High Glass Transition Temperature Polyolefins Obtained by the Catalytic Hydrogenation of Polyindene

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ABSTRACT: Polyindene was prepared by the controlled cationic polymerization of indene initiated with cumyl methyl ether/$TiCl_4$ in CH_2Cl_2 at −65 °C. The number-average molecular weight was controlled by the ratio of monomer to cumyl methyl ether; polydispersity indicies ranged from 1.8 to 3. Polyindene samples prepared by this technique were characterized by ^1H and ^{13}C NMR spectroscopy, and a corrected assignment of chemical shifts in these spectra was made with respect to previous literature reports. Polyindene samples ranging from $M_n = 5$ to $M_n = 70$ kg/mol were hydrogenated to high levels of phenyl ring saturation using a heterogeneous catalyst consisting of silica-supported Pt. Characterization of polyindene and its hydrogenation product by size exclusion chromatography using a light-scattering detector showed that the hydrogenation proceeded without change in the degree of polymerization. The relationship between molecular weight and the glass transition temperature for these polymers was established, and T_g values of 207 °C for polyindene and 268 °C for hydrogenated polyindene were predicted in the limit of infinite molecular weight.

Introduction

The polymerization of indene (and copolymerization with its ethereal analogue coumarone) is among the oldest known polymerization reactions; commercial production dates to at least 1917.[1,2] Early polymerization reactions initiated with sulfuric acid or Lewis acids such as $SnCl_4$ and $SbCl_5$ provided low molecular, oligomeric materials.[3,4] The ability to obtain high molecular weight polyindene (PIn) through the use of Lewis acid catalysts in high dielectric constant solvents (notably $TiCl_4$ in CH_2Cl_2) at low temperatures was demonstrated by Sigwalt.[5] Control of the initiation process in these polymerizations was later brought about by the use of a co-initiator, an organic species designed to react with the Lewis acid to give a stable carbocation that in turn initiates the polymerization. A variety of these agents have been examined with regard to the polymerization of indene.[6−9] Recent work has focused on the use of cumyl methyl ether/$TiCl_4$[10] and cumyl chloride/$TiCl_4$[11] to initiate indene polymerization in methylene chloride at low temperature. These systems are characterized by rapid polymerization rates and low chain transfer to monomer; in addition, a linear relationship between M_n and monomer conversion has been observed.[12] Variations on this chemistry that employ difunctional initiator fragments have been used to prepare α,ω-dichloropolyindenes[13] and poly(indene-*b*-isobutylene-*b*-indene)[14] structures. The preparation of discrete structures along with the ability to control molecular weight by control of the initiator/monomer ratio suggests that, at least under some conditions, the cationic polymerization of indene is at least controllable and perhaps "living".[15]

The advent of efficient catalysts for the hydrogenation of polystyrene has led to renewed interest in this transformation.[16−18] The saturation of polystyrene and polystyrene containing block copolymers provides polymers with microphase-separated morphologies.[19] Polyolefin structures of this type are challenging to prepare directly from monomeric species and have potential utility in a variety of applications.[20] Attempts to increase the heat distortion characteristics of these saturated hydrocarbon polymers have focused on the hydrogenation of poly(α-methylstyrene) (PAMS).[16,21] A recent effort to hydrogenate narrow polydispersity PAMS and block copolymers containing PAMS showed that, for molecular weights higher than a few thousand, degradation of molecular weight and increase in polydispersity always accompanied saturation.[22] This difficulty can be mediated by copolymerizing styrene with α-methylstyrene, as the resultant copolymer can be saturated without degradation.[22]

The underlying process that leads to chain cleavage in PAMS has not been elucidated. High molecular weight PS (ca. 6×10^5 kg/mol) can be hydrogenated without displaying any degradation. In the case of PAMS, control reactions have suggested that simple thermal depolymerization is not occurring; subjecting monodisperse polymer to the reaction conditions but without catalyst leads to recovery of unchanged starting material. Work with PAMS of various molecular weights shows that polymers with molecular weights up to 2.5 kg/mol can be hydrogenated without degradation.[22,23] The presence of the quaternary center at the benzylic position in PAMS may play a role; either this backbone structure is not stable to the hydrogenation conditions, or some intermediate forms that can undergo degradative side reactions leading to disruption of the backbone structure. Alternatively, the relative bulk of the hydrogenated PAMS structure may be such that it cannot withstand this steric congestion and degrades to relieve the strain imposed by the bulky substituents.

The purpose of this work was to prepare a PIn of relatively high molecular weight and to hydrogenate

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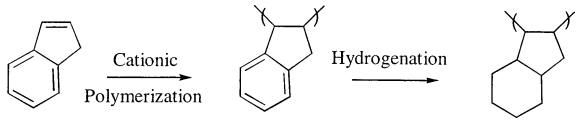
Scheme 1



that polymer using a heterogeneous Pt catalyst on a porous silica support (Scheme 1). The hydrogenation of low molecular weight PIn has been reported,[24] but we are not aware of any detailed study of the hydrogenation of high molecular weight polymer or characterization of the saturated polymer. In particular, we were interested in determining whether this structure could be hydrogenated without chain degradation. Like PAMS, backbone motion is restricted; the PIn backbone is severely constrained by the incorporation of the cyclopentane ring into the polymer chain. This restricted motion results in a very "stiff" polymer chain with a high glass transition temperature and relatively long carbon rotational correlation times τ_c (short spin−lattice relaxation times T_1).[25] Unlike PAMS, however, there is no quaternary carbon in the backbone. This work should elucidate the detailed mechanistic features of the saturation reaction and address the question of whether the quaternary center in the PAMS backbone, or the constrained backbone structure, limits the ability to perform hydrogenation chemistry without chain degradation.

Experimental Section

Materials. Methylene chloride (HPLC grade, Mallinckrodt) was distilled away from CaH_2 prior to use. Indene (98%, Aldrich) was doubly distilled from CaH_2 prior to use. Cumyl methyl ether was prepared from α-methylstyrene and methanol using the method of Ziegler and co-workers;[26] careful fractional distillation was required to isolate the ether, and the material used in the cationic polymerizations contained traces of α-methylstyrene (4%) that was detectable by ^{1}H NMR. The ether was distilled away from CaH_2 prior to use. $TiCl_4$ (Aldrich, 99.9%) was used as obtained. Silica-supported Pt catalyst was obtained from the Dow Chemical Company and was used as received. Ultrahigh-purity grade (99.9995%, Air Products and Chemicals) hydrogen gas was used without further purification.

Characterization. NMR spectra were obtained using a Varian VXR-300 NMR spectrophotometer using $CDCl_3$ solutions (60 mg/mL for ^{1}H spectra and 140 mg/mL for ^{13}C spectra). Size exclusion chromatography (SEC) was performed using a Hewlett-Packard 1100 series liquid chromatograph with THF as the mobile phase. This SEC was equipped with three Jordi divinylbenzene columns (pore sizes 500, 10^3, and 10^4 Å; column temperature 40 °C), and output was detected with an HP1047A differential refractive index detector, an eluent flow rate of 1 mL/min, and a 50 μL injection loop. This instrument was calibrated using narrow polydispersity polystyrene standards (Polymer Laboratories) with molecular weights ranging from 5000 to 1×10^6 g/mol. UV analyses were performed using a Spectronic Instruments Genesys 5 spectrophotometer. SEC/light scattering was performed in THF at an eluent flow rate of 1 mL/min using an Alltech 426 HPLC pump with a 100 μL injection loop, a Wyatt Technology Corp. Dawn DSP-F laser photometer, and a Wyatt Technology Corporation Optilab DSP interferometric refractometer with 3 Phenomonex Phenogel columns (pore sizes 5×10^3, 5×10^4, and 5×10^5 Å) at ambient temperature. The differential refractive index increment (dn/dc) was determined by pumping THF solutions of PIn and hydrogenated PIn of known concentration through the Wyatt Technology Corp. Optilab DSP interferometric refractometer, with a wavelength of 633 nm and a temperature of 40 °C throughout the measurement. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer Pyris 7 DSC that was calibrated using high purity indium at a heating rate of 10 °C/min. Preliminary heating scans were performed to determine the position of the T_g; final scans were performed at 10 °C/min after heating the sample above T_g to remove the influence of thermal history on the DSC analysis.

Table 1. Molecular Characteristics of Cationically Prepared Polyindene

aim[a]		SEC (kg/mol)[b]			light scattering (kg/mol)			%	T_g
(kg/mol)	[M]	M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	yield	(°C)
5	1.03	3.2	8.8	2.76	5.1	10.0	1.97	75.0	178
9.9	0.98	12.8	38.7	3.04	17.1	45.4	2.65	83.0	197
20	1.25	19.4	35.7	1.84	26.4	41.0	1.58	95.4	203
50	0.79	43.4	92.0	2.12	59.2	108	1.82	93.8	204
65.6	1.03	57.5	154	2.68	69.5	170	2.45	87.2	204

[a] Calculated from mass of indene with respect to moles of methyl cumyl ether. [b] Compared to polystyrene standards.

Cationic Polymerization. In a typical polymerization, a 250 mL three-neck round-bottom flask was equipped with a magnetic stirring bar, a gas inlet adapter, and a thermometer. This apparatus was heated in a convection oven and then removed and was allowed to cool under a stream of dry nitrogen. The flask was capped with a septum and attached to a nitrogen bubbler with a Firestone valve. Then, 150 mL of methylene chloride was transferred to this flask by cannula. Following this, 17.4 g of indene (17.5 mL, 150 mmol) was added using a gastight syringe, and 0.l3 g of cumyl methyl ether (0.87 mmol) was added with a gastight syringe. This mixture was stirred, and the flask was placed in a dry ice/2-propanol bath. Polymerization was initiated at −65 °C by the addition of 0.1 mL of $TiCl_4$ ($d = 1.73$ g/cm^3, 0.17 g, 0.9 mmol) using a gastight syringe. The solution instantly became deep red and the temperature increased by 10 °C in less than 30 s. The polymerization was allowed to proceed for 45 min. After this time, the reaction was terminated by the addition of 1 mL of deoxygenated methanol, and the solution became colorless. The polymer was isolated by slow addition of the polymer solution into 800 mL methanol using a disposable pipet. The polymer was a white powder, and was collected in a Buchner funnel and was dried in a vacuum oven at 110 °C. The isolated polymer weighed 16.6 g. UV analysis: λ_{max} 256 nm in THF solution. The differential refractive index increment (dn/dc) was obtained by measuring the refractive index difference between a series of samples ranging in concentration between 0.05 and 1.0 mg/mL in THF. The dn/dc for polyindene was found to be 0.24 mL/g.

Hydrogenation. A typical hydrogenation reaction was performed in a 300 mL Pressure Products Industries high-pressure reactor equipped with baffles and a gas dispersion impeller and stirred with a Dyna/Mag magnetic drive mixer at a stirring rate of 1500 rpm. A solution of 3.0 g of polyindene was dissolved in 25 mL of toluene, and was added to the reactor. This solution was diluted with 150 mL of cyclohexane, and the reactor was sealed. The solution was purged with Ar three times with stirring. The reactor was reopened and a slurry containing 0.6 g of Pt/SiO_2 catalyst in 25 mL of cyclohexane was added to the reactor. The reactor was sealed and purged three times with 60 psig Ar, then pressurized to 800 psig with H_2 and sealed. The reactor was heated to 150 °C over 30 min. During this time the pressure was returned to 800 psig of H_2 when it dropped below 500 psig. The hydrogenation was then allowed to proceed for 16 h in the sealed reactor. The excess hydrogen was vented and the reactor was cooled to room temperature. The polymer solution was separated from the catalyst using a Millipore high-pressure filter with a 0.22 μm porous Teflon filter. The hydrogenated polymer was isolated by pouring the filtered solution directly into 600 mL of methanol. The polymer was isolated in a Buchner funnel, and the polymer was dried in a vacuum oven at 120 °C for 4−8 h. The dn/dc of this polymer was measured as 0.153 mL/g.

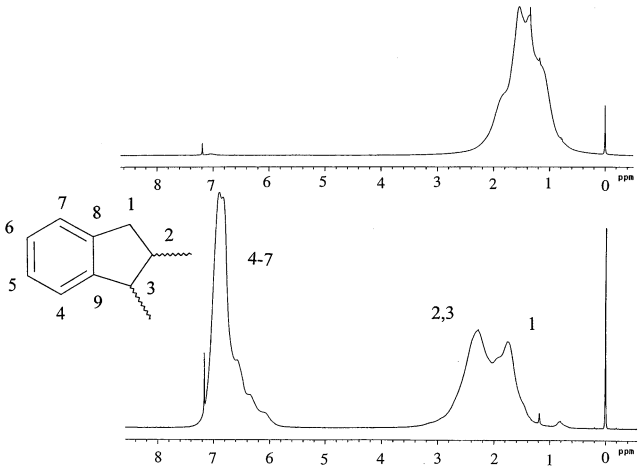


Figure 1. ^{1}H NMR spectra of polyindene (bottom) and hydrogenated polyindene (top) in $CDCl_3$.

Results and Discussion

Polyindene Synthesis and Characterization. A series of polyindenes was prepared by cationic polymerization initiated with cumyl methyl ether and $TiCl_4$. Data obtained from the characterization of these polymers are given in Table 1. Control of molecular weight was attempted by varying the ratio of monomer to initiating species (an equimolar combination of cumyl methyl ether and $TiCl_4$). Both apparent molecular weight (compared to polystyrene standards) and absolute molecular weight (via multiple angle light-scattering detection) were obtained for these samples. The number-average molecular weights of these polymers was uniformly slightly higher than those predicted from the ratio of monomer to cumyl methyl ether/$TiCl_4$; this may be due to deactiviation of some of the initiating species prior to initiation. Polymerization reactions were performed at monomer concentrations of about 1 M (Table 1), and the initiator concentration was varied as required to provide the desired molecular weight. The molecular weight distributions were monomodal, and polydispersities were consistent with previous reports, ranging from 1.8 to 3.0. The relatively broad polydispersity observed for this polymerization system (in the absence of chain transfer and with a sufficiently large R_i/R_p)[10] has been attributed to exchange between active (a carbocation$-TiCl_4OCH_3^-$ ion pair) and inactive (chlorinated) chain ends at rates slower than polymerization. It may also be that the extremely fast rate of propagation brings about deviation from a Poisson type distribution ($1 + 1/\nu$, where ν is the number-average degree of polymerization) resulting from inhomogeneities in the polymerization medium, such that not all chain ends incorporate the same amount of monomer.[27] Apparent molecular weights obtained by SEC analysis and compared to polystyrene standards are consistently lower than the actual molecular weight determined by SEC with light-scattering detection.

Polyindene samples were also characterized by spectroscopic analysis. Figure 1 shows the ^{1}H NMR spectrum of polyindene (M_n = 26.4 kg/mol) obtained in $CDCl_3$ at room temperature, and Figure 2 shows the ^{13}C NMR spectrum.[28] The ^{1}H spectrum shows a single broad resonance in the aromatic region (6.5−7.2 ppm) due to the four aryl protons; the aliphatic protons on the cyclopentane ring appear as two broad, unresolved resonances centered at 2.3 and 1.7 ppm. The two methyl groups arising from the initiating cumyl fragment are also clearly visible at 0.8 ppm. Previous workers[8] have assigned the methine protons to both the 2.3 and 1.7 ppm multiplets and the methylene to a sharp single resonance at 1.5 ppm. High-temperature NMR analysis (100 °C in 1,1,2,2-tetrachloroethane-d_2) at lower polymer concentrations narrows the line widths and allows for a better estimate of the area due to these resonances, suggesting that each of these peaks are equivalent to two protons. We therefore assign the broad peak at 2.3 ppm to the two methine protons on the cyclopentane rings, and the peak at 1.7 ppm to the two protons from the methylene.

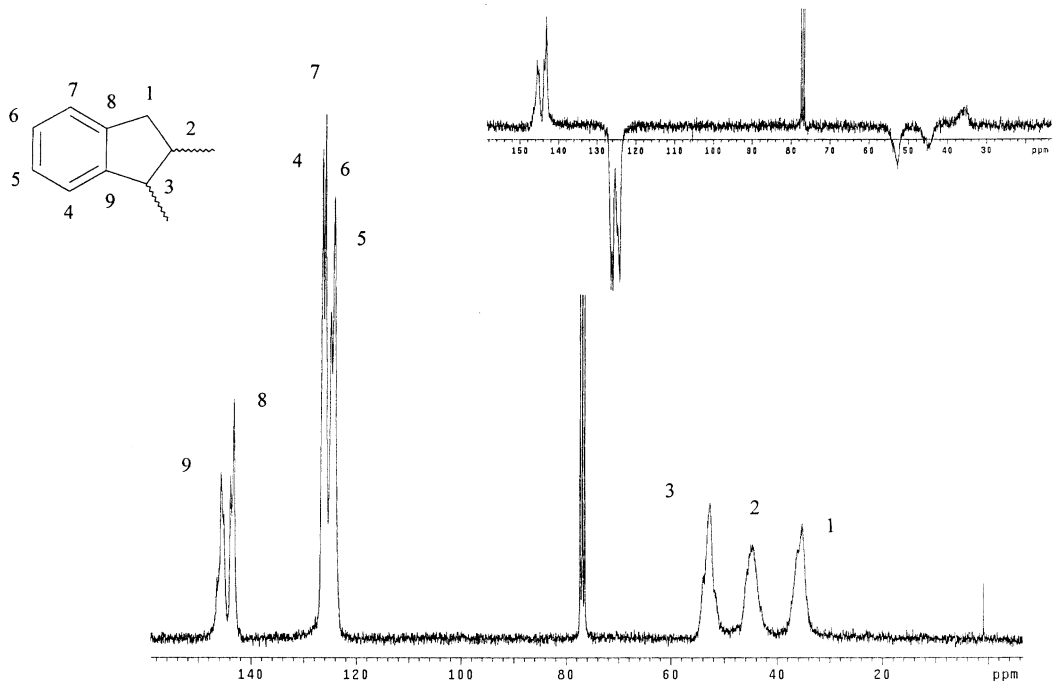


Figure 2. ^{13}C NMR spectrum and ^{13}C APT spectrum (inset) in $CDCl_3$.

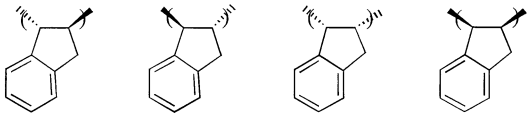


Figure 3. Possible cis and trans repeat unit stereoisomers for polyindene.

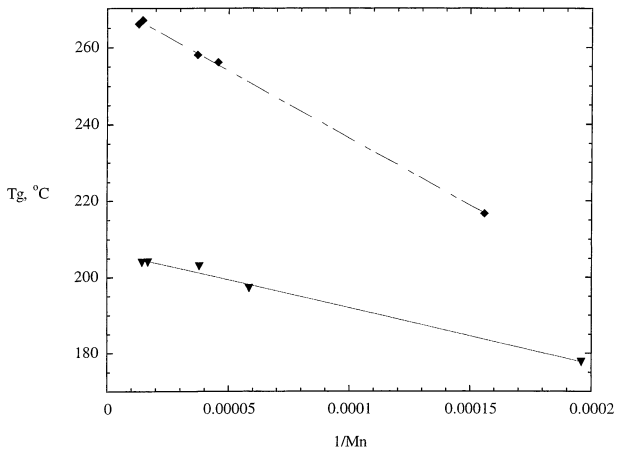


Figure 4. Glass transition temperatures of polyindene (▼) and hydrogenated polyindene (◆) with respect to $1/M_n$. Linear regression analysis for polyindene data gave a best fit of $y = 206.6 - (1.4747 \times 10^5)x$ ($R^2 = 0.9899$) and for hydrogenated polyindene data gave a best fit of $y = 271.5 - (3.511 \times 10^5)x$ ($R^2 = 0.9989$).

The ^{13}C NMR spectrum shows four distinct single resonances due to the aromatic ring methine carbons (carbons 4−7) ranging from 123.5 to 126.0 ppm. These can be assigned tentatively based on the relative chemical shift influence of the substituents attached to the benzylic methine carbon on the cyclopentane ring (3).[29] The carbons in the cyclopentane ring provide more complex signals. The two ring junction carbons appear as broad multiple resonances, centered at 145.6 and 147.0 ppm. There are also three distinct, resolved broad resonances at higher field due to the cyclopentane ring carbons 1−3. Previous workers[8,30] have assigned these as follows; the benzylic methylene carbon (1) centered at 54 ppm, the benzylic methine carbon (3) at the highest field, centered around 36 ppm and the cyclopentyl methine β to the ring junction (2) at 45 ppm. We assign the methylene carbon to the broad resonance at 36 ppm, and the benzylic methine carbon to the broad resonance at 54 ppm. Further support of this assignment was obtained by applying the attached proton test (APT)[31] pulse sequence, which allows for the elucidation of ^{13}C resonances with respect to the number of attached protons. This analysis (inset, Figure 2) clearly shows the 36 ppm peak to be due to a methylene, while the two downfield groupings are methines.

The multiplicity of NMR signals in the carbons in the cyclopentane ring results from the variety of stereoisomers that can be incorporated in polyindene backbone. Staudinger recognized that polyindene can be incorporated such that the repeat units are associated with adjacent repeat units in either a cis or trans configuration.[4] Consideration of these structures shows that two distinct steroisomers can theoretically be incorporated for each of the cis and trans conformers (Figure 3). Further work will be required to elucidate the sequence distribution of these polymers.

The reported glass transition temperature of PIn ranges from as low as 160 °C to as high as 220 °C.[8,32,33]

Table 2. Molecular Characteristics of Hydrogenated Polyindene

SEC (kg/mol)[a]			light scattering (kg/mol)			%	
M_n	M_w	M_w/M_n	M_n	M_w	M_w/M_n	hydrog[b]	T_g (°C)
3.6	9.3	2.60	6.4	11.8	1.86	99	217
11.8	35.2	2.97	21.9	52.9	2.42	99	256
19.9	34.0	1.73	26.9	43.0	1.60	97	258
44.6	81.0	1.81	68.0	122	1.80	99	267
46.1	113	2.46	76.6	171	2.96	99	266

[a] Compared to polystyrene standards [b] From ^1H NMR integration.

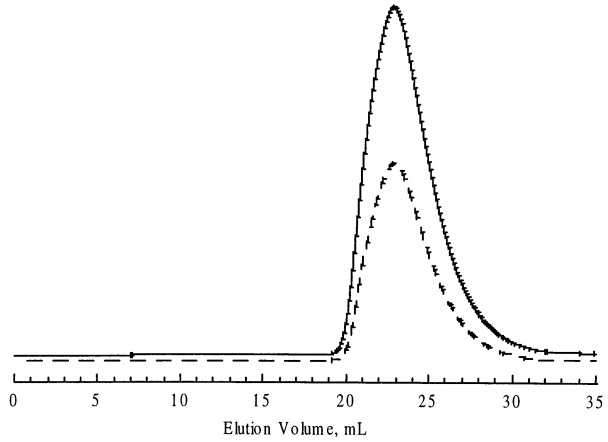


Figure 5. SEC chromatograms of polyindene (solid line) and hydrogenated polyindene (dashed line) obtained using a refractive index detector.

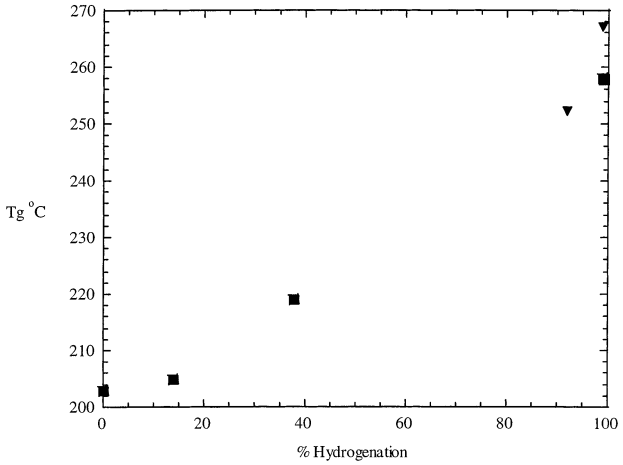


Figure 6. Glass transition temperatures of partially hydrogenated polyindenes obtained from starting material M_n 26.4 kg/mol (■) and M_n 59.20 kg/mol (▼).

Analysis of the T_g data we obtained for the series of PIn samples (Figure 4) prepared in this study shows that the glass transition temperature of PIn approaches 207 °C in the molecular weight regime where chain-end contributions to T_g become negligible (i.e., infinitely high molecular weight or $1/\nu \rightarrow 0$).[34] These data are in excellent agreement with the one previously reported T_g (204 °C) value for which an apparent M_n (27 kg/mol) was also reported.[8]

Polyindene Hydrogenation and Characterization. The hydrogenation of PIn was performed under conditions very similar to those used to saturate polystyrene.[18] High levels of hydrogenation were achieved over the molecular weight range of PIn samples studied (Table 2). Comparison of SEC data for individual PIn

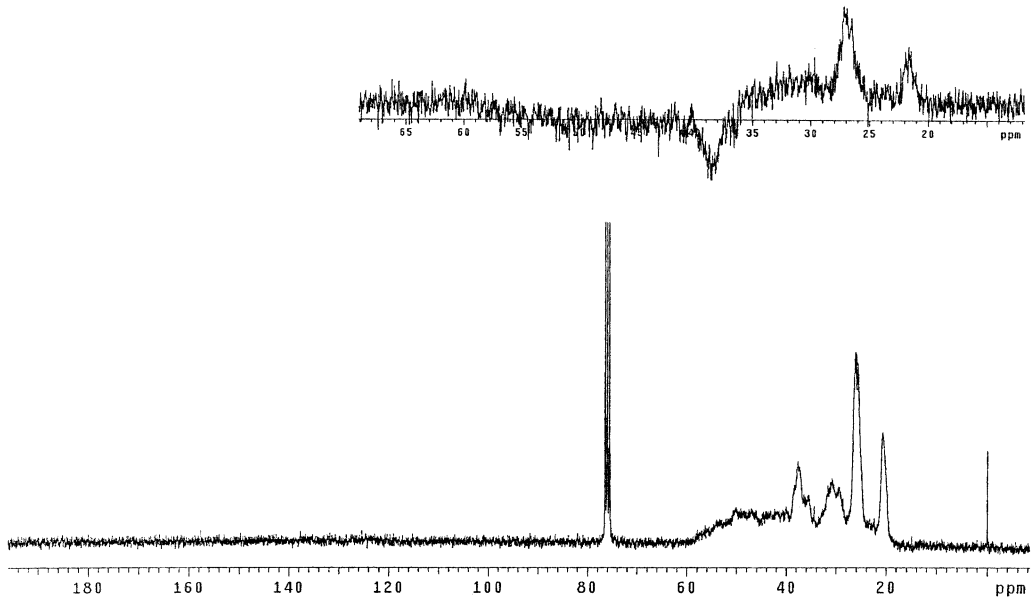


Figure 7. ^{13}C NMR spectrum and ^{13}C APT spectrum (inset) of hydrogenated polyindene in $CDCl_3$.

samples and their hydrogenated products (HPIn) showed only minor changes in polydispersity with no obvious change in peak shape (Figure 5). In THF, there is no significant change in the hydrodynamic volume of the hydrogenated polymer compared to the starting material; this is in contrast with both the hydrogenation of PS and PAMS, where the saturated polymer has a significantly smaller hydrodynamic volume in THF compared to the starting polymer.[35]

Characterization by SEC with light-scattering detection offers an opportunity to determine the absolute molecular weight of the product in comparison to that of the starting material. The addition of 3 mol of H_2/mol of repeat units leads to an increase in the molecular weight by 5.2%. M_n values for the product were in all cases higher than those of the starting material, and in most cases were slightly higher than expected for a fully hydrogenated sample based on hydrogen mass addition alone. These differences may be due to differences in part to the molecular weight dependence of the specific refractive index increment for these two polymers.[36]

The glass transition temperature of polyindene increases dramatically upon hydrogenation. Over the range of molecular weights used in this study, an increase of about 60 °C over the starting material was observed. As with PIn, the relationship between T_g and the reciprocal of M_n is linear with a high degree of correlation (Figure 4); in the limit of high molecular weight, the T_g of HPIn approaches 268 °C. Hydrogenation of the PIn aryl ring leads to a structure in which constraint of backbone motion is even more severe than that apparent in the starting material. This influence can be rationalized based on the repeat unit structure; the hydrogenated polymer contains a saturated hexahydroindanyl bicyclic ring, which is considerably bulkier than the planar indenyl ring. The bicyclic hydroindanyl ring structure can potentially include a cis or trans fused ring junction in addition to the cis or trans chain connections, increasing the number of possible stereochemically distinct repeat units to 16.

Partially hydrogenated samples also show increases in T_g as compared to their respective precursors. Figure 6 shows the glass transition temperatures recorded for PIn samples that were partially hydrogenated. The T_g increases proportionally with the level of hydrogenation (even at 14% saturation a measurable increase is observed). This trend has also been observed in the hydrogenation of PS.[37]

The hydrogenated polymers were characterized by ^1H (Figure 1) and ^{13}C NMR spectroscopy. The proton spectrum shows little differentiation between individual protons; one broad resonance from 0.8 to 2.4 ppm is observed. The ^{13}C NMR spectrum is shown in Figure 7, along with the APT spectrum. Two distinct methylene resonances are oberved at 20 and 27 ppm, with methine resonances covering a chemical shift range of about 30 ppm. We tentatively assign carbons 1, 7, and 4 to the methylene peak at 27 ppm and carbons 5 and 6 to the methylene peak at 20 ppm. Further work will be required to elucidate the polymer structure and to determine the influence of repeat group sequencing on the NMR spectrum.

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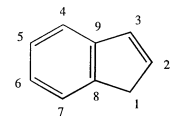

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