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Heterogeneous Catalytic Hydrogenation of Poly(styrene): Thermodynamics of Poly(vinylcyclohexane) Containing Diblock Copolymers

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ABSTRACT: Heterogeneous catalytic hydrogenation of 1,4-poly(isoprene) (PI), atactic poly(styrene) (PS), and two poly(styrene)-poly(isoprene) (PS-PI) diblock copolymers was performed using two palladium supported catalysts. In each case fully saturated materials were obtained with no chain degradation. The dynamic and thermodynamic properties of these materials were investigated using differential scanning calorimetry and dynamic mechanical spectroscopy. Saturated poly(styrene), denoted poly(vinylcyclohexane) (PVCH), exhibited a glass transition temperature (T_g) that is 40 deg higher than that of poly(styrene). For diblock copolymers of PVCH and poly(ethylene-propylene) (PEP) this increase in T_g is accompanied by a slight increase in the order-disorder transition temperature, T_{ODT}, relative to that characterizing the PS-PI precursor. Estimates of the associated segment-segment interaction parameters based on group contribution methods anticipate a steep reduction in T_{ODT} with saturation, contrary to this result.

Introduction

Polyolefins (e.g. poly(ethylene) and poly(propylene) are saturated hydrocarbon polymers that exhibit superior stability toward thermal, oxidative, and radiation induced degradation. Low glass transition temperatures, T_g, and high crystallinity make these materials suitable for a wide range of applications including packaging, household uses, and polymer property modification. Recently, polyolefins also have been recognized as excellent materials for use in fundamental polymer studies, and a variety of compounds have been developed with controlled microstructures and molecular architectures. These materials have been instrumental in investigating various aspects of polymer science and engineering.[1-4]

Several polymerization and post polymerization techniques are used to synthesize polyolefins. Free radical and Ziegler-Natta polymerizations produce polyolefins with a wide polydispersity and little control of the molecular architecture, although with the latter high stereospecificity is readily achieved.[5] In contrast, polyolefins with low polydispersity and controlled molecular architecture can be made by the post polymerization technique of hydrogenating anionically polymerized polydienes.[6-8] Two methods of hydrogenation are practiced in this route to polyolefins, homogeneous and heterogeneous. Homogenous hydrogenation uses a soluble transition metal complex to activate the reaction between molecular hydrogen and the carbon-carbon double bond. Homogeneous hydrogenation yields high conversions; however, this method sometimes causes chain scission and often leads to metal contamination due to catalyst extraction difficulties.[9-11] Heterogeneous hydrogenation relies on an insoluble transition metal catalyst to promote hydrogen addition to the unsaturated double bond. This technique yields high conversions and, in certain cases, is more tractable than homogeneous hydrogenation due to minimal chain scission, no metal contamination, and ease of catalyst extraction. However, the reaction rates of the heterogeneous reactions are slower than in homogeneous hydrogenations, and as a result, more vigorous reaction conditions are required. Furthermore, heterogeneous hydrogenation methods have had little success in fully saturating high molecular weight poly(isoprene) and block copolymers containing poly(styrene).[12]

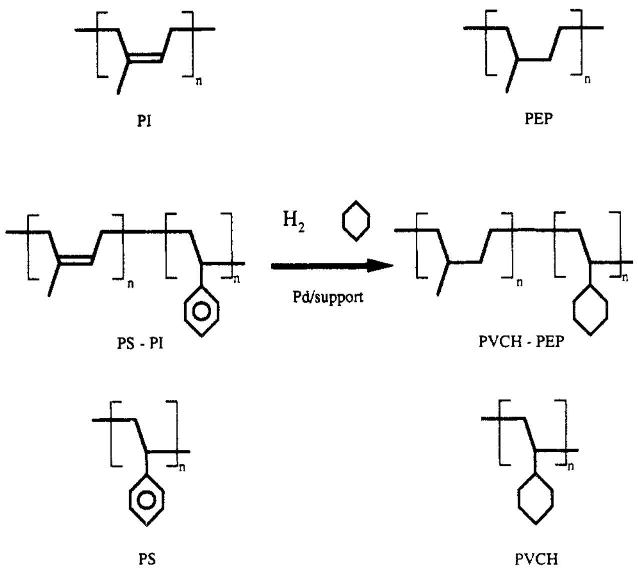

Figure 1. Reaction schematic of the heterogeneous hydrogenation chemistry.

Although many investigators have prepared several types of polyolefins using homogeneous and heterogeneous hydrogenation techniques, very few have dealt with heterogeneous methods in the saturation of poly(styrene) or poly(styrene) containing polymers. In this paper, we report the complete hydrogenation of poly(styrene) and two poly(styrene)-poly(isoprene) (PS-PI) block copolymers to poly(vinylcyclohexane) (PVCH) and poly(vinylcyclohexane)-poly(ethylene-propylene) (PVCH-PEP), respectively, using $CaCO_3$ and $BaSO_4$ supported palladium catalysts at moderate pressures and temperatures. Figure 1 shows a reaction schematic of the hydrogenation chemistry that will be the focus of this publication. In addition, the thermodynamic and dynamic properties of the saturated materials were investigated using dynamic mechanical spectroscopy and differential scanning calorimetry (DSC). To our knowledge the successful use of heterogeneous hydrogenation techniques on poly(styrene)

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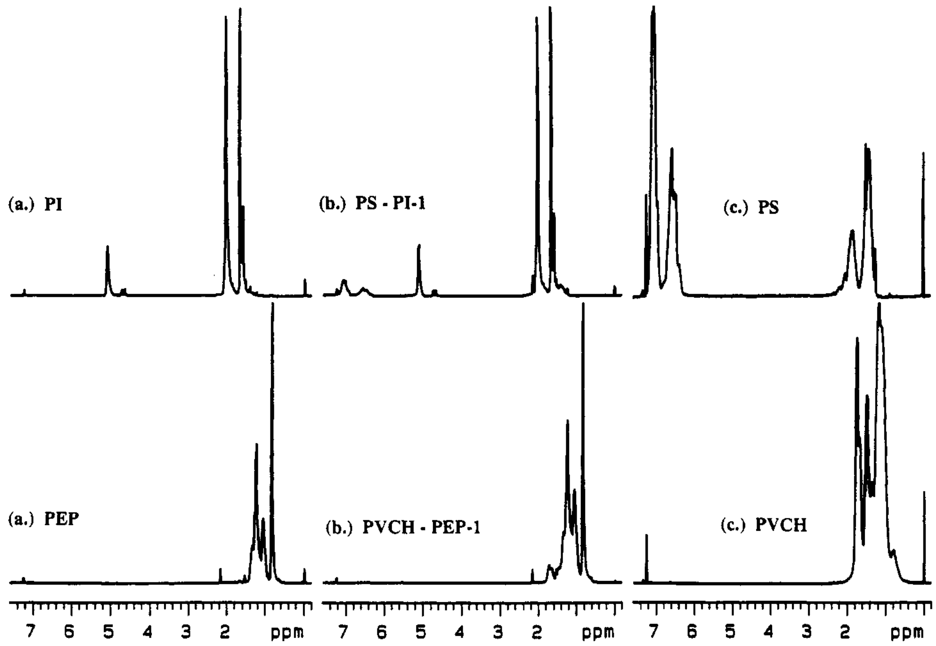

Figure 2. ^{1}H NMR spectra for the unsaturated (top) and saturated (bottom) materials. The olefin and aromatic resonances (4.5-7 ppm) are converted to aliphatic and cyclic resonances after hydrogenation.

based polymers and the physical properties of the saturated materials have not been reported.

Experimental Section

Two monodisperse homopolymers, 1,4-*cis*-poly(isoprene) (PI), atactic poly(styrene) (PS), and two PS–PI diblock copolymers denoted PS–PI-1 and PS–PI-2, were anionically polymerized in cyclohexane using a lithium counterion following established methods.[13] Under these reaction conditions the PI microstructure should be 75% cis-1,4, 20% trans-1,4, and 5% 3,4 addition,[13] these values were confirmed by NMR analysis. Dr. Jimmy Mays kindly provided us with the PS–PI-2 specimen.

Hydrogenation reactions were accomplished using a $CaCO_3$ or $BaSO_4$ supported palladium catalyst (5% Pd, Strem) suspended in cyclohexane under 500 psi of hydrogen. Reaction temperatures were 105 °C for the PI and PS–PI and 140 °C for the PS reactions. The polymer solution concentration and catalyst loading for all cases were 8 g/L and 2.5 g of catalyst/g of polymer, respectively. The reactants and catalyst were vigorously mixed in a newly designed 0.1-L reactor for approximately 12 h. During the course of our research we discovered that mass transfer limitations in commercial reactors play a detrimental role in the heterogeneous catalytic hydrogenation of polymers. In order to circumvent this problem a reactor was designed and developed to minimize mass transfer effects thereby optimizing the product conversion. A description of this equipment will be presented elsewhere.[14]

Gel permeation chromatography (GPC) traces of PI, PS, the PS–PI diblock copolymers, and the saturated homologues were obtained from a Waters 150C instrument fitted with Phenogel columns operated at 25 °C with tetrahydrofuran as the mobile phase. Calibration was accomplished using a set of monodisperse poly(isoprene) (Goodyear Chemical Co.) and poly(styrene) (Pressure Chemical Co.) standards. The volume fraction of PS in the PS–PI block copolymer is reported as the polymerization reaction stoichiometry which was verified by ^{1}H NMR. ^{1}H NMR (Varian VXR-300) spectra were obtained at 25 °C from 10% solutions in $CDCl_3$ with TMS as the internal reference. ^{1}H NMR spectra were used to characterize the polydiene microstructure and the saturation efficiency of the hydrogenation reactions.[15] Molecular characterization results of the four polymers are reported in Table I.

Viscoelastic properties were determined for the PS–PI-1, PS–PI-2, PVCH–PEP-1, and PVCH–PEP-2 block copolymers using a Rheometrics Solids Analyzer (RSA II) operated in the dynamic mode ($0.01 < \omega < 100$ rad/s) with a 0.5-mm shear sandwich test fixture. Glass transition temperatures, T_g, associated with the glassy component in the PS–PI and PVCH–PEP diblock copolymers were determined by measuring G' at a fixed frequency ($\omega_{PS-PI} = 0.08$ rad/s, $\omega_{PVCH-PEP} = 1$ rad/s) and 2% strain amplitude while the specimens were slowly heated (1 °C/min) in nitrogen. The order–disorder transition temperature, T_{ODT}, was determined by measuring G' at a fixed frequency and strain amplitude ($\omega = 0.5$ rad/s, 2%) while the specimens, were slowly heated (1 °C/min). Selected isothermal frequency scans were also acquired for the PS–PI-2 and PVCH–PEP-2 specimens. The glass transition temperatures for the homopolymers and block copolymers were also determined by differential scanning calorimetry (DSC) using a Perkin-Elmer System DSC-7. The test specimens (15 mg) were heated from 60 to 200 °C at a rate of 10 °C/min.

Table I. Polymer Characterization Results

polymer	wt % PI	10^3M_w	M_w/M_n
PI	100	50	1.05
PS–PI-1	75	90	1.06
PS–PI-2	50	18	1.06
PS	0	105	1.05

Results

Four monodisperse polymers, PI, PS–PI-1, PS–PI-2, and PS, were hydrogenated using two different palladium supported catalysts, Pd–$CaCO_3$ and Pd–$BaSO_4$, at two temperatures, 105 and 140 °C. PI and PS were fully saturated to poly(ethylene–propylene) (PEP) and poly(vinylcyclohexane) (PVCH) using either catalyst at 105 and 140 °C, respectively. However, PS–PI-1 at 105 °C showed different results with each catalyst support. Pd–$CaCO_3$ yielded incomplete saturation, while Pd–$BaSO_4$ yielded a fully saturated material. PS–PI-2 was fully saturated utilizing the optimized reaction conditions in the PS–PI-1 case (i.e. Pd–$BaSO_4$, 105 °C).

^{1}H NMR was used to characterize the saturation efficiency of the hydrogenation reaction. Upon hydrogenation, the resonances associated with olefin (4-5.5 ppm) and aromatic (6-7 ppm) protons are converted to aliphatic (1-2 ppm) and cyclic (1-2 ppm) protons. Thus the saturation efficiency can be measured by analyzing the remaining olefin and aromatic proton resonances.[16] Figure 2 shows the ^{1}H NMR spectra prior to and following the hydrogenation reaction for all three polymers under

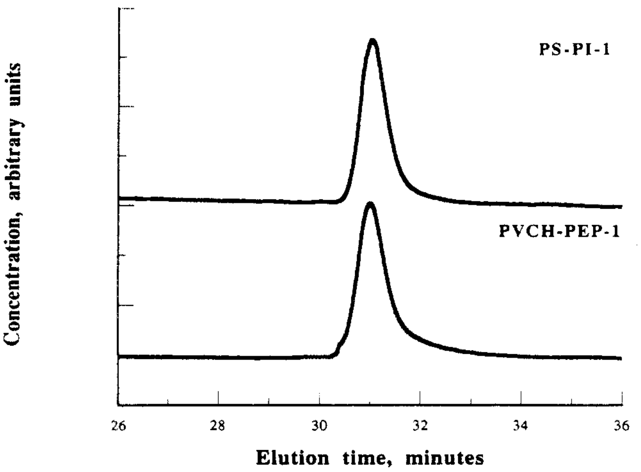

Figure 3. Gel permeation chromatographs of PS–PI-1 and PVCH–PEP-1. The molecular weight distribution remains monodisperse following hydrogenation, verifying the absence of chain scission.

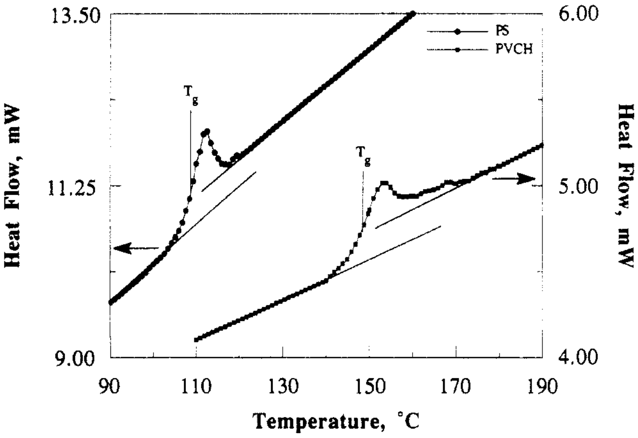

Figure 4. Differential scanning calorimetry traces for poly(styrene) (PS) and poly(vinylcyclohexane) (PVCH) homopolymers obtained at a heating rate of 10 °C/min. The T_g for PS was determined to be 108 °C, while the hydrogenated product, PVCH, possesses a T_g of 148 °C.

conditions leading to complete saturation. The figure reveals the disappearance of the aromatic and olefin protons following the reaction. These ^{1}H NMR spectra confirm >99% saturation efficiency for all three polymers.

GPC traces were obtained from the precursors and the saturated products. Figure 3 shows a representative example (PS–PI-1) of a GPC trace taken prior to and following the hydrogenation reaction, verifying the absence of carbon–carbon bond cleavage.

DSC was used to determine T_g for the PS and PVCH homopolymers, as shown in Figure 4. Defining T_g as the midpoint of the rise in the heat capacity, we find T_g = 108 and 148 °C for PS and PVCH, respectively. Dynamic mechanical spectroscopy was used to establish T_g for the glassy component in the strongly microphase separated PS–PI-1 and PVCH–PEP-1 diblock copolymers (see below) since this transition is somewhat difficult to establish by DSC alone (not shown). Representative isochronal temperature scans of the dynamic elastic modulus G', are presented for PS–PI-1 and PVCH–PEP-1 in Figure 5. Based on the midpoint between the two inflections in G' that occur at the glass transition, T_g was graphically determined to be 101 °C for PS in PS–PI-1 and 141 °C for PVCH in PVCH–PEP-1. These values are only slightly lower than those determined for the homopolymers but reflect the same overall difference of 40 deg between the aromatic and aliphatic species.

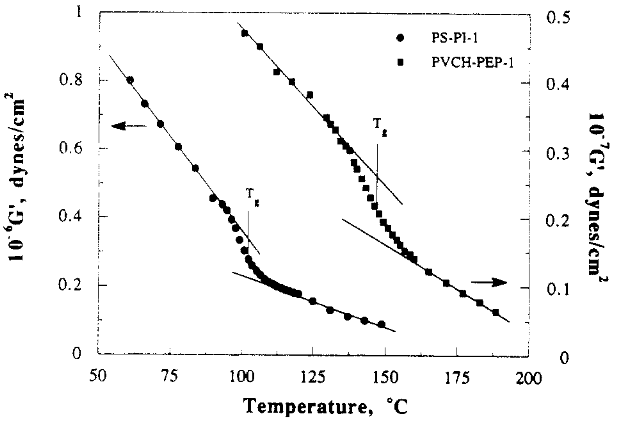

Figure 5. Isochronal temperature scans (2% strain amplitude) of the dynamic elastic modulus, G', for strongly microphase separated PS–PI-1 (ω = 0.08 rad/s) and PVCH–PEP-1 (ω = 1 rad/s). The T_g for the glassy components was determined for PS as 101 °C and for PVCH at 141 °C.

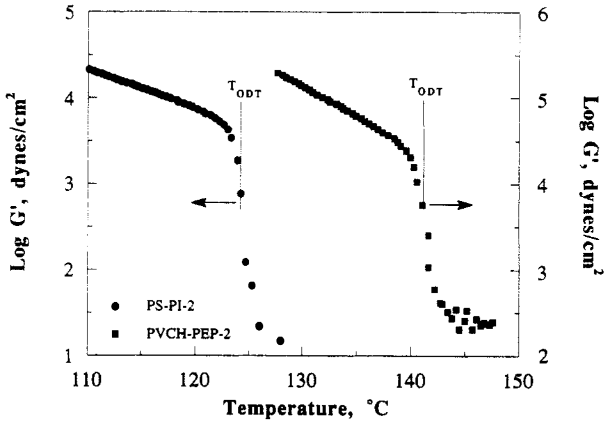

Figure 6. Temperature dependence of the low frequency dynamic elastic modulus for the PS–PI-2 and PVCH–PEP-2 diblock copolymers (2% strain amplitude, ω = 0.5 rad/s). The order–disorder transition temperature, T_{ODT}, is determined as the discontinuity in G'; for PS–PI-2 T_{ODT} = 124 ± 2 °C and for PVCH–PEP-2 T_{ODT} = 140 ± 2 °C.

Order–disorder transition (ODT) temperatures were determined following the procedure established in earlier studies.[4,17–19] Low frequency isochronal dynamic elastic shear moduli were obtained while a specimen was slowly heated. At the ODT the elasticity drops discontinuously, signifying the "melting" of the ordered state to the disordered state. PS–PI-1 and PVCH–PEP-1 displayed rheological behavior characteristic of microscopically ordered materials over the entire experimental temperature window, indicating T_{ODT} > 300 °C for both materials. The results of the measurements for PS–PI-2 and PVCH–PEP-2 are shown in Figure 6. In both cases the drop in G' occurs over a 2-deg interval, providing an accurate determination of T_{ODT}. For PS–PI-2 T_{ODT} = 124 ± 2 °C, while the hydrogenated homologue, PVCH–PEP-2, is characterized by T_{ODT} = 141 ± 2 °C.

The dynamic mechanical properties of PS–PI-2 and PVCH–PEP-2 were also investigated using isothermal frequency scans. In Figures 7 and 8 the representative dynamic elastic (G') and loss (G'') data for PS–PI-2 and PVCH–PEP-2 are shown. These data have been temperature and density corrected[20] and time–temperature superpositioned[21] using high frequency ($\omega > \omega_c$) branches of the spectra based on a common reference temperature (T_0 = 120.7 °C). The crossover frequencies ω_c' and ω_c'' are identified in Figures 7 and 8, respectively, separating the low and high frequency viscoelastic regimes. At high

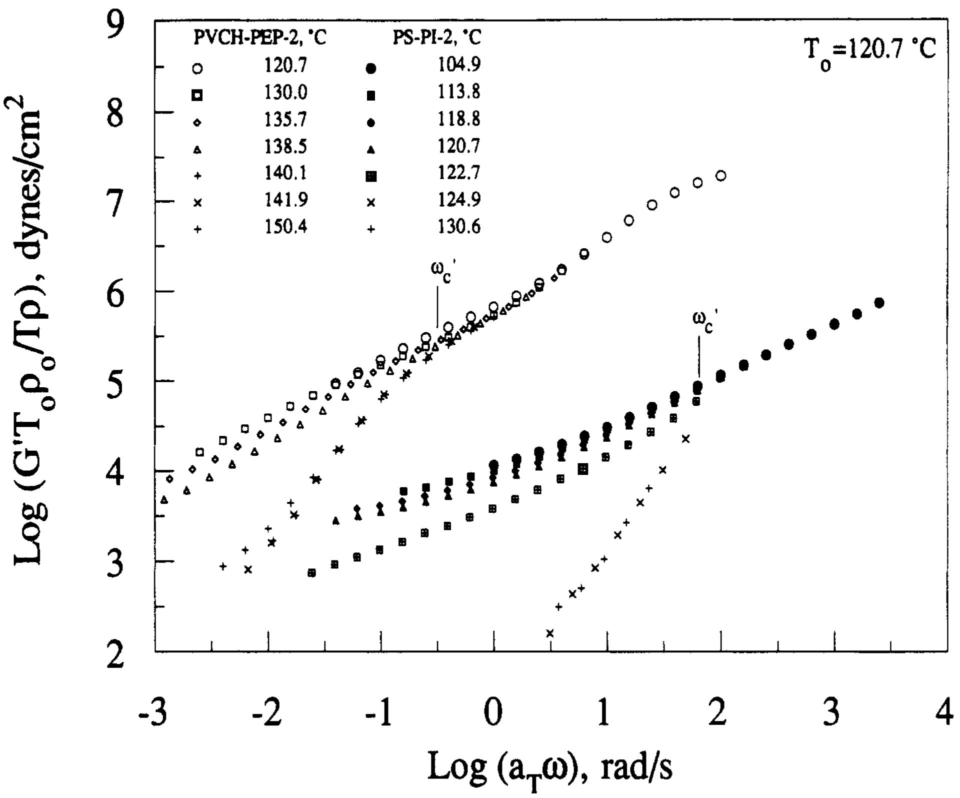

Figure 7. Reduced-frequency plot for dynamic elastic data obtained for PS–PI-2 and PVCH–PEP-2. The G' data are temperature and density corrected and time–temperature superpositioned to 120.7 °C using the high frequency portion ($\omega' > \omega'_c$) of the data. The G' spectra for PS–PI-2 occur at higher frequencies and lower moduli than those for PVCH–PEP-2 due to the decrease in entanglement molecular weight upon saturation of PI.

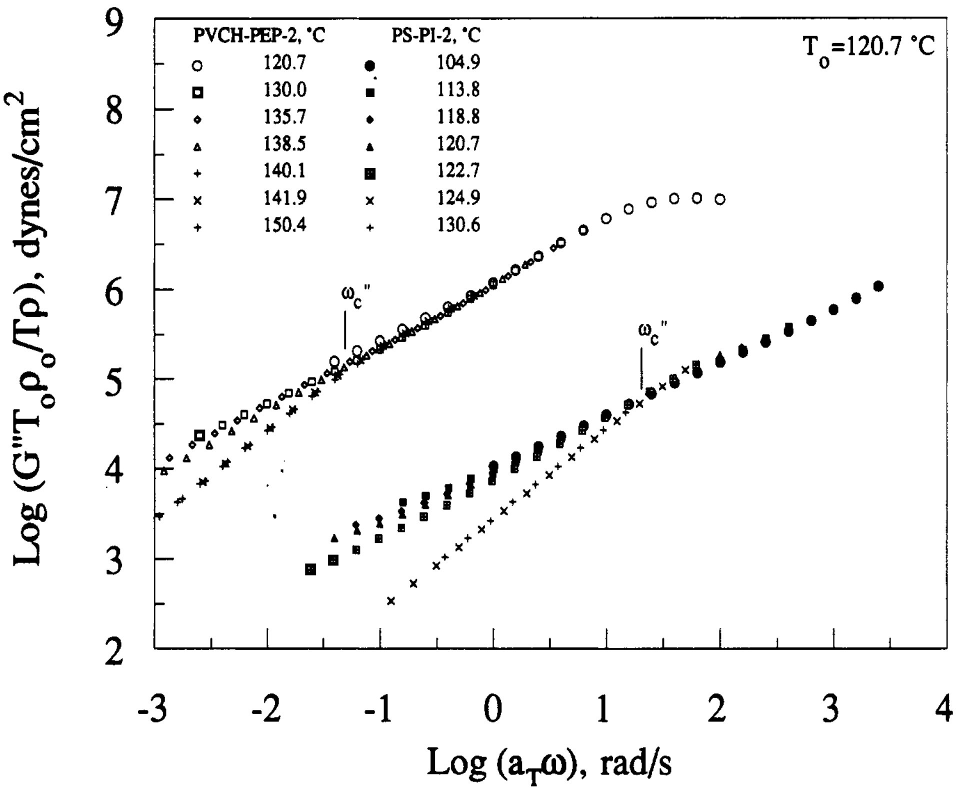

Figure 8. Reduced-frequency plot for dynamic loss data obtained for PS–PI-2 and PVCH–PEP-2. The G'' data are temperature and density corrected and time–temperature superpositioned to 120.7 °C using the same shift factors employed in Figure 7.

frequencies ($\omega > \omega_c$) the response is dominated by entanglement effects which are not affected by microdomain structure. At low frequencies ($\omega < \omega_c$) the rheological response is governed by the microdomain structure, presumed to be lamellar for these symmetric specimens. For PS–PI-2 and PVCH–PEP-2 the low frequency regimes display ordered and disordered characteristics; furthermore, the drops in G' and G'' occur at the same temperature, as shown for the isochronal temperature scans, verifying our assignment of T_{ODT}. The G' and G'' values shown in Figure 7 and 8 for PVCH–PEP-2 occur at lower frequencies and higher moduli than those for PS–PI-2. We attribute this result to a decrease in entanglement molecular weight upon saturation.

Discussion

The hydrogenation of polymers is an old technique that has recently become popular in polymer synthesis. In the past decade many investigators have utilized fully saturated polymers to study various topics in polymer science including rheology,[18] chain dimensions,[7] and block copolymer thermodynamics.[2] However, to our knowledge very few studies have investigated the key variables that effect the hydrogenation chemistry.

Two hydrogenation techniques, heterogeneous and homogeneous, have been shown to be effective methods for attaining saturated polymers. In a study comparing these techniques the homogeneous method led to the incorporation of metal fragments into the polymer chain.[9] Furthermore, viscosity measurements verified chain scission was significant. Heterogeneous hydrogenation was the only technique that alleviated these problems and resulted in a fully saturated material. As a result, heterogeneous hydrogenation has become the method of choice for synthesizing saturated polymeric materials for use in basic research. However, this technique currently finds limited commercial applications.

Heterogeneous hydrogenation has been used to saturate many types of polydienes including 1,4- and 3,4-poly(isoprene)[8] and 1,2- and 1,4-poly(butadiene).[22] The reaction conditions are usually those established by the pioneering work of Rachapudy et al.:[9] 70 °C, 500 psi, Pd–$CaCO_3$ in a commercial Parr reactor. Poly(butadiene)s with molecular weights up to 5×10^5 can be completely saturated[23] at these conditions while poly(isoprene)s with molecular weights greater than about 2×10^5 are only partially saturated.[12] Evidently, the methyl group on the PI plays a role in the reaction sequence that slows the kinetics of the reaction or otherwise deactivates the catalyst.

The synthesis of PVCH using heterogeneous hydrogenation techniques has only been studied in a few instances, and to our knowledge the synthesis of PVCH–PEP has never been reported. In all cases that report the saturation of PS, the reaction conditions are much harsher (200 °C, 2000 psi)[24,25] than those in polydiene hydrogenations and often lead to chain scission. Four previous investigators have reported the T_g for PVCH as 80 °C,[26,27] 119 °C,[28] and 138 °C.[24] Comparing our result of 140 °C it is clear that chain scission played a role in two of the previously reported experiments. Therefore, while the benefits of an increased T_g in PVCH are apparent, reaction conditions must be conservative in order to avoid large scale degradation.

The heterogeneous catalytic hydrogenation of polymers is a complex function of several reaction variables. In a comprehensive study currently being conducted in our laboratory, we have identified five factors that play a significant role in the hydrogenation process: (i) mass transfer limitations, (ii) reaction temperature, (iii) catalyst support, (iv) polymer type, and (v) polymer molecular weight. Preliminary experiments demonstrate that varying these variables has a profound impact on the overall saturation efficiency. These experiments have also identified reaction conditions that lead to the complete saturation of high molecular weight PI ($M_n \approx 8.5 \times 10^5$).[1] This molecular weight is significantly higher than that achievable using the conventional conditions and led us to investigate PS containing polymers. A more complete discussion of our findings regarding these hydrogenation reactions will be presented in a future publication.[14]

Returning to the presently reported work, PI was hydrogenated at 105 °C, 500 psi for 12 h. In other experiments we have demonstrated that room temperature reactions with PI for 1 h are sufficient for complete reaction. Therefore, the reported conditions for PI are conservative and are used for comparison. As previously mentioned, the hydrogenation of PS containing polymers required more vigorous reaction conditions than those of the polydienes. However, the temperatures and pressures in our study are significantly lower than those in previous PS hydrogenations. PS was fully saturated using both support materials at 140 °C, while PS–PI showed different results on each support at 105 °C. The following discussion offers a preliminary analysis of the reported results.

Interpretation of the temperature effects on the saturation efficiency relies on understanding the temperature dependence on each step of the hydrogenation process. The hydrogenation mechanism consists of five steps: diffusion, adsorption, reaction, rearrangement, and desorption. Clearly, temperature influences each step of this process. However, separating and identifying the temperature effect on each step cannot be accomplished with these experiments. In the case of PS at 105 °C, evidently the entire process of adsorption, reaction, and desorption is too slow to proceed to completion given the reaction time. However, at 140 °C the reaction process is successfully completed in the given reaction time. A possible scenario for the complex sequence may be that at 105 °C the chains are becoming immobile on the metal surface, slowing the processes of rearrangement and desorption and thereby causing deactivation.[29] At 140 °C we speculate that some or all of the barriers are reduced and the PS adsorbs, reacts, rearranges, and desorbs, allowing other chains to interact with the surface.

The PS–PI-1 result verifies that some difference in the catalyst support has an effect on the kinetics of hydrogenation. An obvious difference between Pd–$CaCO_3$ and Pd–$BaSO_4$ is the role of the energetics of the support materials on polymer adsorption. The PS–PI-1 result on Pd–$CaCO_3$ suggests that the strongly adsorbing aromatic character of the PS blocks excludes the PI blocks from the surface, causing deactivation of the hydrogen addition to the polymer. In contrast in the case of PS–PI-1 using Pd–$BaSO_4$ the PS blocks do not cause deactivation; thus all the reactants can be replaced at the metal surface, resulting in a completely saturated product. A delicate balance between adsorption and desorption energy is required for a sufficient turnover and reaction of the polymer chains. We feel this delicate balance can be affected by changing the energetics of the support and hence could explain the experimental results reported.

Our principal objective in optimizing the heterogeneous hydrogenation chemistry is simply to create new, model polymer systems. PVCH synthesized via anionic polymerization followed by heterogeneous hydrogenation yields monodisperse, saturated materials with a controlled molecular architecture. These materials also possess greater stability toward oxidative and thermal degradation and offer a higher use temperature associated with the increased T_g. Incorporation of PVCH into block copolymers would expand the use of conventional thermoplastic elastomers into higher temperature applications. A key element in the success of PVCH–PEP block copolymers is the magnitude of the segment–segment interaction parameter, χ. Group contribution calculations show $\chi_{PS-PI} = 0.118$ while $\chi_{PVCH-PEP} \approx 0.0175$ at 27 °C.[30] This analysis would lead one to conclude that PVCH–PEP block copolymers would not constitute commercially competitive thermoplastic elastomers since nearly 7 times the molecular weight necessary to achieve desirable properties with PS–PI materials (e.g. Kraton) would be required.[31] However, we have demonstrated that PS–PI-2 has an T_{ODT} at 124 °C while the saturated homologue, PVCH–PEP-2, disorders at 141 °C. Therefore $\chi_{\mathrm{PVCH-PEP}}$ does not decrease upon hydrogenation, as predicted by group contribution, but instead slightly increases. Thus the PVCH–PEP block copolymers will segregate into glassy and rubbery domains that are characteristic of PS–PI–PS thermoplastic elastomers. The morphological characteristics and the properties of the PVCH–PEP thermoplastic elastomers will remain intact, while the PVCH will enhance the stability and increase the usage temperature. A study comparing the PVCH and PS based thermoplastic elastomers is currently being conducted in our laboratory, and the results will be reported in a future publication.[14]

A likely explanation for the higher than expected $\chi_{\mathrm{PVCH-PEP}}$ relies on a recent analysis by Bates et al.[32] The segment–segment interaction parameter, χ, consists of several terms that accommodate the excess free energy of mixing. Bates et al. have shown that for polyolefins the difference in statistical segment length, Δa, between distinct monomer units in block copolymers (here a is based on a common segment volume), as well as in homopolymer mixtures, is closely correlated with the χ parameter. The argument originates from the ability for each block to occupy space in the melt. If Δa is large, a frustrated situation, the two blocks must accommodate this discrepancy by conformational adjustments that cost entropy, leading to a larger χ parameter.

The a values for all four polymers discussed here have been measured. For PS, PI, and PEP a = 5.5,[20] 6.0,[20] and 7.2 Å,[33] respectively, based on a common segment volume of 1.08×10^{-22} cm^3. We have recently measured $a = 5.0 \pm 0.1$ Å for PVCH using SANS measurements.[34] Therefore, hydrogenation decreases the statistical segment length by about 9%. As a result, $\Delta a/a$ increases from 0.087 (PS–PI) to 0.361 (PVCH–PEP). We believe this increase in conformational asymmetry makes $\chi_{\mathrm{PVCH-PEP}}$ larger than that predicted by group contribution methods. Additional experiments using block copolymers containing PVCH and other polyolefins possessing a range of statistical segment lengths support this interpretation and will be presented in a separate report.[14]

Summary

The heterogeneous catalytic hydrogenation of poly(isoprene) (PI), poly(styrene) (PS), and PS–PI diblock copolymers was performed using two different supported palladium catalysts, Pd–CaCO$_3$ and Pd–BaSO$_4$. Both catalysts behave similarly in the case of PI and PS, although differences in effectiveness were observed with one of the PS–PI diblock copolymers. The Pd–BaSO$_4$ catalyst appears to be somewhat more effective than Pd–CaCO$_3$. Hydrogenated PS, denoted poly(vinylcyclohexane) (PVCH) was successfully prepared using some of the mildest reaction conditions ever reported. The T_g of PVCH was found using DSC and dynamic mechanical spectroscopy to be 140 °C. A fully saturated PVCH–PEP diblock copolymer was also produced using heterogeneous hydrogenation techniques. The thermodynamics of PS–PI and the saturated homologue, PVCH–PEP, were compared using dynamic mechanical spectroscopy. The order–disorder transition temperature for PVCH–PEP was 17 deg higher than that for the unsaturated precursor. This observation confirms that $\chi_{\mathrm{PVCH-PEP}} \approx \chi_{\mathrm{PS-PI}}$, which is not predicted by group contribution arguments. This larger than predicted $\chi_{\mathrm{PVCH-PEP}}$ can be qualitatively explained using a recent hypothesis regarding differences in statistical segment length between monomer units in the diblock copolymer. We conclude that the incorporation of PVCH into thermoplastic elastomers would offer superior stability, higher use temperatures, and sufficient demixing to make these materials potentially useful in many applications.

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