Another Synthesis Route to New Materials: Hydrogenation of Heteroaromatic Polymers

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Introduction

Hydrogenation of unsaturated polymer is a powerful modification method that introduces into precursor polymers unique chemical and physical features which might not be able to obtain through polymerization of monomers alone. Kraton® and saturated ROMP are examples of commercial success of hydrogenation of polymers. Gehlsen and Bates[1] reported in 1993 that polystyrene and poly(styrene-*b*-isoprene) were fully hydrogenated with $Pd/CaCO_3$ and $Pd/BaSO_4$ at 140 °C under 500 psig of hydrogen which were much milder conditions than those previously reported.[2,3] While hydrogenation of polymers have been mostly done on unsaturated double bonds, not many attempts have been made on aromatic polymers except for polystyrene.[4,5]

We have been interested in hydrogenation of heteroaromatic polymers possessing nitrogen in the ring because the saturated polymers would be secondary amines which cannot be obtained easily from the corresponding monomers. Poly(vinylpyridine)s were chosen as the materials to start since they are versatile polymers and have structures analogous to polystyrene. Pyridine moiety was used as a practical precursor to secondary amines. In this paper, we would like to report the synthetic methodology and physical properties of the amine polymers/copolymers synthesized using hydrogenation.

Experimental

Hydrogenation of Polystyrene, (PS). 0.2 g of Polystyrene was dissolved in 15 mL of cyclohexane in a glass vial with a magnetic stir bar. 0.2 g of Pt/C was also added and stirred for 10 minutes. The charged vial was placed in a 300 mL Parr® pressure vessel that was then pressurized with H_2 gas and heated to 120 °C for desired reaction time. When quenched the reaction, the pressure vessel was immersed in iced water and released the pressure. After the catalyst was removed by filtration, all the solvent was removed and then dried up by vacuum.

Hydrogenation of Poly(2-vinylpyridine), (P2VP). 0.2 g of Poly(2-vinylpyridine), 15 mL of methanol, 0.2 mL (2.4 mmol) of HCl were added in a glass vial with a magnetic stir bar. After the polymer was completely dissolved in solution, 0.2 g of Pt/C was also added and stirred for 10 minutes. The charged vial was placed in a 300 mL Parr® pressure vessel that was then pressurized with H_2 gas and heated to 120 °C for desired reaction time. After the catalyst was removed by filtration, all the solvent was removed and redissolved in 5 mL of methanol and precipitated in cold acetone. The white precipitate was filtered and dissolved in fresh methanol (20 mL). This polymer solution was stirred with the ion exchange resin (OH^- type) for 2 hours to get free amine form. The resin was then separated and the polymer was dried up by vacuum.

Hydrogenation of Poly(styrene-b-2vinylpyridine), (PS-P2VP). 0.5 g of the block copolymer, 40 mL of Cyclohexane, 40 mL of Methanol, and 0.5mL of HCl were mixed in a glass vial. After observing continuous milky phase, 0.5 g of Pt/C was added. The charged vial was placed in a 300 mL Parr® Pressure vessel that was then pressurized with H_2 gas and heated to 120 °C for 72 hours.

Characterization methods. Molecular weight and molecular weight distributions of polystyrene and poly(2-vinylpyridine) were measured via gel permeation chromatography using a JASCO PU-1580 pump and a JASCO RI-1530 refractive index detector at a flow rate of 1 mL/min at room temperature. DMF with 0.1% (w/v) tetrabutylammonium bromide for Poly(2-vinylpyridine) and chloroform for Polystyrene were used as the eluents. Calibration was accomplished using a set of monodisperse Polystyrene standards (Pressure Chemical) and Poly(2-vinylpyridine) standards (Polymer Standards Service-USA, Inc.). The degree of hydrogenation was calculated from the integration of aromatic proton and aliphatic proton peaks of ^{1}H-NMR. ^{1}H-NMR spectra were obtained using a Varian Mercury 400 (400MHz) Spectrometer at 25 °C in $CDCl_3$ with TMS as the internal reference. The thermal properties of polymers were analyzed using DSC 2920, Differential Scanning Calorimeter and TGA 2950, Thermogravimetric Analyzer (TA Instruments). The glass transition temperatures (T_g) and the decomposition temperatures (T_d) were determined when the sample was heated at 10 °C/min under nitrogen. TEM was performed on a PHILIPS CM12 electron microscope operated at 100kV.

Results and Discussion

Hydrogenation of homopolymers. Poly(2-vinylpyridine) and poly(4-vinylpyridine) were hydrogenated using Pd/C, Rh/C, RuC, Pt/C, PtO_2 at 120 °C and 1000-1200 psig. In acidic aqueous or methanolic solution, the complete hydrogenation of P2VP and P4VP to P2VPip and P4VPip could be accomplished in a relatively rapid fashion (**Figure 1**).

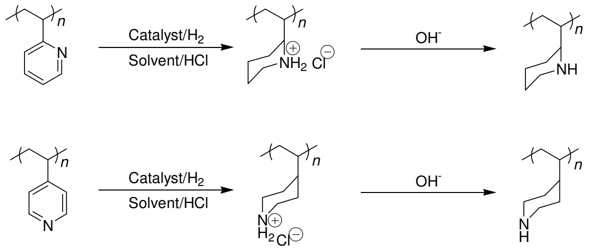


Figure 1. Reaction scheme of hydrogenation of Poly(2-vinylpyridine) and Poly(4-vinylpyridine).

Under these acidic conditions, the protonated P2VPip and P4VPip are readily separated from the catalyst by filtration as opposed to their difficult separation in neutral media. After the treatment with ion exchange resin, the free amine P2VPip and P4VPip are soluble to water, lower alcohols, DMF, DMAC and chloroform. P2VPip and P4VPip showed pH~11 in water and alcohol.
DSC was used to determine the glass transition temperatures (T_g) for P2VP, P4VP, P2VPip, and P4Vpip, as shown in **Figure 2.**

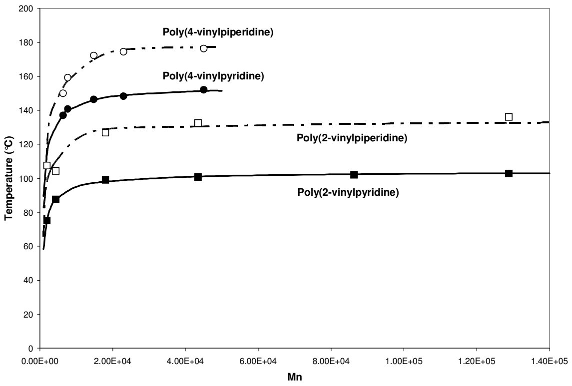


Figure 2. Glass Transition Temperatures of P4VP, P4VPip, P2VP, and P2VPip.

The T_gs of the hydrogenated polymers are 33°C higher for P2VPip and 24°C higher for P4VPip than P2VP and P4VP respectively. Saturated pendant groups, piperidinyl rings are much bulkier than unsaturated pyridinyl rings so that they impede bond rotation and stiffen the chain. Chain stiffening increases the energy necessary for cooperative motions of monomer units, and thus increases the T_g.

Hydrogenation of Poly(styrene-b-2vinylpyridine). Polystyrene, Poly(2-vinylpyridine), and Poly(styrene-*b*-2vinylpyridine) were anionically polymerized to give well defined polymers.

Table 1. Polymer Characterization results.

Polymer	Mn	Mw	PDI	St/2VP
PS	14,600	15,600	1.07	100/0
P2VP	18,900	20,700	1.10	0/100
PS-P2VP	38,700	42,100	1.09	64/36
PS-P2VP	104,000	112,300	1.08	63/37
PS-P2VP	108,000	116,600	1.08	56/44

Hydrogenation of PS and P2VP was carried out in Cyclohexane and methanol solution with Pt/C respectively. **Figure 3** shows that both PS and P2VP were converted to polyvinylcyclohexane and Poly(2-vinylpiperidine) (P2VPip) with the similar profile. However, if the two solutions of PS and P2VP were combined in the same vial, the hydrogenation reaction scheme was altered completely (**Figure 4**). Hydrogenation of PS was suppressed minimal and the reaction of P2VP was accelerated instead. This is because pyridine rings of P2VP are strongly binded to the catalyst surface so that they prevent access of PS. As the result, all the catalyst in the system was used for hydrogenation of P2VP which led the faster conversion.

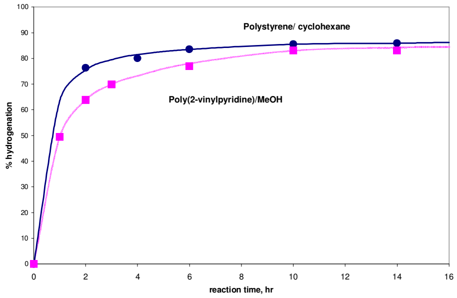


Figure 3. Hydrogenation of PS and P2VP. PS/Cyclohexane, P2VP/Methanol.

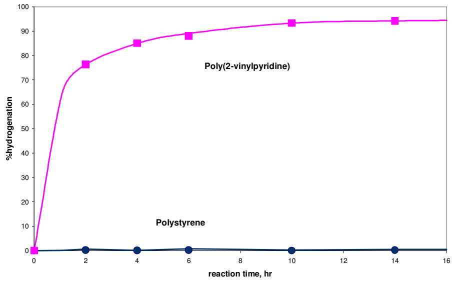


Figure 4. Hydrogenation of PS and P2VP in the mixed solvent of Cyclohexane and Methanol.

We have found that this selectivity of hydrogenation of P2VP over PS was able to be utilized for the block copolymer. PS-P2VP was hydrogenated with Pt/C providing the exclusive reduction of P2VP block. The **Figure 5** shows the ^{1}NMR spectra of before and after hydrogenation.

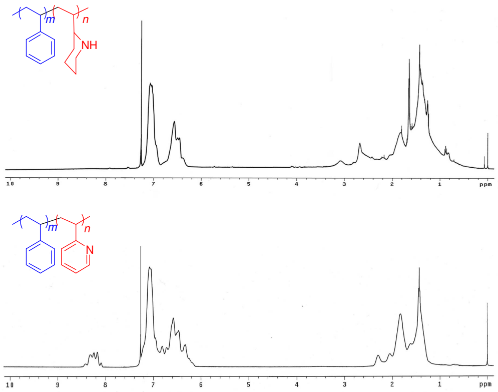
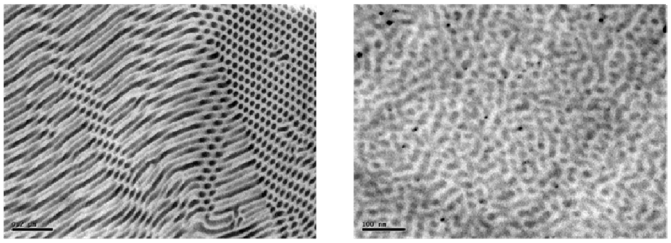


Figure 5. ^{1}H-NMR spectra of before (bottom) and after (top) hydrogenation of PS-P2VP.

After hydrogenation, the peak at 8.2 ppm which is an aromatic proton of the pyridine ring was disappeared and the resonances of aromatic region (6~8 ppm) is identical of those of polystyrene.

The phase behavior of Poly(styrene-*b*-2vinylpyridine) system has been extensively studied by Shull and Schulz.[6,7] According to the phase diagram, the prepared diblock copolymers in **Table 1** have either lamella structures or hexagonal cylinders based on the volume fraction ratio of PS/P2VP. **Figure 6** shows TEM images of hydrogenated block copolymer with the ratio of PS/P2VP at 63/37. After hydrogenation, P2VP block becomes P2VPip block which is more polar and more immiscible with PS block.



Before Hydrogenation

After Hydrogenation

Figure 6. TEM images of for PS-P2VPip with PS/P2VPip=63/37.

Light and dark regions correspond to PS- and P2VP- (or P2VPip-) rich microdomains, respectively. The domain size of hydrogenated copolymer is smaller than the original polymer. This was not initially expected since the repulsion between ST and 2VPip is bigger than ST and 2VP. Piperidine have secondary amine NH group which generates inter and intra molecular attraction by hydrogen bonds. We assume that the piperidine blocks aggregate to form sphere like domains in the Polystyrene matrix. The similar phenomena were observed in the block copolymers with strongly interacting groups such as ion-containing polymers.[8,9,10]

Conclusions

Heterogeneous catalytic hydrogenation of Poly(2-vinylpyridine) (P2VP) and Poly(4-vinylpyridine) (P4VP) was successfully achieved using various group VIII metals supported on carbon at relatively mild conditions. There was no sign of chain degradation upon hydrogenation reaction. The saturated polymers P2VPip and P4VPip show high solubility to water as well as some polar organic solvents. Incorporation of amine group to polymer chain makes the further functionalization easier. The glass transition temperatures of P2VPip and P4VPip are found to be higher than the original polymers. The selective hydrogenation of PS-P2VP was successfully accomplished using heterogeneous catalyst. Catalyst poisoning by P2VP block brings to the selectivity of hydrogenation on the P2VP block over the PS block. The hydrogenated block copolymers have non-ionic and amphiphilic nature. They showed sphere like morphology with aggregates of P2VPip block dispersed in PS domain.

Acknowledgments

The authors of this paper would like to thank Duke Energy and NSF for the financial support of this research.

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