of Crosby et al.[3] was used: A 250-mL round-bottomed flask was charged with 2.06 g (8.45 mmol of Br) of macroporous brominated polystyrene (4.1 mmol of Br/g of polymer) and 100 mL of THF. Then the reaction mixture was cooled to −78 °C, 6.4 mL (10.2 mM) of 1.6 N *n*-BuLi was added, and the reaction mixture was shaken at −78 °C for the desired length of time.

General Procedure for the Lithiation of PSHgCl. A modification of the procedure of Burlitch and Winterton[4] was used. The following is representative: First 0.5024 g (1.41 mM Hg) of chloromercurated polystyrene in 10 mL of THF was cooled to −78 °C and treated with 1.0 mL (6.67 mM) of 6.67 N *n*-butyllithium. The reaction mixture was then shaken for 1 h at −78 °C and washed twice with 10 mL of THF, and the resulting poly(styryllithium) was suspended in 10 mL of THF.

General Analytical Procedure. A suspension of metalated polymer containing ca. 30% or more ethereal solvent at −78 °C was allowed to react with 1,2-dibromodecane added slowly at −78 °C, using a syringe. The resulting polymer suspension was allowed to sit at −78 °C for 30 min with occasional shaking and then warmed to room temperature with continuous agitation. Aliquots were withdrawn by syringe and quenched with 10% HCl. After separating the aqueous and ethereal phase, the organic solution was used for GLC analysis.

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Dipole Moment of Poly(methyl vinyl ketone)

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Polymers of alkyl vinyl ketones have been known for a long time,[1] but relatively little attention has so far been paid to their chain-conformational properties. In the present note we present data on the dipole moment of atactic poly(methyl vinyl ketone), PMVK, and its temperature coefficient. Our work was undertaken as a preliminary to measurements of dielectric and nuclear magnetic relaxation, which will be reported at a later time. The keto group also permits the attachment of fluorescent or spin labels, and indeed spin-label dynamic studies of PMVK and of styrene/MVK copolymers have already been published by Bullock, Cameron, and Smith.[2]

After completion of our experiments, we learned that Suter[3] had already made extensive semiempirical calculations of the conformational potential energies of simple and polymeric ketones and had in fact derived a two-state rotational isomeric state model for PMVK based on these calculations. Applied to the dipole moment, his model accounts quantitatively for our results. Here we confine ourselves simply to a presentation of the experimental data.

Table I
Dipole Moments of PMVK and MEK in Dioxane

temp, °C	$\langle\mu^2\rangle/x$[a]
15 (PMVK)	2.42 ± 0.15
25 (PMVK)	2.52 ± 0.03
35 (PMVK)	2.61 ± 0.15
45 (PMVK)	2.71 ± 0.15
55 (PMVK)	2.82 ± 0.15
25 (MEK)	7.83 ± .07

[a] All $\langle\mu^2\rangle$ are in units of D^2.

Experimental Section

A sample of PMVK, prepared by benzoyl peroxide initiation in hexane solution, was purchased from Scientific Polymer Products, Inc., and is presumed to have an atactic, head-to-tail structure.[1] Insoluble colored impurities were removed by dissolving the sample in acetone, filtering, and precipitating in cyclohexane. The resulting polymer IR spectrum matched Aldrich No. P1346A for PMVK. The intrinsic viscosity of the polymer in chloroform at 25 °C was 2.23 dL/g. No viscosity–molecular weight relationship is known to us for the atactic polymer, but if we use the results of Merle–Aubry, Merle, and Selegny[4] for an isotactic polymer (a maneuver which turns out to be essentially correct[3]) we estimate the weight-average molecular weight of our sample to be about 1 × 10^6. In any case, knowledge of the molecular weight is unnecessary for the present purpose, since the mean square dipole moment per repeat unit is independent of chain length except for oligomers; for the same reason, no fractionation was needed or performed.

Capacitances were measured for dilute solutions of PMVK and of its repeat-unit model, methyl ethyl ketone, in freshly distilled dioxane, with a General Radio Model 1620 capacitance bridge assembly at a frequency of 5 kHz. The home-built capacitance cell requires about 10 mL of solution and has been described elsewhere.[5] From results at three concentrations of the order of 1–2%, initial dielectric increments $d\epsilon/dw$ were determined, where w signifies weight fraction. Refractive-index increments dn/dw were measured with a Brice-Phoenix Model BP-1000V differential refractometer at a wavelength of 546 nm. In this instrument, rapid solvent evaporation precluded accurate determinations above 35 °C, so extrapolations based on the data at lower temperatures had to be used.

A simplified form of the equation of Guggenheim[6] and Smith[7] was used to evaluate the mean-square dipole moment per repeat unit:

$$\frac{\langle\mu^2\rangle}{x} = \frac{27kTM_0}{4\pi N_A d_1}\left[\frac{(d\epsilon/dw)}{(\epsilon_1+2)^2} - \frac{2n_1\,(dn/dw)}{(n_1^2+2)^2}\right] \qquad (1)$$

in which d_1 is the density and n_1 the refractive index of the pure solvent, N_A is Avogadro's number, M_0 is the molecular weight of the repeat unit, and kT is the thermal energy. This relation neglects the difference in vibrational ("atomic") polarization between solute and displaced solvent, but the attendant error is surely less than 1% in the present case.

Results and Discussion

Table I gives the mean-square dipole moment per repeat unit of PMVK in dioxane at five temperatures and that of MEK at 25 °C. (The latter is presumed independent of temperature.) The dipole moment ratio at 25 °C is

$$D_\infty = \langle\mu^2\rangle/x\mu_1^2 = 0.32 \pm 0.01 \qquad (2)$$

where μ_1 is the dipole moment of MEK. The temperature coefficient is positive, with a value $d \ln \langle\mu^2\rangle/dT = (4 \pm 2) \times 10^{-3}$ K^{-1}.

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As already stated, our results are nicely explained by Suter's two-state RIS model, in which *tg* and *gt* states at the backbone methine carbon atom are preferred in meso dyads and *tt* and *gg* states in racemic dyads. For complete details and statistical weight parameters, readers are referred to Suter's paper.[3]

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The Unperturbed Dimension–Temperature Coefficient for *trans*-Polyisoprene

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As is well known, the temperature coefficient of a statistical property such as unperturbed dimension, dipole moment, etc., assumes particular importance in the study of the configurations of chain molecules.[1] Experimental values of this coefficient d ln $\langle r^2\rangle_0/\mathrm{d}T$ can be interpreted using the rotational isomeric state scheme to yield chain conformational energies, which, in turn, may be used in the calculation of other configuration-dependent properties of the molecule.

trans-Polyisoprene (*trans*-PIP) is a chain molecule, the configurational study of which has been investigated by Mark[2] and Abe and Flory.[3] However, little has been reported about experimental results of the different configuration-dependent properties.[4-7]

We have carried out viscosity–temperature measurements on *trans*-PIP in cyclohexane. The required information on the thermodynamics of mixing of *trans*-polyisoprene with cyclohexane can be provided by modified Stockmayer–Fixman plots,[8] taking into account the report of Yamakawa and Tanaka[9] about the relationship between the expansion coefficient and the excluded volume parameter.

Experimental Section

A sample of *trans*-polyisoprene was generously provided by Polysar Ltd. (Sarnia, Ontario, Canada). According to its infrared and NMR spectra,[10,11] it contains a large percentage (97%) in trans units.

The polymer was fractionated, using fractional precipitations of the toluene solution of the sample at 28 °C. The solution contained approximately 1% by weight of polymer, and the nonsolvent was methanol. The separations were observed to involve two liquid phases, as required. Five fractions were chosen and designated FPIP-1 through FPIP-5.

Table I
Number-Average Molecular Weights and Temperature Coefficients of Intrinsic Viscosity for Five Fractions of *trans*-PIP in Cyclohexane

fraction	$10^{-5}M$, g mol^{-1}	10^3 d ln $\lvert\eta\rvert$/ dT, K^{-1}
FPIP-1	2.650	−0.75
FPIP-2	2.119	−0.41
FPIP-3	1.370	−1.16
FPIP-4	0.911	−0.72
FPIP-5	0.390	−0.84

The osmotic pressures of dilute solutions of the trans PIP fractions in toluene at 35 °C were measured using a high-speed osmometer (Knauer) containing a conditioned semipermeable membrane. Concentrations c were expressed in g cm^{-3}; osmotic pressures Π were expressed in dyn cm^{-2}.

Solutions of the polymer usually were prepared directly by dissolving a known weight of *trans*-PIP in the solvent at approximately 35 °C and subsequently adding solvent to adjust the total volume to the desired value at 25 °C. Values of c at temperatures other than 25 °C were calculated using the appropriate values of specific volumes and thermal expansion coefficients. All of the solvents were dried and distilled before use. Values of the cyclohexane specific volume $\bar{v}_1$ and thermal expansion coefficient β_1 were determined by pycnometer at several temperatures. The value of the *trans*-PIP thermal expansion coefficient β_2, in the liquid state, was calculated according to Van Krevelen.[12] β_1 and β_2 were 1.23×10^{-3} and 7.76×10^{-4} K^{-1}, respectively.

Viscosities of the cyclohexane solvent and *trans*-PIP solutions were measured at 25, 30, 35, 40, and 45 °C by means of an Ubbelhode viscometer. At least five concentrations were investigated for each fraction. Intrinsic viscosities $\lvert\eta\rvert$ were obtained in the usual manner by extrapolation of both η_{sp}/c and ln $(\eta_{\mathrm{rel}})/c$ to infinite dilution.

Results and Discussion

In the analysis of the osmotic pressure data in toluene at 35 °C, $(\Pi/c)^{1/2}$ was found to show a linear dependence on concentration c. The data were therefore analyzed according to the equation[13]

$$\Pi/c = RT/M(1 + \tfrac{1}{2}A_2M\,c)^2 \qquad (1)$$

where R is the gas constant. Values of the number average molecular weights M obtained from the interceps of these curves are presented in Table I.

According to the theory,[14] the intrinsic viscosity is given by the relationship

$$\lvert\eta\rvert = \Phi\langle r^2\rangle_0{}^{3/2}\alpha_\eta{}^3\mathrm{M}^{-1} \qquad (2)$$

where Φ is the hydrodynamic constant, and α_η characterizes the extent to which polymer–solvent interactions expand the chain dimensions over their unperturbed values. The temperature dependence of the expansion factor can be obtained from the theoretical expression[9,15]

$$\alpha_\eta{}^3 = 1 + 1.06z \qquad (3)$$

with

$$z = [4/3^{3/2}]C_{\mathrm{M}}(\tfrac{1}{2} - \chi_1)M^{1/2} \qquad (4)$$

and

$$C_{\mathrm{M}} = [27/2^{5/2}\Pi^{3/2}](\bar{v}_2{}^2/V_1N_{\mathrm{A}})\lvert\langle r^2\rangle_0/M\rvert^{-3/2} \qquad (5)$$

where N_{A} is Avogadro's number, $\bar{v}_2$ is the specific volume of the polymer, and V_1 is the molar volume of the solvent. χ_1 is a parameter characterizing the interactions between polymer and solvent.

Substitution of the temperature coefficient of α_η obtained from eq 3, 4, and 5 into the expression for the

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