) recorded by a CCD video camera. 2 μL of water was dropped onto the film surface of each polymer sample at dosing rate of 1 μL s^{-1}, and at least three measurements were made on each sample. IR spectra were recorded on a Thermo Scientific Nicolet iS10 FTIR Spectrometer. Typically, 16 scans were signal-averaged to reduce spectral noise.

Monomer A Synthesis. *o*-Nitrobenzyl alcohol (100 g, 0.65 mol) was dissolved in 300 mL of 1,4-dixoane followed by addition of tetrabutylammonium bromide (10.5 g, 32.7 mmol) and 200 g of a 40 wt % aqueous sodium hydroxide sodium (80 g (2 mol) of NaOH in 120 g of H_2O). Epichlorohydrin (200 mL, 2.6 mol) was subsequently added dropwise to the cold mixture (0 °C), and the resulting mixture was allowed to warm to room temperature. The progress of the reaction was monitored by thin layer chromatography (ligroin (50–70)/diethyl ether (5/3 by volume)). After stirring for 48 h, the reaction progress had subsided, and the mixture was extracted with two portions of 500 mL of diethyl ether. The combined ether fractions were extracted with excess of water, saturated sodium bicarbonate, and saturated sodium chloride and were dried over magnesium sulfate, filtered, and concentrated by rotary evaporation. The oily product was purified by column chromatography with solvent (ligroin (50–70)/diethyl ether (5/3 by volume)) on silica, resulting in monomer **A** in a yield of 37 g (27.2% mole ratio based on *o*-nitrobenzyl alcohol) of a light yellow liquid at room temperature. ^{1}H NMR (δ, ppm, $CDCl_3$): 8.00 (d, 1H, ONB), 7.75 (d, 1H, ONB), 7.65 (t, 1H, ONB), 7.40 (t, 1H, ONB), 4.92 (s, 2H, ONB($\boldsymbol{CH_2}$)OCH_2CHCH_2O), 3.86, 3.89 (m, 2H, $ONBCH_2O(\boldsymbol{CH_2})CHCH_2O$), 3.20 (m, 1H, $ONBCH_2OCH_2(\boldsymbol{CH})CH_2O$), 2.63, 2.81 (m, 2H, $ONBCH_2OCH_2CH$-($\boldsymbol{CH_2}$)O). ^{13}C NMR (δ, ppm, $CDCl_3$): δ 147.16, 134.69, 133.73, 128.67, 128.08, 124.67, 71.74, 69.79, 50.65, 44.21.

Scheme 1. Synthesis of 2-[[(2-Nitrophenyl)methoxy]methyl]oxirane (Monomer A); TBAB = Tetrabutylammonium Bromide



Polymerization. Terpolymerization of **A**, PO, and CO_2 was achieved using a zinc glutarate (ZnGlu) catalyst. The catalyst was prepared as described in ref 37. The copolymerization was carried out in a stainless steel reactor of 300 mL volume (Parr). The reactor was charged with 100 mg of ZnGlu and various amounts of **A**. Prior to reaction, a dynamic vacuum was applied to the reactor at room temperature for 1 h to remove any volatiles. Dry toluene (30 mL) was allowed to enter the reactor, and the pressure was raised with gaseous carbon dioxide (3.5 N) to 2.0 MPa. Propylene oxide (10 mL) was added using an HPLC pump. The mixture was heated to 60 °C, and the final pressure was adjusted with carbon dioxide to 3.0 MPa. The temperature and pressure were held for 8 h, after which the reactor was cooled in an ice bath. The pressure was released and the reaction mixture subjected to a dynamic vacuum for 2 h at room temperature to remove the volatiles. The resulting solid was sampled for NMR analysis. The crude polymer was precipitated from acetone into methanol three times, collected, and dried in an oven under vacuum for 24 h at 40 °C. The purified products appear as white to dark yellow powders at high content of comonomer **A** (Table 1). A corresponding series of larger scale polymerizations were successfully achieved with the same ZnGlu catalyst. PPC-ONB polymers at a scale of 40–65 g were produced in each batch with various amounts of **A** (see Supporting Information). For a Fineman–Ross analysis, terpolymerizations of **A**, PO, and CO_2 were carried out in toluene as solvent with 25 mg of zinc glutarate catalyst for 2 h. The conversion was lower than 5% for monomer **A** (see Supporting Information).

Hydroxyl-Functionalized PPC. The *o*-nitrobenzyl groups were removed by exposing 10% (w/v) THF solutions of the purified polymers to 313 nm UV light at room temperature. THF solutions were deoxygenated by stripping with argon gas before UV light irradiation to prevent possible photo-oxidative degradation. The hydroxyl-functionalized PPCs were separated by precipitation into cold ligroin, dissolved in acetone and reprecipitated into ligroin twice, and finally dried as for PPC-OH. The yield was over 90% in all cases (Table 1). PPC-OH samples were analyzed by proton NMR to ensure the absence of aromatic entities (Figure 2).

Contact Angle (CA). CA measurements were performed on thin films of PPC-ONB and PPC-OH samples. These were prepared by spin-coating on a silica wafer from THF solutions of the polymers (10% w/v). Static contact angles to water (distilled twice) were measured by placing a small droplet on the surface and recording the angle between the horizontal plane and the tangent to the drop at the point of contact to the substrate.

RESULTS AND DISCUSSION

Terpolymers of **A**, PO, and CO_2 were prepared in toluene using a zinc glutarate of high activity as catalyst.[36,37] Zinc glutarate is a heterogeneous catalyst that we prefer to use; it has a moderate activity for the copolymerization, is easy to prepare and handle, contains no heavy metals, and residues are readily removed. Reaction times of about 8 h at 60 °C and 3 MPa of pressure (CO_2) with 100 mg of ZnGlu catalyst typically yielded 10–20 g of terpolymer. These conditions are in the optimum range for PO/CO_2 copolymerizations mediated by zinc glutarate.[36] Larger scale preparations (65 g) were successful

Table 1. Characterization Data of Copolymer Samples

sample	A/PO feed (mol %)	A/PO^a in polymer (mol %)	conv A^b (%)	conv PO (%)	activity (g PPC g ZnGlu h^{-1})	carbonate linkages^c (%)	M_n^{d} PPC-ONB (g mol^{-1})	M_w/M_n^{d} PPC-ONB	M_n PPC-OH (g mol^{-1})	M_w/M_n PPC-OH
P1	0	0	0	86.5	15.6	92	89 600	3.9	87 600	3.9
P2	2.5	0.9	61.0	90.1	18.9	93	62 600	3.1	63 400	3.1
P3	5.0	2.2	66.3	90.3	18.1	92	35 500	3.6	37 800	3.4
P4	10	4.6	55.0	65.4	14.1	89	32 300	3.6	32 700	4.0
P5	16	7.0	44.0	69.7	15.6	90	27 000	3.3	26 400	3.4
P6	20	10.6	35.7	34.5	8.1	92	22 700	3.4	23 600	3.6
P7^e	30									

^{a}Comonomer **A** content, calculated from ^{1}H NMR spectra of the PPC-ONB polymer samples; residual **A** could be recycled from the precipitation solvent residue; residual PO was removed in vacuum. ^{b}Calculation based on ^{1}H NMR spectra of samples after polymerization and yields. ^{c}By ^{1}H NMR spectroscopy. ^{d}By gel permeation chromatography (GPC) calibrated to polystyrene standards in THF at room temperature. ^{e}No polymer obtained.

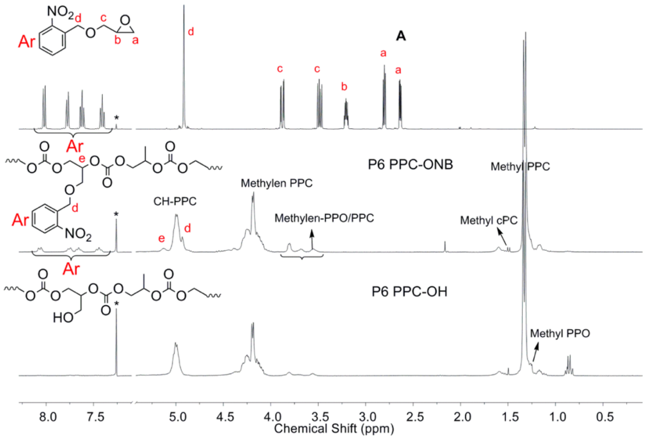


Figure 2. ^{1}H NMR spectra of monomer **A**, ONB-protected polymer **P6 PPC-ONB**, and deprotected polymer **P6 PPC-OH**.

too (see Supporting Information). The terpolymers were readily purified from residual **A** and the formed cyclic carbonate by precipitation into methanol.[55,56] The molar ratio of **A** to PO was varied in a range from 0 to 0.2 to give a range of products **P1** to **P6** (Table 1). An analysis by ^{1}H NMR showed that the resulting polymers were polycarbonates with 89−93% of carbonate linkages. The composition with respect to **A** entities and PO related units ranges up to 10.6 mol % of **A** when the feed **A**/PO had a molar ratio of 20/100. Higher concentrations of **A** entities in the polymer could not be reached under these conditions as a higher ratio of **A**/PO in the feed (>30/100) deactivated the catalyst.

The productivity of the catalyst is strongly dependent on the concentration of **A**. It decreases from 15.6 g PPC/g ZnGlu h^{-1} to 8.1 g PPC/g ZnGlu h^{-1} at a concentration of **A** of 0.72 mol/L (Table 1). It is assumed that **A** coordinates stronger to zinc centers than PO, i.e., next to the epoxide also with (nitro and) ether moieties, thereby blocking the surface.[57] Epoxides are known to be weakly coordinating and are readily displaced from Lewis acids by many functionalities.[58] Without coordination and concomitant activation, epoxides are not undergoing ring-opening at the reaction conditions used.[35,59] The molecular weight of the products varied between 22 700 and 62 600 g mol^{-1}, and molecular weight dispersities (M_w/M_n = 3.1−3.9) were in the typical range of zinc glutarate-based polypropylene carbonates.[60,61] The number-average molecular weight of the samples decreases congruently with the yield at higher concentration of **A**. This is thus probably related to a lower rate of insertion of the monomers affected by the coordination of **A** to the catalyst. Larger scale preparation results showed the same trends in productivity and molecular weight. A Fineman−Ross analysis gives the copolymerization reactivity ratios r_1 and r_2 of PO respectively of **A** at 1.46 and 0.64 (see Supporting Information Figure S5). There is thus a mild preference for incorporation of PO into the terpolymer, but nevertheless it may be expected that the functional groups are substantially randomly distributed in the terpolymer.

The ONB groups can be readily removed from the polymer in THF solution by irradiation with UV light of a wavelength around 313 nm. The product of this reaction is a poly(propylene carbonate) with hydroxyl groups on the methyl substituent (PPC-OH, Figure 2). It was found possible to quantitatively transform the ONB groups into hydroxyl entities. The progress of the reaction is obvious from a color change to dark brown, the typical color of the side product (and decomposition product of) nitroso benzaldehyde.[51,62] The polymer could effectively be separated from the reaction mixture by repeated precipitation from acetone into ligroin, yielding purified PPC-OH.

The transformation of **P6 PPC-ONB** to **P6 PPC-OH** was also monitored by UV−vis spectrometry (Figure 3). A THF solution of the polymer **P6 PPC-ONB** with **A**/PO at 10.6% in molar ratio (2.0 mg/mL) under UV light irradiation was sampled at intervals, and spectra were immediately recorded. A characteristic absorption related to the ONB-protecting group is found around 260 nm (present before UV light irradiation at

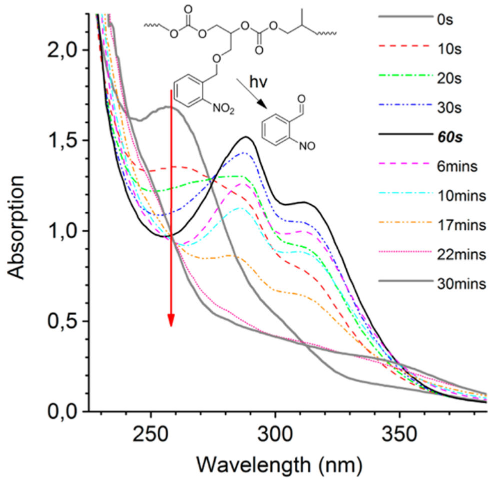


Figure 3. UV−vis spectra of the irradiation process on **P6 PPC-ONB** at room temperature in THF.

Table 2. Contact Angle and Glass Transition Temperature of Polymer Samples

sample based on	A/PO[a] in polymer (mol %)	CA[b] (deg) before UV PPC-ONB	CA (deg) after UV PPC-OH	ΔCA[c] (deg)	T_g[d] (°C) before UV PPC-ONB	T_g (°C) after UV PPC-OH	ΔT_g[e] (°C)
P1	0	76.8	76.4	−0.4	29.3	29.4	0.1
P2	0.9	75.9	71.8	−4.1	30.8	32.9	2.1
P3	2.2	74.1	70.4	−3.7	30.9	35.3	4.4
P4	4.6	74.4	68.5	−5.9	30.3	35.1	4.8
P5	7.0	73.6	65.1	−8.5	25.9	31.4	5.5
P6	10.6	73.8	60.8	−13.0	27.7	35.8	8.1

[a] Comonomer **A** content in polymers. [b] Contact angle. [c] Contact angle change by deprotection. [d] Glass transition temperature (T_g) determined by DSC. [e] Glass transition temperature change, $\Delta T_g = T_{g(\text{PPC-OH})} - T_{g\,(\text{PPC-ONB})}$.

0 s). An isosbestic point is observed of spectra recorded from samples in the first minute, indicative of a direct transformation to hydroxyl groups. The photoreaction is very effective as after 1 min the vast majority of the ONB-protecting groups are already cleaved. Change of absorbance band at 290 and 315 nm in Figure 3 can be attributed to the formation of nitroso benzaldehyde derivative as a byproduct of the released protecting groups.[62] The nitroso side product is very reactive, leading to consecutive reactions not including the polymer as irradiation is prolonged and the concentration of the nitroso compound decreases.[51,63−66]

The molecular weights determined by GPC of the PPC-OH samples were very comparable to corresponding PPC-ONB samples (Table 1). It may thus be anticipated that main chain degradation is not notably taking place during UV light irradiation. Note that the molecular weight should have decreased after UV light irradiation due to the loss of the ONB-protecting (max of 12.3 wt % for polymer **P6**). The molecular weights obtained from GPC are nevertheless almost equal to those of the corresponding PPC-ONBs, which is attributed to a larger hydrodynamic volume of PPC-OH samples with increasing hydroxyl amount. A similar small increase is documented for other postfunctionalized polycarbonates[17,27,59] and hydroxylated polyesters.[67] A severe degradation of poly(glycerine carbonate) has been observed in solution of organic solvents.[25,27] We find that **P6 PPC-OH** is stable in THF for at least 2 weeks. This attributed to the lower concentration of reactive hydroxyl groups and the mild (neutral pH) conditions of the preparation procedure.

PPC-ONB polymers show a single glass transition temperature (T_g) in the same range as for neat PPC.[60,68] The glass transition temperature of PPC-ONB samples increases from 29.3 °C of neat PPC **P1** to 30.9 °C of **P4 PPC-ONB** with 4.6 mol % ONB content and then decreases to 27.7 °C (Table 2) of entities **P5** and **P6** with a higher content of ONB. The small changes may be explained by the opposing effect of the ONB groups acting as bulky side groups increasing T_g and the decreasing molecular weight decreasing T_g.[69] The glass transition temperatures of hydroxyl-functionalized PPC-OH polymers are somewhat higher than those of PPC-ONB polymers. The shift of T_g (ΔT_g) increases with the increasing content of hydroxyl groups in PPC-OH polymers. This could be explained by the presence of the increasing number of hydrogen bonds.[31,59,70,71] IR spectra of **P1**, **P6 PPC-ONB**, and **P6 PPC-OH** were obtained (Figure 4) and show e.g. in **P6 PPC-OH** broad absorptions in the 3500−3000 cm^{-1} region. These are attributed to self-H-bonded O−H groups (3350 cm^{-1}), inter-H-bonded O−H groups (3340 cm^{-1}), and free O−H groups.[72−75]

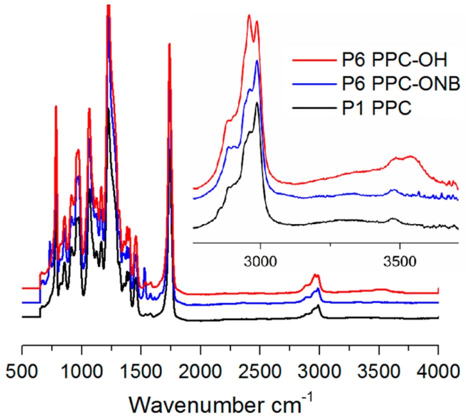


Figure 4. FTIR spectra of **P1** (PPC), **P6 PPC-ONB** (before UV light irradiation), and **P6 PPC-OH** (after UV light irradiation).

Consistently, the polarity of the respective polymers **P1−P6 PPC-ONB** and **PPC-OH** are different. The change in polarity is for example expressed in the contact angle of polymer thin films to water. Water contact angles on polymer surfaces were measured on spin-coated films (Table 2). Contact angles of PPC-ONB polymers are found in the narrow range of 73.8°−76.8°, close to those reported for water contact angle on PPC films.[76] The PPC-OH polymers have a significantly decreased contact angle. The higher the content of comonomer units in the PPC-OH polymers, the lower the contact angle is (Figure 5).

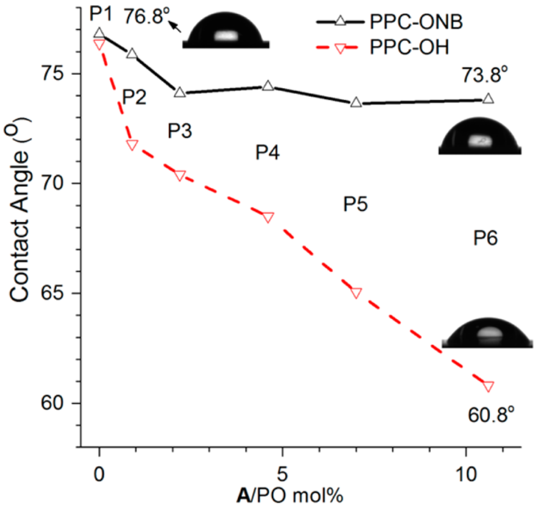


Figure 5. Contact angle analysis of PPC-ONB and PPC-OH samples.

CONCLUSIONS

Hydroxyl-functionalized PPCs have been synthesized via terpolymerization of CO_2-, PO-, and ONB-protected glycidol monomer mediated by a standard zinc glutarate catalyst. It provides a general method for synthesis hydroxyl-functionalized PCs through UV light deprotecting ONB epoxide monomers. The primary hydroxyl group content could be adjusted by varying the molar ratio feed of ONB monomer. ONB-protecting groups could be removed by UV light irradiation completely with no impact on the molecular weight of PPC. Larger scale preparations of about 50 g were easily performed. The composition, thermal properties, deprotection kinetics, and hydrophilicity of the synthesized polymers have been studied: compared to ONB-protected polymers, hydroxyl-functionalized PPCs have higher T_g and higher polarity. IR spectra and DSC results indicate that the hydrogen bonds from inter- and intrapolymer chains may be responsible for the increase of T_g in PPC-OH polymers. The introduction of hydroxyl groups provides hydrophilic PPC with potential applications and a general precursor for various postfunctionalized PPCs, for example methyl sulfonation (see Supporting Information).

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experiment details, polymer characterization, Fineman−Ross analysis, and large-scale polymerizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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