Macromolecules **1980**, *13*, 560–564

Chain Dimensions and Dipole Moments of Poly(*tert*-butyl vinyl ketone)[‡]

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ABSTRACT: The characteristic ratio $C_\infty = \langle r^2 \rangle_0 / nl^2$ of atactic poly(*tert*-butyl vinyl ketone) is determined from light-scattering and viscosity measurements in *sec*-butyl alcohol as 8.6 ± 0.5 at 300 K, and at this temperature in benzene the dipole moment ratio $D_\infty = \langle \mu^2 \rangle / x\mu_1^2$ is measured to be 0.18 ± 0.01, with a temperature coefficient of $\mathrm{d}\ln D_\infty/\mathrm{d}T = (3 \pm 1) \times 10^{-3}\ \mathrm{K}^{-1}$. Calculations of C_∞ and D_∞ based on a two-state rotational isomeric state model, with parameters independently derived from a previously developed semiempirical potential energy surface and from epimerization equilibrium measurements for dimeric and trimeric oligomers, are in excellent agreement with the experimental results. The predicted temperature coefficient is positive but lower in magnitude than that observed.

Although poly(alkyl vinyl ketones) have been known for a considerable number of years, it is only recently that detailed investigations of their configurational and conformational properties have been made. Some equilibrium properties of poly(methyl vinyl ketones) have been reported, among them the vicinal proton–proton coupling constants in the isotactic chain,[1] the dipole moment ratio of the atactic polymer,[2] and a rough estimate of the unperturbed dimensions of isotactic samples.[3,4] More recently the conformational characteristics of the polymer and of simple model ketones have been investigated theoretically.[5]

In our laboratories some attention has now been paid to poly(*tert*-butyl vinyl ketone), hereinafter PTBVK. At the ETH, theoretical calculations of the conformational potential energy[6] were reinforced by determinations of crystal structure and epimerization equilibria for model compounds.[6,7] At about the same time, an independent experimental study of the conformational properties of PTBVK in solution was carried out at Dartmouth.[8] These experiments are described below and are compared to calculated values based on the Zürich investigations, with gratifying accord.

The calculations of the conformational potential for dyads of PTBVK have shown[6] that the conformational characteristics of this polymer are unusual as compared to other vinyl polymers. In the meso dyad, the (helical) conformations $|tg|$ and $|gt|$ are strongly favored over the other conformations, and $|tt|$ conformations have a very high relative energy. The racemic dyad exhibits a $|gg|$ minimum that is slightly lower in energy than that of $|tt|$, which is usually the "over-all best" conformation. The average energy of the racemic dyad is higher than that of the meso dyad, contrary to the situation in other vinyl polymers. The pivaloyl side group was found always to occupy a conformation in which the carbonyl group "bisects" the two C–C bonds substituent to the α-methine carbon, and in which a methyl of the *tert*-butyl group eclipses the keto group. Oscillations around this position are small. This conformation is depicted in Figure 1.

Subsequently, a two-state rotational isomeric state scheme was constructed from the results of these calculations,[7] and the partial partition functions over the conformational domains assigned to a state were resolved into contributions from individual interactions. The two states, t and g, are located at angles $\Phi_t = 10°$ and $\phi_g = 110°$, and the statistical weight matrices[7,9] for a pair of bonds within a meso and a racemic dyad are given as

$$\mathbf{U}_m'' = \begin{bmatrix} 0 & 1 \\ 1 & \omega/\eta \end{bmatrix} \tag{1}$$

and

$$\mathbf{U}_r'' = \begin{bmatrix} \eta\omega^{\ddagger} & \omega' \\ \omega' & 1/\eta \end{bmatrix} \tag{2}$$

where rows and columns are indexed with the states t and g in that order. The first-order parameter η measures the preference for t over g. The second-order parameters ω and ω' represent the effects of interactions between pairs CH_2/CH_2 and CH_2/pivaloyl, respectively. The second-order parameter $\omega^{\ddagger}$ expresses the special "around the chain" repulsion[6] between two pivaloyl groups in the racemic $|tt|$ conformation. The matrix for a pair of bonds embracing a methine carbon is

$$\mathbf{U}' = \begin{bmatrix} 1 & 1 \\ 1 & 0 \end{bmatrix} \tag{3}$$

The statistical weight parameters ω and ω' were assigned values determined by potential energy calculations:[7]

$$\omega = 0.9 \exp(-850/T) \tag{4}$$

$$\omega' = 1.9 \exp(-1400/T) \tag{5}$$

which give, at 300 K, $\omega \approx 0.05$ and $\omega' \approx 0.02$. For η and $\omega^{\ddagger}$, satisfactory values were found through fitting of the conformational model to the results of equilibrium epimerization of the "dimer" 2,4-dipivaloylpentane at 100, 150, and 175 °C and of the "trimer" 2,4,6-tripivaloylheptane at 150 °C. They are

$$\eta = 0.6 \exp(-E_\eta/RT) \tag{6}$$

$$\omega^{\ddagger} = 2.9 \exp(-E_\omega{}^{\ddagger}/RT) \tag{7}$$

where $E_\eta = -0.6\ (\pm\ 0.1)\ \mathrm{kcal\ mol^{-1}}$ and $E_\omega{}^{\ddagger} = 1.5\ (\pm\ 0.2)\ \mathrm{kcal\ mol^{-1}}$, and the limits are independent.[7] At 300 K, $\eta \approx 1.6$ and $\omega^{\ddagger} \approx 0.23$. The C–C–C valence angles are 114° at CH_2 and 112° at CH.

The above parameters were used without modification in the calculations described below.

Experimental Section

Monomeric *tert*-butyl vinyl ketone was prepared[10] by Hofmann elimination from the Mannich base obtained with pinacolone,

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[‡] Dedicated to Paul J. Flory on his 70th birthday.

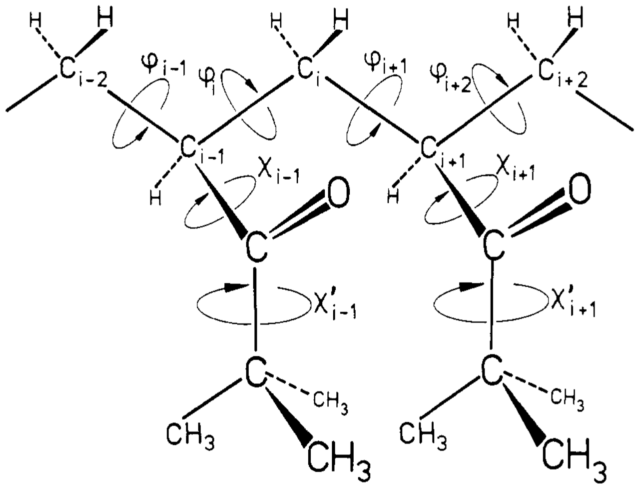

Figure 1. A meso dyad of PTBVK in its *tt* conformation.

Table I
Weight-Average Molecular Weights and Intrinsic Viscosities at 25 °C of PTBVK Fractions

fraction no.	$M_w \times 10^{-5}$	$[\eta]$, dL g^{-1} in *sec*-butyl alcohol	$[\eta]$, dL g^{-1} in benzene
F-1	9.5	0.57	1.26
F-2	6.9	0.51	1.17
F-4	5.6	0.43	0.91
F-6	4.3	0.39	0.78
F-8	2.65	0.293	0.56
F-9	1.54	0.221	0.376
F-10	0.71	0.153	0.208

Table II
Dipole Moments of PTBVK and Pinacolone in Benzene at Several Temperatures

temp, °C	moments, D: pinacolone, μ	PTBVK, $\langle\mu^2\rangle/x$: F-1	F-9
15	2.75	1.26	1.35
25	2.76	1.35	1.36
35	2.77	1.37	1.41
45	2.76	1.41	1.46
55	2.76	1.45	1.49

dimethylamine, and formaldehyde. Having been extracted from the reaction mixture with ethyl ether, the monomer polymerized after evaporation of the ether at 50–60 °C without addition of initiator. The polymerization is presumed to have occurred by a free-radical pathway, probably because of traces of peroxides in the ether. After dissolution in chloroform and precipitation in methanol, the PTBVK was divided into 11 fractions with acetone/methanol.

Benzene, *sec*-butyl alcohol, and pinacolone (Eastman) were distilled before use.

Solution viscosities were determined in Ubbelohde dilution viscometers at 25 °C in a bath controlled to ±0.02 °C. A Brice-Phoenix differential refractometer Model BP-1000V was used to obtain refractive-index increments at temperatures in the range 15–35 °C. For PTBVK in *sec*-butyl alcohol at 25 °C at a wavelength of 546 nm, the value obtained was $dn/dc = 0.097 \pm 0.002$ cm^3 g^{-1}.

Light-scattering intensities of PTBVK solutions in *sec*-butyl alcohol were measured at room temperature for light of 546 nm wavelength with a Brice-Phoenix Model 1000 light scattering photometer. Four different concentrations were measured for each fraction. The fraction of highest molecular weight was observed over the angular range 30–150° with vertically polarized incident light; the standard Zimm plot gave a molecular weight $M_w = 9.1 \times 10^5$, a second viral coefficient $A_2 = (4 \pm 1) \times 10^{-5}$ mol cm^3 g^{-2}, and a root mean square radius of gyration $\langle S^2\rangle^{1/2} = 24 \pm 2$ nm. Alternatively, measurements of right-angle scattering with unpolarized light, when combined with an estimate of the particle scattering factor $P(\theta)$ from the intrinsic viscosity by a method described by Flory[11] and also previously used by us,[12] yielded for the same fraction a molecular weight $M_w = 9.5 \times 10^5$ and a root mean square radius of gyration $\langle S^2\rangle^{1/2} = 26$ nm. This good agreement supports the latter method, which was used for all the other fractions, with the results shown in Table I.

Dielectric constants were measured with a General Radio 1620 capacitance bridge assembly at a frequency of 5 kHz, the solutions being confined in a home-built capacitance cell with electrodes constructed from concentric cylindrical stainless steel plates separated by Teflon PTFE spacers. The cell volume was about 10 mL and the vacuum capacitance was 17.26 pF. The contribution of the spacers to the measured capacitance was evaluated at each temperature by calibration with benzene. The estimated error in capacitance measurement is ±0.002 pF. Loss factors were not recorded and are of no interest at the low frequencies involved here. Each solute was measured at three concentrations in freshly distilled benzene. Dipole moments per repeat unit were evaluated from a simplified Guggenheim[13]–Smith[14] equation,

$$\frac{\langle\mu^2\rangle}{x} = \frac{27kTM_1}{4\pi N_A d_0}\left[\frac{(d\epsilon/dw)_0}{(\epsilon_0+2)^2} - \frac{2n_0\,(dn/dw)_0}{(n_0{}^2+2)^2}\right] \tag{8}$$

from which corrections for the difference in atomic polarization between solute and displaced solvent have been omitted. In the present case this omission is estimated to produce less than 1% error in the resulting square dipole moments. In the above equation, d_0, ϵ_0, and n_0 are the density, dielectric constant, and refractive index, respectively, of the solvent; w is the weight fraction of solute; N_A is Avogadro's number; M_1 is the molecular weight of the repeat unit; and the increments $(d\epsilon/dw)_0$ and $(dn/dw)_0$ are at infinite dilution.

Results

Weight-average molecular weights obtained from light-scattering measurements in *sec*-butyl alcohol are given for seven PTBVK fractions in Table I. In the same table are shown intrinsic viscosities in *sec*-butyl alcohol and in benzene, which is the better solvent of the two. The corresponding Mark–Houwink relationships are:

$$[\eta] = (7.5 \times 10^{-5})M_w{}^{0.71}\ \mathrm{dL/g} \tag{9}$$

in benzene at 25 °C

$$[\eta] = (4.5 \times 10^{-4})M_w{}^{0.52}\ \mathrm{dL/g} \tag{10}$$

in *sec*-butyl alcohol at 25 °C. The low value of the exponent in eq 10 and the observed second virial coefficients show that *sec*-butyl alcohol is not far from Θ solvent conditions. Thus extrapolation to the unperturbed state by a conventional plot of $[\eta]M^{-1/2}$ against $M^{1/2}$ is very safe and leads to $K_\Theta = 5.6 \times 10^{-4}$ dL mol$^{1/2}$ g$^{-3/2}$. With the value $\Phi = 2.5 \times 10^{21}$ for the viscosity constant, we then find

$$\langle r^2\rangle_0/M = (K_\Theta/\Phi)^{2/3} = (37 \pm 2) \times 10^{-18}\ \mathrm{cm^2\ mol\ g^{-1}} \tag{11}$$

The directly observed radius of gyration for fraction F-1 gives $6\langle S^2\rangle/M = 38 \times 10^{-18}$ cm^2 mol g^{-1}, which with a small correction for excluded volume is in agreement with eq 11, based on intrinsic viscosities, to within the experimental error. Taking the figure given in eq 11, we therefore have for the characteristic ratio

$$C_\infty = (\langle r^2\rangle_0/nl^2)_{n\to\infty} = 8.6 \pm 0.5 \tag{12}$$

As both the polymer and the solvent are polar, it would be useful to have confirmation of this result from measurements in other solvents.

Mean square dipole moments in benzene at several temperatures are displayed in Table II for two different fractions of PTBVK and for pinacolone (methyl *tert*-butyl ketone), the latter serving as a model for the polymer repeat unit. It is seen that the data for the two fractions agree to about 3%, although the figures for F-1 are consistently slightly lower than those for F-9. For polymers of the vinyl structure, with no distinguishable direction along the chain contour, the mean square dipole moment per repeat unit is subject to negligible excluded-volume effects and should therefore be the same at all molecular weights,[15,16] except for oligomers. The dipole moment of pinacolone is found to be 2.76 ± 0.01 D, independent of temperature and in agreement with published results for it and other simple ketones.[17] The dipole-moment ratio of the polymer is then

$$D_\infty = \langle \mu^2 \rangle / x\mu_1^2 = 0.18 \pm 0.01 \text{ at } 25\ ^\circ\text{C} \qquad (13)$$

where μ_1 is the dipole moment of pinacolone. The temperature coefficient of D_∞ is positive, with a value of $(3 \pm 1) \times 10^{-3}$ K^{-1}.

Calculations

Calculations of the characteristic ratio and of the dipole moment ratio of PTBVK were carried out with the *generator matrix* technique.[9,18]

For the characteristic ratio the generator matrix for bond i is

$$\mathbf{G}_i = \begin{bmatrix} 1 & 2\mathbf{l}^{\mathrm{T}}\mathbf{T} & l^2 \\ 0 & \mathbf{T} & \mathbf{l} \\ 0 & 0 & 1 \end{bmatrix}_i \qquad (14)$$

$\mathbf{l}_i$ being the bond vector in column form and $\mathbf{l}_i^{\mathrm{T}}$ its transpose; $\mathbf{T}_i$ is the transformation matrix required to transform the Cartesian coordinates in the system of bond $i + 1$ into the system of bond i. The mean square length of the chain vector is

$$\langle r^2 \rangle_0 = Z^{-1} G_0 [\prod_{j=1}^{x-1} (G' G_k'')_j] G_x \qquad (15)$$

where Z is the conformational partition function

$$Z = \mathbf{U}_0 [\prod_{j=1}^{x-1} (\mathbf{U}' \mathbf{U}_k'')_j] \mathbf{U}_x \qquad (16)$$

and the matrices $\mathbf{G}'$ and $\mathbf{G}_k''$ are defined as

$$\mathbf{G}' = (\mathbf{U}' \otimes \mathbf{E}_5) \begin{bmatrix} \mathbf{G}_t' & 0 \\ 0 & \mathbf{G}_g' \end{bmatrix} \qquad (17)$$

and

$$\mathbf{G}_k'' = (\mathbf{U}_k'' \otimes \mathbf{E}_5) \begin{bmatrix} \mathbf{G}_t'' & 0 \\ 0 & \mathbf{G}_g'' \end{bmatrix} \qquad (18)$$

The subscript k stands for m or r, depending on the stereochemical character of the dyad, and $\mathbf{E}_5$ is the identity of order five. The terminal matrices are defined as

$$\mathbf{U}_0 = [1,0] \qquad (19)$$

$$\mathbf{U}_x = \text{col } (1,1) \qquad (20)$$

$$G_0 = \mathbf{U}_0 \otimes \mathbf{G}_1 \qquad (21)$$

$$G_x = \mathbf{U}_x \otimes \mathbf{G}_x \qquad (22)$$

with $\mathbf{G}_1$ being the first row of $\mathbf{G}$ for the first bond and $\mathbf{G}_x$ being the last column of $\mathbf{G}$ for the terminal bond of the chain.

For the dipole moment ratio the same formulation applies, with the group dipole moment replacing the bond vector in $\mathbf{G}_i$. The "monad" dipole moment μ_1 of the repeating unit is located in the keto group and is colinear with the C–O axis. Since[6] the torsion angle χ in the pivaloyl side group can only assume angles in the close vicinity of the preferred conformation shown in Figure 1, we fixed μ_1 in the reference frame of the following skeletal bond (i.e., i or $i + 2$ in Figure 1). With $\mu_1 = 2.75$ D we have $\mu_1 = 2.75 \text{ col } (-0.234, 0.347, -0.908) D$ in[9,18]

$$\mathbf{G}' = \begin{bmatrix} 1 & 2\mu_1^{\mathrm{T}}\mathbf{T} & \mu_1^2 \\ 0 & \mathbf{T} & \mu_1 \\ 0 & 0 & 1 \end{bmatrix} \qquad (23)$$

while a group dipole moment of zero is used in $\mathbf{G}''$:

$$\mathbf{G}'' = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \mathbf{T} & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad (24)$$

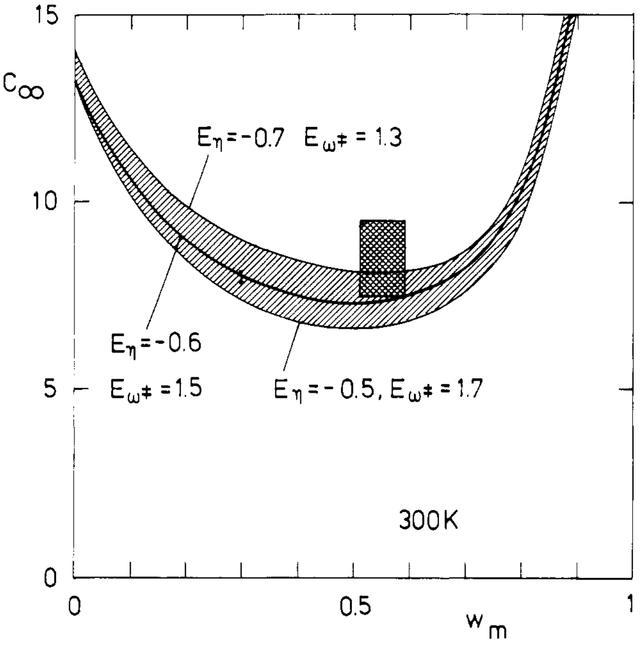

Figure 2. Calculated characteristic ratio $C_\infty = (\langle r^2 \rangle_0 / nl^2)_{n\to\infty}$ as a function of tacticity at 300 K. Values for stereoirregular chains are averages from 30 Monte-Carlo chains with Bernoullian dyad distribution for $n = 200$. Error bars show 2σ limits. Values for purely isotactic and syndiotactic chains are extrapolated from (exact) calculations for x up to 256. The crosshatched rectangle indicates the experimental result (see text).

For stereoregular chains, values were calculated for chain lengths of $x = 4, 8, 16, \ldots, 256$, and C_∞ and D_∞ were obtained by extrapolation against $1/x$. For stereoirregular chains, the conformationally averaged properties for several individual chains of given average stereochemical composition were calculated, the distribution of meso and racemic dyads being determined by a Monte-Carlo procedure assuming a Bernoullian dyad distribution. The probability for a meso placement, w_m, is then independent of the character of the rest of the chain and characterizes the tacticity completely; this assumption has been found valid in general for free-radical polymerized vinyl polymers.[19] We found that the chain length dependence of both C_x and D_x does not extend beyond $x = 100$ for the stereoirregular chains, and the values for C_{100} and D_{100} were identified with C_∞ and D_∞. Monte-Carlo samples of 30 chains for C_∞ and of 15 chains for D_∞ were found to suffice.

Discussion

The calculated curves for C_∞ and D_∞ as functions of w_m at 300 K are displayed in Figures 2 and 3. The heavy central curve in both graphs corresponds to the "best"

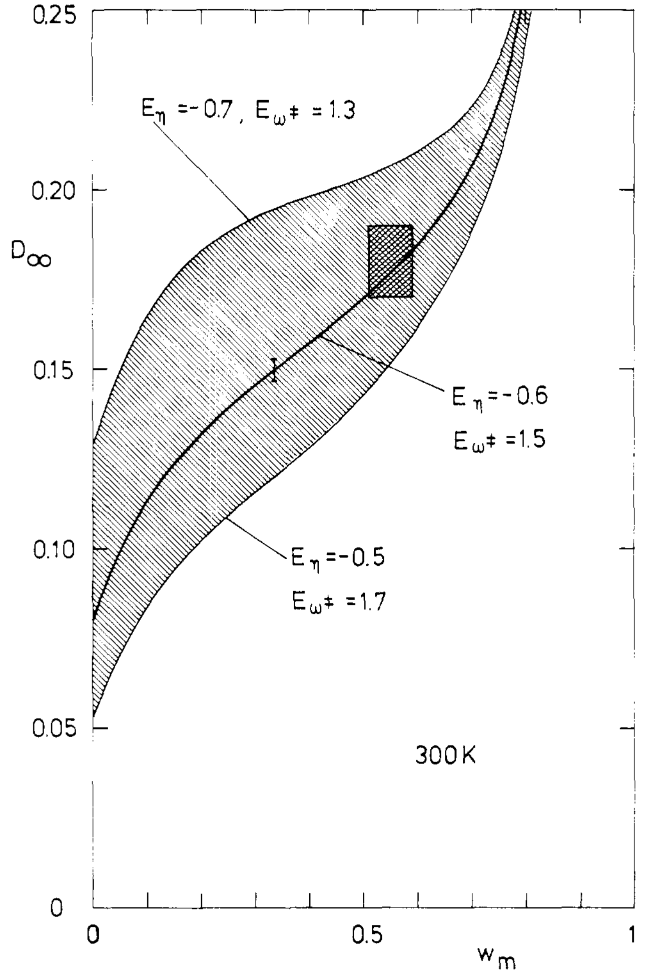

Figure 3. Calculated dipole moment ratio $D_\infty = (\langle\mu^2\rangle_0/x\mu_1^2)_{x\to\infty}$ as a function of tacticity at 300 K. Values for stereoirregular chains are averages from 15 Monte-Carlo chains with Bernoullian dyad distribution for $x = 100$. Error bars show 2σ limits. Values for purely isotactic and syndiotactic polymers are extrapolated from exact calculations for x up to 256. The crosshatched rectangle indicates the experimental results (see text).

values of E_η and $E_\omega^{\ddagger}$ obtained from fitting of the rotational isomeric state model to epimerization data[7] (see eq 6 and 7). The shaded areas surrounding these curves embrace the values calculated when E_η and $E_\omega^{\ddagger}$ are altered independently within their stated limits. The boundaries of these areas are labeled with the corresponding values of E_η and $E_\omega^{\ddagger}$. The two parameters E_η and $E_\omega^{\ddagger}$ are highly correlated, so the particular curve obtained in Figures 2 and 3 is only dependent on the sum $2E_\eta + E_\omega^{\ddagger}$; a change of ±0.2 kcal mol^{-1} in $E_\omega^{\ddagger}$ compensates a change of ∓ 0.1 kcal mol^{-1} in E_η almost exactly.

The characteristic ratio C_∞ and the dipole-moment ratio D_∞ of highly isotactic PTBVK are very large, because of the unusually strong preference for the meso $|tg|$ (or $|gt|$) conformation and the resulting preference for helical conformations: D_∞, for example, is higher than 7 for the purely isotactic chain! The values for highly syndiotactic chains are modest in comparison; those for D_∞ are even unusually small, i.e., ca. 0.1. This is due to the fact that, as in other vinyl polymers, neither the racemic $|tt|$ nor the racemic $|gg|$ conformation possesses a component of the group dipole moment in the direction of the backbone contour (contrary to the meso $|tg|$ conformation), and, additionally, that in the somewhat preferred racemic $|gg|$ conformation neighboring dyads cannot align dipole moments (while in the zigzag planar syndiotactic all-trans chain the dyad moments all interfere constructively). In most other vinyl polymers racemic $|tt|$ is strongly favored over $|gg|$, so that syndiotactic chains have higher D_∞ than those in the present case.

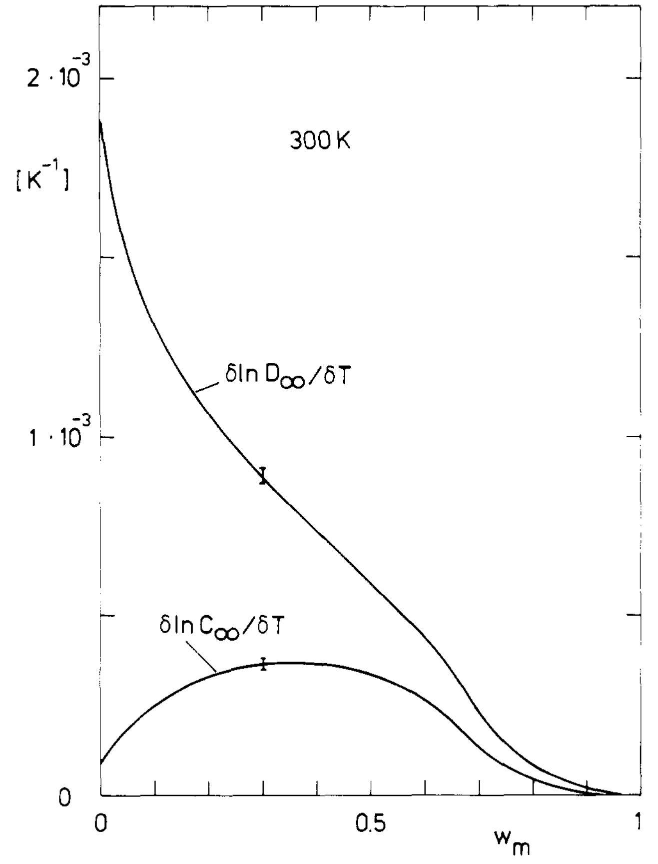

Figure 4. Calculated temperature coefficients $\delta \ln C_\infty/\delta T$ and $\delta \ln D_\infty/\delta T$ as a function of tacticity at 300 K for $E_\eta = -0.6$ kcal mol^{-1} and $E_\omega^{\ddagger} = 1.5$ kcal mol^{-1}. Values for stereoirregular chains are averages from Monte-Carlo samples, the coefficients being calculated separately for every diastereomeric chain of 200 bonds and then averaged. Bernoullian dyad distribution is assumed; error bars indicate 2σ limits. Values for stereoregular chains are extrapolated from exact calculations for x up to 256.

The experimental results are represented in the two graphs by shaded rectangles. The rectangles are delimited by the above stated limits in the experimental values of C_∞ and D_∞ and by the uncertainty in the stereochemical composition of PTBVK polymerized under free-radical conditions,[20] $w_m = 0.55 \pm 0.04$. Experimental and calculated values for D_∞ are in perfect agreement. Agreement is less good for C_∞, but the crosshatched areas still overlap, and the heavy line, representing the "best fit" to the epimerization results, is tangent to the experimental rectangle. We conclude that for both C_∞ and D_∞ calculated values are in substantial agreement with experiment.

Calculations of the temperature coefficients $\delta \ln C_\infty/\delta T$ and $\delta \ln D_\infty/\delta T$ (both at 300 K) for chains of different average Bernoullian stereochemical composition yielded the results shown in Figure 4. Unusual for vinyl polymers, both temperature coefficients are *positive* over the whole range of tacticity, and both become very small as w_m approaches unity. The insensitivity to temperature of the values for isotactic polymers is a result of the nearly exclusive population of meso $|tg|$ (or $|gt|$) only. The sizable positive temperature coefficients of the nonisotactic chains, on the other hand, are due to the facts that in the racemic dyad $|gg|$ is favored over $|tt|$ and that an increase in temperature increases the relative population of $|tt|$. Sequences of $|tt|$ contribute large dipole moments to $\langle\mu^2\rangle_0$

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and increase $\langle r^2 \rangle_0$ because of an almost straight backbone contour for these conformations. Hence, the experimentally observed positive temperature coefficient of D_∞ finds support in the calculations, even though the predicted magnitude is appreciably lower than the observed value.

In view of the now well-established knowledge of the conformational potential energy of PTBVK, observations of dynamical properties would also be of obvious interest. Measurements of dielectric and nuclear magnetic relaxation on solutions of this polymer are in progress and will be reported later. Spin relaxation in solutions of nitroxide-labeled poly(methyl vinyl ketone) has already been described by Bullock, Cameron, and Smith.[21]

Acknowledgment. The work at Dartmouth College was supported by the National Science Foundation under Grant No. DMR76-22987 A01 of the Polymers Program, Division of Material Research.

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Crossover from the Θ to the Excluded Volume Single Chain Statistics: New Experimental Evidences and a Modified Blob Model

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Received December 14, 1979

ABSTRACT: A fortuitous situation created by unexpected results in the study of the poly(acrylamide)–water system in a large range of well-characterized fractions has developed into the proposal of a modified blob model which should be valid for any polymer–solvent system in the range of N/N_c from 0 to 100. Here, as in the simple blob theory, N_c is the chemical distance below which the pair correlation function is supposed to be Gaussian. The experimental results force us, however, to replace the simple jump from Gaussian to excluded volume statistics by a more progressive crossover. Numerical fitting of the whole set of results including the molecular weight dependence of the static and dynamic dimensions as well as the single chain scattering function is consistent for a rather broad crossover up to $N/N_c = 15$.

The consideration of polymer chains as critical objects[1] has greatly revised our picture of polymer solutions. In the dilute regime, the scaling laws coincide with the asymptotic results of Flory's mean-field two-parameter theory, $\alpha^5 - \alpha^3 \propto z$, where z is proportional to $M^{1/2}$ and to the reduced temperature $\tau = (T - \Theta)/\Theta$.[2,3] The description of a single chain as a succession of Gaussian blobs, each made of N_c segments, with excluded volume interaction between the blobs,[4] introduces, however, some differences at small values of z. A theory based on a very simple model with an abrupt change in the pair correlation function for two segments i and j at $|i - j| = N_c$ constitutes a first approach to the problem of the crossover from the Gaussian scaling law at $N < N_c$ to the excluded volume scaling law at $N \gg N_c$ and has been shown[5] to give a consistent explanation of the difference in the exponents of apparent scaling laws obtained for static and dynamic quantities, when measured in a range of values of N/N_c that is not high enough. This is the case for both the q dependence[6] ($q = 4\pi/\lambda \sin \Theta/2$) and M dependence of the diffusion coefficient as measured by quasielastic light scattering.[7] The blob picture is further substantiated by the observation of a spatial crossover in the static neutron scattering law, $S(q)$, which changes from an excluded volume behavior $[S(q) \propto q^{-5/3}]$ to a Gaussian behavior $[S(q) \propto q^{-2}]$ at $q^* \sim R_c^{-1}$, where R_c is the radius of gyration of a blob.[8]

There are however very few experimental studies with sufficient data at small values of α for a very conclusive comparison of the predictions of the blob and the Flory theories. Such a comparison has nevertheless been published recently by Ackasu and Han[9] and seems to be consistent with the blob hypothesis.

In the course of a systematic study of fractions of poly(acrylamide) (PAM) in water,[10] over a large range of molecular weight, we have obtained new unexpected results concerning the exponent in the apparent scaling law for the molecular weight dependence of the radius of gyration R_G. Further investigation, including dynamic measurements, has led us to interpret them in terms of a modified blob theory,[12] which takes into account a progressive

0024-9297/80/2213-0564$01.00/0