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## The Configuration of Vinyl Polymers. Experimental Results

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*The characteristic ratio  $\langle r^2 \rangle_0/nl^2$  for isotactic poly(*n*-pentene-1) deduced from intrinsic viscosities of fractions in 2-pentanol at the  $\Theta$ -point (62.4°) is  $9.2 \pm 0.5$ . This result, though larger than the characteristic ratios for polyethylene, polyisobutylene, and poly(dimethylsiloxane), is less than would be expected on the basis of steric interactions within the isotactic chain structure. The temperature coefficients,  $d \ln \langle r^2 \rangle_0/dT$  in  $10^{-3} \text{ deg.}^{-1}$ , determined for several isotactic and atactic vinyl polymers from stress-temperature measurements on cross-linked networks in the amorphous state, are found to be positive but small with values as follows: isotactic poly(butene-1), 0.09; isotactic poly(*n*-pentene-1), 0.34; atactic poly(butene-1), 0.50; atactic poly(*n*-pentene-1), 0.53; and atactic poly(isopropyl acrylate), 0.25. The temperature coefficient for isotactic poly(*n*-pentene-1) deduced from the temperature dependence of its intrinsic viscosity in *n*-hexadecane is in satisfactory agreement with the stress-temperature value. The significance of these results is discussed in relation to those for other vinyl polymers and also with reference to predictions from analysis of the chain structure and the interactions of its substituents.*

### Introduction

The studies reported in this paper have been concerned with several vinyl polymer<sup>2</sup> chains  $(-\text{CH}_2-\text{CHR}-)_{n/2}$ , namely, poly(butene-1), poly(*n*-pentene-1), and poly(isopropyl acrylate). The isotactic and atactic forms of the first two polymers and the atactic form of the third have been investigated. The occurrence of asymmetric atoms within these chains presents a feature not shared by the examples previously interpreted.<sup>3,4</sup> Pendant substituents greatly increase the steric interactions as compared with polyethylene or polyoxyethylene.<sup>3</sup> They are not, however, so great as in the polyisobutylene chain which bears two substituent methyl groups on alternate atoms. In poly(dimethylsiloxane), which likewise bears two substituents, steric interactions are alleviated by greater bond lengths and bond angles and by the smaller van der Waals radius of the O atom.<sup>5</sup>

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(2) A preliminary report on a part of this investigation has been published: J. E. Mark and P. J. Flory, *J. Phys. Chem.*, **67**, 1396 (1963).

(3) J. E. Mark and P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1415 (1965).

(4) For a bibliography of previous investigation on this subject, see the footnotes given in ref. 3.

Main emphasis has been placed on determination of the temperature coefficient of the unperturbed mean-square, end-to-end length  $\langle r^2 \rangle_0$ . The temperature coefficient may be a more significant quantity than the characteristic ratio  $\langle r^2 \rangle_0/nl^2$  from the standpoint of establishing the connection between chain configuration and structure. The value of the ratio has been determined however for isotactic poly(*n*-pentene-1).

### Experimental

**Polymer Samples.** Both of the isotactic polymers were recrystallized to obtain material of the highest possible tacticity. Isotactic poly(butene-1),<sup>6</sup> having a molecular weight of *ca.*  $10^6$  according to its intrinsic viscosity, was purified by taking advantage of the solubility of atactic poly(butene-1) in both benzene and diethyl ether. A solution containing approximately 1% of the polymer in benzene was cooled gradually to room temperature; diethyl ether was added to complete the crystallization of the more stereoregular material. Recovery exceeded 90%, indicating absence of a substantial proportion of atactic constituents in the polymer as received. The precipitated portion was redissolved in hot benzene, passed through a coarse, fritted-glass filter, and freeze-dried. The density at 25°, determined by flotation in a liquid of matching density, was 0.93 g. cc.<sup>-1</sup>. The melting point, determined with a polarizing microscope, was *ca.* 134°. The size and perfection of the spherulites in the sample indicated a high degree of crystallinity and, hence, of tacticity.

The isotactic poly(*n*-pentene-1) sample<sup>7</sup> (presumably ether-extracted) was dissolved in toluene, and the resulting solution, *ca.* 1% polymer by weight, was cooled to -25°. It was stirred at this temperature for 30 min. Precipitated (crystalline) polymer was separated using a cloth filter. It was redissolved in benzene, passed through a coarse, fritted-glass filter, and freeze-dried. Approximately 90% of the original material was recovered. The intrinsic viscosity of the polymer indicated a molecular weight in the range 2 to  $3 \times 10^6$ . The density at 25° of a carefully annealed sample was found to be 0.890 g. cc.<sup>-1</sup>, in good agree-

(5) P. J. Flory, V. Crescenzi, and J. E. Mark, *J. Am. Chem. Soc.*, **86**, 146 (1964).

(6) This sample was made available by the Avisun Corp. of Marcus Hook, Pa.

(7) All samples of poly(*n*-pentene-1) were prepared for this studies by Professor G. Natta and co-workers of the Polytechnic Institute of Milan. Their cooperation and assistance is gratefully acknowledged.

ment with results of Danusso and Gianotti.<sup>8</sup> Polarizing microscopic examination of a film obtained by slowly evaporating a benzene solution of the polymer revealed large, well-defined spherulites enveloping the entire specimen. Absence of an appreciable proportion of atactic material is thus indicated.

Atactic samples of poly(butene-1)<sup>9</sup> and of poly(*n*-pentene-1)<sup>7</sup> were used as received. Atactic poly(isopropyl acrylate) of molecular weight *ca.*  $3 \times 10^6$  was prepared by free-radical polymerization at 60°, using azobisisobutyronitrile as initiator. Details of the polymerization are described elsewhere.<sup>10</sup>

**Preparation of Networks.** Each polymer, prepared as described above, was pressed at 100 to 150° into a sheet approximately 0.1 cm. thick. Dumbbell-shaped samples cut from these sheets were then cross linked either with  $\gamma$ -radiation from a Co<sup>60</sup> source or by ultraviolet light with the aid of benzophenone as sensitizer. In one instance, high energy electrons from a resonant transformer were used. All irradiations were performed at room temperature in the absence of air (*i.e.*, under vacuum or under nitrogen). The dose rates were *ca.* 0.28 mrad hr.<sup>-1</sup> for the  $\gamma$ -irradiations and *ca.* 100 mrad hr.<sup>-1</sup> in the electron beam bombardments. In the case of samples cross linked by ultraviolet light, approximately 1% by weight of benzophenone was incorporated in the polymer during the molding of the sheet, in accordance with directions of Oster and co-workers.<sup>11</sup> These irradiations were carried out under nitrogen using a high pressure, quartz mercury vapor lamp (Hanovia Model A, 550 w.) placed 10 cm. from the sample.

In order to assure network uniformity, the electron beam and ultraviolet irradiations were carried out by exposing opposite sides of the sample for equal lengths of time. The uniformity of swelling of such networks in a good solvent attested to the efficacy of this procedure. The cross-linked butene-1 polymers were extracted with benzene at about 70° in order to remove soluble constituents. Their amount did not exceed 17% of the sample by weight. Since extraction tended to damage the networks, the *n*-pentene-1 and isopropyl acrylate polymers were used without extraction. All samples were swollen in a 5% solution of *N*-phenyl- $\beta$ -naphthylamine in benzene. This antioxidant was thus incorporated in the network as a safeguard against oxidative degradation during the stress-temperature measurements subsequently to be carried out at elevated temperatures. Reference marks for length measurements were provided by two very fine wires piercing the sample at a distance of about 3 cm. apart within the mid-section of the specimen. The wires were inserted while the sample was swollen with benzene from the antioxidant solution in order to minimize mechanical damage to the network. The weight of the strips after drying indicated that between 0.1 and 0.5% by weight of inhibitor had been absorbed.

Atactic and isotactic forms of the same polymer differed greatly in the degree of cross linking after identical irradiation treatment at room temperature. Compari-

(8) F. Danusso and G. Gianotti, *Makromol. Chem.*, **61**, 164 (1963).

(9) We are indebted to the Petro-Tex Co. and to Professor J. B. Kinsinger of Michigan State University for supplying samples of this polymer.

(10) J. E. Mark, *Dissertation Abstr.*, **23**, 1205 (1962).

(11) G. Oster, G. K. Oster, and H. Moroson, *J. Polymer Sci.*, **34**, 671 (1959).

son of the forces required to obtain a given elongation of the respective amorphous networks, and also of their degrees of swelling in good solvents, indicated the efficiency of cross linking of the isotactic form of a polymer to be at least two to three times that of its atactic isomer. The difference is doubtless due to the crystallinity of the isotactic polymer, and not to the structural differences *per se* between the two forms. This conclusion agrees with those reached by Mandelkern and co-workers on the relative efficiency of cross linking of amorphous and crystalline polyethylene<sup>12</sup> at high temperatures and of natural rubber.<sup>13</sup>

**Stress-Temperature Measurements.** The apparatus and procedure have been described in detail elsewhere.<sup>3,14</sup>

**Intrinsic Viscosities.** Viscosities of dilute solutions were measured in Cannon-Ubbelohde viscometers with capillary sizes so chosen as to render kinetic energy corrections negligible throughout. The temperatures were controlled to  $\pm 0.01^\circ$ , and efflux times (137 to 575 sec., corresponding to specific viscosities  $\eta_{sp}$  of 0.20 to 0.82) were reproducible to  $\pm 0.05\%$ . Intrinsic viscosities were obtained by extrapolating reduced specific viscosities  $\eta_{sp}/c$  to infinite dilution by the usual procedure.

*n*-Hexadecane (Matheson Coleman and Bell, 99% assay, olefin-free) was used as a solvent without purification. 2-Pentanol (Matheson Coleman and Bell, practical grade) was distilled through a 12-in. Vigreux column, and the center cut, having a boiling range from 118 to 120°, was retained for use.

Each solution was prepared by weighing both polymer and solvent. The specific volumes and thermal expansion coefficients used for calculating the concentration *c* in g. dl.<sup>-1</sup> at each temperature are given in Table I. About 0.01% of *N*-phenyl- $\beta$ -naphthylamine was added to the *n*-hexadecane.

**Table I.** Specific Volumes and Thermal Expansion Coefficients<sup>a</sup>

Material	Temp., °C.	Specific volume, cm. <sup>3</sup> g. <sup>-1</sup>	$\beta \times 10^3$ , deg. <sup>-1</sup>
Poly(butene-1) <sup>b</sup>	170	...	0.80
Poly( <i>n</i> -pentene-1) <sup>c</sup>	110	1.248	0.75
	90.0	1.229	0.75
	64.0	1.206	0.75
Poly(isopropyl acrylate) <sup>b</sup>	70.0	0.982	0.67
<i>n</i> -Hexadecane <sup>d</sup>	63.8	1.344	0.89
2-Pentanol <sup>d</sup>	64.0	1.294	1.20

<sup>a</sup> All values for polymers refer to the amorphous state. <sup>b</sup> Dilatometric results. <sup>c</sup> Results taken from dilatometric data of Danusso and Gianotti.<sup>8</sup> <sup>d</sup> Pycnometric results.

**Fractionation of Isotactic Poly(*n*-pentene-1).** The initial polymer, recrystallized as described above, proved to be too high in molecular weight for a source of fractions suitable for the osmotic molecular weight determination. It was therefore degraded thermally by heating under vacuum at 185° for about 2 hr. The resulting material was dissolved in sufficient toluene to

(12) R. Kitamaru, L. Mandelkern, and J. Fatou, *ibid.*, **2B**, 511 (1964); R. Kitamaru and L. Mandelkern, *J. Am. Chem. Soc.*, **86**, 3529 (1964).

(13) D. E. Roberts and L. Mandelkern, *ibid.*, **80**, 1289 (1958).

(14) J. E. Mark and P. J. Flory, *ibid.*, **86**, 138 (1964).

give a solution of 0.5% polymer by weight. If the fractionation had been carried out under conditions permitting crystallization during the phase separations, variations in tacticity of the fractions could have occurred. The entire fractionation was therefore carried out at 80°. The nonsolvent, 2-propanol, was heated to 80°, then added slowly with stirring to the toluene solution at the same temperature until a polymer-rich phase appeared. The mixture was heated to about 86° to redissolve the precipitated phase, then cooled gradually to 80° with stirring. The polymer-rich phase was allowed to settle overnight, whereupon the supernatant liquid was siphoned off. Fractions thus obtained were dissolved in hot benzene, precipitated into methanol, redissolved in benzene, passed through a coarse, fritted-glass filter, and finally freeze-dried. The five fractions (F1 through F5) constituted 16, 21, 22, 13, and 22% of the recrystallized material, respectively.

**Osmotic Molecular Weights.** Osmotic pressures were measured at 37° on toluene solutions of isotactic poly(*n*-pentene-1) fractions F2 through F5 using a Mechrolab 502 automatic membrane osmometer. The cellulose membranes (Schleicher and Schuell super dense, No. 08) were conditioned by gradually changing the medium in which they were immersed from water to acetone, to benzene, to toluene. Flow of solvent through the membrane separating solvent and solution compartments in the osmometer is monitored by an optical system in the osmometer, and the pressure is adjusted automatically to arrest the flow. Approximately 10 min. is required to establish the equilibrium osmotic pressure. Measurements were carried out at no fewer than five concentrations for each fraction, and the  $\pi/c$  ratios were extrapolated to  $c = 0$  in the usual manner.

**Precipitation Temperatures.** The quantities of isotactic poly(*n*-pentene-1) and distilled 2-pentanol required to give the highest concentration desired were placed in a Pyrex tube, 0.6 cm. in diameter and 12 cm. in length. The mixture was heated with stirring until dissolution was complete after which the temperature was slowly lowered until phase separation occurred. The point of maximum turbidity was recorded as the precipitation temperature  $T_p$ . The ready reversibility of the precipitation with temperature and the voluminous nature of the precipitated phase indicated that the separation was liquid-liquid and not liquid-crystalline. The concentration of the solution was determined by weighing the entire apparatus after the determination of each  $T_p$ . Solvent was added in the amount required for the next lower concentration at which  $T_p$  was to be determined, etc. Values of  $T_p$  were thus determined over suitable ranges of polymer concentration.

## Results

**The Temperature Coefficient of  $\langle r^2 \rangle_0$  from Stress-Temperature Measurements.** Results of stress-temperature measurements on samples of isotactic and atactic poly(butene-1) are shown in Figure 1. Similar experiments were conducted on networks of poly(*n*-pentene-1) and poly(isopropyl acrylate); graphs of the data for these polymers are not included, however. The best straight line representing the points for each experi-

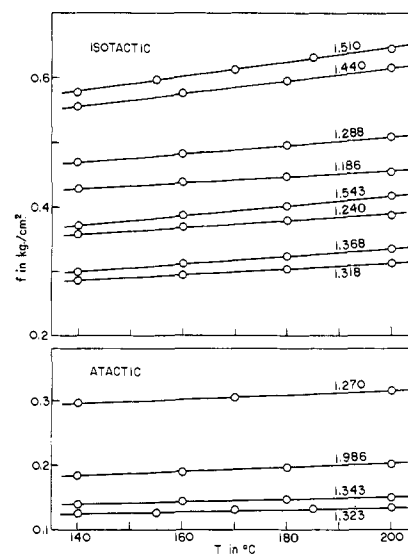


Figure 1. The force  $f$  for cross-linked poly(butene-1) stretched to fixed length vs. temperature. Extension ratios  $\alpha$  indicated for each line permit identification of the experiment as reported in Table II.

ment was located by the method of least squares. Results for all samples are summarized in Tables II through IV. Temperature ranges, chosen to exclude the possibility of crystallization, are given in the heading or subheading of each of these tables. In order to facilitate comparison of samples cross linked to different extents, forces were divided by the cross-sectional area of the sample at the highest temperature. The forces  $\bar{f}$  at the mean temperature for the experiment and the coefficients  $(\partial f/\partial T)_{p,L}$  representing the slope of the experimental points (see Figure 1) are given in the third and fourth columns of Tables II-IV. The coefficients  $[\partial \ln (f/T)/\partial T]_{p,L}$  calculated from  $\bar{f}$  and  $(\partial f/\partial T)_{p,L}$  are given in the fifth column of each table. Values of  $f_e/f$  and  $d \ln \langle r^2 \rangle_0/dT$  calculated as detailed in the preceding paper<sup>3</sup> are presented in the last two columns of each table.

In several of the experiments on isotactic and atactic poly(butene-1) the stress-temperature cycles were not precisely reversible, presumably because of degradation during exposure of the samples to elevated temperatures; tensions  $f$  for the temperature-increasing phase of the cycle were slightly lower than those found during the previously traversed, temperature-decreasing phase. Corrections were applied assuming that this slight decrease was linear with time. Experiments for which this correction was greater than 6% of the total change in force were discarded. Results for all other polymers, given in Tables III and IV, represent experiments which were reversible within limits of observation. Small positive temperature coefficients  $d \ln \langle r^2 \rangle_0/dT$  are found for both isotactic and atactic polymers; values for the latter exceed those for the former.

**The Temperature Coefficients of  $\langle r^2 \rangle_0$  from Intrinsic Viscosity-Temperature Measurements.** The intrinsic viscosity  $[\eta]$  of unfractionated isotactic poly(*n*-pentene-1) in *n*-hexadecane is plotted against temperature in Figure 2. This solvent was chosen because of its similarity to the polymer; its solutions should thus be approximately athermal. The treatment of the results is simplified by this circumstance (see below).

**Table II.** Force-Temperature Results for Poly(butene-1)

Irradiation	$\alpha$ , at 200°	$\bar{f}$ , kg. cm. <sup>-2</sup>	$(\partial f/\partial T)_{p,L}$ × 10 <sup>3</sup>	$-\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{p,L}$ × 10 <sup>3</sup>	$\left(\frac{\beta}{\alpha^3 - 1}\right)$ × 10 <sup>3</sup>	$f_e/f$	$\left(\frac{d \ln \langle r^2 \rangle_0}{dT}\right)$ × 10 <sup>3</sup>
Isotactic, temperature range: 140–200°							
e, 195 mrads	1.510	0.613	1.13	0.42	0.33	0.04	0.09
Ultraviolet, 3.3 hr.	1.368	0.318	0.580	0.44	0.51	-0.03	-0.07
	1.543	0.395	0.765	0.32	0.30	0.01	0.02
$\gamma$ , 54 mrads	1.318	0.301	0.438	0.80	0.62	0.08	0.18
$\gamma$ , 70 mrads	1.240	0.374	0.500	0.92	0.88	0.02	0.04
	1.440	0.586	1.00	0.55	0.40	0.07	0.15
$\gamma$ , 77 mrads	1.288	0.489	0.655	0.92	0.70	0.10	0.22
$\gamma$ , 85 mrads	1.186	0.443	0.420	1.31	1.19	0.05	0.12
					Av.	0.04 (±0.03)	0.09 (±0.07)
Atactic, temperature range: 140–200°							
Ultraviolet, 12 hr.	1.270	0.305	0.317	1.22	0.76	0.20	0.46
$\gamma$ , 77 mrads	1.986	0.193	0.325	0.58	0.12	0.20	0.46
$\gamma$ , 85 mrads	1.323	0.131	0.147	1.14	0.61	0.23	0.53
$\gamma$ , 85 mrads	1.343	0.145	0.165	1.12	0.56	0.25	0.56
					Av.	0.22 (±0.02)	0.50 (±0.04)

**Table III.** Force-Temperature Results for Poly(*n*-pentene-1)

Irradiation	$\alpha$ , at 140°	$\bar{f}$ , kg. cm. <sup>-2</sup>	$(\partial f/\partial T)_{p,L}$ × 10 <sup>3</sup>	$-\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{p,L}$ × 10 <sup>3</sup>	$\left(\frac{\beta}{\alpha^3 - 1}\right)$ × 10 <sup>3</sup>	$f_e/f$	$\left(\frac{d \ln \langle r^2 \rangle_0}{dT}\right)$ × 10 <sup>3</sup>
Isotactic, temperature range: 80–140°							
$\gamma$ , 70 mrads	1.318	0.858	1.54	0.82	0.57	0.10	0.25
	1.395	1.06	1.98	0.74	0.43	0.12	0.31
	1.440	1.21	2.20	0.79	0.37	0.16	0.42
$\gamma$ , 70 mrads	1.317	0.812	1.37	0.92	0.58	0.13	0.34
	1.370	0.892	1.62	0.79	0.47	0.12	0.32
	1.404	0.975	1.77	0.79	0.42	0.14	0.37
					Av.	0.13 (±0.02)	0.34 (±0.04)
Atactic, temperature range: 40–140°							
$\gamma$ , 130 mrads	1.242	0.276	0.330	1.41	0.80	0.23	0.61
	1.327	0.358	0.535	1.12	0.55	0.22	0.57
	1.422	0.434	0.770	0.84	0.39	0.17	0.45
	1.522	0.511	0.920	0.81	0.29	0.20	0.52
	1.641	0.608	1.14	0.73	0.22	0.20	0.51
					Av.	0.20 (±0.02)	0.53 (±0.05)

**Table IV.** Force-Temperature Results for Atactic Poly(isopropyl acrylate)

Irradiation	$\alpha$ , at 100°	$\bar{f}$ , kg. cm. <sup>-2</sup>	Temperature range: 40–100°				$f_e/f$	$\left(\frac{d \ln \langle r^2 \rangle_0}{dT}\right)$ × 10 <sup>3</sup>
			$(\partial f/\partial T)_{p,L}$ × 10 <sup>3</sup>	$-\left[\frac{\partial \ln(f/T)}{\partial T}\right]_{p,L}$ × 10 <sup>3</sup>	$\left(\frac{\beta}{\alpha^3 - 1}\right)$ × 10 <sup>3</sup>			
$\gamma$ , 60 mrads	1.134	0.345	0.390	1.78	1.50	0.10	0.28	
	1.214	0.482	0.885	1.07	0.87	0.07	0.20	
	1.256	0.535	1.02	1.00	0.70	0.10	0.30	
	1.305	0.595	1.25	0.81	0.56	0.09	0.25	
	1.364	0.656	1.46	0.68	0.45	0.08	0.23	
					Av.	0.09 (±0.01)	0.25 (±0.03)	

The value of  $d \ln \langle r^2 \rangle_0/dT$  was calculated<sup>15</sup> from the temperature coefficient of  $[\eta]$  using the equations<sup>16</sup>

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

$$\alpha^5 - \alpha^3 = 27(2\pi)^{-3/2} (v^2/N_A V_1) [\langle r^2 \rangle_0 / M]^{-3/2} M^{1/2} \times \psi_1(1 - \Theta/T) \quad (2)$$

(15) P. J. Flory, A. Ciferri, and R. Chiang, *J. Am. Chem. Soc.*, **83**, 1023 (1961).

(16) P. J. Flory and T. G. Fox, *ibid.*, **73**, 1904, 1909, 1915 (1951).

where  $\Phi$  is a constant<sup>17</sup>  $\cong 2.5 \times 10^{21}$  with  $[\eta]$  in dl. g.<sup>-1</sup>,  $r$  in cm., and  $M$  in g. mole<sup>-1</sup>,  $\alpha = [\langle r^2 \rangle_0 / \langle r^2 \rangle_0]^{1/2}$  measures the expansion of the polymer molecule over

(17) The value  $\Phi = 2.5 \times 10^{21}$ , applicable at the  $\Theta$ -point, is based primarily on the careful light-scattering and viscosity studies on polystyrene carried out by D. McIntyre, A. Wims, L. C. Williams, and L. Mandelkern, *J. Phys. Chem.*, **66**, 1932 (1962). Use of approximate theoretical values  $\Phi = 2.8 \times 10^{21}$  [B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956)] or  $\Phi = 2.2 \times 10^{21}$  [J. E. Hearst, *ibid.*, **40**, 1506 (1964)] would not affect the calculation of  $d \ln \langle r^2 \rangle_0/dT$ . It would, of course, alter the value calculated for the characteristic ratio (see following section).

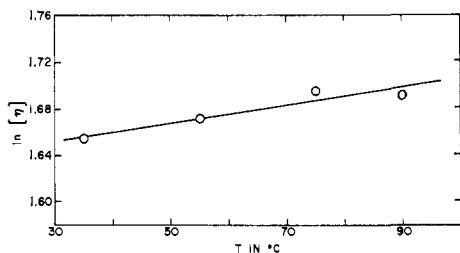


Figure 2. The intrinsic viscosity of unfractionated isotactic poly(*n*-pentene-1) in *n*-hexadecane vs. temperature.

its unperturbed dimensions,<sup>18</sup>  $\nu$  is the specific volume of the polymer,  $V_1$  is the molar volume of the solvent,  $N_A$  is the Avogadro number,  $\psi_1$  is the entropy of mixing parameter, and  $\Theta$  is the  $\Theta$ -temperature, which is proportional to the ratio of the enthalpy and entropy of dilution parameters. In view of the similarity of solvent and polymer,  $\Theta$  has been equated to zero as a first approximation. Differentiation of eq. 1 and 2 then yields<sup>14, 15</sup>

$$d \ln \langle r^2 \rangle_0 / dT = \frac{5}{3} d \ln [\eta] / dT - d \ln (\nu^2 / V_1) / dT - \alpha^{-2} \{ d \ln [\eta] / dT - d \ln (\nu^2 / V_1) / dT \} \quad (3)$$

The value of  $d \ln [\eta] / dT$  was obtained from the slope of the line in Figure 2 and  $d \ln (\nu^2 / V_1) / dT$  from the data of Table I. The expansion factor  $\alpha$  at the average temperature for these measurements, 63.8°, was calculated from eq. 2 taking  $(\langle r^2 \rangle_0 / M)^{1/2} = 78.5 \times 10^{-10}$  cm. (g./mole)<sup>-1/2</sup> on the basis of results described below and assuming  $\psi_1 = 0.2$ . For this nearly athermal system the expression in braces in the last term of eq. 3 is  $0.15 \times 10^{-3}$  deg.<sup>-1</sup>, and the value of this term consequently is quite small. The insensitivity of  $d \ln \langle r^2 \rangle_0 / dT$  to  $\alpha$  indicates that neither  $\psi_1$  nor the numerical constant<sup>19</sup> in eq. 2 needs to be known accurately. Similarly, the modification of eq. 1 suggested by Kurata and co-workers,<sup>20</sup> namely,  $[\eta] = 2.9 \times 10^{21} [(\langle r^2 \rangle_0 / M)^{3/2} M^{1/2} \alpha^{2.43}]$  alters  $d \ln \langle r^2 \rangle_0 / dT$  by only a few per cent. The value of  $d \ln \langle r^2 \rangle_0 / dT$  obtained from these viscosity-temperature measurements,  $0.52 \times 10^{-3}$  deg.<sup>-1</sup>, is in reasonable agreement with that obtained from stress-temperature measurements,  $0.34 \times 10^{-3}$  deg.<sup>-1</sup>. The disparity between these results is, in fact, within the range of error associated with the assumption that  $\Theta = 0$ . Comparison of equation of state parameters for the polymer and the solvent suggests a small positive value of the enthalpy of dilution,<sup>21</sup> and hence that  $\Theta > 0$ . Adoption of  $\Theta = 30^\circ\text{K}$ . would bring the result from the temperature coefficient of the intrinsic viscosity into agreement with that deduced by the stress-temperature method.

**The Characteristic Ratio  $\langle r^2 \rangle_0 / nl^2$ .** Molecular weights of the isotactic poly(*n*-pentene-1) fractions, determined by osmometry as set forth in the Experimental section, are given in Table V. The uncertainty in these values

(18) The present  $\alpha$  must not be confused with the  $\alpha$  used in preceding sections to specify the extension ratio for the network.

(19) Stockmayer's expression [*J. Polymer Sci.*, **15**, 595 (1955); *Makromol. Chem.*, **35**, 54 (1960)] differs from that given by eq. 2 by the reduction of the numerical constant by a factor of one-half. This modification is thus unimportant in the present calculations.

(20) M. Kurata and H. Yamakawa, *J. Chem. Phys.*, **29**, 311 (1958); M. Kurata, H. Yamakawa, and H. Utiyama, *Makromol. Chem.*, **34**, 139 (1959).

(21) P. J. Flory, unpublished.

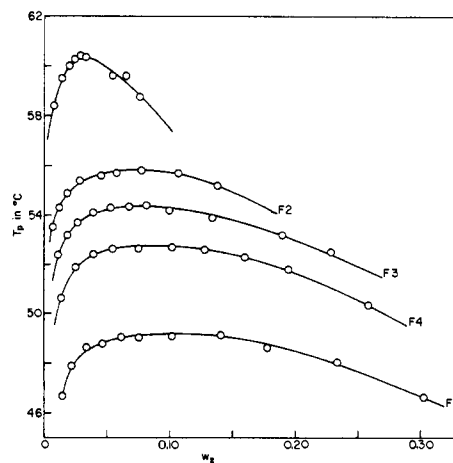


Figure 3. Precipitation temperatures for solutions of isotactic poly(*n*-pentene-1) in 2-pentanol plotted against the weight fraction  $w_2$  of polymer. The uppermost curve is for the undegraded, unfractionated polymer. Other curves are for fractions as indicated; see Table V.

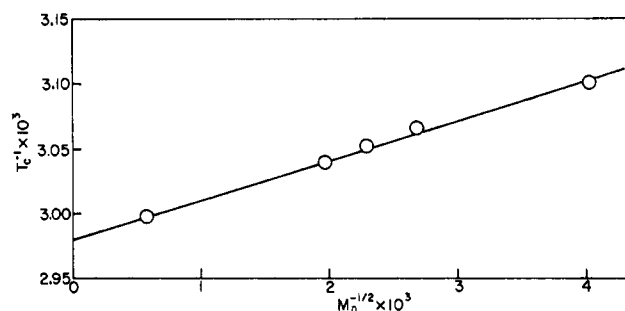


Figure 4. Reciprocal critical solution temperatures obtained from Figure 3 vs. the reciprocal of the square root of the molecular weight.

is estimated to be  $\pm 5\%$ . Precipitation temperatures  $T_p$ , reproducible to  $\pm 0.1^\circ$ , for solutions of the fractions in 2-pentanol are plotted against the weight fraction of polymer in Figure 3. Also included is the curve for the undegraded, unfractionated polymer having a molecular weight of  $3.06 \times 10^6$  according to its intrinsic viscosity in 2-pentanol at 64°. The maximum of each binodal defines the critical miscibility temperature for the polymer fraction,  $T_c$ ; these temperatures are recorded in Table V. Their reciprocals are plotted in Figure 4 against  $M_n^{-1/2}$  in the usual manner.<sup>22</sup> The limiting value of  $T_c$  for  $M = \infty$  is the  $\Theta$ -temperature. By extrapolating the results obtained from Figure 3, we thus find  $\Theta = 62.4 \pm 0.5^\circ$ .

Intrinsic viscosities of the fractions in 2-pentanol, determined at 64°, are given in the fourth column of Table V. The small departure of this temperature from the  $\Theta$ -point is of no importance, inasmuch as the temperature coefficient of  $[\eta]$  in the vicinity of  $\Theta$  is only  $1.3\%$  deg.<sup>-1</sup> according to measurements of fraction F3 at 58, 64, and 70°. As shown in the last column of Table V, the intrinsic viscosities vary approximately as  $M^{1/2}$ , as expected at the  $\Theta$ -point. Thus, we deduce from these results:  $[\eta]_\Theta / M^{1/2} = 1.21 \times 10^{-3}$  dl. g.<sup>-1</sup> (g. mole<sup>-1</sup>)<sup>-1/2</sup>. Adoption of  $\Phi = 2.5 \times 10^{21}$  as the best experimental value<sup>17</sup> for this constant gives

(22) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 541-548.

**Table V.** Molecular Weights, Critical Solution Temperatures, and Intrinsic Viscosities of Isotactic Poly(*n*-pentene-1) and Its Fractions

Sample	$M \times 10^{-5}$	$T_c$ in 2-pen- tanol, °C.	$[\eta]^a$	$([\eta]/M^{1/2}) \times 10^3$
Undegraded <sup>c</sup>	30.6 <sup>b</sup>	60.4	2.11	..
F2	2.58	55.8	0.652	1.28
F3	1.91	54.4	0.515	1.18
F4	1.39	52.8	0.432	1.16
F5	0.613	49.2	0.299	1.21

<sup>a</sup> In 2-pentanol at 64°, dl. g.<sup>-1</sup>. <sup>b</sup> Calculated from  $[\eta]$  at 64° according to eq. 1 with  $\alpha = 1$ . <sup>c</sup> Undergraded, unfractionated polymer.

$\langle r^2 \rangle_0/nl^2 = 9.2$  for isotactic poly(*n*-pentene-1).<sup>23</sup> This result is corroborated by observations of Moraglio and Brzezinski<sup>24</sup> on intrinsic viscosities of fractions of this polymer in isoamyl acetate at 31.5°, the  $\theta$ -point for this system. They find  $\langle r^2 \rangle_0/nl^2 = 9.5$ .

### Discussion

The present results provide a further instance of agreement between the values for  $d \ln \langle r^2 \rangle_0/dT$  deduced by two quite independent methods, the one involving measurements on linear polymer molecules dispersed in a dilute solution and the other the stress for a cross-linked network. Similar agreement has been demonstrated heretofore for polyethylene,<sup>15, 25</sup> poly(dimethylsiloxane),<sup>14</sup> and, recently, for atactic polystyrene.<sup>26</sup> In their investigation of the latter polymer, Orofino and Ciferri<sup>26</sup> observed  $[\eta]_\theta$  in a series of structurally similar solvents whose  $\theta$ -temperatures embraced a suitable range for ascertaining  $d \ln [\eta]_\theta/dT$  directly. Good agreement with the results of stress-temperature measurements was obtained.

The now substantial body of evidence showing that these diverse methods for determining the temperature coefficient of  $\langle r^2 \rangle_0$  yield concordant results lends strength to the opinion that the configurations of long-chain molecules are but little affected by the constraints imposed on them in the bulk polymer (as opposed to the dilute solution), where they must perforce pack with other chains to high density.<sup>15, 25, 27</sup> This is a conclusion of the foremost importance to interpretation of macromolecular materials, as we have pointed out on previous occasions.

Small positive temperature coefficients for  $\langle r^2 \rangle_0$  appears to be the rule among vinyl polymers  $(CH_2-CHR)_{n/2}$  where  $R \cong H$ . For atactic polystyrene Orofino and Ciferri<sup>26</sup> found  $d \ln \langle r^2 \rangle_0/dT = 0.4 \times 10^{-3} \text{ deg.}^{-1}$ , a value remarkably similar to our results for three other atactic vinyl polymers. A recent survey of stress-temperature coefficients,<sup>28</sup> some of

dubious accuracy, for a lengthy list of vinyl polymers supports this generalization. Values for poly(vinyl alcohol)<sup>29, 30</sup> appear to be in the range from 0 to  $0.5 \times 10^{-3} \text{ deg.}^{-1}$ . For various atactic acrylate polymers<sup>28, 31</sup> coefficients of  $-0.4$  to  $1.0 \times 10^{-3} \text{ deg.}^{-1}$  are indicated.

The stress-temperature coefficients for poly(*n*-pentene-1) reported by Tobolsky, Carlson, and Indictor<sup>31</sup> lead to the small negative value  $-0.2 \times 10^{-3} \text{ deg.}^{-1}$  for  $d \ln \langle r^2 \rangle_0/dT$ . Ciferri<sup>28</sup> finds  $-0.3 \times 10^{-3} \text{ deg.}^{-1}$  for the same polymer. We believe our results, indicating a small positive coefficient for this polymer, supersede the others cited in accuracy. In any case, the evidence available suggests slightly lower values for the coefficients for isotactic polymers compared to their atactic isomers. The coefficients are close to zero but are probably slightly positive.

Our value of 9.2 for  $\langle r^2 \rangle_0/nl^2$  for isotactic poly(*n*-pentene-1) is confirmed by the results of Moraglio and Brzezinski cited above.<sup>24</sup> Krigbaum, Kurz, and Smith<sup>32</sup> reported intrinsic viscosities and second virial coefficients for isotactic poly(*n*-butene-1) fractions in good solvents (toluene and *n*-nonane), both osmotic and light-scattering methods being used. Correction of their intrinsic viscosities for molecular expansion according to the method of Orofino and Flory<sup>33</sup> and use of  $\Phi = 2.5 \times 10^{21}$  as above yields  $\langle r^2 \rangle_0/nl^2 = 9.4$ , in remarkably close agreement with our result for the isotactic poly(*n*-pentene-1). Kurata and Stockmayer<sup>34</sup> have estimated values of 10.6 and 5.2 for isotactic polystyrene and isotactic polypropylene, respectively, on the basis of lengthy extrapolations from data of questionable accuracy. Hence, these results are of questionable reliability. Kinsinger and Hughes<sup>35</sup> reported 7.4 for the characteristic ratio of isotactic polypropylene on the basis of measurements at the  $\theta$ -point, 145° in diphenyl ether. Degradation at the high temperature of their experiments may have lowered their result.

The balance of evidence indicates the characteristic ratio for isotactic vinyl polymers to be only a little greater than the value, 6.8, for polyethylene.<sup>15, 36</sup> The much more severe steric restrictions in the former, tending to perpetuate a form close to the Natta-Corradini helix, lead to the expectation of larger values for this ratio. A greater incidence of other rotational conformations may, of course, be invoked to account for the observed value of the ratio. Examination of models emphasizes that such alternative bond conformations should be of considerably greater energy than the preferred form, and this leads, at once, to prediction of a pronounced negative temperature coefficient of  $\langle r^2 \rangle_0$  contrary to the compelling array of experimental evidence. It is essentially on this basis that a large negative temperature coefficient of  $\langle r^2 \rangle_0$  has been predicted<sup>37</sup> in the past for isotactic chains.

(23) The theoretical values (see footnote 17) of  $\Phi = 2.8$  and  $2.2 \times 10^{21}$  yield  $\langle r^2 \rangle_0/nl^2 = 8.55$  and 10.0, respectively.

(24) G. Moraglio and J. Brzezinski, *J. Polymer Sci.*, **B2**, 1105 (1964).

(25) A. Ciferri, C. A. J. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961).

(26) T. A. Orofino and A. Ciferri, *J. Phys. Chem.*, **68**, 3136 (1964).

(27) For a more detailed discussion of this issue, see P. J. Flory, "Lectures in Materials Science," P. Leurgens, Ed., W. A. Benjamin, Inc., New York, N. Y., 1963, pp. 27-50. The contrary view is recurrent in much of the literature on the configurations of chain molecules and morphology of the bulk state of polymers. See, for example, M. V. Volkenstein, "Configurational Statistics of Polymeric Chains," Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 8.

(28) A. Ciferri, *J. Polymer Sci.*, **2A**, 3089 (1964).

(29) H. Abe and W. Prins, *ibid.*, **C2**, 527 (1963).

(30) A. Nakajima and H. Yanagama, *J. Phys. Chem.*, **67**, 654 (1963).

(31) A. V. Tobolsky, D. W. Carlson, and N. Indictor, *J. Polymer Sci.*, **54**, 175 (1961).

(32) W. R. Krigbaum, J. E. Kurz, and P. Smith, *J. Phys. Chem.*, **65**, 1984 (1961).

(33) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

(34) M. Kurata and W. H. Stockmayer, *Fortschr. Hochpolymer.-Forsch.*, **3**, 196 (1963).

(35) J. B. Kinsinger and R. E. Hughes, *J. Phys. Chem.*, **67**, 1922 (1963).

(36) R. Chiang, private communication of results as yet unpublished.

(37) T. M. Birshtein and O. B. Ptitsyn, *Zh. Tekhn. Fiz.*, **29**, 1075 (1959); O. B. Ptitsyn, *Vysokomolekul. Soedin.*, **4**, 1445 (1962).

This pronounced disagreement between theory and experiments for isotactic polymers has yet to be resolved.

Theoretical treatment of the configurations of stereoregular chains will be the subject of a later paper.

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## Structure and Fundamental Vibrations of Cage Molecules.

### I. 1,4-Diazabicyclo[2.2.2]octane<sup>1</sup>

M. P. Marzocchi, G. Sbrana, and G. Zerbi

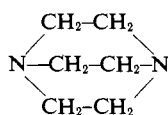
*Contribution from the Departments of Physical Chemistry and Organic Chemistry, Firenze, Italy, and of the Industrial Chemistry Department of the Politecnico, Milan, Italy. Received September 25, 1964*

*Infrared spectra of diazabicyclooctane in the gas solution and solid phases as well as Raman spectra of the solution were obtained. By thermal treatment, solid samples with most of the crystallites oriented with the principal axis perpendicular to the cell window were obtained and their spectra studied. The infrared spectrum is compatible with a  $D_{3h}$  structure. All the  $A_2''$  and  $E'$  infrared active fundamentals and 4 out of the 15 expected frequencies only active in the Raman spectrum have been assigned and discussed. The information obtained from the spectrum of the oriented crystal is more reliable than that obtained from band contours of the gas-phase spectra.*

#### Introduction

Molecules with a "cage structure" exhibit unusual physical properties which can be attributed to their high molecular symmetry. If one or more heteroatoms like nitrogen are present in the ring, the molecule acquires outstanding chemical properties such as complexing ability and catalytic activity.<sup>2</sup>

The purpose of this paper is to discuss the vibrational spectrum of 1,4-diazabicyclo[2.2.2]octane or triethylenediamine (TED), which, to our knowledge, has not been previously studied.



Whereas a large amount of work on the chemistry of TED can be found in the literature, comparatively little is known on its physical chemistry.<sup>3,4</sup> A vibrational assignment and approximated normal coordinate calculation have been carried out by MacFarlane and Ross<sup>5</sup> on the parent molecule bicyclo[2.2.2]octane.

(1) This work was supported by the Consiglio Nazionale delle Ricerche of Italy.

(2) Technical Report of Houdry Process and Chemical Co., Philadelphia, Pa.

(3) A. Farkas, G. A. Mills, W. E. Erner, and H. B. Maerker, *J. Chem. Eng. Data*, **4**, 334 (1959).

(4) S.-S. Chang and E. F. Westrum, Jr., *J. Phys. Chem.*, **64**, 1551 (1960).

(5) J. J. MacFarlane and I. G. Ross, *J. Chem. Soc.*, 4169 (1960).

Only very recently Mirone has studied the Raman spectrum of TED.<sup>6</sup>

#### Experimental

Samples of TED, purchased from Chemical Procurement Laboratories and from Houdry Chemical Co., were carefully purified by repeated sublimation under vacuum. Spectra were recorded with Perkin-Elmer spectrometers, Models 421, 337, and 301, in the frequency ranges 4000–550, 550–400, and 400–70  $\text{cm}^{-1}$ , respectively.

Gas-phase samples were contained in a heated 5-cm. cell at a temperature of 90°. Spectra were also taken in a solution of  $\text{CCl}_4$  and  $\text{CS}_2$ . Solid samples were examined as Nujol mulls, KBr disks, and crystalline films. TED is very hygroscopic and readily absorbs atmospheric water. Even if all the manipulations were performed in dryboxes and great care was taken so as to avoid any humidity, spectra of samples suspended in KBr disks always showed bands due to absorbed water. Crystalline films with no trace of humidity were obtained by melting the substance between two NaCl or KBr windows and by subsequent cooling in a drybox. With the same thermal treatment we were able to obtain oriented crystalline samples as we shall discuss later in this paper. Gas-phase,  $\text{CCl}_4$ - $\text{CS}_2$  solution, and crystalline spectra are shown in Figures 1, 2, and 3, respectively. Figure 3 also shows the infrared spectra of unoriented, partially oriented, and completely oriented crystalline samples.

In addition to the Raman data from Mirone,<sup>6</sup> we have also obtained the Raman spectra of saturated solutions in chloroform and benzene with a Cary 81 Raman spectrometer.

*Structure and Selection Rules.* For this kind of cage molecule two molecular structures must be considered. The first is a  $D_{3h}$  model in which each pair of  $\text{CH}_2$  groups is in the eclipsed configuration. By a suitable rotation of the two  $\text{NC}_3$  pyramids in opposite directions about the threefold axis, a new model is obtained in which the hydrogens are in a staggered configuration. The latter model belongs to the  $D_3$  point group.

(6) G. Mirone, to be published.