

Supplementary Information

Materials and General Methods. *tert*-Butyl acrylate (Aldrich, 98%), was distilled before polymerization. Other reagents from Aldrich, Sigma, and Acros were used as received. All the solvents were HPLC grade. Attenuated Total Reflectance (ATR) spectra were obtained using a Mattson Galaxy 4201 spectrometer with a Wilks Model 10 ATR accessory at an angle of 45° using a KRS-5 crystal. Spectra were recorded at 4 cm⁻¹ resolution between 4000 and 400 cm⁻¹ and were the sum of 256 individual scans.

Preparation of α,ω -Diamino Poly(*tert*-Butyl Acrylate) (NH₂R-PTBA-RNH₂). 4',4'-Azobis(4-cyanovaleric acid) (380 mg, 1.36 mmol), 1,4-dioxane (60 mL), and 20 mL (136 mmol) of *tert*-butyl acrylate were added to a flame-dried, 3-necked flask under nitrogen. The solution was allowed to reflux for 20 h. The polymer was recovered by precipitation into a CH₃OH-H₂O (1:1) mixture. The acid-terminated polymer was further purified by three successive cycles of dissolution in acetone and precipitation in CH₃OH-H₂O (1:1). To form the diamine-terminated polymer, a solution containing 5.0 g of the above polymer in 30 mL of CH₂Cl₂ was added to a flame-dried flask under nitrogen. Activation of the terminal carboxylic acid groups with 324 mg of 1,1'-carbonyldiimidazole (CDI) was followed by addition of 0.2 mL of ethylenediamine and overnight stirring. After the reaction was complete, 100 mL of CH₂Cl₂ was added. The organic layer was washed with H₂O (3 x 30 mL) and dried over anhydrous MgSO₄. The solvent was evaporated, and the product was further dried overnight under vacuo. The product was analyzed by ¹H NMR spectroscopy and FT-IR spectroscopy. The molecular weight (*M_n*) of final diaminoterminated polymer was 20,000 (determined by titration). FTIR (KBr, cm⁻¹): 3438, 1734, 1633, 1262, 1155.

Preparation of Oxidized Polyethylene (PE) Powder. The PE powder was first extracted with CH_2Cl_2 in Soxhlet apparatus overnight and then dried under vacuum. The PE powder was then oxidized using $\text{CrO}_3/\text{H}_2\text{O}/\text{H}_2\text{SO}_4$ (1:2:1) at 90°C for 30 min, washed with water and acetone, and the powder was allowed to air dry. The oxidized PE powder was extracted with CH_2Cl_2 in Soxhlet apparatus overnight and dried under vacuum.

Preparation of PAA/PE Powders. The oxidized PE powder (1 g) was activated using ethyl chloroformate (1 mL) and N-methylmorpholine (1 mL) in 60 mL of DMF for 1 h. The powder was then filtered, and washed with ethyl acetate and dried under vacuum. The activated powder was then put into a solution of 3 g of $\text{NH}_2\text{R-PTBA-RNH}_2$ in 60 mL of DMF for 6 h. After grafting, the powder was extracted with CH_2Cl_2 in Soxhlet apparatus overnight. The powder was then hydrolyzed using 2 mL of MeSO_3H in 60 mL of CH_2Cl_2 at room temperature for 1 h. The product 1PAA/PE powder was washed with water and ethanol and dried under vacuum. The activation, grafting and hydrolysis steps were repeated in order to make higher stages of the hyperbranched PAA/PE powder.

Preparation of Amidated 3-PAA/PE Powder. 3-PAA/PE powder (1 g) was first activated with ethyl chloroformate (see above procedure). The activated PE powder was then immersed in 60 mL of 2.0 M isopropyl amine solution in DMF at room temperature for 3h. After reaction, the PE powder was washed with ethanol, treated with 0.1 N HCl in $\text{H}_2\text{O-EtOH}$ (1:1) for 1 h, washed with ethanol, dried under vacuum. In order to achieve high levels of amidation, the above three-step procedure was repeated twice more.

Reduction of COOH on 4-PAA/PE Powder. The 4-PAA/PE powder was

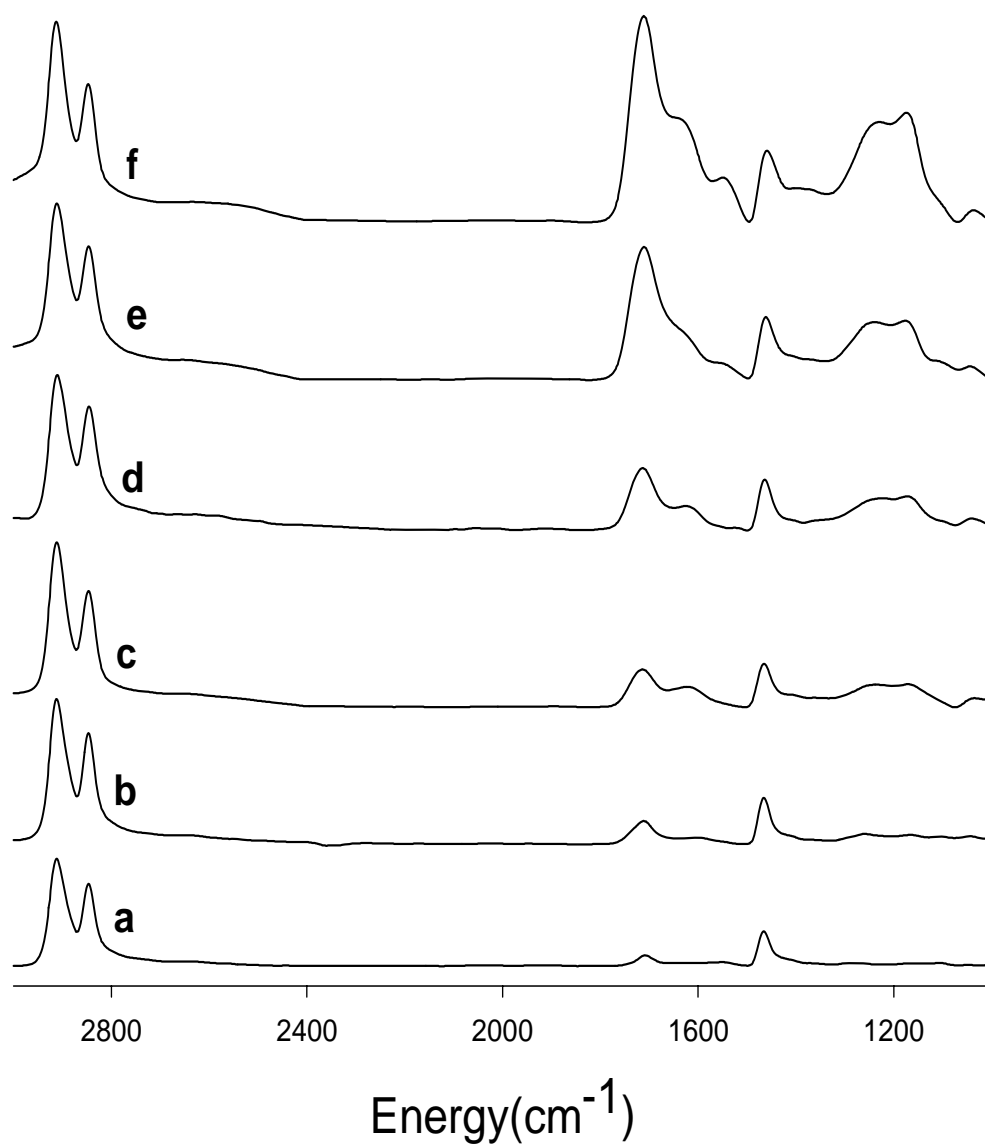
first activated with ethyl chloroformate (see above activation procedure). Then the activated PE powder was immersed in 2.0 M $\text{BH}_3\text{-SMe}_2$ in dry THF and the suspension was allowed to reflux overnight. After the reaction, the PE powder was washed with H_2O and 0.1 M HCl and dried under vacuum.

Preparation of Esters on a 3-PAA/PE Powder. The 3-PAA/PE powder was immersed in ethanol in the presence of 0.2 M H_2SO_4 , and the mixture was refluxed for 24 h. After reaction, the powder was washed with ethanol, dried under vacuum. IR spectroscopy showed ca. 90% conversion of the $-\text{CO}_2\text{H}$ groups into ethyl ester groups for the 3-PAA/PE powder. Allyl esters of a 3-PAA/PE powder were obtained in 80-90% yield using a similar procedure, substituting allyl alcohol for ethanol.

Preparation of Pd Catalyst on a 4-PAA/PE Powder. A 4-PAA/PE powder sample (1 g) was first stirred with a pH 9 buffer for 2 h to deprotonate the $-\text{CO}_2\text{H}$ groups of the graft. The resulting carboxylate-containing polymer was then suspended in EtOH with 15 mg of $\text{Pd}(\text{OAc})_2$ at r.t. for 3 h. Filtration and washing with dilute acid and EtOH yielded a Pd-containing powder that formed Pd(0) on reduction with H_2 . Combustion of a powder sample and analysis of the residue for Pd showed that Pd loadings was ca. 1×10^{-3} g of Pd/g of powder (ca. 0.01 mg-atom of Pd/g of powder).

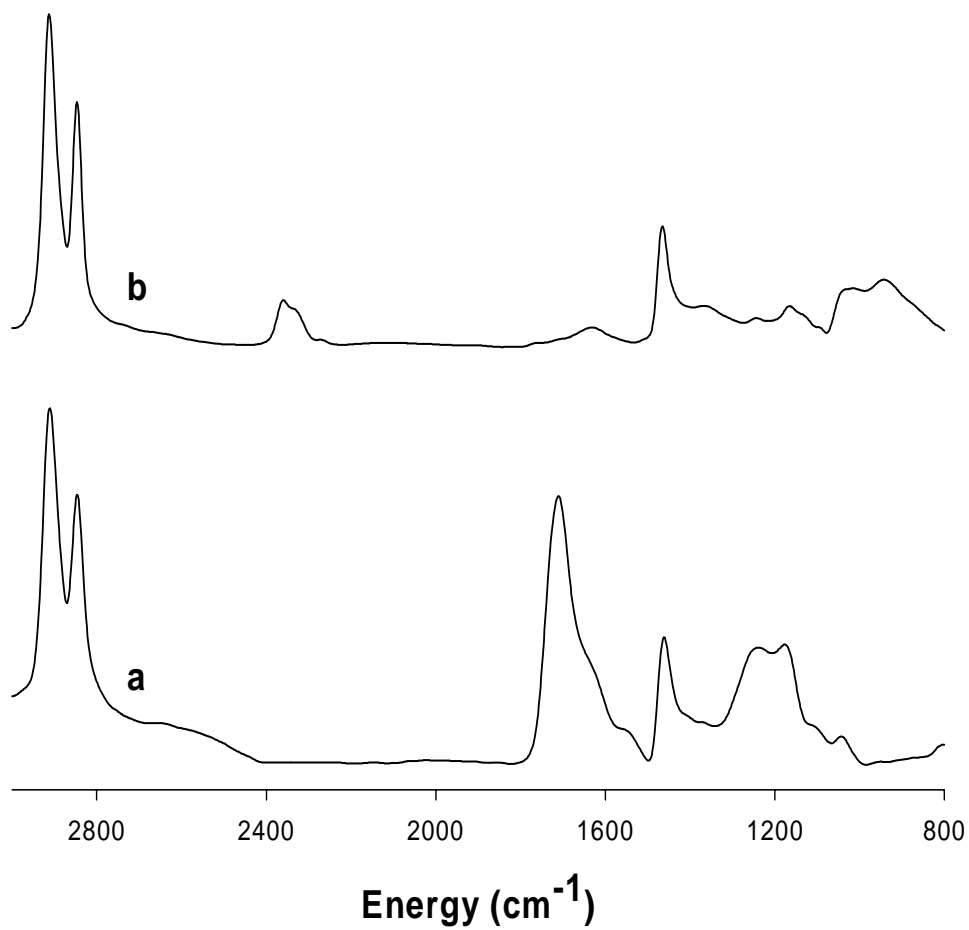
Preparative Scale Hydrogenation of 9-Undecenol Using Pd/4-PAA/PE Powder. 50 mg of a Pd catalyst prepared from a 4-PAA/PE powder as described above (0.0005 mg-atom of Pd) was suspended in 20 mL of ethanol containing 1.45 g (8.51 mmol) of 9-undecenol. Hydrogenation was carried out using a Parr apparatus for 48 h. At that point, H_2 uptake had ceased. The product undecanol was isolated in 84% yield after filtration to remove the catalyst (which could be recycled) followed by removal of the EtOH

solvent under reduced pressure. ^1H NMR and ^{13}C NMR spectroscopy showed the product was identical to authentic undecanol and that the alkene was completely reduced.



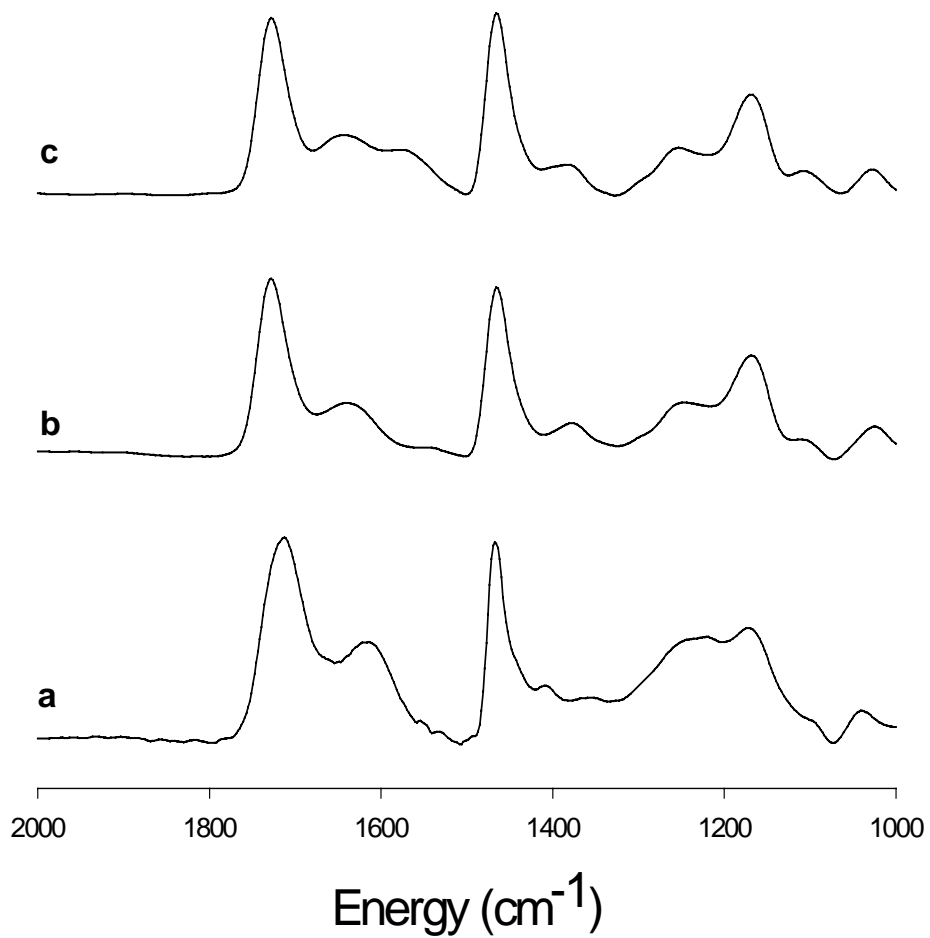
Hyperbranched poly(acrylic acid) onto polyethylene powder

a. oxidized PE; b. 1-PAA/PE; c. 2-PAA/PE; d. 3-PAA/PE; e. 4-PAA/PE; f. 5-PAA/PE



Reduction of 4-PAA/PE powder

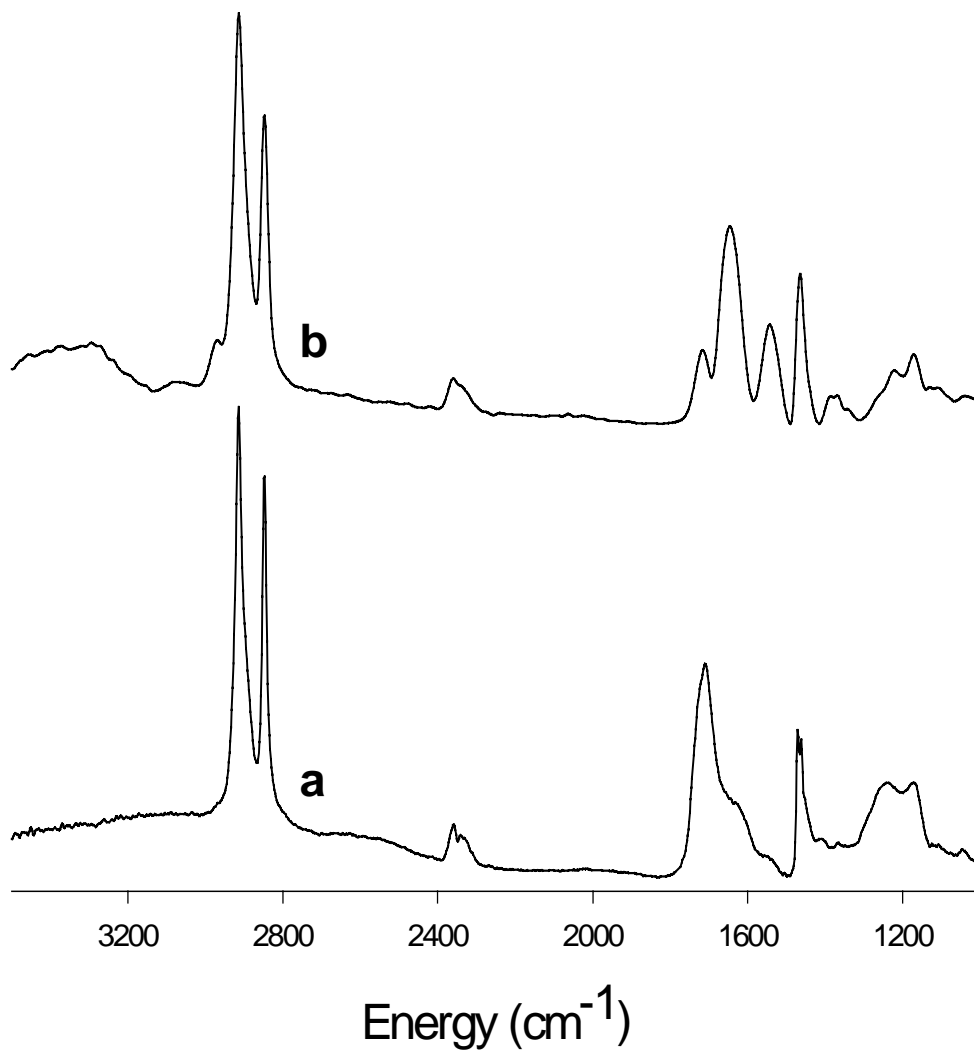
a. 4-PAA/PE; b. 4-P(CH₂CH-CH₂OH)/PE



Preparation of ethyl ester on 3-PAA/PE powder

a. 3-PAA/PE; b. 3-P($\text{CH}_2\text{CHCOOEt}$)/PE;

c. 3-P($\text{CH}_2\text{CHCOOEt}$)/PE after treatment with base



Amidation of 3-PAA/PE powder

a. 3-PAA/PE; b. 3-P(CH₂CHCONHCH(CH₃)₂)/PE