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Temperature Coefficients of Unperturbed Dimensions for Atactic Polypropylene and Alternating Poly(ethylene–propylene)

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ABSTRACT: Polypropylenes with Bernoullian chain statistics and alternating poly(ethylene–propylenes) were prepared by the hydrogenation of 1,4-poly(2-methylpentadiene) and 1,4-polyisoprene, respectively. These materials served as model materials for the evaluation of the temperature coefficient for the unperturbed chain dimensions, d ln $\langle r^2\rangle_0/\mathrm{d}T$. This parameter for polypropylene, -2.7×10^{-3} K^{-1}, is more than twice as large as the maximum value predicted by the Suter–Flory five-state rotational isomeric state model. Conversely, this value of -2.7×10^{-3} K^{-1} is in fair agreement with the average of two previous experimental determinations on "atactic" polypropylene. The value of -1.0×10^{-3} K^{-1} found for alternating poly(ethylene–propylene) agrees with that derived by Mark via the use of the three-state model.

Introduction

The stereochemical constitution of tactic polyolefins can exert a strong influence on chain statistics and upon the variation of chain parameters with temperature. For polypropylene the nonbonded (steric) repulsions in play between methyl groups as well as interactions between methyl groups and the chain backbone will control, depending on tacticity, the preference for certain sequences of conformations of the skeletal bonds. The configurational statistics of polypropylene (PP) and alternating poly(ethylene–propylene) (PEP) have been the subject of theoretical studies[2-19] based, in the main, on the rotational isomeric state (RIS) approach.[20-22] For the case of PP, correlation of theory[2,4-19] and experiment[23-28] has been complicated by the lack of reliable experimental values for chain dimensions and temperature coefficients as a function of tacticity. Other experimental difficulties include a lack of fractionated samples of known polydispersities and, in the case of semicrystalline material, the need to conduct experiments at temperatures where the potential for chain degradation exists.

This work reports on the determination of the temperature coefficient of unperturbed dimensions, $\kappa = \mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T$, for atactic polypropylene with Bernoullian chain statistics (κ is a chain parameter dependent upon the energy and entropy differences of the various rotational isomeric states). Intrinsic viscosities were measured as a function of temperature in the apparent athermal solvents, 2,4-dimethylheptane and 2,2,4-trimethylpentane, and in a series of homologous solvents (alkyl alcohols) under Θ or near-Θ conditions. In a complementary fashion κ was measured for alternating poly(ethylene–propylene) by the determination of K_Θ as a function of temperature. The solvents used were benzene and *n*-alkyl acetates.

Experimental Section

The preparation of the alternating poly(ethylene–propylene) and atactic polypropylene samples has been described.[29,30] 2-Methyl-1,3-butadiene or (*E*)-2-methyl-1,3-pentadiene (Wiley Organics) were polymerized in benzene by using purified *sec*-butyllithium as the initiator. The polyisoprenes were found via ^{1}H NMR spectroscopy to contain the anticipated 91–93% 1,4 and 7–9% 3,4 modes of addition while the poly(2-methylpentadiene) samples contained only the 1,4 addition structures (cis and trans), a finding in accord with previous results.[30-32] Hydrogenation was carried out with Pd on $CaCO_3$ (Strem) under reaction conditions similar to those described by Rachapudy et al.[33] ^{1}H NMR and ^{13}C NMR analysis showed that the essentially alternating poly(ethylene–propylene) (hereafter referred to as poly(ethylene–propylene) or PEP) samples were, within experimental uncertainties, completely saturated whereas the polypropylenes contained no more than 0.4% residual unsaturation.

Table I
Molecular Characteristics of Poly(ethylene–propylene) and Polypropylene

sample	$M_n \times 10^{-4}$,[a] g mol^{-1}	$M_w \times 10^{-4}$,[b] g mol^{-1}	M_z/M_w[c]	M_w/M_n[c]
PEP-1[d]	2.25	2.45	1.03	1.03
PEP-2		2.75	1.02	1.03
PEP-3[e]	3.46	3.63	1.03	1.03
PEP-4		12.1	1.04	1.03
PEP-5	14.7	15.0	1.04	1.05
PEP-6		16.8	1.05	1.06
PEP-7		39.1	1.05	1.07
PP-1		2.30[c]	1.02	1.02
PP-2		2.68	1.02	1.02
PP-3		5.60	1.02	1.03
PP-4	9.9	11.8	1.21	1.27
PP-5		17.0	1.04	1.05
PP-6	24.2	26.8	1.05	1.06
PP-7		42.0	1.32	1.35

[a] Osmometry. [b] Light scattering. [c] SEC. [d] Sample 6A-20 of ref 29. [e] Sample 1-JM of ref 29.

The weight-average molecular weights were measured at 23 °C by using a Chromatix KMX-6 low-angle laser light scattering instrument (λ = 633 nm). Tetrahydrofuran (Burdick and Jackson; dn/dc = 0.0788 mL g^{-1})[29] was the solvent for PEP. The molecular weights of the polypropylene samples were measured in 1-chlorobutane (Fluka 99.9% by GC analysis; dn/dc = 0.0885 mL g^{-1}). The number-average molecular weights were measured in toluene at 25 or 37 °C by using a Hewlett-Packard 502 membrane osmometer with regenerated cellulose membranes (Schleicher-Schuell RC-51).

The molecular characteristics of the poly(ethylene–propylenes) and polypropylenes are given in Table I. In regard to the latter, the polydispersity of samples PP-4 and PP-7 is greater than those[34] used in previous works of ours.[30,35] Flory et al.[36] have indicated that moderate polydispersities are of no consequence in the evaluation of κ via the athermal solvent approach.

Polydispersities were examined by using two Waters 150C size exclusion chromatography (SEC) units each having a differential refractometer. One column set consisted of two Shodex AT-80 M/S mixed-bed columns with equal amounts of 10^3-, 10^4-, 10^5-, and 10^6-Å packings and an additional column packed with 500-Å μ-Styragel. The mobile phase was 1,2,4-trichlorobenzene containing BHT (1.5 g L^{-1}) at a flow rate of 0.5 mL min^{-1} and a temperature of 145 °C. The second SEC unit was equipped with seven ultra-Styragel columns and tetrahydrofuran at 30 °C as the mobile phase at a flow rate of 1.0 mL min^{-1}. That column set covered the nominal porosity range of 10^6–10^2 Å.

Intrinsic viscosities, [η], were measured in Ubbelohde viscometers by methods previously described.[29,30,37] 2,4-Dimethylheptane

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Table II
Intrinsic Viscosities and Huggins Coefficients of Polypropylenes in Athermal Solvents

sample	solvent	parameter	temp, °C 10	25	40	55	70
PP-4	DMH[a]	$[\eta]$, dL g^{-1}	1.11	1.08	1.04	1.01	0.99
PP-4	DMH	k_H	0.33	0.34	0.37	0.38	0.37
PP-6	DMH	$[\eta]$, dL g^{-1}	2.10	2.05	1.96	1.93	1.88
PP-6	DMH	k_H	0.36	0.35	0.40	0.38	0.41
PP-6	TMP[b]	$[\eta]$, dL g^{-1}	2.10	2.03	1.98	1.94	1.87
PP-6	TMP	k_H	0.33	0.34	0.39	0.33	0.37

[a] 2,4-Dimethylheptane. [b] 2,2,4-Trimethylpentane.

was obtained from Wiley Organics in 99% purity (as evaluated by GC) and was used as received. The density, ρ, of this solvent was measured as a function of temperature with a Mettler/Paar Model DMA 46 digital density meter. At 25.0 °C, $\rho = 0.7108$ g mL^{-1} and the thermal expansion coefficient is as follows:

$$\beta_1 = -\frac{\mathrm{d} \ln \rho}{\mathrm{d}T} = 1.3 \times 10^{-3}\ \mathrm{K}^{-1} \qquad (1)$$

2,2,4-Trimethylpentane (Aldrich) was HPLC grade (99.9% pure by GC) material and was used as received. Densities at various temperatures were taken from Riddick and Bunger.[38] The calculated thermal expansion coefficient is

$$\beta_1 = -\frac{\mathrm{d} \ln \rho}{\mathrm{d}T} = 1.2 \times 10^{-3}\ \mathrm{K}^{-1} \qquad (2)$$

The density of PP was found, by weighing in air and water, to be 0.854 g mL^{-1} at 25 °C.[35] The thermal expansion coefficient (β_2) for the atactic PP was derived from published data[39] and the above result:

$$\beta_2 = -\frac{\mathrm{d} \ln \rho}{\mathrm{d}T} = 7.9 \times 10^{-4}\ \mathrm{K}^{-1} \qquad (3)$$

The temperature dependence of polypropylene unperturbed chain dimensions was also evaluated via the determination of K_Θ in a homologous series of Θ solvents: 1-octanol, 2-octanol, and 3-nonanol. The solvents were obtained from Alfa and were used as received. The intrinsic viscosity measurements were done at 5 and 77 °C and combined with the results of ref 30. All data were evaluated via unweighted linear regression analysis.

The poly(ethylene–propylene) materials were examined in benzene, n-decyl, n-octyl, and n-heptyl acetate under Θ or near-Θ conditions. These results were combined with those available elsewhere in n-hexyl acetate[29] to yield a temperature range of ca. 55 °C over which K_Θ was measured. The n-heptyl acetate (Penta Manufacturing Co.) was found to be 99.2% pure via GC analysis. The remaining n-alkyl acetates (Aldrich or Pfaltz and Bauer) were found to be 99.7% pure, while benzene (Burdick and Jackson) was found to exhibit a purity in excess of 99.9%. All solvents were used as received. Solvent densities were determined by using the Mettler/Paar Model DMA 46 digital density meter.

Θ temperatures were established via cloud point studies. The critical temperature, T_c, was determined and the Θ temperatures estimated from plots of T_c^{-1} vs the square root of molecular weight. This method worked reasonably well for all solvents with the exception of benzene, where the accuracy of the extrapolation procedure is limited by the relatively high freezing point of this solvent. However, the initial results for the PEP–benzene system led to a second series of measurements done under virtual Θ conditions.

It must be emphasized that the poly(ethylene–propylene) samples do not possess strictly alternating structures as a consequence of the 7–9% 3,4 content of the parent polyisoprenes. However, for the sake of convenience, the presence of the isopropyl groups is not noted in the nomenclature used in this work. The comparable situation does not exist for the polypropylenes since the parent polydiene was found, within the usual experimental uncertainties, to exhibit only the 1,4 mode of addition.[30]

Results

The measurement of κ by the use of an athermal solvent was first done for polyethylene by Flory and co-workers.[36]

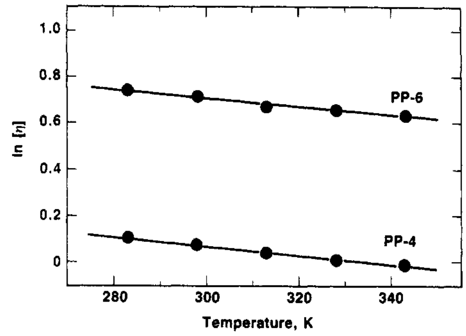

Figure 1. Plot of ln $[\eta]$ as a function of temperature for Bernoullian polypropylenes in the athermal solvent 2,4-dimethylheptane.

Following that procedure we determined the intrinsic viscosities of two polypropylene samples (PP-4 and PP-6) as a function of temperature (10–70 °C) in 2,4-dimethylheptane. Intrinsic viscosity measurements were conducted in 2,2,4-trimethylpentane for PP-6 over the same temperature range. Concentrations were calculated at each temperature from the solvent expansion coefficient, eq 1 and 2. These results are given in Table II and Figure 1.

From the slopes of the lines in Figure 1 κ can be evaluated by using the method of Flory and co-workers.[20,36] This approach begins with the Flory–Fox relationship:[40]

$$[\eta] = \Phi(\langle r^2\rangle_0/M)^{3/2}M^{1/2}\alpha^3 \qquad (4)$$

$$\alpha^5 - \alpha^3 = 27(2\pi)^{-3/2}(\nu^2/N_A V_1)(\langle r^2\rangle_0/M)^{-3/2}M^{1/2}(1/2 - \chi_1) \qquad (5)$$

where $\Phi = 2.5 \times 10^{21}$ (for $[\eta]$ in dL g^{-1}[41-44] and $\langle r^2\rangle_0$ in cm), M is molecular weight, α is the expansion factor $[\langle r^2\rangle/\langle r^2\rangle_0]^{1/2}$, ν and V_1 are, respectively, the specific volume of the polymer and the molar volume of the solvent, N_A is Avogadro's number, and χ_1 describes the thermodynamic interaction of polymer and solvent.

By solving eq 4 for the temperature dependence of $\langle r^2\rangle_0$ and using eq 5 to eliminate the temperature dependence of α, Flory and co-workers obtained[36]

$$\mathrm{d} \ln \langle r^2\rangle_0/\mathrm{d}T = (5/3 - \alpha^{-2})\ \mathrm{d} \ln [\eta]/\mathrm{d}T - (1 - \alpha^{-2})[2\beta_2 - \beta_1 - (1/2 - \chi_1)^{-1}(\mathrm{d}\chi_1/\mathrm{d}T)] \qquad (6)$$

The parameter $\mathrm{d}\chi_1/\mathrm{d}T$ was taken to be zero in view of the chemical similarity of solvent and polymer. This approach has also been made in other athermal solvent based determinations[45-47] of κ. Values of α were calculated at 40 °C, the median temperature used in this work, and from the previously reported[30] unperturbed dimensions of PP measured at 37.6 °C. Thus, the data of Figure 1 lead to values of d ln $[\eta]$/dT of -1.88×10^{-3} and -1.97×10^{-3} K^{-1}, for samples PP-4 and PP-6 in 2,4-dimethylheptane, respectively. For sample PP-6 in 2,2,4-trimethylpentane the value of d ln $[\eta]$/dT was found to be -1.85×10^{-3} K^{-1}. These results lead to an average value of -2.4×10^{-3} K^{-1} for the polypropylene κ.

Table III
Intrinsic Viscosity and Huggins Coefficients for Polypropylene[a]

PP sample	$[\eta]^{5.0°C}_{3\text{-NON}}$, dL g^{-1}	k_H	$[\eta]^{77.0°C}_{1\text{-OCT}}$, dL g^{-1}	k_H
1	0.242	0.57	0.172	0.63
2	0.264	0.55	0.185	0.69
3	0.406	0.47	0.283	0.72
4	0.563	0.48	0.397	0.75
5	0.729	0.70	0.473	1.01
6	0.938	0.57	0.629	0.99
7	1.13	0.60	0.723	1.13

[a] Symbols for solvent identification: 3-NON = 3-nonanol; 1-OCT = 1-octanol.

The apparent athermal solvent approach was complimented by the determination of K_Θ in various alkyl alcohols. These values were based on the intrinsic viscosity results given in Table III and ref 30. The parallel results for poly(ethylene–propylene) are based on the intrinsic viscosity findings given in Table IV and ref 29. The K_Θ and chain dimension parameters for both PP and PEP are summarized in Table V. The K_Θ values are derived in all cases by the use of the Burchard–Stockmayer–Fixman[48-50] extrapolation procedure in order to eliminate errors caused by deviations from true Θ conditions. The resultant values of κ are given in Table VI along with literature values. These κ values are obtainable from

$$\mathrm{d}\ln\langle r_0^2\rangle/\mathrm{d}T = 2/3\ \mathrm{d}\ln[K_\Theta]/\mathrm{d}T \qquad (7)$$

Figures 2 and 3 show respectively the plots of K_Θ as a function of temperature for the PP and PEP studied in this work and the literature values[23-26] for "atactic" polypropylene.

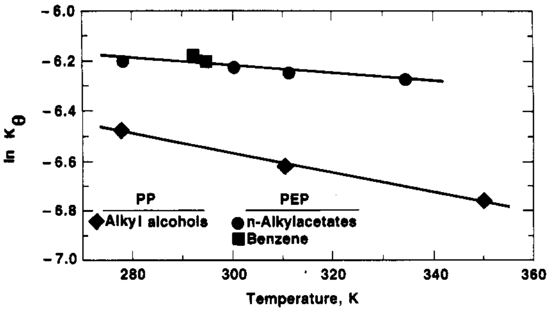

Figure 2. Plot of K_Θ as a function of temperature for alternating poly(ethylene–propylene) and Bernoullian polypropylene.

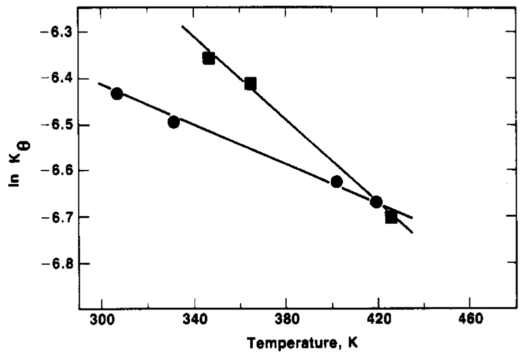

Figure 3. Plot of ln K_Θ as a function of temperature for "atactic" polypropylenes: (●) ref 23–25; (■) ref 26.

Discussion

A comparison of our value for the PP κ of -2.7×10^{-3} K^{-1} and those available in the literature reveals good agreement with that of Kinsinger and Hughes[26,51] (Table VI). The result of Moraglio et al.[23-25] is about one-half of our value. Some possible reasons for these differences exist. As mentioned, the magnitude of κ can be sensitive to the tacticity of the examined samples. Neither tacticity nor sequence distribution data are available for the polypropylenes used in the earlier work. The polymers used in our study are truly atactic[30] and not the amorphous

Table IV
Intrinsic Viscosities and Huggins Coefficients for Poly(ethylene–propylene)[a]

PEP sample	$[\eta]^{5.0°C}_{DA}$, dL g^{-1}	k_H	$[\eta]^{19.0°C}_{BEN}$, dL g^{-1}	k_H	$[\eta]^{21.4°C}_{BEN}$, dL g^{-1}	k_H	$[\eta]^{27.0°C}_{OA}$, dL g^{-1}	k_H	$[\eta]^{38.0°C}_{HA}$, dL g^{-1}	k_H
1					0.325	0.60	0.309	0.59	0.305	0.68
2	0.340	0.79	0.336	0.78	0.344	0.72	0.323	0.73	0.325	0.64
3	0.385	0.80	0.391	0.72	0.400	0.68	0.368	0.75	0.369	0.66
4	0.734	1.34	0.702	1.24	0.799	1.03	0.743	0.66	0.716	0.84
5	0.830	1.56	0.815	1.60	0.875	1.34	0.817	1.30	0.808	0.97
6	0.902	1.43	0.839	1.65	0.945	1.19	0.845	1.36	0.863	0.86
7	1.32	1.85	1.27	1.93	1.42	1.43	1.20	1.59	1.25	1.23

[a] Symbols for solvent identification: DA = *n*-decyl acetate; BEN = benzene; OA = *n*-octyl acetate; HA = *n*-heptyl acetate.

Table V
Intrinsic Viscosity and Unperturbed Parameters for Polypropylene and Poly(ethylene–propylene)

$K \times 10^3$, (g mol wt)$^{-1/2}$	a[a]	$K_\Theta \times 10^{-3}$,[b] (g mol wt)$^{-1/2}$	temp, °C	solvent	$[\langle r^2\rangle_0/M_w] \times 10^3$, nm^2	C_∞[c]
			PP			
1.13	0.53_6	1.58	5.0	3–nonanol	7.35	6.5_9
1.50	0.48_8	1.34	37.6	2-octanol[d]	6.59	5.9_2
1.10	0.50_4	1.15	77.0	1-octanol	5.97	5.3_5
			PEP			
1.62	0.52_3	2.03	5.0	*n*-decyl acetate	8.70	6.7_8
2.01	0.50_2	2.06	19.0	benzene	8.79	6.8_5[e]
1.36	0.54_3	2.03	21.4	benzene	8.70	6.7_8[e]
1.75	0.51_2	1.98	27.0	*n*-octyl acetate	8.56	6.6_6
1.56	0.52_2	1.94	38.0	*n*-heptyl acetate	8.44	6.5_7
1.68	0.51_2	1.89	60.9	*n*-hexyl acetate[f]	8.30	6.4_6[g]

[a] Exponent in the Mark–Houwink equation. [b] Via the Burchard–Stockmayer–Fixman extrapolation procedure; ref 48–50. [c] Calculated for PEP by taking the 3,4 content of the parent chain as 8%. The value of l was 0.153 nm. [d] Reference 30. [e] A value of 6.9 is found via neutron scattering in this temperatures range (Bates, F. S.; Fetters, L. J. unpublished results). [f] Reference 29. [g] This value was mistakenly given as 6.2 in ref 29. This was due to either a typographical or computational error. The value of K_Θ in ref 29 is correct.

Table VI
Temperature Coefficients for Atactic Polypropylene and Poly(ethylene-propylene)

temp coeff $\kappa \times 10^3$, K^{-1}	method	temp range, °C	ref
		PP	
−2.4 (±0.2)	athermal solvents	10–70	this work
−2.9 (±0.3)	Θ solvent series	5–77	this work and ref 30
−3.0	Θ solvent series	74–153	26
−1.4[a]	Θ solvent series	34–146	23–25
		PEP	
−1.0 (±0.2)[b]	Θ solvent series	5–60.9	this work and ref 29

[a] A value of −1.5 × 10^{-3} K^{-1} is obtained by using intrinsic viscosity results in 2,2,4-trimethylpentane (near-athermal solvent); ref 24. [b] A value of −0.9 × 10^{-3} K^{-1} is obtained by not including the benzene-based results of Table V.

Table VII
Unperturbed Dimensions of Isotactic Polypropylene at Various Temperatures

$K_\Theta \times 10^3$,[a] dL g$^{-1/2}$ mol$^{1/2}$	C_∞[b]	temp, °C	solvent	ref
1.43	6.2	125	diphenyl	25
1.52	6.4	125.1	diphenyl	27
1.37	6.0	142.8	diphenyl ether	27
1.30	5.8	143	diphenyl ether	25
1.43	6.2[c]	145	diphenyl ether	26
1.06	5.1	183.2	dibenzyl ether	27

[a] Data from ref 25 and 26 were corrected for small deviations from Θ by the Burchard–Stockmayer–Fixman[48-50] extrapolation procedure. Data from ref 27 were not corrected because values of [η] were not tabulated. [b] C_∞ is the characteristic ratio $\langle r^2\rangle_0/nl^2$. These values were calculated by taking Φ = 2.5 × 10^{21} (for [η] in dL g^{-1}). [c] A value of 4.7 has been reported: Heatley, F.; Salovey, R.; Bovey, F. A. *Macromolecules* **1969**, *2*, 619. That value was based on a single sample of undetermined polydispersity.

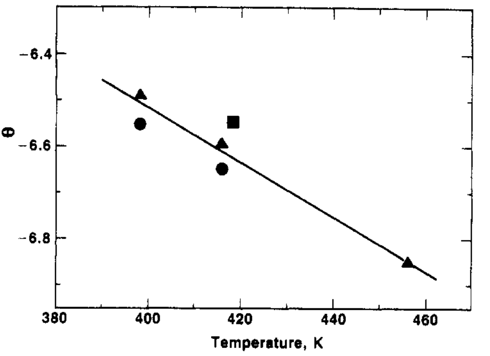

Figure 4. Plot of ln K_Θ as a function of temperature for isotactic polypropylenes: (▲) ref 27; (●) ref 25; (■) ref 26.

stereoirregular PP that is often called atactic. The influence of specific solvent effects on unperturbed dimensions makes evaluation of κ from data obtained in a series of Θ solvents hazardous unless a family of chemically similar Θ solvents is used.[52] No attempt to minimize or evaluate the potential of specific solvent effects was done in the earlier work.[23-25] In addition, number-average molecular weights were used in the previous work;[23-26] intrinsic viscosity results are better treated with weight-average values.[53]

Before our experimental results are compared with the RIS predictions, it is appropriate to review the existing data for κ of isotactic polypropylene.[54] These results,[25-27] which are summarized in Table VII and Figure 4, yield a κ of −3.7 × 10^{-3} K^{-1}.[55] This value is in good agreement with the value −4.1 × 10^{-3} K^{-1} reported by Nakajima and Saijyo[27] but is somewhat larger than the value of κ of −3.0 × 10^{-3} K^{-1} determined by Moraglio and co-workers.[25] No definite conclusion about specific solvent effects can be made but at least for diphenyl ether and dibenzyl ether such effects should be minimized. The experimental findings for our Bernoullian atactic and the isotactic PPs at 130 °C are found to be in fair agreement with values derived from the semiempirical three-state model of Biskup and Cantow[14] when the following RIS parameters are utilized: η = 0.9, ω = 0.0932, τ = 0.6, $\Delta\phi$ = 5°, $(S/R)_\omega$ = 0.5, and ΔF_η = 0.[56] Experimental values and various theoretical results are given in Table VIII.

It is significant to note that the parameters given above are also in agreement with parameters for the three-state RIS model parameters derived by Suter et al.[57] and used in interpreting studies of the epimerization of low molecular weight model compounds. Thus, the three-state model accounts reasonably well for both sets of experimental data (model compounds and polymers).[58,59]

Even in view of its apparent success in treating the configurational statistics of PP, it must be emphasized that the three-state model is approximate.[20,22] Suter and Flory[19] derived a five-state model to more rigorously account for the conformational energies of PP. That model predicts characteristic ratios (C_∞) at 140 °C of about 4.0 and about 5.5 for isotactic and atactic PPs, respectively, and a maximum κ value of about −1 × 10^{-3} K^{-1} for atactic PP and values ranging between −1.3 × 10^{-3} and −2.3 × 10^{-3} K^{-1} for isotactic PP. These findings are not supported by the results summarized in Tables VI–VIII. In particular, the other findings yield larger values of C_∞ for isotactic PP than for the atactic form.

Recently, Wittwer and Suter[60] applied the five-state PP RIS model[19] to atactic (in the Bernoullian sense)[62,63]

Table VIII
Results for C_∞ and κ for Polypropylene from RIS Models and Experiment

	isotactic PP		atactic PP[a]			
RIS model	C_∞	$\kappa \times 10^3$, K^{-1}	C_∞	$\kappa \times 10^3$, K^{-1}	temp, °C	ref
			RIS Values			
Abe	8.5	−3.9	6.3	~0	*b*	11
Allegra et al.	5.6	−3.5	6.5	−0.5	150,[c] 100[d]	16, 10
Biskup–Cantow	6.2	−3.8	5.3	−1.8	130	14
Boyd–Breitling[e]	5.8	−1.0	5.0	−0.6	145	13
Mark	9.4	−4.0	6.7	−1.2	25	2
Suter–Flory[f]	4.2	−1.7	5.5	−0.9	140	19
Wittwer–Suter	5.1	−2.5	4.5	−0.9	127	60
			Experimental Values			
			4.5[g]	−2.7	145	this work and ref 30
	6.2[h]	−3.7			145	26, 27

[a] Defined as material with Bernoullian distribution of the diad configuration. [b] Temperature not given. [c] Isotactic PP. [d] Atactic PP. [e] For E_ω = 1300 cal. [f] Parameters of set A in ref 19. [g] Calculated value based on the data in Table V. [h] Neutron scattering results, ref 61, also yield this value.

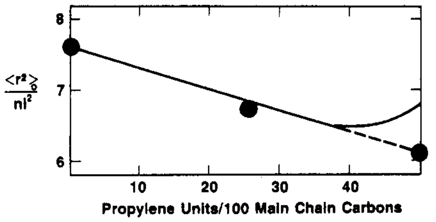

Figure 5. Influence of propylene content on the characteristic ratio of the poly(ethylene–propylene) chain at 25 °C. The solid line represents the three-state RIS predictions of Mark; ref 2.

poly(1-butene)[64] and derived therefrom a value (at 300 K) for C_∞ of 4.5, a value also reported by Mattice and colleagues[65,66] via the use of a three-state RIS approach. Conversely, unperturbed chain dimension measurements based on Θ condition intrinsic viscosity measurements[62] and neutron scattering in the melt[67,68] yield values of 5.3 and 5.2, respectively, for C_∞ (at ca. 300 K). These experimental results combined with those for PP serve to indicate that refinements in the respective RIS models are needed. It must be mentioned that Suter and Flory[19] noted the shortage of reliable data for PP and emphasized the potential need to reassess and refine their five-state model when more dependable results became available.

We feel that some justification of our choice of 2,4-dimethylheptane and 2,2,4-trimethylpentane as athermal or near-athermal solvents is in order. Mark–Houwink–Sakurada exponents for PP in 2,4-dimethylheptane may be derived as a function of temperature from the data in Tables I and II. A constant value of 0.780 ± 0.006 is obtained, and no upward or downward trends are found with increasing temperature. This finding, coupled with the magnitude and near-constant nature of the Huggins coefficients (Table II), suggests that 2,4-dimethylheptane is a very good solvent for PP over the temperature range of interest. The intrinsic viscosity results for sample PP-6 are essentially identical in both solvents at a given temperature.

It has been accepted that polymer/solvent systems chosen on the basis of chemical similarity will exhibit zero or near-zero values for the heat of dilution parameter[37,47,48,69] with $d\chi_1/dT$ equal to zero as the subsequent outcome. Chemical similarity of solvent and polymer is, alone, not a guarantee of the temperature independence of χ_1; e.g., we have found that neither squalene nor squalane serves as an athermal solvent for 1,4-polyisoprene or PEP, respectively. The behavior in both solvents (increasing values for the Huggins coefficients to those anticipated for near-Θ conditions with increasing temperature) suggests an approach to LCST behavior at high temperature for these polymer–solvent pairs.

Danusso and Moraglio[24] found a near-zero heat of mixing for "atactic" PP in 2,2,4-trimethylpentane and *n*-heptane ($\chi_1 = 0.0094$). Such measurements have not been done for the PP/2,4-dimethlheptane system. In view of the agreement of the viscosity results (Table II), our assumption that $d\chi_1/dT \simeq 0$ over the temperature range used may be valid. Nonetheless, in view of this uncertainty, the evaluation of κ for PP was also done via the determination of K_Θ as a function of temperature in a series of structurally similar Θ solvents.

Poly(ethylene–propylene) materials have received less theoretical attention[2,3] than polypropylene[2,4–19] with regard to unperturbed chain dimensions and temperature coefficients. The most extensive effort is that of Mark,[2] who evaluated both of the foregoing parameters for ethylene–propylene copolymers as a function of composition, sequence distribution (expressed in terms of copolymerization reactivity ratios), and tacticity of the propylene segments.

Our evaluation of κ for the alternating ethylene-propylene copolymers involved the determination of K_Θ as a function of temperature under Θ or near-Θ conditions (Table V). The plot of these values is given in Figure 2 and leads to a value of κ of $-1.0\ (\pm 0.2) \times 10^{-3}\ \mathrm{K}^{-1}$ (Table VI). This value is in good agreement with $-1.1 \times 10^{-3}\ \mathrm{K}^{-1}$, which was derived from the three-state model used by Mark.[2] It is duly noted that, within the usual experimental uncertainties, at most a very slight specific solvent effect is detectable for the benzene-based results when compared to those derived from the *n*-alkyl acetate solvents. Thus, in view of what is at best a threshold specific solvent effect, the value of κ reported above is based on all data points (benzene and *n*-alkyl acetates).

The three-state RIS model as used by Mark[2] leads to a correct evaluation of κ and C_∞ for the alternating ethylene–propylene copolymers and isotactic polypropylene (Table VIII). However, that three-state model overestimates the value of C_∞ (at 25 °C) for Bernoullian polypropylene. This is shown in Figure 5, where a monotonic decrease in chain dimensions is observed as the propylene content increases in the ethylene–propylene copolymers (for the case where the polyethylene C_∞ at 140 °C was taken as 6.7 and a κ of $-1.1 \times 10^{-3}\ \mathrm{K}^{-1}$ was used).[36,70–73] Mark's[2] calculations are accurate until the propylene content in the copolymer reaches ca. 70%, the point beyond which the theoretical and experimental chain dimensions deviate (Figure 5). The three-state RIS-based calculations of κ for Bernoullian polypropylene yield a value for this parameter of $-1.2 \times 10^{-3}\ \mathrm{K}^{-1}$ (Table II of ref 2), a value that is about one-half that found in this work. Thus, insofar as Bernoullian polypropylene is concerned, the three-state RIS approach of Mark[2] requires refinement.

In summary, the temperature coefficient of unperturbed dimensions for Bernoullian polypropylene derived from intrinsic viscosity measurements is shown to be large and negative. Our value of κ, $-2.7 \times 10^{-3}\ \mathrm{K}^{-1}$, is reasonably consistent with the semi-empirical three-state RIS model of Biskup and Cantow[14] and Suter et al.,[57] this latter model being based on results of epimerization studies on low molecular weight analogues of polypropylene. These three-state models[12,14,16,57] and that used by Mark,[2] even though they are only approximate, successfully predict C_∞ and κ for isotactic PP. The five-state RIS model of Suter and Flory[19] requires refinement in view of the experimental results for Bernoullian polypropylene. For example, bond and torsion angles have generally been considered to be temperature invariant. Thus a potential refinement may be, as Cook and Moon have suggested,[74,75] the inclusion of torsional oscillations into the configurational statistics of the RIS models.

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(55) It must be mentioned that $\kappa = -1.6 \times 10^{-3}\ \mathrm{K}^{-1}$ has been reported for isotactic PP by F. Hamada (see, for example, ref 11 and 19) using the athermal solvent approach. To the best of our knowledge, this result has not yet appeared in its own right in the literature.

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