Macromolecules **2001,** *34,* 1737−1741

Thermal and Viscoelastic Behavior of Hydrogenated Polystyrene

Jin Zhao, Stephen F. Hahn,* Dennis A. Hucul, and David M. Meunier

Corporate Research and Development, The Dow Chemical Company, Midland, Michigan 48674

Received September 14, 2000; Revised Manuscript Received December 18, 2000

ABSTRACT: Fully saturated hydrocarbon polymers often exhibit superior stability toward thermal, oxidative, and radiation-induced degradation. Recent improvements in catalyst technology allow for the convenient synthesis of the saturated hydrocarbon poly(cyclohexylethylene) (PCHE) from polystyrene (PS) by heterogeneous catalytic hydrogenation. The focus of this report was to prepare nearly monodisperse samples of polystyrene by anionic polymerization and to fully saturate those materials by catalytic hydrogenation. The thermal and viscoelastic properties of these materials were then evaluated using differential scanning calorimetry and dynamic mechanical spectroscopy. On the basis of these experimental results, the glass transition temperature of PCHE has been found to approach 148 °C at high molecular weight. Relationships between the zero shear viscosity, steady-state compliance, and rubbery plateau modulus of PCHE with respect to molecular weight have been determined, and entanglement spacing and packing length have been calculated from these data. PCHE shows an entanglement spacing (M_e) of 40 200 g/mol, compared to 18 700 g/mol for the starting material PS. This increase in glass transition temperature and entanglement length can be attributed to the increase in steric bulk of the cyclohexyl substituent compared to the phenyl ring present in the starting material.

Introduction

Fully saturated hydrocarbon polymers are technologically and commercially important materials, which often exhibit superior stability toward thermal, oxidative, hydrolytic, and radiation-induced degradation. One such material that has recently received renewed interest is poly(cyclohexylethylene) (PCHE), which can be prepared from polystyrene (PS) by heterogeneous catalytic hydrogenation (Scheme 1).[1−10] Although the catalytic hydrogenation of PS has been reported previously, the recent development of an efficient catalyst that facilitates the rapid hydrogenation of PS without chain degradation allows for controlled synthesis of PCHE.[11] Of particular interest is the approach taken by Gehlsen and Bates[8] and Bates et al.,[9] in which narrow polydispersity polystyrene and variously substituted polystyrenes were hydrogenated; the narrow polydispersity of these starting materials simplifies the detection of chain cleavage reactions.

The focus of this project was to prepare nearly monodisperse samples of polystyrene by anionic polymerization and to fully saturate those materials by catalytic hydrogenation. After determining that the hydrogenation process had not degraded the polymeric backbone structure, these well-defined samples were characterized by thermal and rheological methods. Reports of the glass transition behavior of this material have varied rather widely, so one particular aim of this work was to attempt to establish the relationship between the glass transition temperature with molecular weight. The viscoelastic properties of these materials were evaluated using dynamic mechanical spectroscopy (DMS).[12,13] Characterization of fundamental viscoelastic parameters such as zero shear viscosity, steady-state compliance, and rubbery plateau modulus with respect to molecular weight was performed from these data. These experimental data were then used to interrogate some of the fundamental characteristics of this polymer chain. It is particularly useful to consider the properties of PCHE in comparison to the starting material, atactic polystyrene, which is one of the most thoroughly studied amorphous linear hydrocarbon polymers.[14−17]

Scheme 1

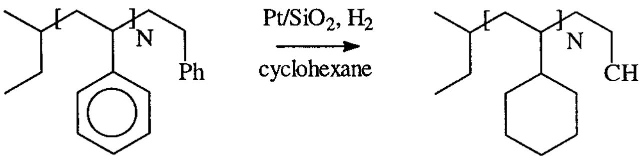

Table 1. Molecular Characteristics of PCHE Samples

M_n (g/mol)	M_w (g/mol)	M_w/M_n	% hydrogenation	T_g (°C)
4 400	5 000	1.13	99.4	127
13 400	14 100	1.05	99.9	140
19 700	20 500	1.04	99.9	141
48 100	50 100	1.04	99.0	145
101 800	110 700	1.09	99.9	146
133 700	141 300	1.06	99.9	146
198 000	217 600	1.09	99.9	146
287 700	313 100	1.09	99.8	147
370 400	435 000	1.17	99.8	148

Experimental Section

Materials. A series of polystyrenes with varying molecular weights were prepared by anionic polymerization of styrene monomer in cyclohexane solvent with *sec*-butyllithium initiator. The molecular weights of these materials were determined by size exclusion chromatographic (SEC) analysis with THF as eluent. Molecular weights were determined by comparison to observed elution volumes of narrow polydispersity polystyrene standards. These polymers were then hydrogenated in cyclohexane solution using a silica-supported Pt catalyst.[11] The extent of hydrogenation was measured by UV analysis; in all cases, the degree of hydrogenation was greater than 99%. GPC analysis showed no change in polydispersity in the hydrogenated materials due to the hydrogenation process. Molecular weights of the hydrogenated polystyrene samples were calculated from the molecular weight of the parent polystyrene by using a molecular weight per styrene residue of 110.11 g/mol. Molecular weight data for all of the polymer samples used in this investigation are listed in Table 1. The difference in the apparent molecular weight of the hydrogenated polymer relative to the starting PS is due to differences in the

10.1021/ma0015929 CCC: $20.00

hydrodynamic volume of the THF solvated PCHE compared to THF solvated PS. Figure 1 shows molecular weight distributions from SEC analyses of PS and the PCHE prepared from it, giving both the apparent molecular weights and absolute molecular weights determined using an SEC/differential viscometer and the universal calibration method.[18] The molecular weight distributions shown in Figure 1 were not corrected for band broadening. Nevertheless, it is clear from this characterization that the hydrogenation has proceeded without chain cleavage and that the hydrogenated polymer has a smaller hydrodynamic volume in THF compared to PS of the same degree of polymerization.

A small amount of butylated hydroxytoluene (BHT ~0.2 wt %) was added as an antioxidant to delay the onset of thermal degradation at high temperatures during the dynamic mechanical measurements. Characterization of the thermal stability of PCHE when heated in a nitrogen atmosphere showed that, over the time frame of the experiments performed, some degradation of molecular weight begins at 280 °C, and degradation above 300 °C makes experimental work at these temperatures impractical.

Materials Characterization. Differential scanning calorimetry (DSC) was performed using a Seiko model 5100 DSC at a heating rate of 3 °C/min. Each sample was run through a full heating cycle, cooled, and then rerun, with the glass transition temperature determined by the inflection point in the heat capacity during the second heat. Three separate samples of each molecular weight material were analyzed, and the standard deviation of the triplicate analyses was always less than 0.5 °C.

Dynamic mechanical spectroscopy (DMS) was used to probe the viscoelastic properties of narrow polydispersity PCHE polymers. The polymer samples were tested using isothermal frequency sweeps within the temperature range of 140−300 °C and at frequencies ranging from 100 to 0.006 rad/s. To cover a broader frequency range, master curves were obtained by shifting the data along the log frequency axis to produce master curves using the relationship described by Williams−Landel−Ferry:[12]

$$\log a_{\mathrm{T}} = -C_1(T - T_{\mathrm{r}})/(C_2 + T - T_{\mathrm{r}}) \quad \text{for } T > T_{\mathrm{g}} \qquad (1)$$

where a_{T} is the empirically derived shift factor, C_1 and C_2 are constants (8.51 and 104.3, respectively, were used in this work), and T_{r} is a reference temperature (187 °C for this set of experiments). The shift factors for this set of hydrogenated polystyrene samples are shown plotted with respect to temperature in Figure 2.

The DMS measurements described in this report were performed on a Rheometrics mechanical spectrometer (RMS) operated with a 25 mm parallel plate fixture. The lower plate was replaced with a cup, which was used to minimize edge failure. Polymer disks analyzed in this fixture were obtained by compression molding the polymer powders into a 25 mm disk at 200 °C. After assembling the sample and the fixture in the rheometer, a small torsional sinusoidal strain $\gamma = R_{\mathrm{p}}\theta/h$ was applied on the lower plate (where R_{p} is the radius of the plate, h is the thickness between the plates, and θ is the rotating angle). All samples were run at a strain amplitude of less than 0.2% during the frequency scans in a nitrogen environment. Linearity of response was checked repeatedly by measurements of torque for various strain amplitudes; critical strain amplitude was not observed at sinusoidal strains of up to 20%.

Results and Discussion

Thermal and Rheological Characterization of PCHE. The hydrogenated polystyrene samples prepared for this work were analyzed by DSC to establish the relationship between glass transition temperature and molecular weight for PCHE. The glass transition temperatures recorded for polymers with molecular weights above 100 000 g/mol were observed to fall between 146 and 148 °C at a heating rate of 3 °C/min. Figure 3 shows the measured glass transition temperatures of these samples plotted with respect to $1/M_{\mathrm{n}}$; by this analysis, the T_{g} of PCHE approaches 148 °C in the limit of high molecular weight. Previous investigators have reported glass transition temperatures ranging from ca. 80 to 140 °C for this polymer. For hydrogenated, anionically prepared polystyrenes with number-average molecular weights 3.3×10^5 and 5.6×10^5

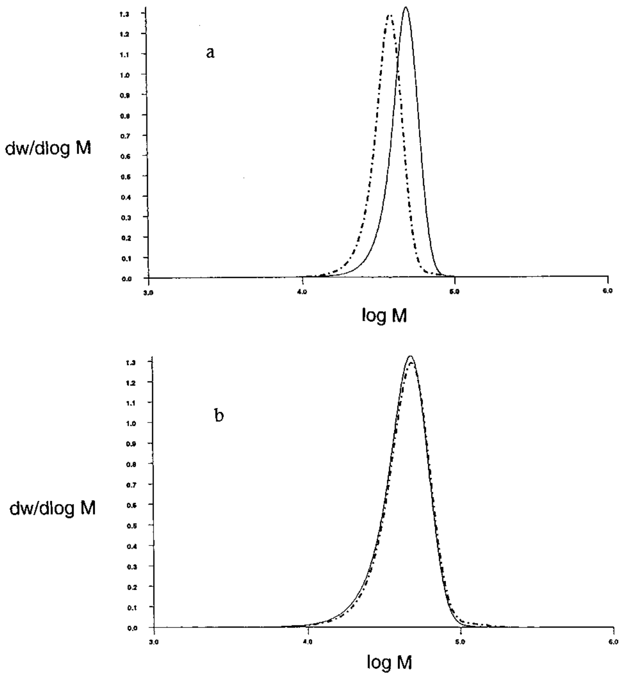

Figure 1. Differential weight fraction vs log molecular weight distribution plots for M_{n} 48 100 PS (solid) and the PCHE (dashed) prepared from it. Plot a shows apparent molecular weight distributions of both samples with respect to PS standards; plot b shows absolute molecular weight distributions obtained by SEC/differential viscometry using the universal calibration method.[18]

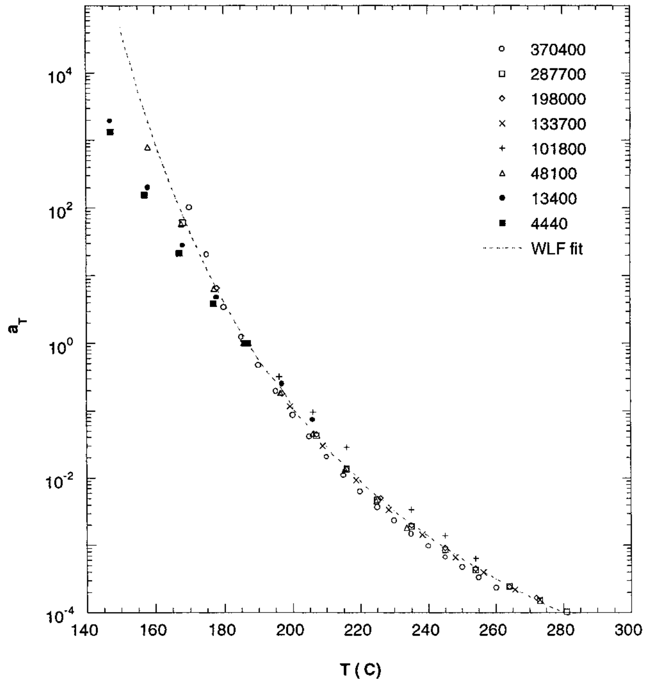

Figure 2. WLF shift factor a_{T} with respect to temperature for nearly monodisperse hydrogenated polystyrenes.

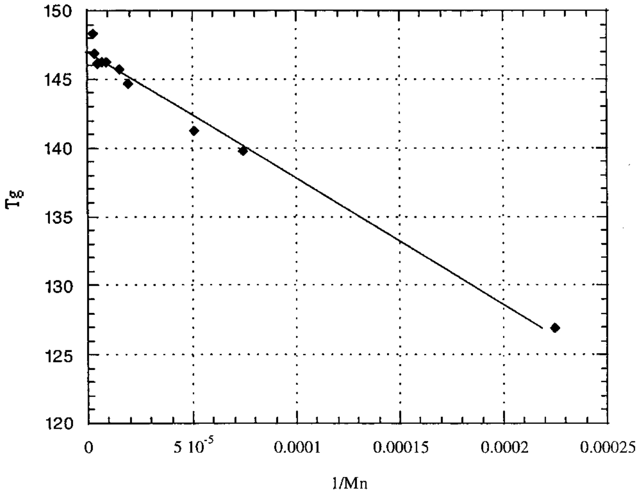

Figure 3. Glass transition temperature with respect to number-average molecular weight for nearly monodisperse PCHE samples as determined by DSC analysis.

g/mol, Bates et al.[9] reported a T_g of 137 °C, slightly lower than the results observed in this work.

Dynamic mechanical spectroscopy has been used extensively to probe polymer structure and properties. The dynamic spectrum of shear storage modulus (G') and shear loss modulus (G'') with respect to frequency (ω) contains information regarding the manner in which a sample responds to small magnitude deformation applied over varying time scales. A typical dynamic spectrum for a linear monodisperse homopolymer that has sufficiently high molecular weight displays three distinct regions of behavior. These are known respectively as the glassy, plateau, and terminal regions when going from high frequency to low frequency (or from low temperature to high temperature). In the glassy region, where the deformation frequency is high compared to the average relaxation time of the polymer chain, the chains cannot adjust quickly enough to dissipate the applied stress, and the observed modulus is high. As the frequency of deformation decreases, storage modulus decreases until a rubbery plateau is observed. In this region a relatively constant storage modulus value is observed over several decades of frequency, indicating that polymer chains have sufficient time to relax locally but (at adequately high molecular weights) are entangled and exhibit behavior consistent with a rubbery network. Finally, at very low frequencies, the shear storage and loss moduli decrease further, corresponding to the complete relaxation of polymer chains. In this low-frequency limit, where the time allowed for relaxation is longer than the longest relaxation time in the polymer sample, the polymer melt behaves like a viscoelastic liquid, with G' proportional to ω^2 and G'' proportional to ω.

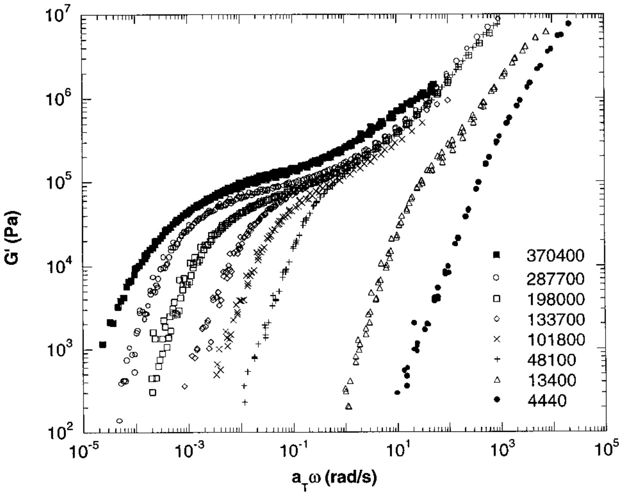

Figure 4. Shear storage modulus G' master curves with respect to reduced frequency for nearly monodisperse PCHE samples (T_r = 187 °C).

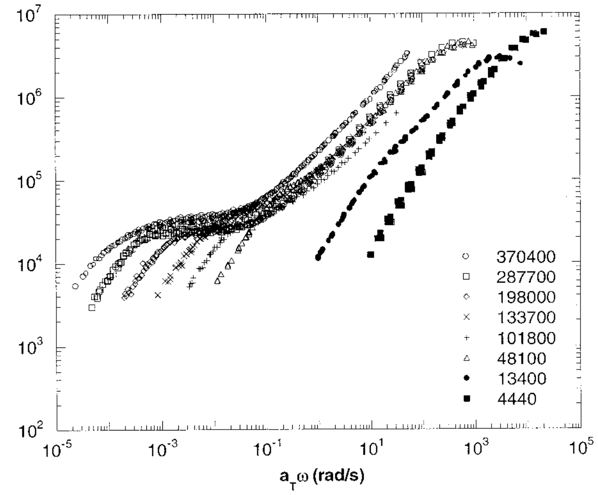

Figure 5. Shear loss modulus G'' master curves with respect to reduced frequency for nearly monodisperse PCHE samples (T_r = 187 °C).

Master curves of G' and G'' (T_r = 187 °C) for the series of PCHE homopolymers at different molecular weights studied in this report are shown in Figures 4 and 5. The master curves of samples with $M_n \geq 134\ 000$ demonstrate behavior consistent with that expected for the terminal zone, rubbery plateau, and glass transition zones. The master curves of samples with $M_n < 134\ 000$ do not manifest the rubbery plateau to any meaningful degree, displaying only terminal and transition zone behavior. As is commonly observed in other linear, monodisperse homopolymer systems, the frequency at which the terminal zone appears shifts progressively to the low-frequency side, and the rubbery plateau becomes longer as the molecular weight of the sample increases. The G' curves for samples with $M_n \geq 48\ 100$ coalesce in the transition zone. The G' curves of samples with $M_n < 134\ 000$ do not overlay with each other, nor do they overlay with the higher molecular weight polymers in the transition zone. It is interesting to note that none of the samples displays a completely flat rubbery plateau, especially when compared to polystyrene.[15] This suggests that the entanglement molecular weight of PCHE is relatively high, and as a result, a much higher molecular weight of PCHE is needed to observe a flat rubbery plateau compared to PS.

Entanglement Spacing of PCHE. Numerous theoretical and experimental investigations into the properties of molten polymers have elucidated the important relationships between chain entanglement and rheological behavior. One of the most frequently cited characteristic parameters for a linear polymeric structure is the entanglement molecular weight, M_e. The melt viscosity of many polymers has been observed to be directly proportional to molecular weight up to a specific value, after which it increases sharply with increasing molecular weight.[13,20,21] The molecular weight of the polymer at this crossover is designated M_c, the

Table 2. Plateau Moduli and Entanglement Molecular Weights for PCHE Homopolymers

M_w (g/mol)	$G_N°$ (Pa)	M_e (g/mol)
110 700	87 800	38 900
141 300	87 700	39 000
217 600	69 400	49 400
313 100	81 400	42 000
435 000	108 100	31 600
		av 40 200

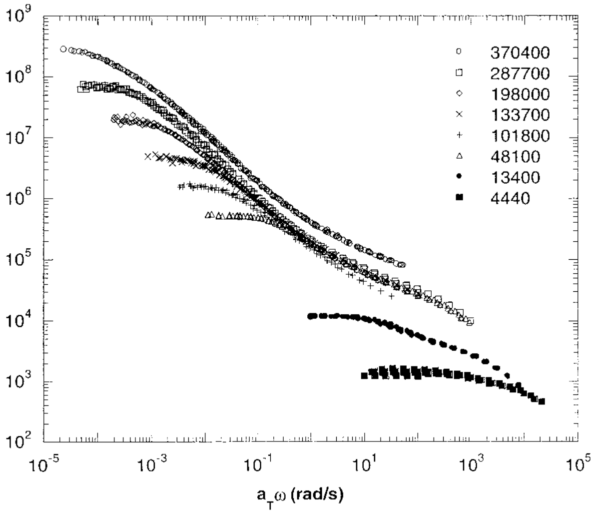

Figure 6. Complex viscosity master curves with respect to reduced frequency for nearly monodisperse PCHE samples (T_r = 187 °C).

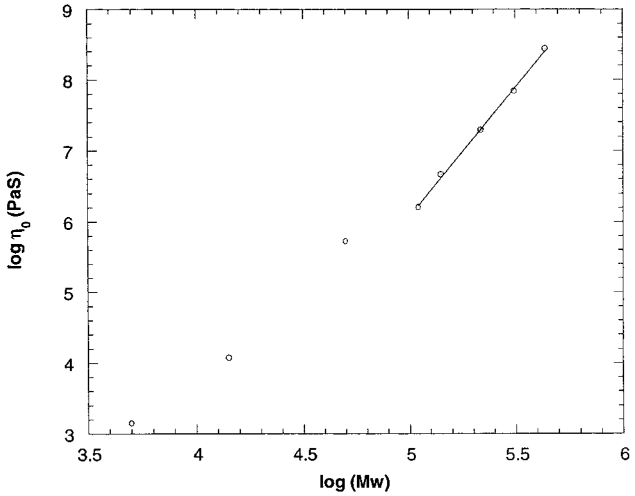

Figure 7. Plot of zero shear viscosity at 187 °C with respect to weight-average molecular weight for nearly monodisperse PCHE. The line serves merely to guide the eye.

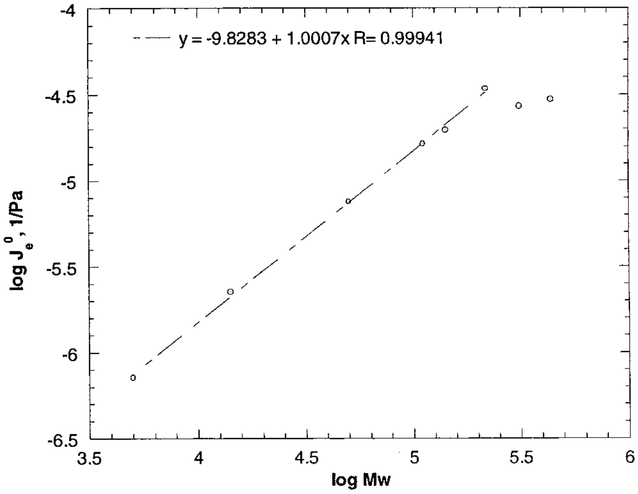

Figure 8. Steady-state compliance with respect to weight-average molecular weight for nearly monodisperse PCHE samples. The line represents the best fit line through data points for M_w 5000−217 600.

critical molecular weight, and is roughly twice M_e. Values for M_e are often calculated[13] from the plateau modulus using the relationship

$$M_e = \rho RT/G_N° \quad (2)$$

where ρ is the melt density, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and $G_N°$ is the plateau modulus. M_e was calculated using eq 2 for those PCHE materials that displayed a clear plateau region; $G_N°$ was determined from the magnitude of G' at the frequency that corresponded to the minimum in the loss tangent. The melt density of PCHE at 187 °C was estimated as 0.894 g/cm^3 based on data reported by Gehlsen et al.[9] The entanglement molecular weights calculated from the data obtained in this work are given in Table 2, ranging from 32 000 to 49 000, with an average value for all entangled samples of about 40 200. The scatter in the evaluated plateau moduli and subsequent calculated entanglement molecular weight may be due to the difficulty in determining the minimum position of the loss tangent, since the breadth of the plateau region for PCHE is relatively narrow. The entanglement spacing of atactic PCHE has been reported as 38 900 from small-angle neutron scattering (SANS) measurements,[19] in good agreement with the data reported here.

Master curves of complex viscosity with respect to frequency for the PCHE series are shown in Figure 6. Figure 7 shows the relationship between the measured zero shear viscosity η_0 for the PCHE series with respect to the weight-average molecular weight at 187 °C. The slope of the viscosity vs M_w for polymers above 110 700 is 3.7, which agrees with that measured for polystyrene[15] but is slightly higher than the value of 3.4 commonly observed.[13]

The entanglement spacing can also be estimated from analysis of the steady-state compliance, $J_e°$, which increases proportionally with molecular weight up to some critical chain length, after which it becomes independent of molecular weight.[12] The point at which the observed steady-state compliance ceases to increase with increasing molecular weight is defined as the critical molecular weight, M_c', and has been observed to be of the order of $5M_e$ determined from the plateau modulus.[13] Figure 8 shows the relationship between steady-state compliance and M_w determined in this work. The value of M_c' determined from juncture of the slopes of $J_e°$ above and below the discontinuity is 199 000, providing an M_e value of 39 800, in good agreement with the value obtained from the plateau moduli for these samples. The steady-state compliance measurement also allows for measurement of the time required for final equilibration of stress in the polymer melt. The characteristic relaxation time, τ_0, is given by

$$\tau_0 = \eta_0 J_e^{\,0} \quad (3)$$

Values for zero shear viscosity, steady-state compliance, and relaxation times determined for this work are given in Table 3.

Table 3. Steady-State Compliance, Zero Shear Viscosity, and Relaxation Times for PCHE Samples at 187 °C

M_w (g/mol)	η_0 (Pa s)	$J_e°$ (1/Pa)	τ_0 (s)
5 000	1.4×10^3	7.2×10^{-7}	1×10^{-3}
14 100	1.1×10^4	2.2×10^{-6}	2.3×10^{-2}
50 100	5.0×10^5	7.6×10^{-6}	3.8
110 700	1.6×10^6	1.6×10^{-5}	27
141 300	4.8×10^6	2.0×10^{-5}	93
217 600	2.0×10^7	3.4×10^{-5}	660
313 100	6.4×10^7	2.7×10^{-5}	1700
435 000	2.5×10^8	3.0×10^{-5}	7400

Table 4. Chain Characteristics for Some Linear Hydrocarbon Polymers

polymer	T (°C)	$G_N°$ (Pa)	M_e (g/mol)	jP_e[a]	p (Å)
polyethylene[b]	140	2.6×10^6	830	30	1.69
s-polypropylene[c]	190	1.35×10^6	2170	52	2.36
a-propylene[c]	190	4.2×10^5	7050	168	3.48
polyisobutylene[b]	140	3.2×10^5	7300	130	3.43
PS[d]	160	2.0×10^5	18700	180	3.99
PCHE[e]	187	8.1×10^4	40200	370	6.0

[a] Backbone atoms between entanglements; $jP_e = jM_e/M_0$, where j is the number of chain atoms per monomer unit and M_0 is the repeat unit molecular weight. [b] Data from ref 19. [c] Calculated using data from ref 24. [d] Data from ref 14. [e] Data from this work.

The influence of polymer structure on physical properties is of fundamental importance to polymer science. The relative influence of substituents on the properties of the polyethylene chain has been the subject of extensive research. Of particular interest is the recent work by Fetters and co-workers[19,22,23] demonstrating that, for flexible, linear Gaussian chain polymers, a universal relationship between entanglement spacing and the newly defined parameter packing length can be expressed as

$$M_e = n_t^2 N_a \rho p^3 \tag{4}$$

where n_t is a temperature-insensitive coefficient, N_a is Avogadro's number, and p is the packing length. The packing length has been defined as the occupied volume of a chain $M(\rho N_a)^{-1}$ divided by the mean-square end-to-end distance $\langle R^2 \rangle_0$ and can be envisioned as a relative measure of chain thickness. In general, as the steric bulk of the pendant substituent increases, the entanglement density decreases and the packing length increases. Table 4 provides several relative measures of entanglement density and packing length for several substituted polyethylene derivatives. It is clear from comparative data such as this that the steric bulk of cyclohexyl ring in PCHE is large compared to most other substituents and results in a pronounced increase in the entanglement molecular weight observed for PCHE compared to the starting material, PS.

Conclusions

The preparation of narrow polydispersity hydrogenated atactic polystyrene samples was used to characterize the thermal and rheological properties of this material. Hydrogenation has been observed to lead to a dramatic increase in the glass transition temperature compared to that of polystyrene, with values at high molecular weight approaching 148 °C. The increased bulk of the cyclohexyl ring compared to the phenyl ring leads to a large increase in the entanglement molecular weight and packing length in PCHE compared to polystyrene.

Acknowledgment. The authors thank Bridget Bartos for GPC analysis, Charles Berglund, Craig Carriere, and Cora Leibig for a careful reading of the manuscript, and Tim Lodge for helpful advice and discussions.

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MA0015929