Characteristic Ratios of Model Polydienes and Polyolefins

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Received January 11, 1984

ABSTRACT: Homogeneous anionic polymerization offers several unique advantages in the polymerization of diene monomers. Polymers prepared by this method possess extremely narrow molecular weight distributions and are free of branching. The microstructure of the polymer may be controlled by the choice of polymerization conditions. Amorphous polyolefins can be obtained by hydrogenation of diene polymers. Polyolefins prepared in this manner retain the desirable characteristics of the parent material, i.e., narrow molecular weight distributions and an absence of branching. Hence these polymers are ideal models for testing molecular theories. Several series of model polydienes and polyolefins have been prepared by the aforementioned techniques. These polymers have been carefully characterized, with particular emphasis on determining the effect of molecular architecture on chain stiffness as defined by the characteristic ratio. Glass transition temperatures are also reported.

Introduction

The rotational isomeric state (RIS) model[2,3] has proven useful for predicting the unperturbed dimensions of polymer chains. Unfortunately, there is a shortage of thorough experimental studies on unperturbed dimensions which employ model polymers. Model polymers are necessary for such studies since branching or compositional heterogeneity can lead to significant errors in the results which are obtained.

Homogeneous anionic polymerization is a powerful tool for the preparation of linear polymers of well-defined structures. Unfortunately, the variety of monomers which are amenable to controllable anionic polymerizations is somewhat limited, e.g., styrenes, some conjugated dienes, and a few others. Olefins are not polymerized to high molecular weights by typical anionic initiators such as butyllithium. However, it has recently been demonstrated[4–6] that quantitative hydrogenation of polydienes can lead to amorphous polyolefins which retain the desirable characteristics of the parent materials, i.e., narrow molecular weight distributions and an absence of branching. Consequently, these materials are model polymers for testing molecular theories such as the rotational isomeric state model.

In this work, several series of polydienes and polyolefins were prepared by the aforementioned techniques. These polymers were carefully characterized, with particular emphasis on determining the effect of molecular architecture on chain posture as defined by the characteristic ratio. A subsequent paper will discuss the viscoelastic properties of these materials.

Experimental Section

Three series of model polydienes were prepared by the general vacuum line procedures described elsewhere.[7] Purified *sec*-butyllithium was the initiator in all the systems. Mixed-microstructure polybutadienes, IUPAC name poly(1-butenylene-*co*-vinylethylene) (12PBD), were prepared by using cyclohexane as the principal solvent and adding triethylamine (TEA) in a 500:1 molar ratio based on initiator concentration. The polymerizations were carried out between 5 and 10 °C for 48–72 h. Microstructure analysis by ^{13}C NMR gave 43% 1,2 units. Cis-1,4 vs. trans-1,4 content was analyzed by infrared spectroscopy and was found to be about 2.3:1 trans to cis.

Mixed-microstructure polyisoprenes, IUPAC name poly(1-methyl-1-butylene-*co*-isopropenylethylene) (50PI), were prepared by using a cyclohexane–TEA mixture (30% TEA by volume) as solvent. Reactions were run at ambient temperatures and were complete after about 24 h. ^{1}H NMR analysis gave about 51% 1,4 units and about 49% 3,4 units. The 1,4 units were revealed by infrared spectroscopy to be present primarily in the trans conformation. The presence of about 1–2% of the 1,2 units should also be noted.

The use of triethylamine as the polar cosolvent in the diene polymerizations was prompted by our observation that the polymer microstructure was insensitive to minor variations in the amine/lithium ratios used in this work. Thus slight fluctuations in the concentration of TEA could be tolerated without incurring a concomitant change in the 1,2:1,4 content. Thus, the requisite series of polydienes were prepared with only molecular weight as the variable.

High-vinyl polyisoprenes, IUPAC name poly(isopropenylethylene-*co*-1-methyl-1-vinylethylene) (34PI) were prepared by using *sec*-butyllithium complexed with 1,2-dipiperidinoethane (DPE) for the polymerization of isoprene in cyclohexane at room temperature. Reactions were allowed to proceed for 24–48 h. A 5/1 molar ratio of DPE/*sec*-BuLi was maintained in each reaction. Previously, polybutadiene of virtually 100% 1,2 content was prepared under similar conditions.[5,8] In the case of polyisoprene, the microstructure of the polymer is more complex. Infrared analysis indicated the microstructure to be 20–25% 1,2, 70–75% 3,4, and <5% 1,4 units. This result is in good agreement with the results reported by Kow et al.[9] and is supported by the ^{13}C NMR results on the hydrogenated analogues of this polyisoprene.

Model polyolefins were prepared by hydrogenating the three series of polydienes described above. A series of anionically prepared 1,4-polyisoprenes (70% cis-1,4, 23% trans-1,4, and 7% 3,4 units) were also hydrogenated. Hydrogenation of 12PBD yields an ethylene–1-butene copolymer, IUPAC name poly(ethylene-*co*-isopropylethylene) (H$_2$12PBD). Similarly, poly(1-methylbutylene-*co*-isopropylethylene) (H$_2$50PI) was obtained from 50PI, poly(isopropylethylene-*co*-1-methyl-1-ethylethylene) (H$_2$34PI) was obtained from 34PI, and poly(methylbutylene) (Et-Prop) was obtained from 1,4-polyisoprene; IUPAC name poly(2-methyl-1-butenylene).

The Pd/CaCO$_3$-catalyzed hydrogenation of dienes has been shown previously to be both quantitative and free of side reactions.[4–6] Both ^{1}H NMR and infrared measurements verified complete hydrogenation for all the polyolefinic samples used in this study.

Figure 1 shows the size exclusion chromatograms (SEC) for a polymer before and after hydrogenation. These chromatograms were obtained with a Waters 150C instrument equipped with six μ-Styragel columns having a nominal porosity range of 10^6–10^2 Å. Purified (by distillation) tetrahydrofuran (THF) was the carrier solvent at a flow rate of 1 mL min^{-1} and a temperature of 30 °C. The shapes of the two chromatograms are identical; the slight low molecular weight tails observed for both samples are presumably due to a chain termination event which occurs during polymerization in the presence of TEA. Any large-scale chain degradation or branching occurring during the hydrogenation event would be detected by the SEC measurements. Some SEC work was performed on a Waters Ana-Prep instrument in THF at 30 °C. In this case a seven-column Styragel set with a continuous porosity range from 10^6 to 10^3 Å was used.

The weight-average molecular weights were measured statically with the Chromatix KMX-6 low-angle photometer and/or the KMX-6 interfaced with the Waters 150C SEC (SEC–LALLS). SEC–LALLS measurements were carried out in THF at 30 °C.

0024-9297/84/2217-2723$01.50/0

Table I
Specific Refractive Index Increments for Model Polymers at 30 °C (λ = 633 nm)

polymer	dn/dc, mL g^{-1} cyclohexane	dn/dc, mL g^{-1} tetrahydrofuran
12PBD	0.1019	
$H_2$12PBD	0.0614	0.0796
50PI	0.1020	
$H_2$50PI		0.0818
34PI	0.1010	
$H_2$34PI		0.0908
Et-Prop		0.0788

Table II
Θ Conditions for Model Polymers

polymer	solvent	Θ temp, °C
12PBD	1,4-dioxane	15.7
$H_2$12PBD	n-hexyl acetate	65.0
50PI	2-octanol	41.3
$H_2$50PI	2-octanol	55.3
34PI	2-octanol	30.5
$H_2$34PI	2-octanol	26.2
Et-Prop	n-hexyl acetate	60.9

Table III
Glass Transition Temperatures of Model Polymers

	T_g, °C				
polymer	20 °C/min	10 °C/min	5 °C/min	2 °C/min	0 °C/min
12PBD	-59	-63	-65		-67
$H_2$12PBD	-58	-64	-67		-70
50PI	-15	-19	-22		-24.5
$H_2$50PI	-20	-22	-23.5		-25
34PI	+16	+14	+13	+12.5	+12
$H_2$34PI	+23	+19	+15.5	+14.5	+13
Et-Prop	-52	-56	-58		-60

The static measurements used cyclohexane as the solvent at 25 °C. The KMX-6 is equipped with a helium-neon laser and operates at a wavelength of 633 nm.

The specific refractive index increments of the polymers were measured with the Chromatix KMX-16 refractometer at 30 °C. These values are given in Table I. The number-average molecular weights were measured with a Hewlett-Packard 503 membrane osmometer with toluene as the solvent at a temperature of 37 °C.

Intrinsic viscosities were obtained for all polymers in both THF and under Θ conditions. Cannon-Ubbelohde semi-micro viscometers with negligible kinetic energy corrections were employed. Solvents for the viscosity measurements and other dilute solution studies were all dried and fractionally distilled just prior to use.

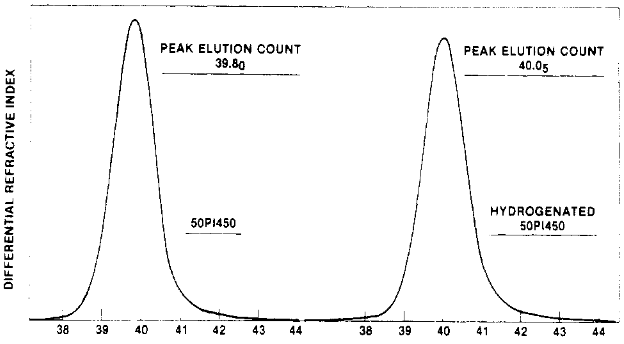

Figure 1. Size exclusion chromatograms of 50PI450 and $H_2$50PI450 samples. The differences in the peak elution counts are a reflection of the values of the respective characteristic ratios.

Θ conditions were determined in purified solvents with the Sofica light scattering photometer. Second virial coefficients were measured as a function of temperature, and the temperature at which $A_2 = 0$ was taken as the Θ temperature. Table II lists the Θ conditions for the various model polymers.

The DuPont 990 DSC was used to determine the thermal properties of the polymers. The instrument was calibrated with indium and mercury as the standards. Glass transition temperatures were determined by extrapolation of the measured values vs. heating rate to zero heating rate. The results are given in Table III. It should be noted that the glass transition temperature was the only transition found for any of these polymers over the temperature range -100 to ca. +150 °C. Consequently, these polymers may be considered amorphous. Solubility in common solvents is further evidence of their amorphous nature. The atactic nature of the polyolefinic materials was also demonstrated by ^{13}C NMR analysis, i.e., no indication was found that long-range stereoregular sequences existed in these materials.

Results and Discussion

The molecular characteristics of the model polymers are given in Tables IV–X. SEC polydispersities ($\bar{M}_w/\bar{M}_n$) are in good agreement with polydispersities determined by absolute methods, i.e., light scattering and osmometry. SEC polydispersities ($\bar{M}_z/\bar{M}_w$) are not listed; suffice it to mention that $\bar{M}_z/\bar{M}_w$ was smaller than $\bar{M}_w/\bar{M}_n$ in all cases. Molecular weights measured before and after hydrogena-

Table IV
Molecular Characteristics of Poly(1-butenylene-*co*-vinylethylene) (12PBD)

			THF		1,4-dioxane			
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ °C}$, dL g^{-1}	k_H	$[\eta]^{15.7\ °C}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]
10		0.88	0.230	0.33	0.166	0.47		1.03
20	1.92	1.94	0.402	0.31	0.256	0.55	1.01	1.03
50	5.27	5.48	0.823	0.35	0.415	0.93	1.04	1.05
100	9.39	9.71	1.30	0.30	0.560	1.08	1.03	1.05
200B	12.9	14.2	1.66	0.27	0.700	1.24	1.10	1.07
300B	20.7	22.0	2.38	0.26	0.839	1.26	1.06	1.09

[a] Absolute measurements. [b] Via Ana-Prep SEC.

Table V
Molecular Characteristics of Poly(butylene-*co*-ethylethylene) ($H_2$12PBD)

			THF		n-hexyl acetate		
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ °C}$, dL g^{-1}	k_H	$[\eta]^{65\ °C}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]
10		0.92	0.238	0.42	0.181	0.52	
20	1.95	1.96	0.388	0.42	0.275	0.61	1.01
50	5.45	5.67	0.729	0.47	0.452	1.02	1.04
100	9.55	10.3	1.07	0.52	0.603	1.25	1.08
200B	12.9	13.7	1.33	0.49	0.755	1.03	1.06
300B	20.9	22.8	1.87	0.51	0.945	1.25	1.09

[a] Absolute measurements.

Table VI
Molecular Characteristics of Poly(1-methyl-1-butenylene-*co*-isopropenylethylene) (50PI)

			THF		2-octanol			
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$[\eta]^{41.3\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]
9	1.04	1.07	0.170	0.39	0.104	0.56	1.03	1.04
16	1.73	1.80	0.236	0.35	0.128	0.78	1.04	1.03
40	3.61	3.70	0.393	0.36	0.193	0.66	1.02	1.04
80	9.83	10.1	0.839	0.32	0.316	0.79	1.03	1.04
120	11.3	12.0	1.01	0.22	0.366	0.72	1.06	1.03
200	21.6	23.2	1.51	0.28	0.465	0.98	1.07	1.05
300	25.8	26.9	1.90	0.25	0.546	1.04	1.04	1.06
450	38.8	41.1	2.60	0.28	0.701	0.88	1.06	1.05

[a] Absolute measurements. [b] Via Waters 150C SEC.

Table VII
Molecular Characteristics of Poly(1-methylbutylene-*co*-isopropylethylene) ($H_2$50PI)

			THF		2-octanol		
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$[\eta]^{53.3\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]
9	1.10	1.13	0.160	0.28	0.102	0.63	1.03
16	1.74	1.76	0.226	0.30	0.124	1.27	1.02
40	3.71	3.78	0.368	0.33	0.185	1.20	1.02
80	9.75	10.1	0.704	0.35	0.311	0.90	1.04
120	11.5	11.9	0.803	0.35	0.345	1.09	1.03
200	21.6	22.7	1.20	0.37	0.402	0.91	1.05
300	27.5	28.6	1.44	0.35	0.567	0.91	1.04
450	39.3	42.5	1.93	0.43	0.728	1.04	1.08

[a] Absolute measurements.

Table VIII
Molecular Characteristics of Poly(isopropenylethylene-*co*-1-methyl-1-vinylethylene) (34PI)

			THF		2-octanol			
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$[\eta]^{30.5\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]
12	1.30	1.34	0.175	0.35	0.120	0.63	1.03	1.05
20	2.46	2.45	0.287	0.37	0.170	0.44	1.00	1.07
65	6.55	6.67	0.582	0.36	0.269	0.64	1.02	1.07
90	9.15	11.2	0.791	0.29	0.342	0.67	1.22	1.16
50	12.1	12.5	0.988	0.24	0.379	0.75	1.03	1.06
125	15.2	16.3	1.26	0.21	0.422	0.71	1.07	1.07
250	25.3	27.0	1.76	0.28	0.553	1.07	1.07	1.09

[a] Absolute measurements. [b] Via Ana-Prep SEC.

Table IX
Molecular Characteristics of Poly(isopropylethylene-*co*-1-methyl-1-ethylethylene) ($H_2$34PI)

			THF		2-octanol		
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$[\eta]^{26.2\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]
12	1.46	1.50	0.140	0.45	0.103	0.76	1.03
20	2.70	2.92	0.225	0.24	0.141	0.64	1.08
65	6.83	7.29	0.423	0.26	0.206	0.99	1.07
90	9.03	10.7	0.536	0.26	0.260	0.60	1.18
50	12.7	13.3	0.664	0.24	0.299	0.86	1.05
125	15.7	17.0	0.868	0.18	0.342	0.78	1.08
250	25.8	27.8	1.27	0.23			1.08

[a] Absolute measurements.

Table X
Molecular Characteristics of Poly(methylbutylene) (Et-Prop)

			THF		*n*-hexyl acetate			
sample	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\eta]^{30\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$[\eta]^{60.9\ ^\circ\mathrm{C}}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]
6A-10	0.82	0.84	0.220[c]	0.36	0.171	0.40	1.02	1.04
6A-15	1.45	1.49	0.305[c]	0.35	0.232	0.39	1.03	1.03
6A-20	2.25	2.45	0.409	0.32	0.294	0.65	1.09	1.06
1-JM	3.46	3.63	0.541	0.31	0.359	0.66	1.05	1.07
WF-1	4.16	4.64	0.631	0.37	0.437	0.54	1.12	1.14
HPI-15	9.14	9.60	1.06	0.42	0.603	0.88	1.05	1.06
L-14	26.7	30.1	2.29	0.57	1.05	1.79	1.13	1.13
1-NS	29.3	31.6	2.60	0.48	1.12	1.56	1.08	1.10
L-12		60.0	3.56	0.46				1.10

[a] Absolute measurements. [b] Via Waters 150C SEC. [c] These data were not used in the calculation of the MHS relation since curvature is present in this molecular weight range.

Table XI
Mark–Houwink–Sakurada and Second Virial Coefficient Parameters for Model Polydienes and Polyolefins

	THF		ideal solvents		A_2[a]	
polymer	$K \times 10^4$	α	$K \times 10^3$	α	$K \times 10^{-2}$	ν
12PBD	3.23	0.72	1.73	0.50	2.96	−0.27
$H_2$12PBD	7.13	0.64	1.71	0.51	0.31	−0.12
50PI	1.46	0.75	0.78	0.52	3.08	−0.30
$H_2$50PI	2.98	0.68	0.74	0.52	2.16	−0.30
34PI	1.16	0.77	1.02	0.50	0.69	−0.11
$H_2$34PI	1.03	0.75	0.92	0.49	0.14	−0.09
Et-Prop	4.22	0.68	1.69	0.51	4.78	−0.34

[a] $A_2 = KM_n^{-\nu}$; A_2 in units of mL mol g^{-2}. A_2 values obtained in toluene at 37 °C.

tion are identical, within experimental error (±5%), after taking into account the slight increase in molecular weight brought about by hydrogenation. This observation supports the conclusion[4] that the Pd/CaCO$_3$ hydrogenation reaction does not envoke changes in large-scale chain structure.

The data in Tables IV–X yield the Mark–Houwink–Sakurada (MHS) and the osmometric second virial coefficient–molecular weight parameters shown in Table XI. Within experimental error the exponents for the measurements done in Θ solvents reveal that the majority of the measurements were done under Θ conditions. The correlation coefficients for the intrinsic viscosity relations were >0.99, while those for the second virial coefficients were >0.97.

It is of interest to note that in some cases the exponents for the $A_2 \propto M^{-\gamma}$ relations are smaller than a predicted[10] limiting value of −0.2 for flexible chains in moderate to good solvents. This behavior has been observed previously for certain methacrylate polymers[11,12] and polystyrene.[13–16] The suggestion of Berry and Casassa[17] that the exponent in the A_2–M relationship has a limiting value of ca. −0.25 in good solvents is apparently borne out by the findings noted above.

The most common method for the determination of the characteristic ratio employs a combination of intrinsic viscosity measurements and weight-average molecular weights. Measurements of $[\eta]$ under Θ conditions directly yielded the unperturbed dimensions.[2] Measurements in non-Θ solvents require the use of one or more of the extrapolation procedures, e.g., the Burchard–Stockmayer–Fixman approach.[8,19] In this work measurements were carried out in both types of solvents, though only results from measurements under Θ or near-Θ conditions were used to calculate C_∞. The accuracy in this case should be higher than where extrapolations for good solvent data are involved.

The ratio $\langle r^2\rangle_0/\bar{M}_w$ is obtained from the Fox–Flory relationship.[20,21]

$$[\eta]_\Theta = \Phi[\langle r^2\rangle_0/\bar{M}_w]^{3/2}M_w^{1/2} = K_\Theta \bar{M}_w^{1/2}$$

where $\langle r^2\rangle_0$ is the unperturbed mean square end-to-end distance of the chain, $[\eta]_\Theta$ is in dL g^{-1}, and Φ is the Flory constant.[21–23] The experimental value[16,24–29] of the Flory constant is 2.5×10^{21} when $[\eta]_\Theta$ is expressed in units of dL g^{-1} and $\langle r^2\rangle_0$ is in cm^2. Consequently, we may write

$$(K_\Theta/\Phi)^{2/3} = \langle r^2\rangle_0/\bar{M}_w$$

with the characteristic ratio, C_∞, being calculated from the following:

$$C_\infty = \lim_{n\to\infty} \frac{\langle r^2\rangle_0}{nl^2}$$

where n is the number of backbone chain bonds and l^2 is the mean square backbone bond length. Values of l^2 were calculated from the bond lengths given by Abe and Flory.[30] Table XII lists values of K_Θ and C_∞ for a series of model polydienes and polyolefins.

Table XII
Unperturbed Chain Parameters for Model Polydienes and Polyolefins

polymer	$K_\Theta \times 10^3$,[a] (g mol wt)$^{-1/2}$	C_∞
1,4-PBD[b]	1.78	5.1
12PBD	1.73	6.0
$H_2$12PBD	1.88	6.3
1,4-PI[c]	1.26,[d] 1.34[e]	5.1,[d] 5.3[e]
50PI	0.96	5.3
$H_2$50PI	0.91	5.0
34PI	1.02	7.9
$H_2$34PI	0.83	7.2
Et-Prop	1.89	6.2
poly(methylethylene)[f]	1.32	5.9
poly(vinylethylene)[g]	1.20	7.0
poly(ethylethylene)[g]	0.74_4	5.3

[a] Evaluated via the Burchard–Stockmayer–Fixman extrapolation process. The values are based on the measurements done under Θ or near-conditions. [b] 1,4-Polybutadiene; PBD microstructure: ca. 36 cis-1,4; 57% trans-1,4; 7% 1,2. [c] 1,4-Polyisoprene. [d] Reference 27; PI microstructure: ca. 70% cis-1,4, 23% trans-1,4; 7% 3,4. [e] Reference 31; PI microstructure: ca. 100% cis-1,4. [f] Reference 6. This sample was prepared by hydrogenating poly(1,3-dimethyl-1-butenylene). The resultant "polypropylene" was shown via ^{13}C NMR spectroscopy to be atactic in the Bernoullian sense. [g] Reference 5.

Mark[32] has published on the configurational statistics of ethylene–propylene copolymers. Using the RIS approach, he calculated $C_\infty = 6.8$ for an alternating ethylene–propylene copolymer at 25 °C. We find $C_\infty = 6.2$ at 61 °C for the Et-Prop samples, and we conclude that, in essence, our results support Mark's[32] predictions. Two points can be made, however. First, Mark's calculations were based on a value $C_\infty = 6.5$ for atactic (Bernoullian) polypropylene. Both current theory[33] and recent experimental results[6] indicate a lower value (5.9) for the characteristic ratio of this polymer. This trend presumably would make the agreement even better between the theoretical and experimental characteristic ratios for Et-Prop. It should be noted, though, that our samples contain ca. 7% isopropylene units[27] and thus are not strictly alternating ethylene–propylene copolymers in an absolute sense.

None of the other polymers studied here have been addressed by the RIS approach. Although direct comparison with theory is thus not possible, some comments regarding general trends are in order. Flory, Mark, and Abe[34] have concluded that an articulated side group in vinyl polymers in which this side group is of a size roughly equivalent to the methylene unit can be readily accomodated if one or both of the backbone bonds adjacent to the methine carbon has a gauche conformation. Since a gauche conformation is more compact than a trans conformation, the net effect is to decrease the characteristic ratio relative to the parent polyethylene chain. Hence, $C_\infty = 7.6$ for polyethylene,[35] while $C_\infty = 5.9$ for atactic poly(methylethylene)[6] and 5.3 for atactic poly(ethylethylene)[5] over the temperature range 23.5–38 °C. On the other hand, the presence of large and/or unarticulated side groups would not be expected to lead to a large decrease in C_∞ since, as Flory, Mark, and Abe[34] have pointed out, steric interactions are not substantially reduced by adopting a higher population of gauche conformations. Observe that $C_\infty = 7.9$ for 34PI, 7.2 for $H_2$34PI, and 7.0 for poly(vinylethylene),[5] where large and/or inflexible side groups are present.

Table XIII
Chain Dimension Parameters for Ethyl-Branched Polyethylene Chains

$\chi_{1,2}$[a]	$\chi_{C_2H_5}$[b]	$K_\Theta \times 10^3$, (g mol wt)$^{-1/2}$	C_∞	T, °C	ref
0	0	3.66[c]	7.6	35	35
0.08	0.042	3.24[c]	7.3	35	36
0.28	0.16	2.64	7.1	35	37
0.43[d]	0.27	1.94	6.4	65	this work
0.52	0.35	1.88	6.6	35	37
0.73	0.57	1.72	7.3	35	37
0.99	0.98[e]	0.77_4	5.3	23.5	5

[a] Mole fraction of vinyl units formed in the parent polymer during the polymerization of 1,3-butadiene. [b] Mole fraction of ethylethylene units in the copolymer; $\chi_{C_2H_5} = \chi_{1,2}/[\chi_{1,2} + 2(1 - \chi_{1,2})]$. [c] Calculated values based on the temperature coefficients given in the corresponding references. [d] $H_2$12PBD. [e] Poly(ethylethylene).

Conversely, the influence of the articulated ethyl side group on the characteristic ratios of the poly(ethylene-*co*-ethylethylene) samples as a function of composition can be seen from the data[5,35-37] collected in Table XIII. With one exception, these results show that the characteristic ratio decreases as the concentration of ethyl side groups is increased. Since the three-state RIS model has proven adequate for poly(methylene)[38] and poly(ethylethylene),[5,34] the influences of the ethyl side group can be explained, in perhaps a simplistic sense, as leading to a progressive increase in the population of gauche conformers at the expense of the more extended trans structure.

In the case of polymers with double bonds in the main chain there can be no rotation about these bonds. Thus, a large population of sterically unfavorable conformations may be "locked in" as a consequence of the polymerization mechanism. On hydrogenation, these double bonds are removed and the resulting single bonds are susceptible to rotation. The chains may then undergo conversion to the less sterically inhibited trans conformer. For example, a *cis/trans*-1,4-polybutadiene ($C_\infty = 5.1$)[27] yields a poly(methylene) ($C_\infty = 7.3$)[36] and in this work, *high-cis*-1,4-polyisoprene ($C_\infty = 5.1$)[27] yields Et-Prop ($C_\infty = 6.2$). It is erroneous to assume that the presence of main-chain double bonds necessarily corresponds to high "stiffness" of the chain. Our results on C_∞ may be qualitatively interpreted in light of the above considerations. Quantitative support from the appropriate RIS calculations is not available.

The various Huggins coefficients have also been reported in Tables III–X. Several comments can be made. In THF the k_H values are generally lower the larger the exponent in the MHS equation, i.e., for the case where THF is the better solvent. These combined results indicate that the Huggins coefficient may show a greater solvent dependence than has hitherto been, to the best of our knowledge, reported. It should also be noted that for the cases where the MHS exponent is >0.70, our k_H values are in accord with predictions[39,40] that this parameter is 0.4 or less.

The Huggins coefficient values obtained under Θ or near-Θ conditions show, in certain cases, a pronounced dependence on molecular weight and achieve values of one or greater. It is of interest to note that the polymer (34PI) with the highest characteristic ratio in Table XII yields Huggins coefficients which are essentially independent of molecular weight, a feature shared with polystyrene,[41,42] which also has a relatively large characteristic ratio.[38] With perhaps one exception,[43] the Huggins coefficients found in this work are not accounted for by theory.[44-47] The treatment of Peterson and Fixman[43] yields a Θ-condition Huggins coefficient of 0.9 assuming penetrable spheres, while under conditions of slight excluded volume the coefficient can increase to a value near 1.1. It should be noted that work[48] on poly(*N*-vinyl-3,6-dibromocarbazole) has also revealed some Θ-condition Huggins coefficients with values of close to one. The remaining theories[44-47] predict limiting values of about 0.7 or less.

It is recognized that K_Θ can sometimes be a function of solvent e.g., as can be seen from results available for polystyrene.[49-51] Clearly, we are currently unable to state whether such solvent effects are present in our results. Suffice it to mention that our combined experience with, for example, 2-octanol (this work and ref 5) has not led to any obvious abnormalities. This conclusion is based, in part, on the observation that the initial slopes of the light scattering second virial coefficient vs. $(1 - \Theta/T)$ were normal. Nonetheless, the question of the potential Θ-solvent effects on K_Θ and k_H cannot be completely ruled out until additional Θ-condition measurements are done in different solvents.

Acknowledgment. This work was supported in part by grants from the National Science Foundation, Polymers Program (Grant DMR-79-08200), and the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Polybutadiene (homopolymer), 9003-17-2; polyisoprene (homopolymer), 9003-31-0.

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Dipole Moments of Poly(*N*-vinylcarbazole)

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ABSTRACT: A sample of poly(*N*-vinylcarbazole) (PVK) was synthesized by radical polymerization in toluene solution using azobis(isobutyronitrile) (AZBN) as initiator. The weight-average molecular weight of the polymer, estimated by light scattering measurements in THF solutions, was 4.36×10^5 and its isotactic fraction, determined by ^{13}C NMR, was $P_i = 0.33$. Dipole moments of PVK in dioxane solutions were measured at several temperatures from 30 to 60 °C. The experimental value at 30 °C of the dipole moment ratio $D_x = \langle \mu^2 \rangle / x\mu_0^2$ (where $\langle \mu^2 \rangle$ represents the mean-square dipole moment of the chains and $x\mu_0^2$ is the same quantity in the idealization that all the skeletal bonds are freely jointed) was found to be 0.43, in very good agreement with the results reported by other authors. The temperature coefficient $\delta \ln \langle \mu^2 \rangle / \delta T$, measured in the vicinity of 30 °C was 2.1×10^{-3}. The rotational isomeric states model, with the 2 × 2 states scheme previously employed to study unperturbed dimensions of PVK, was used here to analyze the dipole moment of this polymer. Calculated values of D_x are in reasonable agreement with the experimental results; however, a negative temperature coefficient is predicted by theory.

Introduction

The discovery of electronic transport in vinyl aromatic polymers has emphasized the need for a better knowledge of the structural characteristics of these materials in order to correlate the nature of the electronic properties and its charge generation. One of the polymers which has focused the attention in many aspects for its dielectric, charge-transfer, or energy-transfer properties is poly(*N*-vinylcarbazole) (PVK). Owing to the photoconductivity of these chains which confers practical uses to the polymer, a few studies have been made on the crystalline structure, electric properties, and microstructure by NMR spectroscopy.[1]

Sundararajan[2] carried out the conformational analysis of PVK in terms of pairwise rotations around the skeletal bonds. As occurs with other vinyl chains bearing bulky planar substituents, the side group imposes severe restrictions on the available conformations so that a 2 × 2 rotational isomeric states (RIS) scheme is suitable for the study of the configurational properties of PVK. By using this approach, the rather large unperturbed dimensions of the polymer were successfully explained. It would be desirable to extend this analysis to the study of the polarity of the chains. The aim of this work was, therefore, to measure the dipole moments of PVK chains and to interpret critically the results, using Sundararajan's statistics.

Experimental Section

***N*-Vinylcarbazole (VK).** *N*-Vinylcarbazole monomer (Fluka, A.G.) was recrystallized from methanol three times before use. It was obtained as a pure crystalline white solid with a melting point of 65.5 °C (by DSC at 10 °C/min).

Poly(*N*-vinylcarbazole) (PVK). PVK was synthesized by radical polymerization of *N*-vinylcarbazole in 30% (w/v) toluene solution containing 0.3% azobis(isobutyronitrile) (AZBN). More detailed information is given elsewhere.[3] The polymer was white and powdered, soluble in the usual organic solvents. The intrinsic viscosity at 25 °C, estimated in THF solution, was 32.5 mL/g. The weight-average molecular weight, M_w, estimated by light scattering measurements in THF at 25 °C was 4.36×10^5.

Microstructure of PVK. The steric microstructure of the PVK sample was determined by following the procedure of Kawamura et al.[4] which has been employed very recently by Terrel and Evers[5] to analyze systematically the free radical polymerization of *N*-vinylcarbazole as a function of solvent power and polymerization temperature. ^{13}C NMR spectra were recorded with a Varian XL-100-12FT spectrometer. The measurements were carried out at 90 °C on undegassed 10-mm-o.d. Pyrex NMR glass tube, using 1,4-dioxane-d_8 as ^{2}H internal lock solvent. Other experimental conditions are similar to those reported by Terrel and Evers.[5] The fraction of isotactic dyads P_i was calculated from the areas of the triad peaks (*rr*, 51.3 ppm; *mr*, 50.0 ppm; *mm*, 49.5 ppm) using the expression $P_i = mm + (mr/2)$, where *mm*, *mr*, and *rr* represent the respective triad mole fractions. It was found that $P_i = 0.33$, in satisfactory agreement with the tacticity reported for other PVKs obtained by free radical polymerization at the same temperature.[5]

Dielectric Measurements. Dielectric constants ϵ of solutions of PVK in dioxane were measured with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cell.[6] The measurements were performed for several frequencies lying in the range 200–20 000 Hz, and no significant dependence of ϵ on frequency was found. Increments in refractive index of the so-