Macromolecules **1980,** *13,* 190–191

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]

Acknowledgment. We thank Dr. U. W. Suter of the ETH, Zürich, for the privilege of seeing his manuscript before publication and for later stimulating discussions. This research was supported by the National Science Foundation under Grant No. DMR76-22987 A01 of the Polymers Program, Division of Materials Research.

References and Notes

(1) C. S. Marvel and C. L. Levesque, *J. Am. Chem. Soc.*, **60**, 280 (1938).

(2) A. T. Bullock, G. G. Cameron, and P. M. Smith, *Makromol. Chem.*, **176**, 2153 (1975).

(3) U. W. Suter, *J. Am. Chem. Soc.*, **101**, 6481 (1979).

(4) L. Merle-Aubry, Y. Merle, and E. Selegny, *Makromol. Chem.*, **176**, 709 (1975).

(5) A. A. Jones, W. H. Stockmayer, and R. J. Molinari, *J. Polym. Sci., Polym. Symp.*, **No. 54**, 227 (1976).

(6) E. A. Guggenheim, *Trans. Faraday Soc.*, **47**, 573 (1951).

(7) J. W. Smith, "Electric Dipole Moments", Butterworths, London, 1955.

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

M. J. FERNÁNDEZ-BERRIDI, F. J. ANSORENA, J. J. IRUIN,* and G. M. GUZMÁN

Departamento de Química Física, Facultad de C. Químicas de San Sebastian, Universidad del Pais Vasco, Apartado 1072, San Sebastian, Spain. Received July 17, 1979

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]

$$\Pi/c = RT/M(1 + {}^1\!/_2 A_2 M\,c)^2 \qquad (1)$$

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

$$z = [4/3^{3/2}]C_{\mathrm{M}}({}^1\!/_2 - \chi_1)M^{1/2} \qquad (4)$$

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

0024-9297/80/2213-0190$01.00/0

temperature coefficient of $|\eta|$ obtained from eq 2 gives the result

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = (2\alpha_\eta^{\,3}/3)\,\mathrm{d}\ln|\eta|/\mathrm{d}T - {}^2\!/_3(\alpha_\eta^{\,3} - 1)|(2\beta_2 - \beta_1) - ({}^1\!/_2 - \chi_1)^{-1}\,\mathrm{d}\chi_1/\mathrm{d}T| \quad (6)$$

This final equation had the limitation that χ_1 and $\mathrm{d}\chi_1/\mathrm{d}T$ must be known with a reasonably high degree of accuracy. These magnitudes can be obtained from the modified Stockmayer–Fixman equation[15]

$$|\eta|M^{-1/2} = K_\Theta + 0.346\Phi(\bar{v}_2^{\,2}/V_1N_A)(1 - 2\chi_1)\mathrm{M}^{1/2} \quad (7)$$

deduced when eq 3 is used in the original SF work[8] instead of the old equation $\alpha_\eta^{\,3} = 1 + 1.55z$.

For the purpose of evaluating the temperature coefficient of the unperturbed dimension, intrinsic viscosities in cyclohexane at five temperatures were determined for each fraction. The dependence of ln $|\eta|$ on temperature is also shown in Table I.

With the data of intrinsic viscosities and number average molecular weights, eq 7 allows us to obtain χ_1 at different temperatures and consequently $\mathrm{d}\chi_1/\mathrm{d}T$ from the slopes of plots $|\eta|M^{-1/2}$ against $M^{1/2}$. The interaction parameter χ_1 showed a little variation with T and $\mathrm{d}\chi_1/\mathrm{d}T$ was 1.0×10^{-4} K^{-1}.

Finally, α_η is available from eq 3, 4, and 5. We calculated the expansion coefficient at 35 °C as a representative temperature of the considered range. At 35 °C $\chi_1 = 0.222$, $V_1 = 109.9$ cm^3 mol^{-1}, and $\bar{v}_2 = 1.078$ cm^3 g^{-1}. The value of $(\langle r^2\rangle_0/M)^{-3/2} = 1.19 \times 10^{24}$ was taken from the literature.[16]

Substitution of these data in the expression for the temperature coefficient, d ln $\langle r^2\rangle_0/\mathrm{d}T$, gives an average value of $(-1.23 \pm 0.41) \times 10^{-3}$ K^{-1}.

We can compare this result with those obtained by Abe and Flory[3] from a preferred set of configurational energies for PIP chains. The configuration-dependent properties so calculated are largely affected by the location of rotational states such as CH_2–$C(CH_3)$ about the planar trans conformation as a reference. The theoretical value of d ln $\langle r^2\rangle_0/\mathrm{d}T$, calculated for the more realistic location (±70 °C), is between -1.02×10^{-3} and -1.44×10^{-3} for the 100% trans polymer, depending on the configurational energy assumed for the states mentioned above.

As a conclusion, our result is in good agreement with the calculated value, taking into account the composition of our samples. As Flory and Mark[17] pointed out, the viscosity–temperature measurements are reliable methods in obtaining values of the cited coefficient when the solvent–polymer interactions are well considered.

References and Notes

(1) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, 1969.
(2) J. E. Mark, *J. Am. Chem. Soc.*, **89**, 6829 (1967).
(3) Y. Abe and P. J. Flory, *Macromolecules*, **4**, 230 (1971).
(4) R. H. Becker, C. U. Yu, and J. E. Mark, *Polym. J.*, **7**, 234 (1975).
(5) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).
(6) T. Ishikawa and K. Nagai, *Polym. J.*, 1, 116 (1970).
(7) D. W. Saunders, *Trans. Faraday Soc.*, **52**, 1414 (1956).
(8) W. H. Stockmayer and M. Fixman, *J. Polym. Sci., Part C*, 1, 137 (1963).
(9) H. Yamakawa and G. Tanaka, *J. Chem. Phys.*, **55**, 3188 (1971).
(10) W. S. Richardson and A. Sacher, *J. Polym. Sci.*, **10**, 353 (1953).
(11) Y. Tanaka, Y. Takeuchi, M. Kobayashi, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **9**, 43 (1971).
(12) D. W. Van Krevelen, "Properties of Polymers", Elsevier, Amsterdam, 1976.
(13) P. J. Flory, "Principles in Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953.
(14) P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).
(15) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, 1971.
(16) Y. Poddubuyi, E. G. Erenburg, and M. A. Eryomina, *Vysokomol. Soedin. Ser. A*, **10**, 1381 (1968).
(17) J. E. Mark and P. J. Flory, *Macromolecules*, **6**, 300 (1973).

Star-Branched Polymers. 4. Synthesis of 18-Arm Polyisoprenes

NIKOS HADJICHRISTIDIS[1a] and L. J. FETTERS*[1b]

The Department of Industrial Chemistry, The University of Athens, Athens (144), Greece, and The Institute of Polymer Science, The University of Akron, Akron, Ohio 44325.

Received October 2, 1979

The use of chlorosilanes is well documented[2,3] with regard to the synthesis of star-branched polymers, using anionic polymerization techniques[4-8] and organolithium initiators. The reaction of the silicon–chlorine groups with the carbon–lithium chain end yields a process free from deleterious side reactions. The only potential difficulty encountered is that due to steric hinderance, e.g., it has been reported that poly(styryllithium) will not react completely with silicon tetrachloride[4] or 1,2-bis(dichloromethylsilyl)ethane[6] while poly(isoprenyllithium) fails to react completely with silicon tetrachloride.[9] This latter observation can be rationalized by the fact that the active chain end is known to exist in the 4,1 form in hydrocarbon solvents.[10,11]

Recently, it was reported[12] that 8- and 12-arm polyisoprenes were synthesized using either an octa- or dodecachlorosilane which were synthesized from tetravinylsilane via the hydrosilation reaction involving either methyl dichloro- or trichlorosilane. The Θ temperature behavior, in dioxane, for these materials has been investigated.[13]

We wish to report, in this note, that an extention of the foregoing procedures has led to the synthesis of 18-branch polyisoprene stars, using a specially prepared decaoctachlorosilane.

Experimental Section

The preparation of the linear polyisoprenes was done in cyclohexane, using purified *sec-* or *tert*-butyllithium. The polymerization procedures used are those presented elsewhere. All polymerizations were performed under vacuum conditions.

The decaoctachlorosilane was prepared using the following reactions:

$$Cl_3SiCH_2CH_2SiCl_3 + 6CH_2{=}CHMgBr \rightarrow 6ClMgBr + (CH_2{=}CH)_3SiCH_2CH_2Si(CH{=}CH_2)_3 \quad \text{(I)}$$

$$\text{I} + 6HSiCl_3 \xrightarrow{H_2PlCl_3} (Cl_3SiCH_2CH_2)_3SiCH_2Si(CH_2CH_2SiCl_3)_3 \quad \text{(II)}$$

It should be noted that the hydrosilation reaction generally proceeds in an anti-Markownikoff fashion. Nonetheless, structure II in the above reaction sequence is probably a mixture of isomers due to some addition to the vinyl group in a Markownikoff fashion. This trend was noted for the octa- and dodecachlorosilanes.[12]

The linking reaction was allowed to proceed at ca. 20 °C for approximately 3 weeks. This reaction time was doubtless excessive since it was observed, by gel permeation chromatography, that near complete linking was apparently achieved after 24–40 h, depending on the molecular weight of the arm.[14] Nonetheless, a conservative approach was followed in order to ensure as complete a reaction as possible.

Characterization of the star-shaped polymers and the linear arms was done by a combination of vapor pressure and membrane osmometry as well as light scattering in both dioxane, at $\theta_{A_2} = 0$, and cyclohexane, a good solvent for polyisoprene. The procedures followed have been presented elsewhere.[6-9,12]

0024-9297/80/2213-0191$01.00/0