Macromolecules 1991, *24*, 6199-6209

Conformational Characteristics of Some Model Polydienes and Polyolefins

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Received May 8, 1991

ABSTRACT: The conformational behavior of model polydienes and their saturated polyolefinic analogues has been studied. The polymers were based on 1,3-butadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-butadiene, and 3-methylene-7-methyl-1,6-octadiene (β-myrcene). The unperturbed chain dimensions of these near-monodisperse polymers were evaluated under Θ or near-Θ conditions via intrinsic viscosity measurements. Consequently, information was obtained regarding the influence of side-chain length on chain dimensions as well as the influence of head-to-head structures in polypropylene. The temperature coefficient (d ln $\langle R^2\rangle_0/\mathrm{d}T$) for chain dimensions of alternating poly(ethylene–butene) was determined. Its value of -0.9×10^{-3} K^{-1} is in consonance with the values for polyethylene and alternating poly(ethylene–propylene). The temperature coefficients for poly(vinylethylene), a butene-rich poly(ethylene–butene) material, and poly(ethylethylene) were also measured. The value for the latter polymer is notably larger (-2.3×10^{-3} K^{-1}) than that predicted (-0.1×10^{-3} K^{-1}) from the five-state rotational isomeric state model. A value of -1.7×10^{-3} K^{-1} was measured for poly(vinylethylene), while -1.4×10^{-3} K^{-1} was found for a butene-rich poly(ethylene–butene) copolymer (40 ethyl branches per 100 backbone carbons).

Introduction

The evaluation of unperturbed chain dimensions and their respective temperature coefficients for polydiene and polyolefinic chains has been the recipient of both theoretical and experimental attention. The former case utilizes the rotational isomeric state (RIS) concept conceived by Volkenstein[2] and Birshtein and Ptitsyn[3] and refined by Flory.[4-6] The majority of the RIS predictions of the above-mentioned parameters have been verified by experiment for polyethylene,[7-10] polybutadiene,[11-14] polyisoprene,[12,15] alternating poly(ethylene–propylene),[16] polyisobutylene,[17-25] poly(dimethylsiloxane),[26-28] polystyrene,[29] and poly(α-methylstyrene).[11,30] Exceptions to this gratifying trend are the apparent failures of various RIS efforts[31-40] to coincide with the experimentally evaluated unperturbed chain dimensions and the corresponding temperature coefficients for atactic[41] (in the Bernoullian sense) polypropylene[16,42] (PP) and, as will be shown, atactic polybutene.

In this study, the polymers were based on 1,3-butadiene, 2,3-dimethylbutadiene, 2-ethyl-1,3-butadiene, and 3-methylene-7-methyl-1,6-octadiene (β-myrcene). The polydienes and their saturated counterparts were evaluated via intrinsic viscosity measurements under (with one exception) Θ or near-Θ conditions. The saturated version of the essentially 1,4-poly(dimethylbutadiene) (1,4-PDMBD) is head-to-head polypropylene (HHPP). The assay of that amorphous polyolefin (which can also be viewed as an alternating copolymer of ethylene and 2-butene) yields information regarding the potential influence of head-to-head structures in atactic polypropylene. Those polymers based on ethylbutadiene and β-myrcene allow the evaluation of increasing branch length on the chain posture of the resulting polydienes and polyolefins. The temperature coefficients of unperturbed chain dimensions for the butadiene- and ethylbutadiene-based polymers were measured.

Table I
Specific Refractive Index Increments for Polydienes and Polyolefins at 30 °C (λ = 633 nm)[a]

polymer	cyclohexane	1-chlorobutane	THF
1,4-PDMBD	0.113		
HHPP			0.090
55-PDMBD	0.104		
$H_2$55-PDMB			0.095
1,4-PEB	0.093		
PEB-26			0.079
1,4-PMYRC	0.109		
$H_2$1,4-PMYRC	0.059		
64-PMYRC	0.103		
$H_2$64-PMYRC	0.0620		
PEB-14	0.0614		0.0796
PEB-40		0.0909	
PVE	0.0873		
PEE	0.0672		

[a] Units in mL g^{-1}.

Experimental Section

The polymerizations were carried out at 0 or 30 °C in cyclohexane or amine/aliphatic hydrocarbon mixtures. Purified *sec*- or *tert*-butyllithium[43] was the initiator. The usual vacuum-line procedures[44,45] were followed. The polymerizations were allowed to proceed for a minimum of 12 h. Active centers were terminated by the addition of degassed methanol.

Initially, polymerizations of β-myrcene were plagued by the formation of branched or gelled product. Findings of Quirk and Huang[46] revealed that exposure of myrcene to sodium dispersion removed the offending impurity (possibly a triene). This procedure led to the formation of polymers having predictable molecular weights and narrow monomodal molecular weight distributions.

Some of the mixed-microstructure polydienes were prepared using a 3/7 vol/vol triethylamine–cyclohexane mixture. This choice was made based on an observation of Tobolsky and Rogers,[47] who reported that such a mixture yielded polyisoprene containing approximately 50:50 3,4 and 1,4 modes of addition. The use of dipiperidinoethane to yield high vinyl polymers from dimethylbutadiene and myrcene failed due to an unavoidable

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Table II
Molecular Characteristics of 1,4-PDMBD

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{CCl_4}$, dL g^{-1}	k_H	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]^{30°C}_{n\text{-HEP}}$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
1.62	1.47	0.295	0.31	0.245	0.30	0.224	0.25	1.05	1.10
8.17	7.69	1.02	0.34	0.790	0.39	0.619	0.44	1.06	1.06
15.2	14.5	1.67	0.31	1.20	0.41	0.94	0.47	1.10	1.05
18.9	17.6	1.80	0.34	1.38	0.36	1.04	0.63	1.09	1.07
24.0	19.7	2.20	0.29	1.60	0.43	1.25	0.41	1.10	1.22
42.5	38.6	3.48	0.31	2.44	0.43	1.82	0.50	1.17	1.10

[a] *n*-Heptane. [b] SEC. [c] Absolute measurements.

Table III
Molecular Characteristics of HHPP

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{CCl_4}$, dL g^{-1}	k_H	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
1.64		0.269	0.24	0.222	0.40	0.157	0.49	1.06	
8.78	8.58	0.887	0.37	0.697	0.38	0.359	0.67	1.08	1.02
15.0	15.1	1.42	0.37	1.05	0.45	0.477	0.97	1.12	0.99
19.4	18.1	1.77	0.41	1.26	0.46	0.549	1.62	1.15	1.07
24.8	24.8	2.00	0.37	1.43	0.48	0.613	1.21	1.09	1.00
43.3	41.8	3.15	0.32	2.20	0.41	0.789	1.36	1.20	1.04

[a] Isoamyl acetate, 56.8 °C. [b] SEC. [c] Absolute measurements.

Table IV
Molecular Characteristics of 55-PDMBD

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{CCl_4}$, dL g^{-1}	k_H	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
2.51	5.11	0.334	0.31	0.277	0.30	0.204	0.55	1.05	1.19
6.21	5.95	0.618	0.33	0.496	0.36	0.325	0.53	1.05	1.04
8.30	7.76	0.729	0.26	0.595	0.39	0.369	0.71	1.06	1.07
12.4	12.0	1.00	0.33	0.829	0.38	0.467	0.67	1.07	1.03
18.0	17.2	1.32	0.31	1.06	0.35	0.559	0.66	1.07	1.05
23.8	21.3	1.61	0.31	1.25	0.39	0.636	0.90	1.11	1.12

[a] Isoamyl acetate, 30.0 °C. [b] SEC. [c] Absolute measurements.

Table V
Molecular Characteristics of $H_2$55-PDMBD

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{CCl_4}$, dL g^{-1}	k_H	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[c]	$\bar{M}_w/\bar{M}_n$[c]
2.42		0.209	0.28	0.179	0.36	0.114	0.59	1.04	
6.06	5.71	0.433	0.24	0.338	0.35	0.177	0.89	1.05	1.06
7.54	7.47	0.498	0.36	0.392	0.36	0.209	0.56	1.06	1.01
12.9	12.4	0.719	0.22	0.580	0.16	0.275	0.61	1.07	1.05
17.8	18.0	0.857	0.30	0.663	0.21	0.295	0.48	1.07	0.99
23.2	21.1	1.13	0.27	0.880	0.17	0.372	0.71	1.11	1.10

[a] 2-Octanol, 22.0 °C. [b] SEC. [c] Absolute measurements.

Table VI
Molecular Characteristics of
Poly(ethylbutadiene) (1,4-PEB)

$\bar{M}_w \times 10^{-4}$	$[\eta]^{25°C}_{C_6H_{12}}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]
1.58	0.210	0.36	0.123	0.61	1.02
4.28	0.383	0.33	0.219	0.45	1.03
5.18	0.445	0.34	0.229	0.46	1.03
5.19	0.455	0.34	0.230	0.56	1.04
5.23	0.456	0.30	0.235	0.52	1.04
13.6	0.940	0.29	0.376	0.52	1.05
30.4	1.73	0.31	0.557	0.54	1.06
40.7	2.38	0.30	0.683	0.56	1.07
66.6	3.10	0.26	0.843	0.75	1.07

[a] *n*-Amyl acetate, 22.0 °C. [b] SEC.

termination event. Comments on those observations are available elsewhere.[48] Dipiperidinoethane was used to prepare essentially 1,2-polybutadiene [poly(vinylethylene) (PVE)], while tetamethylethylenediamine was used to prepare 90% 1,2-polybutadiene.

The molecular weights were determined via, in most cases, membrane osmometry (Hewlett-Packard 503) and low-angle laser light scattering (Chromatix KMX-6). The d*n*/d*c*, at 633 nm, measurements were accomplished using the Chromatix KMX-16. These values are gathered in Table I.

Following preliminary screening, the Θ conditions for the various polymer–solvent systems were estimated via one of two methods. The light-scattering second virial coefficients, A_2, were measured at temperatures above and below Θ. The temperature at which $A_2 = 0$ was thus determined via interpolation. Cloud point measurements were also used with the conventional[49] plotting of the reciprocal cloud point temperature vs the reciprocal of the square root of the weight-average molecular weight. The reciprocal Θ temperature was determined from the intercept. The search for a Θ solvent for the partially crystalline 1,4-PDMBD proved fruitless. Thus, the chain dimension data were obtained by using the mediocre solvent *n*-heptane. The intrinsic viscosity measurements were conducted using previously described procedures.[9,10,14,27,28,39]

Hydrogenation was carried out via the use of 5% palladium on calcium carbonate (Strem) in cyclohexane at 70 °C under, initially, 700 psi of hydrogen for periods ranging from 12 to 24 h. The reduced form of the catalyst was used. Insightful accounts regarding some of the charcteristics of this hydrogenation process are available from Rosedale and Bates[50] and Rachapudy et al.[51] For the 1,4-PDMBD series 5 g of catalyst mixture per gram of polymer was required for complete hydrogenation, while a 2:1 ratio was used for the mixed-microstructure PDMBD materials. A 1:1 ratio was found to be sufficient for the myrcene-, butadiene-, and ethylbutadiene-based polymers.

Infrared spectroscopy was used as an expedient method to determine the progress of hydrogenation. This was accomplished by noting the disappearance of the unsaturation absorption bands in the region 1600–1650 cm^{-1} from spectra obtained after hydrogenation. No attempt was made to determine polymer

Table VII
Molecular Characteristics of Random Poly(ethylene-*co*-butene) (PEB-14)

$\bar{M}_w \times 10^{-4}$	$[\eta]_{OA}$,[a] dL g^{-1}	k_H	$[\eta]_{HA}$,[b] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[c]
0.92	0.181	0.55	0.181	0.52	1.02
1.96	0.286	0.67	0.275	0.61	1.03
5.67	0.484	0.97	0.452	1.02	1.04
10.3			0.603	1.3	1.05
13.7	0.713	0.86	0.755	1.0	1.05
22.0	0.963	1.2			1.05
22.8			0.945	1.3	1.08
52.0	1.47	1.1			1.06

[a] *n*-Octyl acetate, 37.1 °C. [b] *n*-Hexyl acetate, 65.0 °C. [c] Via SEC.

structure from the infrared spectra, though it was noted that the presence of 3,4 structures could be easily detected for these polydiene species by absorptions at 1770 and 3075 cm^{-1}.

^{1}H NMR was used for polydiene microstructure determinations and the detection of residual unsaturation in the polyolefin materials. In all cases the degree of saturation was at least 99.5% and in many cases no residual unsaturation was detected. Table XXI lists the structures of the polymers evaluated in this work and the polymer nomenclature used. Examples of the ^{13}C NMR, ^{1}H NMR, and IR spectra of the dimethylbutadiene- and myrcene-based polymers are given elsewhere.[48]

Size exclusion chromatography (Waters 150C) was used to examine the molecular weight distribution of polymers before and after hydrogenation. This was done to verify hydrogenation had not caused degradation. Slight changes in peak elution volume were observed to either a greater or lower volume, outside of experimental error. These changes are caused by an alteration in the polymer chain conformation and thus polymer hydrodynamic volume in the carrier solvent tetrahydrofuran; e.g., see ref 50. Both μ- and ultra-Styragel six-column sets were used with nominal porosities covering the range of 10^6 to 10 nm.

The glass transition temperatures (T_g) were measured via a Perkin-Elmer 2-C DSC equipped with a thermal analysis data station. The estimated error of the instrument determined from standards was ±1 K. The T_g peak onset was essentially the same over the heating rates of 5 and 10 °C/min. Measurements were performed in sealed aluminum pans in a nitrogen atmosphere. No trace of the controversial and generally elusive "liquid–liquid transition" was observed in these measurements. The T_g values are given in Table XXII along with the densities and the density temperature coefficients for the polymers studied in this work.

Results and Discussion

Tables II–XV list the molecular characteristics of the polymers studied in this work. The Mark–Houwink–Sakurada constants, K and α, are given in Table XVI. The Θ-solvent data were evaluated via the Burchard–Stockmayer– Fixman (BSF)[52-54] extrapolation process to ascertain K_Θ for each polymer series. This approach

Table VIII
Molecular Characteristics of Alternating Poly(ethylene–butene) (PEB-26)

$\bar{M}_w \times 10^{-4}$	$[\eta]^{25°C}_{C_6H_{12}}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$[\eta]_\Theta$,[b] dL g^{-1}	k_H	$[\eta]_\Theta$,[c] dL g^{-1}	k_H	$[\eta]_\Theta$,[d] dL g^{-1}	k_H	$[\eta]_\Theta$,[e] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[f]
1.62	0.280	0.31	0.177	0.75	0.171	0.69	0.166	0.63	0.160	0.66	0.157	0.60	1.02
4.38	0.570	0.33			0.265	0.74	0.267	0.69	0.264	0.63	0.258	0.65	1.04
5.31	0.623	0.33					0.287	0.68					1.03
5.32	0.630	0.36	0.343	0.73			0.289	0.70					1.05
5.36	0.643	0.31			0.300	0.80	0.293	0.66	0.290	0.67	0.289	0.45	1.04
13.9	1.30	0.34	0.579	0.73	0.460	0.91	0.483	0.64	0.457	0.68	0.450	0.57	1.05
31.1	2.35	0.30	0.932	0.87	0.626	1.1	0.708	0.82	0.642	0.75	0.660	0.91	1.06
48.1	3.25	0.33	1.20	0.91	0.780	1.2	0.853	0.86	0.843	0.66	0.815	0.76	1.05
68.2	3.99	0.31	1.49	1.08	0.958	1.7	1.00	0.88	0.972	0.97	0.998	1.0	1.06

[a] Benzene, 15.0 °C. [b] *n*-Heptyl acetate, 17.1 °C. [c] *n*-Hexyl acetate, 32.0 °C. [d] *n*-Pentyl acetate, 51.7 °C. [e] *n*-Butyl acetate, 73.2 °C. [f] Via SEC.

Table IX
Molecular Characteristics of 1,4-PMYRC

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
6.66	6.29	0.39	0.28	0.156	0.66	1.05	1.06
15.8	14.7	0.76	0.28	0.235	0.70	1.08	1.07
43.4	41.8	1.67	0.30	0.396	0.64	1.04	1.05
58.3	55.5	2.10	0.33	0.451	0.68	1.07	1.04

[a] 2-Octanol, 35.9 °C. [b] SEC. [c] Absolute measurements.

Table X
Molecular Characteristics of H$_2$1,4-PMYRC

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
7.10	6.42	0.46	0.29	0.192	0.50	1.06	1.10
16.3	15.7	0.824	0.25	0.292	0.80	1.70	1.04
43.0		1.67	0.30	0.455	0.96	1.08	
63.2	57.2	2.22	0.23	0.577	0.79	1.08	1.10

[a] 2-Octanol, 51.0 °C. [b] SEC. [c] Absolute measurements.

Table XI
Molecular Characteristics of 64-PMYRC

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
6.30	5.37	0.370	0.27	0.141	0.66	1.04	1.17
11.9	10.9	0.627	0.25	0.194	0.83	1.05	1.10
13.5	12.7	0.676	0.25	0.205	0.44	1.05	1.06
25.1	22.2	1.10	0.25	0.278	0.90	1.05	1.13
44.2	37.2	1.63	0.29	0.364	0.88	1.06	1.19
55.7	46.1	1.86	0.33	0.385	1.05	1.07	1.21

[a] 2-Octanol, 29.2 °C. [b] SEC. [c] Absolute measurements.

Table XII
Molecular Characteristics of $H_2$64-PMYRC

$\bar{M}_w \times 10^{-4}$	$\bar{M}_n \times 10^{-4}$	$[\eta]^{30°C}_{THF}$, dL g^{-1}	k_H	$[\eta]_\Theta$,[a] dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$[c]
6.85	6.64	0.376	0.26	0.173	0.57	1.05	1.03
12.3	11.2	0.613	0.27	0.238	0.63	1.05	1.10
13.4	13.3	0.644	0.31	0.250	0.72	1.05	1.01
26.7	24.4	1.05	0.21	0.362	0.65	1.07	1.09
44.4	43.8	1.52	0.26	0.454	0.88	1.08	1.01
56.1	48.8	1.79	0.34	0.516	0.60	1.06	1.15

[a] 2-Octanol, 35.0 °C. [b] SEC. [c] Absolute measurements.

Table XIII
Molecular Characteristics of Random Poly(ethylene-*co*-butene-1) (PEB-40)

$\bar{M}_w \times 10^{-4}$	$[\eta]^{30°C}_{CYC}$, dL g^{-1}	k_H	$[\eta]^{5°C}_{3\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{29°C}_{2\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{59°C}_{1\text{-}OCT}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]
1.95	0.215	0.41	0.130	0.89	0.122	0.69	0.116	0.90	1.03
5.23	0.493	0.37	0.214	0.99	0.209	0.75	0.190	0.91	1.04
6.40	0.553	0.36	0.234	0.92	0.221	0.94	0.207	0.73	1.03
12.3	0.954	0.38	0.332	1.11	0.322	0.81	0.292	0.99	1.04
28.6	1.72	0.37	0.495	0.93	0.457	0.93	0.431	0.97	1.05
53.6	2.80	0.39	0.678	0.88	0.655	0.81	0.592	0.96	1.07

[a] Via SEC.

Table XIV
Molecular Characteristics of Poly(vinylethylene) (PVE)

$\bar{M}_w \times 10^{-4}$	$[\eta]^{30°C}_{C_6H_{12}}$, dL g^{-1}	k_H	$[\eta]^{35°C}_{TOL}$, dL g^{-1}	k_H	$[\eta]^{30°C}_{CYC}$, dL g^{-1}	k_H	$[\eta]^{16.0°C}_{3\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{32.8°C}_{2\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{66.0°C}_{1\text{-}HEX}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]
1.12[b]	0.201	0.27	0.181	0.34									
2.70	0.117	0.37	0.354	0.34	0.393	0.42	0.236	0.83	0.211	0.88	0.199	0.61	1.03
3.30[b]	0.460	0.25	0.403	0.32									
4.40	0.601	0.35	0.523	0.34	0.580	0.40	0.319	0.89	0.286	0.86	0.268	0.64	1.05
7.10	0.840	0.37	0.760	0.34	0.800	0.40	0.392	1.04	0.363	0.83	0.339	0.73	1.05
8.44[b]	0.960	0.30	0.845	0.36									
10.4	1.12	0.36	1.01	0.34	1.064	0.39	0.482	1.08	0.444	0.97	0.407	0.86	1.05
20.4[b]	1.88	0.32	1.65	0.31									1.05
27.3	2.24	0.36	2.11	0.36	2.135	0.39	0.798	1.15	0.723	1.12	0.655	1.02	1.06
48.9	3.44	0.40	3.28	0.34	3.356	0.38	1.045	1.15	0.901	1.33	0.828	1.16	1.07

[a] Via SEC. [b] Samples and data from: Roovers, J.; Toporowski, P. M. *Rubber Chem. Technol.* **1990**, *63*, 734.

Table XV
Molecular Characteristics of Poly(ethylethylenes)

$\bar{M}_w \times 10^{-4}$	$[\eta]^{30°C}_{C_6H_{12}}$, dL g^{-1}	k_H	$[\eta]^{5.0°C}_{3\text{-}NON}$, dL g^{-1}	k_H	$[\eta]^{5.0°C}_{3\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{21.0°C}_{2\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{23.5°C}_{2\text{-}OCT}$, dL g^{-1}	k_H	$[\eta]^{53.0°C}_{1\text{-}OCT}$, dL g^{-1}	k_H	$\bar{M}_w/\bar{M}_n$[a]
5.20	0.455	0.39											1.03
7.34	0.595	0.40	0.272	0.60	0.259	0.69	0.226	0.65	0.226	0.70	0.204	0.65	1.05
9.50			0.321	0.520	0.291	0.84	0.258	0.71	0.272	0.46	0.230	0.77	1.03
13.4	0.846	0.39	0.395	0.43	0.357	0.57	0.300	0.69	0.313	0.64	0.274	0.73	1.05
32.5	1.69	0.38	0.658	0.45	0.583	0.60	0.477	0.80	0.514	0.61	0.424	0.97	1.06
53.0			0.908	0.49	0.750	0.66	0.604	1.19	0.652	0.61	0.533	0.93	1.08
54.5	2.50	0.37	0.915	0.47	0.780	0.70	0.624	0.81	0.669	0.54	0.557	0.83	1.11

[a] Via SEC.

minimizes errors introduced by measurement made at temperatures deviating from the true Θ temperature. The evaluation of K_Θ allows the determination of the unperturbed dimensions of a polymer chain via the expression

$$K_\Theta = \Phi[\langle R^2\rangle_0/M]^{3/2} \qquad (1)$$

where Φ, the Flory hydrodynamic constant, is taken as 2.5 × 10^{21}. The values for the unperturbed chain dimensions are given in terms of the root-mean-square end-to-end distance, $\langle R^2\rangle_0$, the corresponding characteristic ratio, C_∞

$$C_\infty = \langle R^2\rangle_0/nl^2 \qquad (2)$$

where n is the number of main-chain bonds, and l, the average bond length.

The polymers studied in this work, with the exception of HHPP and PEE, have not been evaluated via RIS methods. Thus comparison with theory is not possible. Also, there are apparently only two experimental studies which pertain to polymers studied in this work. That of Ansorena and co-workers[56] reports a characteristic ratio for 1,4-PDMBD, while those of Arichi and co-workers[57,58] report values for the hydrogenated versions of poly(2,4-hexadiene) and poly(2,3-dimethyl-1,3-butadiene). Both 1,4-polydienes yield on saturation the HHPP structure.

Ansorena and co-workers reported[56] a C_∞ value of 8.5 for essentially 1,4-PDMBD. The two samples evaluated were obtained by fractional precipitation from a polydisperse sample. The method of sample preparation was not stated, and the polydispersity indices of the two fractions were not determined. The molecular weights used were number-average values rather than the more appropriate weight-average values. Furthermore, a solvent/nonsolvent mixture was used to simulate Θ conditions. The use of such mixtures has not been thoroughly investigated although evidence exists[59-62] that the good solvent in such mixtures may preferentially solvate the polymer chain, thus leading to expanded-chain dimensions relative to

Table XVI
Mark-Houwink-Sakurada Parameters

polymer	solvent	temp, °C	$K \times 10^4$, dL g^{-1}	α
1,4-PDMBD	THF	30.0	2.81	0.700
	CCl_4	30.0	2.10	0.749
	n-heptane	30.0	4.53	0.639
HHPP	THF	30.0	2.50	0.699
	CCl_4	30.0	1.76	0.754
	isoamyl acetate	56.8	12.5	0.498
55-PDMBD	THF	30.0	2.75	0.681
	CCl_4	30.0	2.69	0.701
	isoamyl acetate	30.0	11.7	0.509
$H_2$55-PDMBD	THF	30.0	1.73	0.688
	CCl_4	30.0	1.44	0.723
	isoamyl acetate	62.0	6.63	0.510
1,4-PEB	cyclohexane	25.0	1.02	0.773
	n-amyl acetate	22.0	9.00	0.511
PEB-26	cyclohexane	25.0	2.30	0.729
	benzene	15.0	7.17	0.567
	n-heptyl acetate	17.1	21.5	0.452
	n-hexyl acetate	32.0	14.6	0.487
	n-amyl acetate	51.7	15.5	0.479
	n-butyl acetate	73.2	14.1	0.487
1,4-PMYRC	THF	30.0	0.746	0.772
	2-octanol	35.9	6.42	0.494
$H_2$1,4-PMYRC	THF	30.0	0.968	0.752
	2-octanol	51.0	7.69	0.494
64-PMYRC	THF	30.0	1.05	0.742
	2-octanol	29.2	8.05	0.469
$H_2$64-PMYRC	THF	30.0	1.13	0.731
	2-octanol	35.0	5.26	0.521
PEB-14	*n*-octyl acetate	37.1	17.6	0.511
	n-hexyl acetate	65.0	17.0	0.512
PEB-40	cyclohexane	30.0	1.13	0.768
	3-octanol	5.0	9.50	0.498
	2-octanol	29.0	8.96	0.499
	1-octanol	59.0	9.14	0.491
PVE	toluene	35.0	1.51	0.760
	THF	30.0	1.91	0.747
	cyclohexane	30.0	1.79	0.746
	3-octanol	16.0	10.7	0.525
	2-octanol	32.8	10.6	0.516
	1-hexanol	66.0	11.4	0.503
PEE	cyclohexane	30.0	1.80	0.721
	3-nonanol	5.0	3.05	0.607
	3-octanol	5.0	5.14	0.555
	2-octanol	21.0	7.62	0.508
	2-octanol	23.5	5.71	0.536
	1-octanol	53.0	7.78	0.497

those obtained under conventional Θ conditions.

It could be argued that our value of 7.0 for 1,4-PDMBD is distorted as a consequence of four failure to find a Θ solvent for this polymer. The application of the BSF approach must be used with caution when good-solvent data are evaluated as a result of the recognized inadequacy of the two-parameter theory at large excluded volumes. As seen in Figure 1, this leads to obvious deviations from linearity for the tetrahydrofuran and carbon tetrachloride systems with the potential for inflated values of K_Θ. However, a statistical analysis of the *n*-heptane results indicates that the curvature apparent in the other two solvents is not present—at least over the molecular weight range studied. It should be noted that although the BSF procedure was initially developed for use above Θ, work has shown[30] this method to be valid below the Θ temperature as well.

Although RIS calculations for 1,4-PDMBD are not available, such evaluations are found[63-65] for the 1,4-trans forms of polyisoprene. These RIS results lead to characteristic ratios of ca. 7 for high trans-1,4 content chains. This must be considered good agreement with our value if, within the framework of the RIS evaluations, the assumption[63] is correct that an additional methyl group at the double-bond site exerts little influence on chain dimensions for the trans polydiene structures. Nevertheless, the value of 7.0 determined in this work should be considered provisional until verified by results obtained closer to or, if possible, at a Θ state.

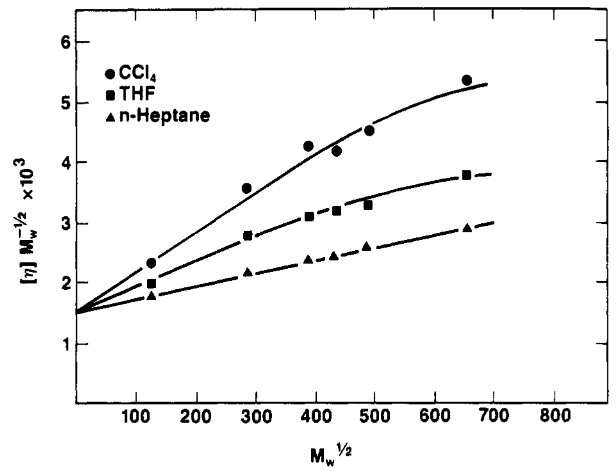


Figure 1. Burchard-Stockmayer-Fixman plots for 1,4-PDMBD.

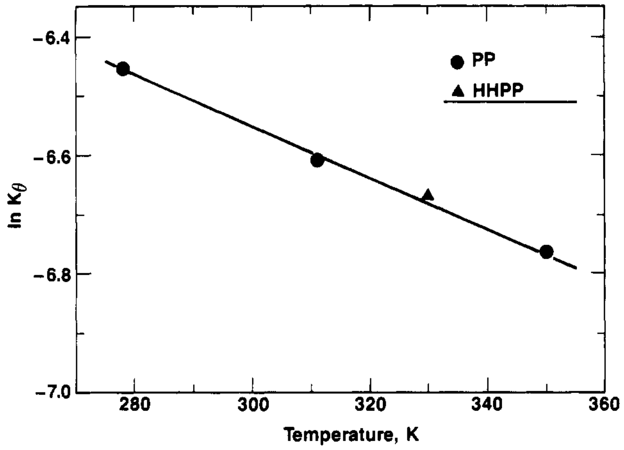


Figure 2. Plot of ln K_Θ vs temperature for polypropylene[16] and head-to-head polypropylene.

Arichi et al.[57,58] reported values for the HHPP characteristic ratio of 3.7, 4.0, and 4.5 (the latter obtained by Θ measurements) for HHPP at 30 and 43 °C (Θ), respectively. Our results, at 56.8 °C, lead to a value of 5.8, which is identical with that derived via the data of Mays et al.[16,42] for atactic polypropylene (Figure 3). The plot of ln K_Θ vs temperature leads to the temperature coefficient for chain dimensions (κ = d ln $\langle R^2 \rangle_0$/dT), which in the case of PP is -2.5×10^{-3} K^{-1}. Inclusion of the HHPP value of K_Θ leads to the same value. However, the chain dimension temperature coefficients for the two forms of polypropylene cannot be taken as identical since such a claim lacks validity in the absence of K_Θ values at additional temperatures for HHPP. The apparent agreement between the PP and HHPP K_Θ values is also subject to the absence of specific solvent effects; the chain dimension data of the former were obtained in aliphatic alcohols, while the latter are based on isoamyl acetate solutions.

The foregoing must be considered within the framework of the known configurational charcteristics of these two types of polypropylenes. The head-to-tail form exhibits chain statistics[42] which are Bernoullian with P_m of 0.502. That stereoirregular material is in contrast to the configurational characteristics of the HHPP chain. Khlok et al.[66] have shown that this polymer (prepared by the hydrogenation of poly(2,3-dimethylbutadiene)) contains

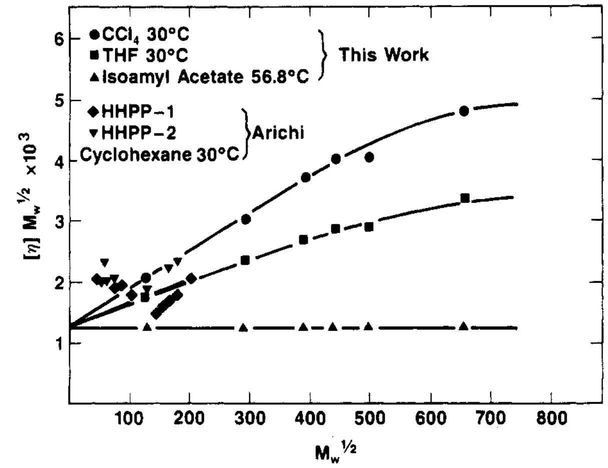
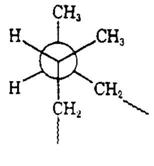


Figure 3. Burchard–Stockmayer–Fixman plots of head-to-head polypropylene. Samples of Arichi et al.[57,58] were made from poly(2,4-hexadiene) (HHPP-1) and poly(2,3-dimethylbutadiene) (HHPP-2).

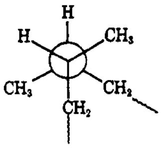
Table XVII
Unperturbed Chain Parameters

polymer	temp, °C	$K_\Theta \times 10^4$, dL g^{-1}	$\langle R^2\rangle_0/M$, 10^3 nm^2 mol g^{-1}	C_∞
1,4-PDMBD	30.0	15.5	7.26	7.0
HHPP	56.8	12.6	6.35	5.8
55-PDMBD	30.0	12.6	6.34	8.4
$H_2$55-PDMBD	62.0	7.08	4.31	5.6
1,4-PMYRC	35.9	6.28	3.98	6.3
$H_2$1,4-PMYRC	51.0	7.14	4.34	6.7
64-PMYRC	29.2	5.71	3.74	7.6
$H_2$64-PMYRC	35.0	6.55	4.10	8.3
1,4-PEB	22.0	10.0	5.43	5.4
PEB-14	37.1	19.6	8.49	6.5
	65.0	18.8	8.28	6.3
PEB-26	15.0	13.4	6.60	6.1
	17.1	13.5	6.67	6.1
	32.0	13.0	6.45	5.9
	51.7	12.8	6.37	5.8
	73.2	12.5	6.27	5.7
PEB-40	5.0	9.36	5.20	5.6
	29.0	8.92	5.03	5.4
	59.0	8.37	4.82	5.2
PVE	16.0	13.5	6.64	7.7
	32.8	12.5	6.30	7.3
	66.0	11.8	6.08	7.0
PEE	5.0	8.79	4.98	5.9
	5.0	8.89	5.02	6.0
	21.0	8.22	4.76	5.7
	23.5	8.18	4.75	5.6
	53.0	7.49	4.48	5.3

both erythro and threo configurations:



ERYTHRO



THREO

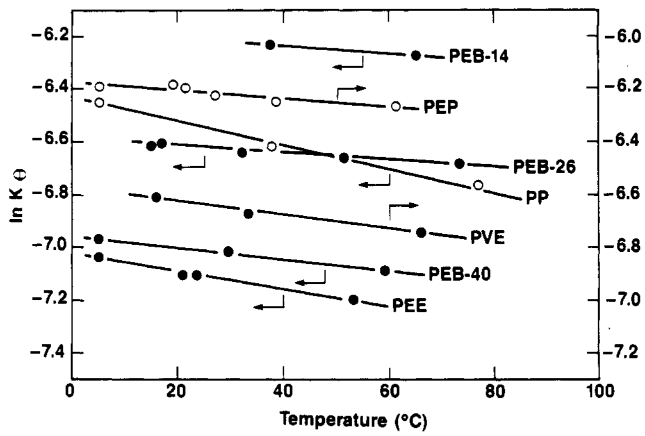


Figure 4. Plots of ln K_Θ vs temperature for ethyl-, methyl-, and vinyl-branched polyolefins. See Table XVIII for references.

Table XVIII
Chain Dimension Temperature Coefficients for Branched Polyethylenes

polymer	temp range, °C	d ln $\langle R^2\rangle_0$/dT, K^{-1} expt	RIS	refs[a]
PE	120–190	−1.2	−1.1	10/70
PEB-14	37.1–65.0	−1.0		this work
PEP	5.0–60.9	−1.0[b]	−1.1 to −1.3	16/72
PEB-26	15.0–73.2	−0.9		this work
PEB-40	5.0–59.0	−1.4		this work
PP	5.0–77.0	−2.5	~0 to −1.8	16/32–37
PEE	5.0–53.0	−2.3	−0.1	this work/39
PVE	16.0–66.0	−1.7		this work

[a] References before the slash refer to the experimental values while those after it pertain to the RIS results. [b] Small-angle neutron scattering over the temperature range 24–180 °C for PEP in the melt yields a value of -1.1×10^{-3} K^{-1}. At higher temperatures (>180 °C) κ is observed to diminish as temperature increases, a facet not heretofore expressly considered for this parameter in the RIS models. Butera, R.; Fetters, L. J.; Huang, J.; Richter, D.; Pyckhout-Hintzen, W.; Zirkel, A.; Farago, B.; Ewen, B. *Phys. Rev. Lett.* **1991**, *66*, 2088. Zirkel, A. Thesis, Rheinischen Friedrich Wilhelms Universität, Bonn, Germany, March 1991.

The ^{13}C NMR spectrum exhibited two major resonances for each type of carbon (CH_3, CH_2, CH) present. Their analysis indicated an erythro/threo ratio of about 1.3, a conclusion which is fortified by our ^{13}C NMR results.[48] Thus, their soluble hydrogenation catalyst (Al/Co) and the heterogenous palladium/calcium carbonate system lead to cis and trans additions resulting in HHPP materials having a virtually identical configuration mix. It is pertinent to note that despite structural and configurational differences PP and HHPP appear to exhibit similar conformational behavior.

The results of Arichi et al.[57,58] and ours differ. A BSF plot of their cyclohexane data is given in Figure 3 along with our results for HHPP. The Θ temperature intrinsic viscosity data of those authors were not tabulated. The value of 4.0 for the characteristic ratio determined by them in cyclohexane is not apparent from the BSF plot of their data (Figure 3). An additional difference is their reported value of 43 °C as the Θ temperature in isoamyl acetate. Suffice it to note that in our hands the highest molecular weight HHPP was found to precipitate from that solvent (1/4% w/v solutions) at that temperature. A potential explanation for this difference is the influence of the higher concentration of non-1,3 units (6–11%) in the polydienes prepared by Arichi and co-workers.[57,58]

The question of the influence of HHPP units on the chain dimensions has been addressed by Asakura et al.,[55] who, via a modified RIS approach, investigated the effect of up to 50% head-to-head linkages in polypropylene. Two models were chosen for their calculations. In one the characteristic ratio decreases with an increase in head-to-head linkages, while the other model predicts virtually no change in that parameter. Thus, strictly speaking, the Asakura et al.[55] findings cannot be used to rationalize experimental results as Arichi and co-workers[57,58] have done since both their results and ours can be accommodated depending on which model and variables are selected.

Table XIX
Conformational Characteristics of Ethyl-Branched Polyethylenes at 300 K

ethyl branches per 100 backbone C's	$\langle R_G^2\rangle_0/M$, 10^4 nm^2 mol g^{-1}	$\bar{M}_w \times 10^{-5}$,[a] g mol^{-1}	$\langle R_G^2\rangle_0$,[a] nm^2	g^b	g^c	C_∞	refs
0	21.6[d,e]	2.80	604.8	1	1	7.7_5	7–9, 79
2	19.8[d,f]	2.91	575.0		0.95_1	7.3_9	80
5	18.1[g]	3.08	557.5	0.95–0.97	0.92_1	7.1_4	
7	17.3	3.19	551.9		0.91_2	7.0_8	80
10	15.7[g]	3.36	527.5	0.91–0.95	0.87_2	6.7_6	
13	13.8	3.53	486.9		0.80_5	6.2_4	80
14	14.2	3.58	508.4		0.84_1	6.5_1	29
18	13.0	3.81	495.0		0.81_8	6.3_4	80
20	12.5[g]	3.92	490.0	0.86–0.91	0.81_0	6.2_8	
26	10.8	4.28	462.2		0.76_4	5.8_9	this work
30	9.92[g]	4.48	444.4		0.73_5	5.7_0	
40	8.38	5.04	422.4		0.69_8	5.3_3	this work
49	7.82	5.54	433.2		0.71_6	5.5_5	this work/81

[a] For DP$_w$ of 10^4. [b] Reference 78. [c] Experimental values. [d] $\kappa = -1.2 \times 10^{-3}$ K^{-1} used to calculate $\langle R_G^2\rangle_0/M$ at 300 K. [e] $\langle R_G^2\rangle/M = 19.35 \times 10^4$ nm^2 mol g^{-1} at 415 K. [f] $\langle R_G^2\rangle/M = 17.70 \times 10^4$ nm^2 mol g^{-1} at 413 K. [g] Interpolated values.

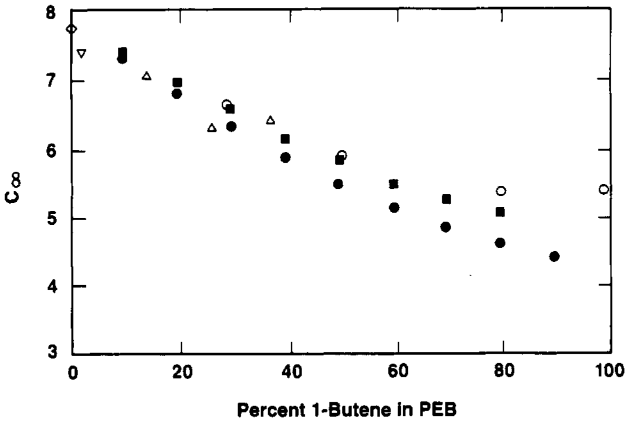


Figure 5. Characteristic ratios (at 300 K) of ethyl-branched polyethylenes as a function of 1-butene content. Solid symbols are RIS calculations for the statistical weights $\tau = 0$ (●) and 0.43 (■). Open symbols denote experimental values: (△) refs 7–9; (▽) ref 79; (△) ref 80; (○) this work, ref 81. This figure is based on Figure 1 in ref 39.

The present state of play regarding the dilute-solution Θ-condition behavior of HHPP indicates remarkable similarity with PP insofar as the unperturbed chain dimensions are concerned. From the viscoelastic standpoint, a similar correspondence is observed in the plateau modulus where values of G_N° of 5.7×10^6 and 5.6×10^6 dyn cm^{-2} are found[67,68] for PP and HHPP. In terms of the reptation model[69] both forms of polypropylene exhibit, at 330 K, the same tube diameter, d_T, of 4.6 nm, where

$$d_T^2 = [\langle R^2\rangle_0/M][M_e] \quad (3)$$

and M_e denotes the entanglement molecular weight as derived from the plateau modulus.

The majority of the polymers studied in this work have not been the subject of RIS treatments. Nonetheless, potentially useful observations can be made. The increase in side-chain length—methyl, ethyl, and 4-methyl-3-pentyl—for the high *cis*-1,4-polydienes yields a gradual increase in the characteristic ratio (Table XVII). Conversely, the chain dimensions of the saturated analogues of these polydienes show a different sensitivity to side-chain length. The replacement of the methyl group with the ethyl side unit leads to an attenuation in the characteristic ratio (Table XVII and Figure 4). This indicates that the articulated side group leads, via nonbonded interactions, to an enhancement (in terms of the three-state model) of the gauche conformer population in the backbone. This influence on chain dimensions is identical to what is observed for the "conversion" of polyethylene to alternating poly(ethylene–propylene) (Table XVII) where the addition of the methyl group leads to a decrease in the characteristic ratio. If the chain dimension data for PE, PEP, and PEB are compared at 35 °C, the resultant characteristic ratios range from 7.7 (PE), to 6.6 (PEP), to 6.0 (PEB). It is also of interest to note that the temperature coefficients for chain dimensions are similar for these three polyolefins (Table XVII).

Table XX
Polydiene Microstructure

polymer	trans-1,4	cis-1,4	3,4	1,2
1,4-PDMBD	74	23		3
55-PDMBD	23	32	45	
1,4-PEB	14	75	11	
1,4-PMYRC	90		10	
50-PMYRC	64	36		
1,2-1,4-PBD	10			90
PVE	1–2			98–99

A reversal of the above trend is seen when the 4-methylpentyl side group is present; the characteristic ratio is increased relative to that of PEB. The increase in the number of rotational degrees of freedom in this side chain would appear to strongly influence the statistics of the backbone conformation. Another contributing factor is the possible interdependence of the conformations of neighboring side groups as has been suggested for long-side-chain poly(1-alkenes).[38] This latter feature may well be an important facet in the relatively high value for C_∞ of 8.3 found for the H$_2$50-PMYRC material. Such qualitative comparisons and conclusions must be considered within the framework of the respective chain dimension temperature coefficients of these polymers.

The unperturbed chain dimension temperature coefficients for butadiene- and ethylbutadiene-based polyolefins were evaluated via intrinsic viscosity measurements. Use of the same samples throughout each series leads to the cancelation of the errors involved (ca. ±5%) in the molecular weights insofar as the relative comparison of K_Θ is concerned. The BSF procedure also eliminates errors in K_Θ caused by deviations from true Θ conditions. The measurements were also run using chemically similar Θ solvents to minimize or eliminate the impact of specific solvent effects.

The temperature coefficient findings are given in Table XVIII and Figure 4. For the sake of comparison, the values of κ for alternating poly(ethylene–propylene)[16] (PEP)[70] and atactic polypropylene[16] (PP) are included. For PE and PEP, where RIS-based results are available,[71,72] experiment and theory are in reasonable consonance. Also, PEB-26 (for which no RIS evaluation is available) exhibits

Table XXI
Polydiene and Polyolefin Structure and Nomenclature

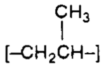
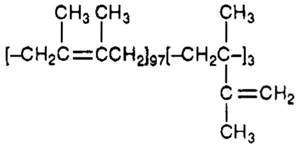
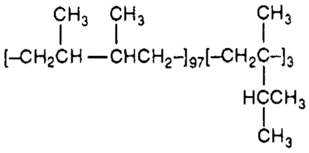
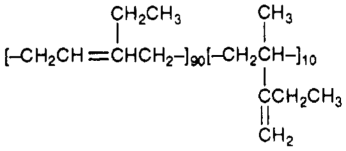
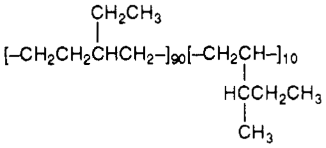
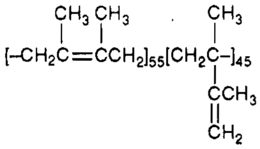
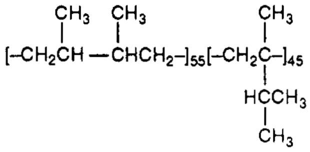
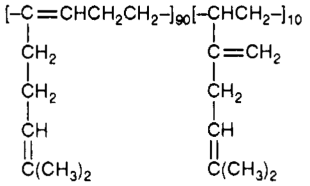
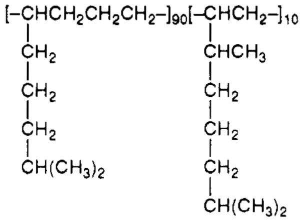
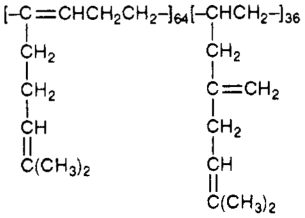
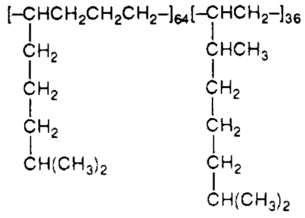
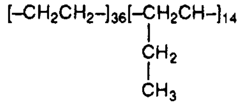
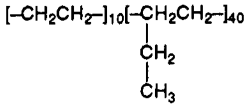
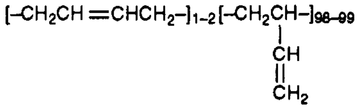
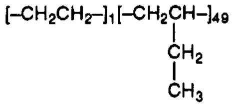
common or IUPAC name	structure	nomenclature
polypropylene	 $[-CH_2CH(CH_3)-]$	PP
1,4-poly(dimethylbutadiene)	 $[-CH_2C(CH_3){=}C(CH_3)CH_2]_{97}[-CH_2C(CH_3)(C(CH_3){=}CH_2)-]_3$	1,4-PDMBD
head-to-head polypropylene	 $[-CH_2CH(CH_3)-CH(CH_3)CH_2-]_{97}[-CH_2C(CH_3)(HC(CH_3)CH_3)-]_3$	HHPP
1,4-poly(ethylbutadiene)	 $[-CH_2CH{=}CH(CH_2CH_3)CH_2-]_{90}[-CH_2CH(CH_3)(C(CH_2CH_3){=}CH_2)-]_{10}$	1,4-PEB
poly(ethylene–butene)	 $[-CH_2CH_2CH(CH_2CH_3)CH_2-]_{90}[-CH_2CH(HC(CH_2CH_3)CH_3)-]_{10}$	PEB-26ᵃ
1,4–1,2-poly(dimethylbutadiene)	 $[-CH_2C(CH_3){=}C(CH_3)CH_2]_{55}[CH_2C(CH_3)(C(CH_3){=}CH_2)-]_{45}$	55-PDMBD
poly(1,2-dimethyl-1-butylene-*co*-1-(1-methyl-1-isopropyl)ethylene	 $[-CH_2CH(CH_3)-CH(CH_3)CH_2-]_{55}[-CH_2C(CH_3)(HC(CH_3)CH_3)-]_{45}$	$H_2$55-PDMBD
1,4-polymyrcene	 $[-C(CH_2CH_2CH{=}C(CH_3)_2){=}CHCH_2CH_2-]_{90}[-CH(C(=CH_2)CH_2CH{=}C(CH_3)_2)CH_2-]_{10}$	1,4-PMYRC
poly(1-(4-methylpentyl)-1-butylene-*co*-1-(1,5-dimethylhexyl)ethylene)	 $[-CH(CH_2CH_2CH_2CH(CH_3)_2)CH_2CH_2CH_2-]_{90}[-CH(CHCH_3CH_2CH_2CH_2CH(CH_3)_2)CH_2-]_{10}$	$H_2$1,4-PMRYC
poly(1-(4-methyl-3-pentenyl-1-butenylene-*co*-1-(1-methylene-5-methyl-4-hexenyl)ethylene)	 $[-C(CH_2CH_2CH{=}C(CH_3)_2){=}CHCH_2CH_2-]_{64}[-CH(CH_2C(=CH_2)CH_2CH{=}C(CH_3)_2)CH_2-]_{36}$	64-PMYRC
poly(1-(4-methylpentyl)-1-butylene-*co*-1-(1,5-dimethylhexyl)ethylene	 $[-CH(CH_2CH_2CH_2CH(CH_3)_2)CH_2CH_2CH_2-]_{64}[-CH(CHCH_3CH_2CH_2CH_2CH(CH_3)_2)CH_2-]_{36}$	$H_2$64-PMRYC

Table XXI (Continued)

common or IUPAC name	structure	nomenclature
poly(ethylene-*co*-butene)	 $[-CH_2CH_2-]_{36}[-CH_2\underset{\substack{\vert\\ CH_2\\ \vert\\ CH_3}}{C}H-]_{14}$	PEB-14[a]
poly(ethylene-*co*-butene)	 $[-CH_2CH_2-]_{10}[-\underset{\substack{\vert\\ CH_2\\ \vert\\ CH_3}}{C}H_2CH_2-]_{40}$	PEB-40[a]
poly(vinylethylene)	 $[-CH_2CH{=}CHCH_2-]_{1-2}[-CH_2\underset{\substack{\vert\\ CH\\ \Vert\\ CH_2}}{C}H-]_{98-99}$	PVE
poly(ethylethylene)	 $[-CH_2CH_2-]_1[-CH_2\underset{\substack{\vert\\ CH_2\\ \vert\\ CH_3}}{C}H-]_{49}$	PEE

[a] The number in the PEB series denotes the number of ethyl branches per 100 backbone carbons.

Table XXII
Glass Transition Temperatures and Density Parameters for Polydienes and Polyolefins

polymer	glass transition temp, °C				
	peak onset	peak midpoint	ρ, g cm^{-3} (20 °C)	$-$d ln $\rho/\mathrm{d}T$, 10^4 K^{-1}	refs
PP[a]	-5	-3	0.857	7.9	14, 39, 67
HHPP[b]	-28	-26	0.878	7.2	this work
PEP	-65	-62	0.586	7.0	83, 77
1,4-PEB	-65	-64	0.891		this work
PEB-26	-61	-59	0.861		this work
55-PDMBD	14	16	0.918	5.8	this work
$H_2$55-PDMBD	5	10	0.892	6.3	this work
1,4-PMYRC	-71	-68	0.895	6.7	this work
$H_2$1,4-PMYRC	-57	-54	0.856	9.2	this work
64-PMYRC	-66	-65	0.897	6.0	this work
$H_2$64-PMYRC	-46	-45	0.853	7.5	this work
PVE	0	2	0.889	6.0	75, this work
PEE	-30	-28	0.870	6.0	this work

[a] T_g values of -6 °C (Cowie, J. M. G. *Eur. Polym. J.* **1973**, *9*, 1041) and -5 °C (Burfield, D. R.; Doi, Y. *Macromolecules* **1983**, *16*, 702) have been reported for amorphous polypropylene. [b] A T_g of -27 °C has been reported for HHPP.[61] That value is via extrapolation to the 0 K min^{-1} heating rate. Arichi et al.[56] gave T_g's of -10 °C (HHPP-1) and -17 °C (HHPP-2) (see caption of Figure 3 for nomenclature identification).

a κ similar to that seen for PE and PEP. Pronounced discrepancies exist for both PP and PEE, where the RIS models[31-37] lead to underestimates of the respective values of κ (and at 300 K an overestimate of C_∞ for PP and, conversely, an underestimate of the same parameter for PEE[38] (Table V)).

Our value for PEE κ of -2.3×10^{-3} K^{-1} is markedly different from that of 0.5×10^{-3} K^{-1} determined from the stress-temperature measurements (140-200 °C) of Mark and Flory.[73] As noted, disagreement is also present with the RIS value, -0.1×10^{-3} K^{-1}, of Wittwer and Suter.[38] Conversely, neutron scattering results of Bates, Rosedale, and Frederickson[74] over the temperature range 27-187 °C are compatible with our value for κ. For PVE, the PEE parent, no RIS model is available nor is any direct experimental evidence. Roovers and Toporowski[75] have, though, offered the value of -1.6×10^{-3} K^{-1}, which was derived from the temperature dependence of the plateau modulus, G_N. Their method relied on the Graessley-Edwards[76] approach that relates G_N with the chain contour length, main-chain bond length, average mass per main-chain bond, chain concentration per unit volume, and the Kuhn step length. This approach also was effective for polystyrene and 1,4-polybutadiene when the known values of κ were used.

A cautionary note must be offered regarding the apparent disagreement existing in the values of κ for PEE. Small-angle neutron scattering (SANS) results[77] for the temperature dependence of R_G (the radius of gyration) for PEP over the temperature range 24-270 °C have been obtained. It was found[77] that κ was constant (-1.1×10^{-3} K^{-1}; see Table XVIII) from 24 to ca. 180 °C; thereafter κ was observed to diminish over the temperature range 180-270 °C. This facet of κ has not been expressly considered in the RIS approach.

It could be argued that the PEE κ could show similar behavior with κ commencing to diminish in value at perhaps a lower temperature than does PEP. The minimum value that C_∞ for a polyolefinic chain can assume is about 4 (see Appendix). Thus with a projected value of the PEE C_∞ of 4.7 at 100 °C, this chain may already have entered the temperature range where κ varies in value. It is worthwhile to note that the Graessley-Edwards[76] treatment of the PEE chain yields good agreement between measured and calculated values of b_T (where $b_T = (G_N{}^\circ)_T/(G_N{}^\circ)_{T_0}$) when the theoretical value[38] of -0.1×10^{-3} K^{-1} is used. Clearly resolution of these questions must await SANS measurements of the PEE R_G as a function of temperature. Relative to the Θ-solvent method SANS has the ability to track R_G in the realistic melt environment (and thus eliminate the potential influence of specific solvent effects) over a much wider temperature range than is possible in dilute solution.

The influence of ethyl branches on the conformational behavior of PEB copolymers was apparently first addressed by Tonelli.[78] The mean-square unperturbed radii of gyration of branched polyethylenes were calculated via an RIS approximation. The numbers of ethyl branches per 100 backbone carbons were 5, 10, and 20. The influence of these branches was expressed in terms of $g = \langle R_G^2 \rangle_{0,b} / \langle R_g^2 \rangle_{0,l}$, where the subscripts b and l denote the branched and linear polymers, respectively. The values of R_G were for polymers having equal *degrees* of polymerization.

Table XIX summarizes the experimental influence on polyethylene conformation of the frequency of ethyl branching. In terms of g, the RIS method used by Tonelli[78] tends to underestimate the influence of ethyl branching upon R_G. Conversely, the RIS model of Mattice[39] shows good agreement, in terms of C_∞, between theory and experiment over the ethyl branch range covered in Tonelli's work. This is shown in Figure 5, where σ and τ are the statistical weights involving first-order interactions involving methylene units and those involving the ethyl groups, respectively. Good agreement is obtained for the case where $\sigma = \tau$, an event repeated latter for PEP.[72] However, Mattice's three-state model[39] tends to lead to an underestimation of C_∞ for PEB-40 and PEE, a disagreement reminiscent of the previously noted apparent failure of the five-state model to lead to a correct value for the temperature coefficient of PEE chain dimensions. Additional work would seem to be needed to modify these discrepancies.

Appendix

The microstructures for the polydienes are given in Table XX. The ^{13}C NMR analysis of 1,4-polymyrcene published by Newmark and Majumdar[82] has been particularly helpful in the elucidation of the structure of that polydiene. The polymer structures and corresponding nomenclature used in this paper are shown in Table XXI. The glass transitions, densities, and density temperature coefficients are given in Table XXII. Polymer densities were measured by weighing in water or by the use of a density gradient column.

For the case[4] of a polyolefinic backbone with free rotation and bond angles (θ) fixed at the regular tetrahedral value

$$C_\infty = \frac{1 - \cos\theta}{1 + \cos\theta} = 2 \qquad (1A)$$

This unrealistic model can readily be modified to include hindrance to backbone bond rotation as follows: The average values of the torsional angle ϕ are trans = 0° and gauche = 120°. Thus

$$\cos\phi = (1 - \sigma)/(1 + 2\sigma)$$

where σ denotes $\exp(-E_g/RT)$ and E_g the energy of a gauche state relative to that of the trans state (500 cal/mol). At 298 K $\sigma = 0.43$. Thus, for this elementary three-state model[84-86]

$$C_\infty = \left[\frac{1 - \cos\theta}{1 + \cos\theta}\right]\left[\frac{1 + \overline{\cos\phi}}{1 - \overline{\cos\phi}}\right] = 3.76 \qquad (2A)$$

Thus, C_∞ of ca. 4 represents the "floor" value that a polyolefin chain can achieve.

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