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i.e., one for the PLA at +53 °C and another for the PCL at −53 °C. Table III shows some physical and mechanical properties of ABA and AB block copolymers for comparison. It is interesting to find that the elongation at break of the ABA block copolymer is much higher than that of the AB block copolymer of similar CL/LA ratio with the highest value of 600% without sacrifice of tensile strength.

Conclusion

The "living" behavior of LA polymerization by Teyssie's catalyst has been proved, yet the growing PLA–OAl< intermediate could not initiate the block copolymerization of CL directly. Instead, HO-terminated PEO end-capped polylactide was prepared and reactivated by the modified catalyst as the real active prepolymer to initiate the CL block copolymerization. Thus, it provides a pathway to the synthesis of ABA triblock copolymers of lactone and lactide. The ABA block copolymers of CL and LA prepared by this synthetic method show some interesting properties over the AB diblock copolymers such as the high value of elongation at break. Such ABA block copolymers may be considered as a potential new biomedical material with biodegradable and tough membrane-forming properties for sustained release drug delivery system.

References and Notes

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Model Hydrocarbon Polymers: Rheological Properties of Linear Polyisoprenes and Hydrogenated Polyisoprenes

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ABSTRACT: Hydrogenated polyisoprenes (HPI) with nearly monodisperse molecular weight distributions were prepared by reacting H_2 with anionically prepared linear polyisoprenes (PI) in the presence of a $Pd/CaCO_3$ catalyst. Effects of chemical microstructure on rheological properties were explored with PI and HPI samples of various 3,4 contents (isopropenyl and isopropyl branch frequencies). At low 3,4 content the HPI's are good models for conventional equimolar ethylene–propylene copolymers. They have similar average composition, density ρ, glass transition temperature T_g, plateau modulus $G_N°$, melt viscosity–intrinsic viscosity relationship, and temperature coefficient of viscosity. The temperature dependence within either the PI series or the HPI series was independent of chemical microstructure at a fixed interval of temperature above T_g. Variations in plateau modulus with microstructure for the two series confirmed, at least qualitatively, the expected roles of the characteristic ratio C_∞ and molecular weight (or volume) per backbone bond m_0 in determining $G_N°$. The shift in modulus scale with temperature for HPI was inconsistent with the classical theory for entangled melts, $b_T \propto \rho T$, but in good agreement with a recent prediction: $b_T \propto \rho^d T C_\infty^{2d-3}$, $d \sim 2.0$–2.3.

Introduction

Copolymers of ethylene and propylene comprise an important class of commercial products. For approximately equimolar compositions and approximately random sequence distributions, the EP copolymers are substantially amorphous at and above room temperature.[2] With incorporation of small amounts of a diene monomer they form the basis of the EPDM elastomers. Even without addition of the third monomer, however, the structure of the commercial products can be complicated. Made with Ziegler–Natta catalysts, the copolymers have chemical microstructures and compositional distributions which vary with catalyst and conditions. Also, the distribution of molecular weights is typically broad ($\bar{M}_w/\bar{M}_n \gtrsim 2$), and long-chain branching may be present in some cases. With such materials it is very difficult to examine each of these factors in isolation.

On the other hand, a 1:1 ethylene–propylene microstructure can be obtained by the hydrogenation of polyisoprene (PI). Isoprene can be polymerized anionically to form chains of known and highly uniform architecture. Polymerization in nonpolar solvents gives predominantly 1,4 head-to-tail addition (~92%, the remainder being 3,4 addition). Hydrogenation should give a strictly alternating EP microstructure ($r_1 = r_2 = 0$), interrupted occasionally by isopropyl side groups (~16/1000 backbone carbons from the 3,4 content of the precursor PI). Such polymers are potentially useful as model materials to provide a better understanding of conventional EP copolymers.

The present paper reports the preparation, characterization, and viscoelastic properties of linear hydrogenated polyisoprene (HPI) and compares the results, extrapolated to 0% isopropyl groups in some cases, with those for substantially linear commercial EP copolymers of similar average microstructure. The behavior of HPI with long branches (hydrogenated samples of three-arm star polyisoprene) will be discussed in a later paper.

Experimental Section

A. Polymerization and Hydrogenation. Isoprene (Aldrich, Gold Label) was polymerized in cyclohexane at 50 °C with initiation by *sec*-butyllithium (Alfa Ventron). The "capped-bottle" procedure of Hsieh was used, as described earlier for butadiene polymerization[3] and modified slightly for isoprene.[4] The 3,4 content was increased in selected cases by adding small amounts of tetrahydrofuran to the polymerization solvent. After completion of polymerization (~4 h) the polyisopropenyl anions were ter-

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Table I
Chemical Microstructures and Physical Properties

	polyisoprene (PI)						hydrogenated polyisoprene (HPI)	
sample[a]	%, 3,4	% 1,2	% cis 1,4	% trans 1,4	ρ(25 °C), g/cm^3	T_g, °C	ρ(25 °C), g/cm^3	T_g, °C
PI-0.465L	8	~0	77	15		−68	0.854	−62
PI-0.634L	8	0				−69	0.854	−63
PI-0.729L	8	0				−68	0.854	−61
PI-0.920L	11	0	74	15				
PI-0.922L	8	0	78	14		−66	0.854	−62
PI-0.991L	8	0	7	15	0.898	−65	0.853	−63
PI-1.115L	8	0	74	18	0.899	−67	0.853	−64
PI-1.596L	7	0	80	13		−69	0.853	−63
PI-1.395H	16	~0	56	28	0.898	−61	0.855	−59
PI-0.949H	18	0	44	38	0.899	−59	0.856	−57
PI-0.699H	20	0	57	23		−59	0.855	−56
PI-1.058H	29	0	25	46	0.899	−50	0.858	−49
PI-0.813H	33	~1	37	29		−45	0.858	−45
PI-1.141H	34	~2	19	45	0.899	−44	0.859	−42
JBG-11[b]							0.854	−62

[a] L designates the polymers with low 3,4 content (unmodified polymerization); H designates the polymers with elevated 3,4 content (THF-modified polymerization). [b] Ethylene–propylene copolymer, 53 mol % ethylene units, T_m < 25 °C.

minated by injection of dry 2-propanol. The polymer was then precipitated with an excess of methanol, washed and stabilized with antioxidant (Santonox, Monsanto Co.), dried under vacuum, and stored in a refrigerator. The polyisoprenes were hydrogenated with a Pd/CaCO$_3$ catalyst (Strem Chemical Co.), as described earlier for polybutadiene.[5] Compared with polybutadiene the polyisoprene hydrogenation was more difficult. Sometimes repeated hydrogenation was necessary, and "old" samples seemed particularly resistant. All samples used in subsequent studies had residual unsaturation levels below 1% according to infrared measurements.

B. Microstructure and Physical Properties. Chemical microstructures were obtained by infrared and NMR measurements using established procedures.[6,7] Proton NMR (JEOL, FX-270 MHz) was used to determine the frequencies of cis-1,4, trans-1,4, 1,2 (vinyl) and 3,4 (isopropenyl) additions for the polyisoprenes. Only 3,4 content was determined by infrared, the 1,4 bands being poorly resolved in polyisoprene. Information on 3,4 addition as well as 3,4 sequence distribution was obtained by ^{13}C NMR measurements (Varian CFT-20 MHz) on the hydrogenated polyisoprenes. The results in Table I are consistent with earlier studies showing that unmodified isoprene polymerization by lithium alkyls in nonpolar media gives 75–80% 1,4-cis, ~15% 1,4-trans, ~8% 3,4, and ~0% 1,2 additions.[8] The 3,4 and 1,4-trans contents rise and the 1,4-cis content falls with modification by tetrahydrofuran. The 1,2 content remains undetectably small up to ~30% 3,4 content. We were somewhat surprised to find definite indications of "blockiness" in 3,4 additions for the unmodified polymerizations. Thus, for random addition of 8% 3,4 units, only 0.6% of adjacent pairs of mers would both be 3,4, but the observed frequency of 3,4 pairing is 3.3%.[4] The placements become more random with increasing 3,4 content.

The density ρ of selected PI and HPI samples was measured at 25 °C in a density gradient column. Glass transition temperatures, extrapolated to zero heating rate, were obtained by differential scanning calorimetry (Perkin-Elmer DSC-2). No evidence of crystallinity was found; all PI and HPI samples appear from the thermal analysis to be completely amorphous. Values of ρ and T_g are given in Table I. Figure 1 shows T_g as a function of microstructure for PI and HPI. The values for HPI near 0% 3,4 content agree well with the reported T_g ~ −63 °C for approximately equimolar EP copolymers.[2] (See EP sample JBG-11 in Table I.)

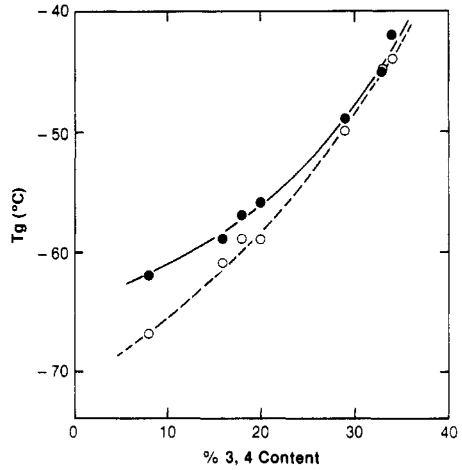

Figure 1. Glass transition temperature as a function of 3,4 content for polyisoprene and hydrogenated polyisoprene. Open circles designate polystyrene; filled circles designate hydrogenated polyisoprene.

C. Molecular Weight and Distribution. Data on average molecular weight and distribution breadth were obtained from intrinsic viscosity, gel permeation chromatography in tetrahydrofuran (Waters Model 200 GPC), and dilute solution light scattering in cyclohexane (Chromatix KMX-6) at or near 25 °C. Association occurs in dilute solutions of EP copolymers near room temperature, so the commercial EP copolymers, and several HPI samples for comparison purposes, were characterized in 1,2,4-trichlorobenzene at 135 °C by intrinsic viscosity and light scattering (Chromatix KMX-6) in-line with GPC (Waters 150C GPC). The data at high temperatures were provided by Dr. Gary VerStrate of Exxon Chemical Co.;[9] instrumental calibration in the high-temperature measurements was confirmed repeatedly by data on a polyethylene standard sample, NBS-1484.

Universal calibration and axial dispersion corrections[10] were used to interpret the tetrahydrofuran–GPC results for both PI and HPI. In tetrahydrofuran[11,12]

$$[\eta]_{\mathrm{THF}} = 1.77 \times 10^{-4} M^{0.735} \quad \text{(PI)} \qquad (1)$$

$$[\eta]_{\mathrm{THF}} = 3.88 \times 10^{-4} M^{0.686} \quad (\sim 1{:}1\ \text{EP}) \qquad (2)$$

Molecular weights for several PI samples were also estimated from intrinsic viscosity measurements in toluene:[13]

$$[\eta]_{\mathrm{TOL}} = 1.72 \times 10^{-4} M^{0.74} \quad \text{(PI)} \qquad (3)$$

For EP copolymers (40–60% ethylene) at 135 °C[14]

$$[\eta]_{\mathrm{TCB}} = 2.92 \times 10^{-4} M^{0.726} \quad (\sim 1{:}1\ \text{EP}) \qquad (4)$$

Light scattering molecular weights for the polyisoprenes were obtained with dn/dc values (λ = 0.633 nm) from Mays[15] (0.106 cm^3/g for an 8% 3,4 microstructure and 0.102 cm^3/g for a 49% 3,4 microstructure), interpolated linearly as required for inter-

Table II
Molecular Characterization of Polyisoprenes

sample	% 3,4	$[\eta]_{\mathrm{THF}}$, dL/g	$[\eta]_{\mathrm{TOL}}$, dL/g	$\bar{M}_w/\bar{M}_n$(GPC)	$\bar{M}_w$(GPC)	$\bar{M}_w$(LS)	$\bar{M}_v([\eta]_{\mathrm{TOL}})$
PI-0.465L	8	0.47	0.48_5	1.04	45 700	45 400	46 000
PI-0.634L	8	0.63		1.03	76 500		
PI-0.729L	8	0.73	0.77	1.03	86 100	85 600	85 500
PI-0.920L	11	0.92	0.88	1.03	105 000		103 000
PI-0.922L	8	0.92	0.90	1.04	108 000	115 000	106 000
PI-0.991L	8	0.99	1.02	1.04	132 000	133 000	126 000
PI-1.115L	8	1.12	1.24	1.05	164 000	158 000	163 000
PI-1.596L	7	1.60	1.68	1.03	233 000	251 000	245 000
PI-1.395H	16	1.40		1.05	267 000	285 000	
PI-0.949H	18	0.95		1.03	146 000	141 000	
PI-0.699H	20	0.70		1.03	81 000	79 000	
PI-1.058H	29	1.06		1.05	160 000	146 000	
PI-0.813H	33	0.81		1.12	102 000	95 000	
PI-1.141H	34	1.14		1.04	164 000	159 000	

Table III
Molecular Characterization of Hydrogenated Polyisoprenes

sample	% 3,4	$[\eta]_{\mathrm{THF}}$, dL/g	$[\eta]_{\mathrm{TCB}}$, dL/g	$\bar{M}_w/\bar{M}_n$(GPC)	$\bar{M}_w$(GPC)	$\bar{M}_w$(LS)	$\bar{M}_w$(LS,PI)[a]	$\bar{M}_w$(LS, 135 °C)
HPI-0.465L	8	0.59	0.69	1.04	48 000	48 000	46 300	41 000
HPI-0.634L	8	0.84		1.04	74 000			
HPI-0.729L	8	0.92	1.08	1.04	87 000	91 000	88 000	76 000
HPI-0.920L	11	1.01		1.04	107 000	105 000		
HPI-0.922L	8	1.11	1.13	1.05	115 000	115 000	118 000	103 000
HPI-0.991L	8	1.17	1.28	1.03	127 000	134 000	137 000	119 000
HPI-1.115L	8	1.42	1.52	1.04	159 000	174 000	163 000	155 000
HPI-1.596L	7	1.88	2.24	1.03	226 000		258 000	219 000
HPI-1.395H	16	1.67		1.03	262 000	274 000	293 000	
HPI-0.949H	18	1.07		1.03	139 000		145 000	
HPI-0.699H	20	0.77		1.04	78 000		81 000	
HPI-1.058H	29	1.00		1.04	142 000		150 000	
HPI-0.813H	33	0.82		1.11	91 000		98 000	
HPI-1.141H	34	1.03		1.04	147 000	179 000	163 000	
JBG-11			1.67	2.2[b]				155 000

[a] Calculated from $\bar{M}_w$(LS) for the precursor polyisoprene by multiplying by 70/68, the ratio of mer weights. [b] Value obtained by GPC–light scattering in trichlorobenzene at 135 °C; $\bar{M}_z/\bar{M}_w = 1.8$ obtained by the same method.

mediate 3,4 contents. Lacking information on the variation of dn/dc with HPI microstructure, we used the Mayo value, $dn/dc = 0.0618$ cm^3/g for HPI with 8% 3,4 content in cyclohexane,[15] for all samples. For HPI and EP copolymers in trichlorobenzene at 135 °C, $dn/dc = -0.104$ cm^3/g.[14]

The results in Table II show that the PI samples have narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$) and that the average molecular weights obtained by several methods are in good agreement. The results for HPI in Table III show that the distribution does not broaden detectably with hydrogenation. Indeed, the uncorrected GPC traces (THF, room temperature) before and after hydrogenation are indistinguishable except for slight displacements in peak position.

The average molecular weights for HPI obtained by characterization at room temperature are consistent with those for the corresponding PI precursor. However, values obtained by light scattering at 135 °C are somewhat smaller than expected. The difference is about 11% at midrange, decreasing slightly with increasing molecular weight. Despite numerous attempts, we have been unable to account for the discrepancy. Values obtained for other HPI samples by the light scattering procedure at 135 °C are also lower than those obtained by room-temperature light scattering,[15] but only by about 6%. That difference is about the same for all molecular weights and is understandable simply from slight uncertainties in calibration and dn/dc values. In the rest of the paper we will use the HPI molecular weights obtained by room-temperature characterization, but the possibility of a small, systematic discrepancy must be borne in mind.

D. Rheological Characterization. Linear viscoelastic data were obtained with a Rheometrics mechanical spectrometer (eccentric rotating disk method with values corrected for instrumental compliance[16]). The storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were measured at frequencies from as low as $\omega = 10^{-3}$ s^{-1} to $\omega = 250$ s^{-1}. Data were obtained at temperatures of 25, 50, and 75 °C for the PI samples. It was possible to cover a much wider temperature range (up to 205 °C) with the HPI samples because of their greater thermal stability. The usual precautions were taken to ensure bubble-free samples, linearity of response, and absence of degradation. All samples were stabilized with ~0.1% Santonox. Adjustments were made at each temperature for thermally induced changes in the platen spacing.

Time–temperature superposition was excellent for both the PI and HPI samples. Thus[17]

$$G'(\omega,T) = b_T G'(a_T\omega,T_0) \tag{5}$$

$$G''(\omega,T) = b_T G''(a_T\omega,T_0) \tag{6}$$

where T_0 is a suitable reference temperature and a_T and b_T are the temperature-dependent frequency and modulus shift factors. Dynamic moduli for the PI samples were accurately superimposable by shifts in frequency scale alone ($b_T = 1$). Master curves for several samples (~8% 3,4 content) with $T_0 = 25$ °C are shown in Figure 2. A shift in modulus scale was just barely detectable even over the much wider range of temperatures covered by the HPI data. It amounts to a very small but systematic *decrease* in b_T from 25 to 190 °C of ~15%, in contrast with an *increase* of almost 40% expected from the classical modulus shift for polymer melts, $b_T \propto \rho T$.[17] We will return to this observation later. The master curve obtained for one HPI sample is shown in Figure 3. The master curve for an EP copolymer, JBG-11, a sample which has a much broader molecular weight distribution, is shown in Figure 4.

The forms of the master curves for PI and HPI are typical of the terminal and plateau responses for nearly monodisperse linear polymers in the entanglement region.[17,18] The shape is not changed by hydrogenation, as shown by the PI–HPI comparison in Figure

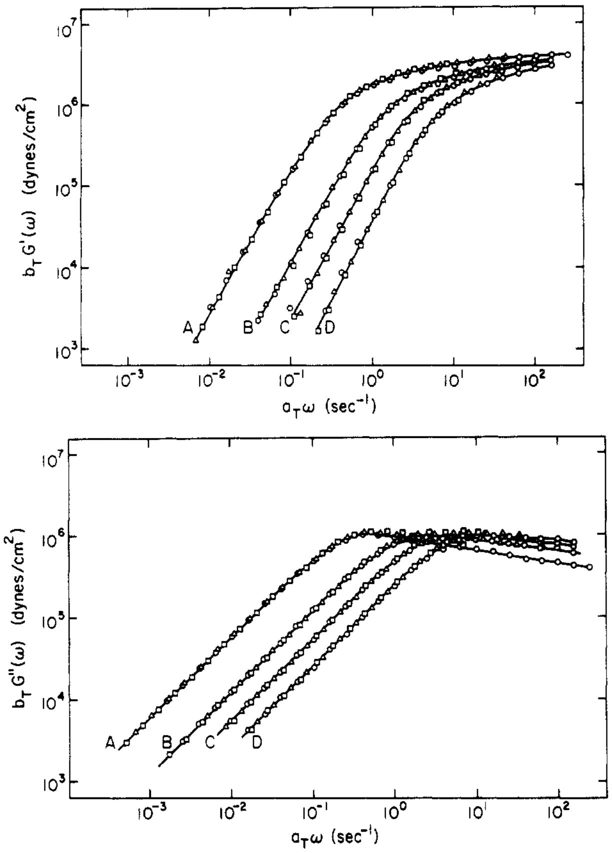

Figure 2. Dynamic modulus master curves for polyisoprenes. Data at 25 (○), 50 (△), and 75 °C (□) for PI-1.596L (A), PI-1.115L (B), PI-0.991L (C), and PI-0.922L (D) at reference temperature 25 °C.

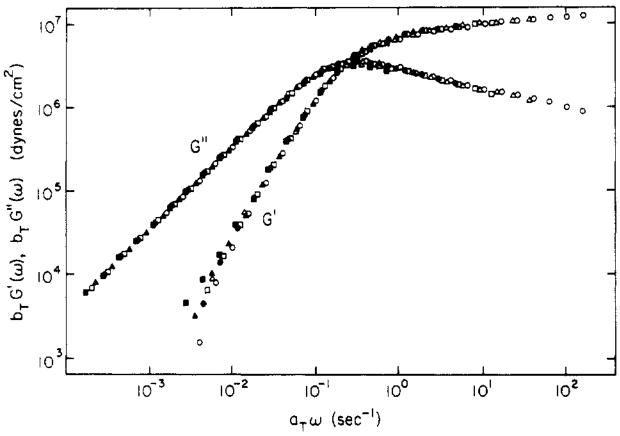

Figure 3. Dynamic modulus master curves for hydrogenated polyisoprene HPI-1.596L. Data at 50 (○), 75 (△), 100 (□), 130 (●), 160 (▲), and 190 °C (■), reduced in this case to 50 °C.

5, supporting the earlier conclusion from dilute solution characterization that the large-scale structure is unaltered. Like T_g, and, as seen in many other linear polymer systems, the temperature shift factors depend on the chain microstructure but not on chain length.[17]

At low frequencies, $G' \propto \omega^2$ and $G'' \propto \omega$, providing values of the zero-shear viscosity η_0 and steady-state recoverable compliance $J_e°$:[17]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{7}$$

$$J_e° = \frac{1}{\eta_0^2} \lim_{\omega \to 0} \frac{G'(\omega)}{\omega} \tag{8}$$

At higher frequencies $G''(\omega)$ passes through a maximum, G_m'' at ω_m. The terminal loss peak becomes progressively more well-defined, i.e., further separated from the transition response, with increasing chain length. The plateau modulus $G_N°$ can be determined by an integration over a fully resolved terminal loss peak:[17]

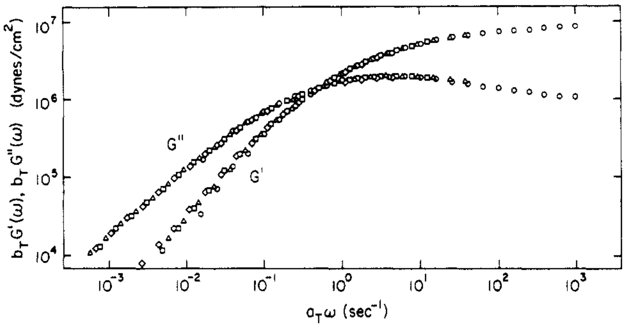

Figure 4. Dynamic modulus master curves for ethylene–propylene copolymer JBG-11. Data at 25 (○), 75 (△), 100 (□), and 130 °C (○) reduced in this case to 25 °C.

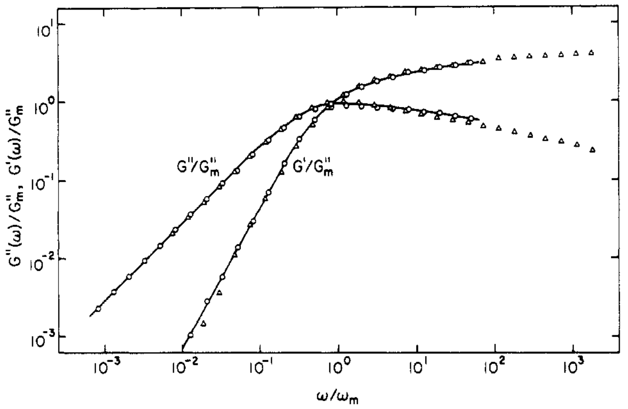

Figure 5. Comparison of reduced master curves for hydrogenated polyisoprene (HPI-1.115L) and its polyisoprene precursor (PI-1.115L). Symbols: (○) PI and (△) HPI.

$$G_N° = \frac{2}{\pi} \int_{-\infty}^{\infty} G''(\omega)\, \mathrm{d} \ln \omega \tag{9}$$

When the resolution is incomplete or uncertain the plateau modulus can still be estimated from $G'(\omega)$ in the upper portion of the plateau. For nearly monodisperse linear polymers, an approximate value of $G_N°$ can also be calculated from G_m'' with a relationship obtained by Raju et al.:[18]

$$G_N° = 3.56 G_m'' \tag{10}$$

The values of $J_e°$ and $G_N°$ are practically independent of temperature because they scale with b_T alone.[19] When $b_T = 1$

$$\eta_0(T) = a_T \eta_0(T_0) \tag{11}$$

so the frequency shift factor parallels the temperature dependence of viscosity. Values of η_0, $J_e°$ and $G_N°$ (from eq 10) at $T_0 = 25$ °C for PI and $T_0 = 100$ °C for HPI and EP are given in Tables IV and V. Values of a_T for the various microstructures, obtained with eq 11, are listed in Tables VI and VII.

Results and Discussion

A. Molecular Weight and Temperature Dependence of Viscosity. Figure 6 shows viscosity vs. molecular weight at 25, 50, and 75 °C for polyisoprenes with the ~8% 3,4 microstructure. All molecular weights are well above the reported M_c of 10 000 for such polyisoprenes,[20] so entangled behavior is expected for the viscosity. The results at 25 °C agree well with the data of Holden[21] and Pearson[22] for similar polyisoprenes in the same range ($45\,000 \leq M \leq 250\,000$). The values of Nemoto et al.,[20] extrapolated to 25 °C from their reference temperature of

Table IV
Rheological Properties of Polyisoprenes at 25 °C

sample	% 3,4	η_0, P	$10^7 J_e°$, cm²/dyn	$10^{-6} G_N°$,[a] dyn/cm²	$J_N° G_N°$
PI-0.465L	8	1.45×10^4	5.80		
PI-0.634L	8	7.26×10^4	5.75	3.56	2.05
PI-0.729L	8	1.11×10^5	6.09	3.42	2.09
PI-0.920L	11	3.02×10^5	5.94	3.75	2.22
PI-0.922L	8	2.64×10^5	6.25	3.54	2.20
PI-0.991L	8	5.50×10^5	5.75	3.44	1.98
PI-1.115L	8	1.23×10^6	6.60	3.33	2.20
pI-1.596L	7	6.07×10^6	7.20	3.63	2.61
PI-1.395H	16	1.30×10^7	5.37	3.72	2.00
PI-0.947H	18	1.55×10^6	5.75	3.72	2.13
PI-0.699H	20	2.00×10^5	5.62	3.76	2.12
PI-1.058H	29	6.03×10^6	5.75	3.48	2.00
PI-0.813H	33	1.51×10^6	7.41	3.24	2.40
PI-1.141H	34	1.24×10^7	5.75	3.47	1.99

[a] Calculated from G_m'' with eq 10.

Table V
Rheological Properties of Hydrogenated Polyisoprenes at 100 °C

sample	% 3,4	η_0, P	$10^7 J_e°$, cm²/dyn	$10^{-6} G_N°$, dyn/cm²	$J_e° G_N°$
HPI-0.465L	8	(9.08×10^3)[a]	2.15	10.6	2.28
HPI-0.634L	8	4.19×10^4	1.92	11.0	2.11
HPI-0.729L	8	7.99×10^4	1.99	11.0	2.21
HPI-0.920L	11	(1.62×10^5)[a]	1.82	11.3	2.06
HPI-0.922L	8	1.62×10^5	2.06	11.0	2.27
HPI-0.991L	8	3.31×10^5	1.90	11.3	2.15
HPI-1.115L	8	7.24×10^5	1.80	11.5	2.07
HPI-1.596L	7	2.76×10^6	2.29	11.7	2.68
HPI-1.395H	16	3.02×10^6	2.51	8.9	2.23
HPI-0.949H	18	3.56×10^5	2.51	8.6	2.16
HPI-0.699H	20	3.63×10^4	2.54	7.9	2.01
HPI-1.058H	29	3.16×10^5	3.55	5.7_5	2.04
HPI-0.813H	33	5.13×10^4	4.79	4.9_5	2.37
HPI-1.141H	34	3.31×10^5	3.98	5.1_5	2.05
JBG-11[b]		1.35×10^6	~20	15.8	~32

[a] Interpolated or extrapolated from data at other temperatures using eq 13. [b] EP copolymer.

Table VI
Frequency Shift Factors for Polyisoprenes (T_0 = 25 °C)

% 3,4	T_g, °C	log a_{50}	log a_{75}
8	-68	-0.68	-1.17
16	-61	-0.82	-1.33
18	-59	-0.77	-1.35
20	-59	-0.80	-1.37
29	-50	-0.98	-1.61
33	-45	-0.97	-1.66
34	-44	-1.02	-1.77

-30 °C, are larger by about a factor of 2, but this may well be caused simply by the uncertainties of such a long extrapolation. Probably for the same reason, that correlation for a_T, obtained from measurements in the vicinity of -30 °C, does not correctly predict the temperature dependence of our viscosities when applied to the range 25–75 °C.

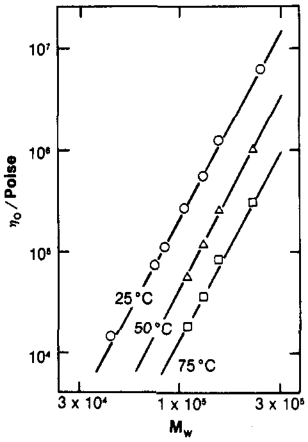

Figure 6. Molecular weight dependence of viscosity for polyisoprene at several temperatures.

Table VII
Frequency Shift Factors for Hydrogenated Polyisoprenes (T_0 = 100 °C)

	% 3,4	T_g, °C	log a_{25}	log a_{50}	log a_{75}	log a_{130}	log a_{160}	log a_{190}
	8	-62	1.93	1.12	0.45_5	-0.45	-0.81	-1.11
	16	-59		1.18	0.53	-0.46	-0.82	-1.11
	18	-57	2.09	1.22	0.53	-0.50	-0.86	-1.17
	20	-56	2.30	1.31	0.55			
	29	-49	2.38	1.39	0.61	-0.53	-0.93	-1.25
	33	-45	2.61	1.46	0.63			
	34	-42		1.46	0.64	-0.53	-0.95	-1.26
JBG-11		-63	1.73	1.00	0.49	-0.43	-0.82	-1.10
JBG-11[a]		-62	2.00	0.95			-0.70[b]	

[a] Data provided by Dr. Pawan Agarwal, Exxon Corporate Science Laboratories. [b] Value of log a_{150}.

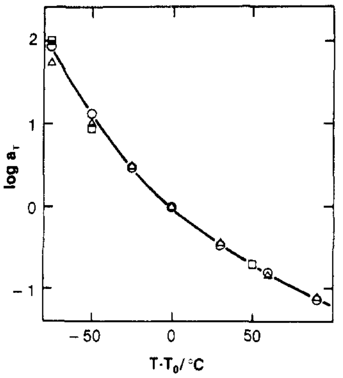

Figure 7. Temperature shift factor a_T for hydrogenated polyisoprene and an ethylene–propylene copolymer. Average of values for several HPI samples (8% 3,4) (○), JBG-11 (△), and JBG-11 results from P. Agarwal (□); T_0 = 100 °C.

The viscosity results for the 8% 3,4 microstructure at 25 °C are described by the equation

$$\eta_0 = 2.37 \times 10^{-13} M^{3.59} \qquad \text{(PI)} \qquad (12)$$

and the temperature shifts by a WLF equation[17]

$$\log a_T = \frac{-4.1(T - T_0)}{122 + (T - T_0)} \qquad \text{(PI)} \qquad (13)$$

with T_0 = 25 °C. Equation 13 also applies for the other PI microstructures if T_0 is adjusted for the change in glass transition temperature: $T_0 = 25 + \Delta T_g$, where ΔT_g is the difference in T_g from −67 °C, the value for the 8% 3,4 microstructure. Thus, the temperature coefficient of viscosity is independent of PI microstructure at a constant distance from T_g.

Temperature shift factors for frequency (and viscosity) in the range 25–190 °C (T_0 = 100 °C) are shown in Figure 7 for hydrogenated polyisoprenes (8% 3,4 microstructure) and an ethylene–propylene copolymer (JBG-11). Values obtained for JBG-11 by Dr. Pawan Agarwal, Exxon Corporate Research Laboratories, are also included. The agreement of HPI and EP shift factors is excellent at elevated temperatures. At the lower temperatures, 25 and 50 °C, the shifts for JBG-11 appear to be slightly smaller, but we believe those differences are due to the experimental problems associated with the large viscosity of JBG-11 at the lower temperatures. The departures in any case are opposite to those expected if incipient crystallizability were somehow influencing the viscosity of JBG-11 at low temperatures.

The solid line in Figure 7 is the fit obtained for the HPI data to a WLF equation (T_0 = 100 °C):

$$\log a_T = \frac{-3.91(T - T_0)}{227 + (T - T_0)} \qquad \text{(HPI)} \qquad (14)$$

Agreement with the WLF form is uniformly good from 25 to 190 °C, a range which corresponds to $T - T_g$ values for HPI from ~90 to ~250 °C. It is sometimes suggested that the temperature dependence of viscosity obeys the Arrhenius equation ($\log \eta_0 \propto T^{-1}$) for $T - T_g > 100$ °C. This is clearly incorrect, at least for HPI, since plots of $\log \eta_0$ vs. T^{-1} curve continuously at least up to $T - T_g$ = 200 °C.[4] Beyond that temperature ($T \sim 140$ °C) we cannot distinguish; the data for HPI and EP are fitted equally well by the WLF form (eq 14) and with $E_v \equiv R\, \mathrm{d} \ln \eta_0 / \mathrm{d}T^{-1}$ = 9.8 kcal/mol (100–190 °C).

As in the polyisoprene series, the equation describing behavior for the 8% 3,4 HPI microstructure (eq 14) also represents the shift factor for other HPI microstructures when the reference temperature is at a fixed distance from T_g. In this case, $T_0 = 100\ °\text{C} + \Delta T_g$, where ΔT_g is the difference from the value of −62 °C for the 8% 3,4 HPI microstructure.

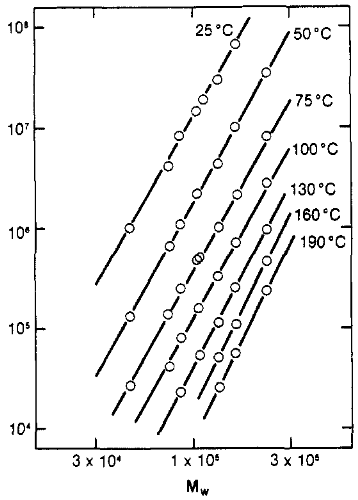

Figure 8. Molecular weight dependence of viscosity for hydrogenated polyisoprene (8% 3,4 content) at several temperatures.

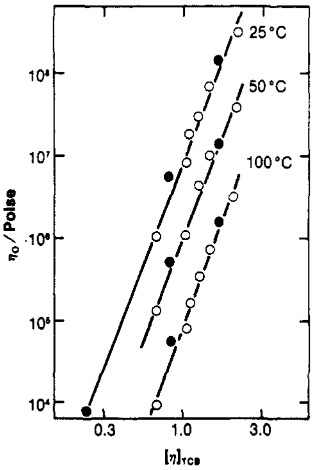

Figure 9. Melt viscosity vs. intrinsic viscosity for hydrogenated polyisoprenes (8% 3,4 content) and nearly equimolar ethylene–propylene copolymers. Symbols: (○) HPI and (●) EP.

The viscosity–molecular weight behavior of HPI with the 8% 3,4 microstructure is shown in Figure 8. The molecular weight exponent is independent of temperature. At 100 °C

$$\eta_0 = 4.86 \times 10^{-13} M^{3.48} \qquad \text{(HPI)} \qquad (15)$$

The values of viscosity for EP copolymers (such as JBG-11) do not agree with eq 15 ($\bar{M}_w$ for the EP sample in place of M). Molecular weights of the EP copolymers were obtainable only by light scattering at 135 °C, and the discrepancy between EP and HPI seems mainly to arise from the unexplained differences in characterization results noted earlier. The apparent disagreement largely disappears when comparisons of melt viscosity are made through the intrinsic viscosity in TCB at 135 °C, as shown by Figure 9.

B. Plateau Modulus and Recoverable Compliance. Figure 10 shows the plateau modulus as a function of microstructure for the PI and HPI polymers. In the PI series the values of $G_N°$ are practically independent of 3,4 content from 8% to 33%; $G_N°$ is considerably larger for 8% 3,4 HPI but decreases rapidly with increasing 3,4 content over the same range.

Table VIII
Values of $G_m''(T)/G_m''(25\ ^\circ C)$ for Hydrogenated Polyisoprene (8% 3,4)

	$G_m''(T)/G_m''(25\ ^\circ C)$						
sample	50 °C	75 °C	100 °C	130 °C	160 °C	190 °C	205 °C
HPI-0.729L	1.03	1.03	1.00				
HPI-0.922L		0.93	0.94				
HPI-0.991L	1.00	0.96	0.90	0.87			
HPI-1.115L	0.99	1.00	1.05	0.98	0.93	0.85	
HPI-1.596L		0.93	0.98	0.96	0.93	0.85	0.85

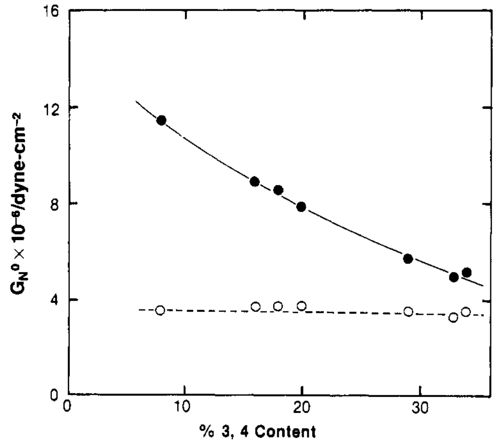

Figure 10. Plateau modulus vs. 3,4 content for polyisoprene and hydrogenated polyisoprene. Symbols: (○) PI and (●) HPI.

These trends with microstructure are consistent with a recent suggestion that plateau modulus is essentially a universal function of the concentration of Kuhn steps in the liquid.[23] The proposed equation is

$$G_N^0 l^3/kT = K(\nu L l^2)^d \tag{16}$$

where ν is the number of chains per unit volume, L is the contour length of the chains, l is the Kuhn step length, K is a universal constant, and the exponent d is in the range 2.0–2.3. The Kuhn step length is related to the characteristic ratio of the polymer:[24] $l = C_\infty l_0$, where l_0 is the average skeletal bond length. Equation 16 implies that, for isothermal variations with microstructure in a series of polymers with similar ρ and l_0,

$$G_N^\circ \propto C_\infty^{2d-3}/m_0^d \tag{17}$$

where m_0 is the average molecular weight per backbone bond. In the PI series, C_∞ increases slightly with 3,4 content, going from a value of 5.1 at 8% 3,4[25] to 5.3 at 49% 3,4.[15] In the corresponding HPI samples, C_∞ decreases with 3,4 content, going from 6.2 to 5.0.[15] The value of m_0 increases with 3,4 content in both series. Thus, changes in C_∞ and m_0 tend to offset one another across the PI series. The result is a much weaker variation in G_N° with microstructure than in the HPI series, where changes in both C_∞ and m_0 act to decrease G_N° with increasing 3,4 content.

The following average values of plateau modulus for polyisoprene at 25 °C and hydrogenated polyisoprene at 100 °C (8% 3,4 microstructure) were obtained with eq 10:

$$G_N^\circ = 3.5_2 \times 10^6 \text{ dyn/cm}^2 \quad \text{(PI)} \tag{18}$$

$$G_N^\circ = 11.4 \times 10^6 \text{ dyn/cm}^2 \quad \text{(HPI)} \tag{19}$$

These values correspond to entanglement molecular weights, $M_e \equiv \rho RT/G_N^\circ$, of 6400 and 1860, respectively. The value for PI agrees fairly well with other reported results on *high-cis*-polyisoprene[22,26] and natural rubber.[17] For HPI-1.596L, the terminal peak was sufficiently well resolved to apply eq 9, and a slightly larger value, $G_N^\circ = 12.2 \times 10^6$ dyn/cm^2, was obtained. Extrapolation of the HPI results to 0% 3,4 content gave $G_N^\circ = 15.1 \times 10^6$ dyn/cm^2, lying between the published values[17,27] for nearly equimolar EP copolymers near room temperature, 12.6×10^6 and 17.0×10^6 dyn/cm^2, respectively. It agrees very well with $G_N^\circ = 15.8 \times 10^6$ dyn/cm^2, estimated from $G'(\omega)$ at high frequencies for JBG-11, and with results obtained from eq 9 for several other EP copolymers.[14] It is larger than the average of values reported recently for a series of EP copolymers and EPDM terpolymers of somewhat higher ethylene content, $G_N^\circ = 11.9 \times 10^6$ dyn/cm^2.[28]

The product $J_e^\circ G_N^\circ$, a measure of the breadth of the terminal spectrum,[18] is practically independent of microstructure (Tables IV and V). Most values lie in the range, $2.0 < J_e^\circ G_N^\circ < 2.5$, which is typical for entangled linear chains with narrow molecular weight distributions. The much larger value of $J_e^\circ G_N^\circ$ for the EP copolymer JBG-11 is clearly the result of its broad molecular weight distribution. The average of recoverable compliance values for the 8% 3,4 microstructure is

$$J_e^\circ = 6.0_3 \times 10^{-7} \text{ cm}^2/\text{dyn} \quad \text{(PI)} \tag{20}$$

$$J_e^\circ = 1.9_5 \times 10^{-7} \text{ cm}^2/\text{dyn} \quad \text{(HPI)} \tag{21}$$

(The somewhat larger values for HPI-1.596L and its polyisoprene precursor were omitted in the averaging.) The PI value agrees fairly well with estimates from the extrapolation of data on concentrated PI solutions,[29] $J_e^\circ = (4.8\text{–}6.3) \times 10^{-7}$ cm^2/dyn, depending on the choice of concentration exponent. An earlier result for undiluted PI samples of similar microstructure, $J_e^\circ = 14 \times 10^{-7}$ cm^2/dyn,[20] is considerably larger for reasons unknown.

C. Temperature Dependence of Plateau Modulus. In the Experimental Section we noted that the modulus shift factor b_T is practically constant for HPI despite the large temperature span of the experiments (25–205 °C); G_m'' actually decreases slightly over this range. It is usual to assume that b_T for the terminal and plateau responses has the temperature dependence associated with the Rouse model:[17]

$$b_T = \rho T/(\rho T)_0 \tag{22}$$

The plateau modulus determines the modulus scale in those regions, and eq 16 gives a different temperature dependence:

$$b_T = \frac{G_N^\circ(T)}{G_N^\circ(T_0)} = \frac{\rho^d T C_\infty^{2d-3}}{(\rho^d T C_\infty^{2d-3})_0} \tag{23}$$

from which factors such as l_0, L, and M, which do not change with temperature, have been canceled.

The temperature coefficients of density and chain dimensions are known for nearly equimolar ethylene–propylene copolymers:[2,30]

$$-\mathrm{d} \ln \rho/\mathrm{d}T = \alpha = 0.75 \times 10^{-3}\ ^\circ\mathrm{C}^{-1} \tag{24}$$

$$\mathrm{d} \ln C_\infty/\mathrm{d}T = \kappa = -1.2 \times 10^{-3}\ ^\circ\mathrm{C}^{-1} \tag{25}$$

Calculations based on the rotational isomeric model suggest that κ would not be much different for the strictly alternating EP (HPI) microstructure ($r_1 = r_2 = 0$).[30] Ex-

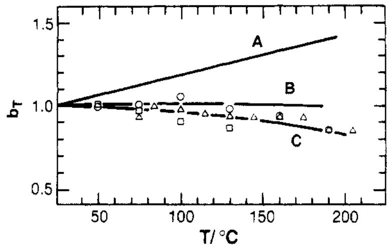

Figure 11. Modulus shift factor vs. temperature for hydrogenated polyisoprene (8% 3,4 content). Symbols: (□), HPI-0.991L (○) HPI-1.115L, and (△) HPI-1.596L. Curve A calculated from eq 22, curve B from eq 23 with d = 2.0, and curve C from eq 23 with d = 2.3.

perimental b_T values for the 8% 3,4 HPI structure, expressed as $G_m''(T)$ normalized to 25 °C (Table VIII), are compared in Figure 11 with values calculated from eq 22 and from eq 23 with $d = 2.0$ and $d = 2.3$. The data quite clearly rule out the Rouse form (eq 22) and agree rather well with the values from eq 23. Agreement for $d = 2.3$ is slightly better, but that distinction almost certainly goes beyond the precision of the data. Scholtens has recently found a very similar behavior in EP copolymers and pointed out a similar consistency with eq 23 for $d = 2$.[28] Similar comparisons have been made for other polymer species, κ being positive in some cases and negative in others.[31] In those cases the behavior of b_T also seems in good agreement with eq 23. Values of b_T must of course be available over a wide range of temperature to make any test; for this reason nothing can be concluded from the polyisoprene results. Finally, we note that departures of a similar nature from eq 22 are suggested by a recent theory of $G_N°$ by Ronca.[32]

Conclusions

We have shown that linear polyisoprene can be reacted with H_2 over a $Pd/CaCO_3$ catalyst to provide nearly monodisperse samples of hydrogenated polyisoprene. They have the same chemical microstructure as a strictly alternating copolymer of ethylene and propylene ($r_1 = r_2 = 0$), interrupted occasionally by isopropyl side groups (~16 per 1000 backbone carbons for HPI's from PI's with ~8% 3,4 content). At low 3,4 levels many properties of HPI closely resemble those of nearly equimolar ethylene–propylene copolymers. They are virtually the same in density, glass transition temperature, plateau modulus, temperature coefficient of viscosity, and relationship between melt viscosity and intrinsic viscosity. Other properties of the melt, such as the shape of the viscoelastic spectrum and recoverable shear compliance, are different, but such differences are expected from the much narrower molecular weight distribution of HPI. Also, unlike EP copolymers of the same average composition, HPI is noncrystalline at all temperatures, reflecting the difference in methylene sequence distribution. There is as yet an unfortunate and unresolved discrepancy in molecular weight determinations which prevents an unambiguous comparison of HPI and EP viscosities at the same molecular weight. Aside from this problem, however, HPI appears to be a good model for nearly equimolar EP copolymers. The differences are either small or quite natural consequences of known variations between HPI and EP copolymers in either large-scale chain structure or chemical microstructure.

Beyond such modeling considerations, we have shown that the time–temperature superposition principle is applicable to linear PI and HPI polymers and that the shift factor for time (frequency) obeys the WLF equation. Moreover, the same WLF coefficient was shown to apply for different PI and HPI microstructures (up to 34% 3,4 content), when the reference temperature is adjusted to the same interval above the glass transition temperature.

We also examined the variations in plateau modulus with chemical microstructure in PI and HPI. In the PI series, $G_N°$ is practically independent of 3,4 content; in the HPI series, $G_N°$ falls rapidly with increasing 3,4 content in the parent PI. This behavior was shown to be qualitatively consistent with microstructurally related changes in Kuhn step length and molecular weight per main chain bond, as suggested recently by Graessley and Edwards.

Finally, we exploited the combination of thermal stability and low glass transition temperature of HPI to test theories of the temperature dependence of modulus scale in entangled liquids. The classical expression for the shift factor, $b_T \propto \rho T$, was shown to be inconsistent with observed behavior in the plateau and terminal viscoelastic regions. The experimental data agree rather well with a result from the Graessley–Edwards analysis of plateau modulus, $b_T \propto \rho^d T C_\infty^{2d-3}$, with d = 2.0–2.3.

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Effects of Chain Microstructure on the Viscoelastic Properties of Linear Polymer Melts: Polybutadienes and Hydrogenated Polybutadienes

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ABSTRACT: Linear viscoelastic properties in the plateau and terminal regions were measured over wide ranges of temperature and chain microstructure in melts of polybutadiene and hydrogenated polybutadiene. All samples were linear with high molecular weights ($M \gg M_c$) and narrow distributions ($\bar{M}_w/\bar{M}_n < 1.1$). The polybutadienes vary in microstructure from 8% to 99% vinyl content; the hydrogenated polybutadienes are equivalent structurally to copolymers of ethylene with 4–99% 1-butene. Primary attention was given to properties that depend on chain microstructure but are insensitive to chain length for long chains—the plateau modulus G_N°, the steady-state recoverable compliance J_e°, and the temperature shift factors for the frequency and modulus, a_T and b_T. The microstructural effects on a_T reflect primarily the location of the glass transition: a_T is a unique function of $T - T_g$ for all microstructures in the PB series and also for the noncrystallizable members of the HPB series. This characteristic was used to estimate T_g values for the crystallizable HPB members and gives, by extrapolation, -70 °C $< T_g \lesssim -105$ °C for amorphous polyethylene. The product $J_e^\circ G_N^\circ$ was found to be practically independent of chain microstructure, reflecting the universal nature of the terminal relaxation spectrum for entangled linear polymers with near-monodisperse distributions. The classical form for the modulus shifts, $b_T \propto \rho T$, was shown to be incorrect in general. Variations in both b_T and G_N° with microstructure were analyzed in terms of a recent theory which associates G_N° with the concentration of polymeric Kuhn steps in the liquid.

I. Introduction

A number of important problems in polymer melt rheology have to do with the effects of chain microstructure. Microstructure of course influences a wide range of physical properties—density, melting temperature, glass transition, crystalline morphology, etc. However, both large-scale structure and local structure play important roles in the determination of the rheological properties. Many studies have dealt with the large-scale contribution,[2,3] but comparatively few with the systematic effects of microstructure. The purpose of the present work was to examine the variation in rheological properties of polymer melts with local chain structure. We have used nearly monodisperse systems of linear chains and have focused on those properties which become independent of chain length for long chains, e.g., the temperature coefficients of viscoelastic response, the plateau modulus G_N°, and the steady-state recoverable compliance J_e°. Two series of samples were used, polybutadienes which had been synthesized with a range of microstructures by anionic polymerization, and fully hydrogenated versions of the same polymers. Depending on polymerization conditions, the polybutadiene (PB) samples range from ~8% to ~99% in vinyl group content. Hydrogenation saturates the backbone double bonds and converts vinyl branches to ethyl branches. The hydrogenated polybutadienes (HPB) are structurally equivalent to copolymers of ethylene and 1-butene with compositions from ~4% to ~99% 1-butene. The proportion of backbone double bonds decreases with increasing vinyl branch frequencies in the PB series; the HPB backbone is of course fully saturated for all ethyl branch frequencies. The effect of long branches will be reported in a later paper on PB and HPB stars.

II. Experimental Procedures

A. Polymerization and Hydrogenation. All samples in this study were prepared by anionic polymerization of butadiene. Conditions were chosen to yield linear chains of high molecular weight ($M > 50\,000$) and narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n < 1.1$). In most cases the polymerizations were conducted at 50 °C in cyclohexane under a nitrogen atmosphere. The capped-bottle technique of Hsieh was used with *sec*-butyllithium as the initiator. The polybutadienyl anions were deactivated with dry 2-propanol stored under nitrogen. Enchainment of butadiene results in three types of structural units–1,4 cis, 1,4 trans, and 1,2 (vinyl). Unmodified polymerization in nonpolar media results in ~8% 1,2 addition. Higher levels of 1,2 addition were obtained by the addition of small quantities of tetrahydrofuran, combined in some cases with a lower polymerization temperature. Samples with nearly 100% 1,2 addition were prepared at the University of Akron by vacuum line techniques. Room-temperature polym-

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