

[CONTRIBUTION FROM MELLON INSTITUTE, PITTSBURGH, PA.]

## Temperature Coefficient of the Polyethylene Chain Conformation from Intrinsic Viscosity Measurements<sup>1</sup>

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RECEIVED AUGUST 17, 1960

Temperature coefficients  $d \ln [\eta]/dT$  of the intrinsic viscosities of linear polyethylenes in *n*-hexadecane, in *n*-octacosane and in *n*-triacontane measured over the range 114 to 170° are  $-1.1(\pm 0.07) \times 10^{-3}$ . The temperature coefficient  $d \ln \langle r^2 \rangle_0/dT$  of the mean-square unperturbed end-to-end distance estimated from these results is  $-1.2(\pm 0.2) \times 10^{-3}$ . This result is compared with the value of the same quantity deduced from stress-temperature measurements on cross-linked networks.

### Introduction

The experiments reported in this paper were undertaken for the purpose of evaluating the temperature coefficient of the mean-square unperturbed end-to-end distance,  $d \ln \langle r^2 \rangle_0/dT$  for the free polyethylene chain. Comparison with the value of this quantity deduced from the stress-temperature coefficient of amorphous polyethylene networks, as set forth in the preceding paper,<sup>2</sup> assumes special importance through its bearing on the premises underlying rubber elasticity theory.

The method adopted in the present investigation requires precise determination of the temperature coefficient of the intrinsic viscosity  $[\eta]$ . Direct dependence of the intrinsic viscosity on a power of the actual mean-square end-to-end distance  $\langle r^2 \rangle$  closely approaching three-halves is now well established. Hence,  $d \ln [\eta]/dT$  leads at once to  $d \ln \langle r^2 \rangle/dT$ . Correction to the temperature coefficient for the unperturbed parameter  $\langle r^2 \rangle_0$  is fraught with vexing difficulties, however. The factor  $\alpha^2 = \langle r^2 \rangle / \langle r^2 \rangle_0$  depends both on  $\langle r^2 \rangle_0$  and on the thermodynamic interaction between polymer and solvent.<sup>3</sup> Precise evaluation of the latter is particularly difficult in the case of polyethylene on account of the necessity for conducting measurements at the elevated temperatures ( $> 100^\circ$ ) required to dissolve the polymer. A different approach has therefore been adopted in the present investigation. Long chain paraffin hydrocarbons, namely, *n*-hexadecane, *n*-octacosane and *n*-triacontane, were selected as solvents in consideration of their similarity with the polymer. In these media, thermodynamic interaction effects should be minimized; in particular, the heat of dilution should be small. Application of the necessary correction for the temperature coefficient for the expansion of the polymer relative to its unperturbed state is thus simplified.

### Experimental

**Polymer Samples.**—Characteristics of the polyethylene samples are listed in Table I. All were of the low pressure variety. Samples 1 and 2 were made available through the courtesy of the Koppers Co. The latter was a fraction separated from the former. The remaining samples were prepared from Marlex-50 produced by the Phillips Petroleum Co. Sample 3 was a coarse center fraction prepared by fractional precipitations to remove low and high molecular weight constituents. Samples 4, 5 and 6 were separated

(1) Partial support from the National Science Foundation Research Grant NSF-G6039 is gratefully acknowledged.

(2) A. Ciferri, C. A. J. Hoeve and P. J. Flory, *THIS JOURNAL*, **83**, 1269 (1961).

(3) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953. Chapters XII and XIV.

TABLE I  
POLYETHYLENE SAMPLES

Sample no.	$[\eta]$ in decalin at 135°	$\bar{M}_v \times 10^{-4}$
1 <sup>a</sup>	1.71	80
2	3.85	240
3	2.76	150
4	1.07	43
5	2.25	126
6	5.98	490

<sup>a</sup> Unfractionated; broad distribution.

from Marlex-50 by the column technique first employed by Desreux<sup>4</sup> and improved by Henry<sup>5</sup>; according to results previously obtained by this method, it may be assumed that  $\bar{M}_w/\bar{M}_n \cong 1.1$  for these fractions. The viscosity average molecular weights given in the last column of Table I were calculated from the intrinsic viscosities in decalin using the equation given by Henry<sup>5</sup> and by Tung.<sup>6</sup> Precise values of the molecular weights are not required for the purposes of the present investigation, and appreciable polydispersity can be tolerated.

**Solvents.**—*n*-Hexadecane and *n*-octacosane were obtained from the Eastman Chemicals Co. The former was redistilled at reduced pressure, m.p. 16.9–17.7°, and the latter, m.p. 59–61°, was used without purification. *n*-Triacontane was kindly provided by W. P. Ridenour of the Petroleum Fellowship, Mellon Institute. It had been purified by fractional distillation and by urea adduction; mol. wt. 419, m.p. 64.15°. Specific volumes and thermal expansion coefficients  $\beta$  in the temperature range of this investigation are given in Table II.

TABLE II

SPECIFIC VOLUMES AND THERMAL EXPANSION COEFFICIENTS

	Spec. vol., cc/g., 140°	$\beta \times 10^3$ , deg. <sup>-1</sup> , ca. 140°
<i>n</i> -C <sub>16</sub> H <sub>34</sub>	1.456	1.13 <sup>7</sup>
<i>n</i> -C <sub>28</sub> H <sub>58</sub>	1.370	0.885 <sup>7</sup>
<i>n</i> -C <sub>30</sub> H <sub>62</sub>	1.364	0.89 <sup>7</sup>
Polyethylene	1.275	0.70 <sup>8</sup>

**Viscometry.**—Preliminary experiments made apparent the necessity for rigorous exclusion of oxygen at the elevated temperatures (114 to 170°) over which the viscosities were to be determined. Cannon-Ubbelohde dilution viscometers eventually were constructed according to the design shown schematically in Fig. 1, which permitted all operations to be performed in an atmosphere of pure helium. As a further precautionary measure, the antioxidant phenyl- $\beta$ -naphthylamine was incorporated in all solutions at a concentration of 0.04%.

Separate viscometers were used for each of the three *n*-paraffin solvents; flow times for the pure solvents in the respective viscometers at 140° were 243.4 sec. for C<sub>16</sub>H<sub>34</sub>, 134.4 sec. for C<sub>28</sub>H<sub>58</sub> and 153.6 sec. for C<sub>30</sub>H<sub>62</sub>. Kinetic

(4) V. Desreux, *Rec. trav. chim.*, **68**, 789 (1949); V. Desreux and M. C. Spiegels, *Bull. soc. chim. Belges*, **59**, 476 (1950).

(5) P. M. Henry, *J. Polymer Sci.*, **36**, 3 (1959).

(6) See also, L. H. Tung, *ibid.*, **36**, 287 (1959).

(7) G. Egloff, "Physical Constants of Hydrocarbons," Vol. V, Reinhold Publishing Corp., New York, N. Y., 1953.

(8) M. G. Gubler and A. J. Kovacs, *J. Polymer Sci.*, **34**, 551 (1959).

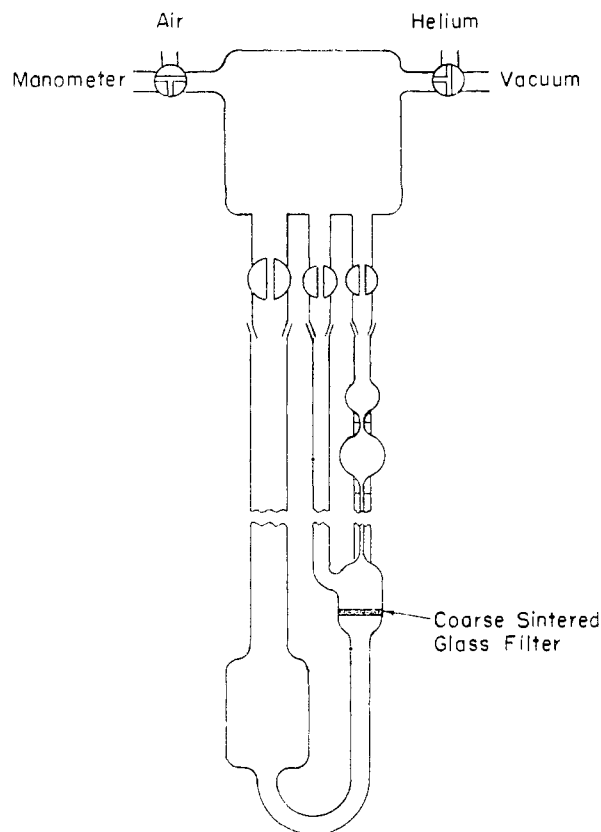


Fig. 1.

energy corrections, established by calibration with aqueous sucrose solutions, were applied. In no case did the kinetic energy correction applied to the flow time amount to more than 0.5%; the temperature coefficients  $d \ln[\eta]/dT$  were affected no more than 10%, which scarcely exceeds the experimental error.

Solutions were prepared by introducing measured quantities of the components into the lower reservoir of the viscometer. After evacuating and filling with helium several times to assure thorough removal of oxygen, the viscometer and contents were placed in a silicone oil thermostat at a temperature of *ca.* 140° until solution was complete and thorough mixing was achieved. The thermostat was adjusted at once to the desired temperature ( $\pm 0.01^\circ$ ) for performance of viscosity measurements. The delivery bulb was filled by application of pressure through the stopcock connecting with the reservoir, thereby forcing the solution upward through the sintered glass filter and the capillary. Upon closing the first stopcock and opening the other two, the liquid was permitted to discharge through the capillary under the force of gravity, the gas pressure being equalized above the bulb and at the suspended level. The flow time between fiducial marks was recorded. A positive pressure of helium was maintained on the system at all times in order to assure exclusion of traces of air.

A solution of the highest concentration was prepared initially and its flow times taken in duplicate at successive temperatures starting at the highest and proceeding to the lowest. Repetition of the determination at the highest temperature yielded the previously observed flow time within experimental error ( $\pm 0.1$  sec.). After completion of the series of measurements at the highest concentration, the viscometer was brought to room temperature, the gas delivery manifold was removed and a measured quantity of solvent added. Measurements at the next lower concentration then were carried out exactly as described above. In this way, viscosities were determined at four concentrations covering approximately a three-fold range in concentration; the specific viscosities ranged from about 0.9 to 0.08. The errors in the specific viscosities did not exceed 1%.

The solution concentration  $c$  in g./100 ml. was calculated at each temperature using the specific volumes and thermal

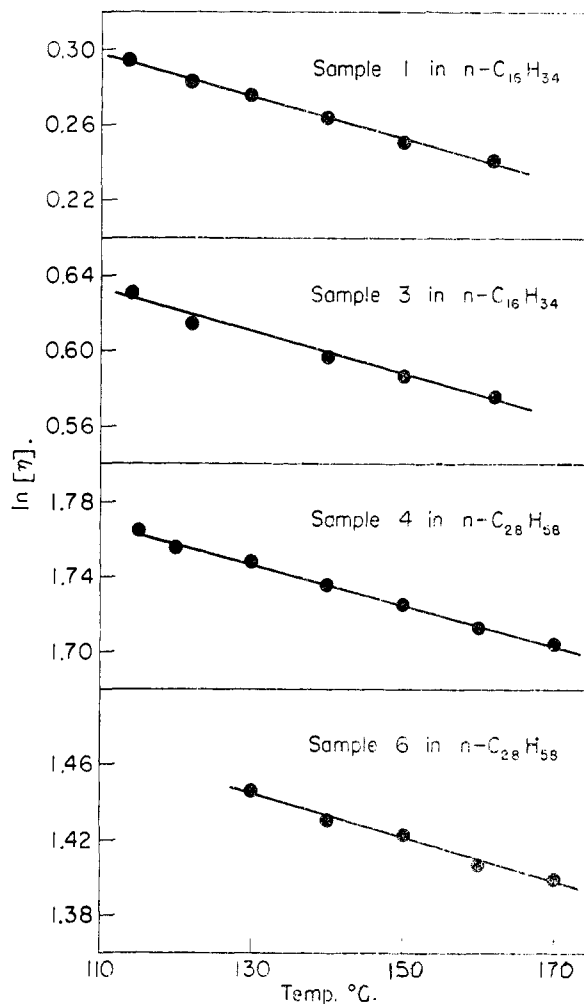


Fig. 2.

expansion coefficients given in Table II. The ratios  $\eta_{sp}/c$  were extrapolated linearly (least squares method) to  $c = 0$  to obtain the intrinsic viscosities  $[\eta]$ . Huggins  $k'$  constants calculated from the slopes were consistently greater than the normal value of *ca.* 0.40; the average was 0.58. This slight abnormality may reflect a small dilution error. It is of no importance insofar as the temperature coefficient is concerned.

## Results

Intrinsic viscosities for each solvent-polymer pair were plotted against temperature as in Fig. 2. Values at 140° (interpolated if not measured) are given in the second column of Table III; slopes  $d \ln[\eta]/dT$  taken from least square straight lines through the experimental points are presented in the third column. There is no discernible trend in these coefficients with either the diluent or the molecular weight of the polymer.

**Treatment of Data.**—The temperature coefficient  $d \ln \langle r^2 \rangle_0 / dT$  of the unperturbed mean-square chain end-to-end distance has been deduced from the intrinsic viscosity-temperature coefficient through use of the relationships<sup>3,9</sup>

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

$$\alpha^5 - \alpha^3 = 27(2\pi)^{-3/2} N_a^{-1} \bar{v}^2 v_1^{-1} \langle r^2 \rangle_0 / M)^{-1/2} M^{1/2} (1/2 - \chi_1) \quad (2)$$

(9) P. J. Flory and T. G. Fox, *THIS JOURNAL*, **73**, 1904, 1909, 1915 (1951); *J. Phys. Colloid Chem.*, **53**, 197 (1949).

TABLE III  
OBSERVED TEMPERATURE COEFFICIENTS OF INTRINSIC  
VISCOSITIES AND CALCULATED TEMPERATURE COEFFICIENT  
OF  $\langle r^2 \rangle_0$

Sample solvent	$[\eta]_{160^\circ}$ dl. g. <sup>-1</sup>	$\frac{-d \ln [\eta]/dT}{\times 10^3}$	$\alpha^2$	$\frac{-d \ln \langle r^2 \rangle_0/dT}{\times 10^3}$
1/ <i>n</i> -C <sub>16</sub> H <sub>34</sub>	1.30	1.11	1.71	1.18
2/ <i>n</i> -C <sub>16</sub> H <sub>34</sub>	2.60	1.07	2.00	1.21
3/ <i>n</i> -C <sub>16</sub> H <sub>34</sub>	1.82	1.11	1.87	1.22
3/ <i>n</i> -C <sub>27</sub> H <sub>54</sub>	1.76	1.04	1.62	1.15
4/ <i>n</i> -C <sub>25</sub> H <sub>50</sub>	0.77	1.10	1.43	1.11
5/ <i>n</i> -C <sub>25</sub> H <sub>50</sub>	1.60	1.17	1.61	1.27
6/ <i>n</i> -C <sub>25</sub> H <sub>50</sub>	4.17	1.15	1.93	1.36

where  $\alpha$  is the expansion factor arising from intramolecular interactions,  $N_a$  is Avogadro's number,  $\bar{v}$  is the specific volume of the polymer,  $v_1$  is the molar volume of the solvent and  $\chi_1$  characterizes the thermodynamic interaction of polymer and solvent. The exponent  $\gamma$  was given as three in the original theory.<sup>8,9</sup> Recent attempts at refinement<sup>10,11</sup> recommend a somewhat lower value in the neighborhood of  $\gamma = 2.5$ . The second of these relationships is approximate; the magnitude of the numerical constant is especially subject to question,<sup>12</sup> a point to which we shall return later. Inaccuracies which may limit the utility of these equations in dealing with the absolute magnitudes of  $\alpha$  and  $[\eta]$  are comparatively unimportant for the purposes of the present analysis, which is concerned only with small *relative* changes due to alteration of the temperature, the polymer and solvent being otherwise unchanged.

The direct effect of a decrease in  $\langle r^2 \rangle_0$  with temperature on  $[\eta]$  as expressed by eq. 1 is compensated in part by the increase in  $\alpha$  due to the increased density of polymer segments. It is on this account that  $\langle r^2 \rangle_0$  occurs in the inverse three-halves power in eq. 2. The factors  $\bar{v}^2/v_1$  and  $1/2 - \chi_1$  occurring in the latter equation also depend on the temperature. The change of  $\alpha$  with temperature may be expected therefore to contribute importantly to the temperature coefficient of  $[\eta]$ . Proper allowance for this contribution is essential for the evaluation of the temperature coefficient of  $\langle r^2 \rangle_0$ .

The temperature coefficient of  $\alpha$  will not however be evaluated explicitly. We shall find it expedient instead to eliminate this coefficient, as given by eq. 2, from the expression for the temperature coefficient of  $[\eta]$  according to eq. 1. In this way we obtain

$$\frac{d \ln \langle r^2 \rangle_0/dT}{d \ln [\eta]/dT} = \frac{2(5\alpha^2/3 - 1)[(5 - \gamma)\alpha^2 - (3 - \gamma)]^{-1}}{(2\beta_2 - \beta_1) - (1/2 - \chi_1)^{-1}d\chi_1/dT} \quad (3)$$

where  $2\beta_2 - \beta_1 = d \ln(\bar{v}^2/v_1)/dT$ ,  $\beta_1$  and  $\beta_2$  being the bulk thermal expansion coefficients (Table II) of solvent and liquid polymer, respectively. If  $\gamma = 3$ , this relationship simplifies to

$$\frac{d \ln \langle r^2 \rangle_0/dT}{d \ln [\eta]/dT} = \frac{(5/3 - \alpha^{-2})}{[2\beta_2 - \beta_1 - (1/2 - \chi_1)^{-1}d\chi_1/dT]} \quad (3')$$

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

(11) O. B. Ptitsyn and V. Y. Eisner, *J. Phys. Chem. (U.S.S.R.)*, **32**, 2464 (1958).

(12) W. H. Stockmayer, *J. Polymer Sci.*, **15**, 595 (1955); *Makromol. Chem.*, **35**, 54 (1960).

**The Expansion Factor  $\alpha$ .**—Before undertaking application of eq. 3, the value of the expansion factor  $\alpha$  must be obtained from eq. 2. The quantities  $\langle r^2 \rangle_0/M$ ,  $M$  and  $\chi_1$  are required. The value of the ratio  $\langle r^2 \rangle_0/M = 1.14 \times 10^{-16}$  cm.<sup>2</sup> mole g.<sup>-1</sup> has been deduced by Orofino's<sup>13</sup> method using the intrinsic viscosity-molecular weight relationship for linear polyethylene in  $\alpha$ -chloronaphthalene established by Henry<sup>5</sup> and by Chiang<sup>14</sup> and supported by the results of Tung,<sup>6</sup> in conjunction with the closely agreeing second virial coefficients found by these authors in the same solvent. We assume  $\chi_1 = 0$  in view of the similarity of the *n*-paraffinic solvents to polyethylene.

Evidence in support of this assumed value is afforded by comparison of the degree of swelling ( $1/v_2 = 3.08$ , at equilibrium in *n*-C<sub>25</sub>H<sub>50</sub> at 140°) with the elastic retractive stress ( $\tau = 1.45$  kg. cm.<sup>-2</sup> at  $\alpha = 1.174$  and  $T = 140^\circ$ , unswollen) exhibited by the same network when stretched. By application of the well-known relationships for swelling equilibrium and for the elastic response of Gaussian networks, we calculate  $\chi_1 = 0.02$ . Accuracy cannot be claimed for the numerical result; the experiments cited assure, however, that  $|\chi_1| < 0.1$ . An interaction parameter of this magnitude would not appreciably alter the values of  $\alpha^2$  calculated from eq. 2 as detailed above and listed in the third column of Table III.

**Calculation of the Temperature Coefficient of  $\langle r^2 \rangle_0$ .**—Calculation of  $d \ln \langle r^2 \rangle_0/dT$  according to eq. 3 requires knowledge of  $d\chi_1/dT$ , in addition to the thermal expansion coefficients  $\beta_1$  and  $\beta_2$  given in Table II and other quantities dealt with above. The quantity  $d\chi_1/dT$  is a measure of the enthalpy of dilution, which should be very small for polyethylene in the higher *n*-paraffins; it must vanish of course as the chain length of the diluent is indefinitely increased. With this in mind we have computed the values of  $-d \ln \langle r^2 \rangle_0/dT$  given in the last column of Table III taking  $d\chi_1/dT = 0$  and  $\gamma = 2.5$ . Choice of  $\gamma = 3$ , enabling use of eq. 3' instead of eq. 3, results in values for  $-d \ln \langle r^2 \rangle_0/dT$  which are raised by about 13%.

**Confirmatory Evidence for Athermal Mixing.**—Experimental proof that the heat of mixing is indeed negligible in these solvents was sought through determination of the temperature coefficient of swelling of polyethylene cross linked with 3 mev. electrons. A sample measuring about  $0.12 \times 0.15 \times 4$  cm. was sealed under vacuum in a cylindrical tube containing a large excess of *n*-octacosane. Tube and contents were placed in a thermostat at 180° until the length became constant when measured with a cathetometer reading to 0.005 mm. This required five days. The length was similarly determined at 160° and then at 140°, after 5 hr. at each temperature. Repetition of the measurements at 160 and 180° confirmed the previous observations.

Assuming swelling to be isotropic, the equilibrium volume fraction  $v_2$  of polymer and its temperature coefficient were calculated from the measured lengths of the sample, swollen and unswollen. The

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

(14) R. Chiang, *J. Polymer Sci.*, **36**, 91 (1959).

results obtained were:  $v_2(180^\circ) = 0.288$ ;  $dv_2/dT = 2.9 (\pm 0.2) \times 10^{-4} \text{ deg.}^{-1}$ .

According to theory

$$(v_1\nu/V^*)(\langle r^2 \rangle_1^*/\langle r^2 \rangle_0)[v_2^{1/3} - (v_2/2)\langle r^2 \rangle_0/\langle r^2 \rangle_1^*] = -[\ln(1 - v_2) + v_2 + \chi_1 v_2^2] \quad (4)$$

where  $\nu$  is the number of moles of network chains in volume  $V^*$  and  $\langle r^2 \rangle_1^*$  is the mean-square chain displacement length in the dry state of this volume. Taking  $\chi_1 = 0 \pm 0.1$ ,  $d\ln\langle r^2 \rangle_0/dT = -1.3 (\pm 0.2) \times 10^{-3} \text{ deg.}^{-1}$  and  $dv_2/dT = 2.9 (\pm 0.2) \times 10^{-4} \text{ deg.}^{-1}$ , we calculated from eq. 4 that  $d\chi_1/dT = 1.5 (\pm 2.5) \times 10^{-4}$ , with full allowance for the stated uncertainties in the quantities involved. Even if the extreme value  $-4 \times 10^{-4}$  were used for  $d\chi_1/dT$  instead of zero, the value of  $-d\ln\langle r^2 \rangle_0/dT$  calculated from eq. 3 would be altered only by about  $+0.2 \times 10^{-3}$ .

The close similarity between the viscosity-temperature coefficients in *n*-hexadecane and in the higher hydrocarbon solvents offers independent assurance that enthalpies of dilution make no significant contribution to the results. If this were not so, their effect should be more prominent in the former than in the latter and therefore apparent in the results.

## Conclusions

The average of the values of  $-d \ln \langle r^2 \rangle_0/dT$  given in Table III is  $1.21 \times 10^{-3} \text{ deg.}^{-1}$ . As already noted, use of  $\gamma = 3$  instead of 2.5 would increase the result somewhat. On the other hand, incorporation of the suggestion of Stockmayer<sup>12</sup> according to which the numerical factor in eq. 2 should be reduced by one half, reduces  $\alpha^2$  by about 15% and  $-d \ln \langle r^2 \rangle_0/dT$  by about 10%. Considering these various sources of uncertainty in the present method, we conclude that  $-d \ln \langle r^2 \rangle_0/dT = 1.2 (\pm 0.2) \times 10^{-3}$ .

The results of stress-temperature studies on polyethylene networks swollen by *n*-triacontane and *n*-dotriacontane presented in the preceding paper yield  $-d \ln \langle r^2 \rangle_0/dT = 1.16 (\pm 0.10) \times 10^{-3}$ . The gratifying agreement between results obtained by these unrelated methods lends substantial support to the assumption that the molecular conformation in the amorphous state is not appreciably affected by interactions between neighboring chains. The related assumption<sup>2</sup> that the chains of a cross-linked network contribute additively to its elastic free energy likewise is validated.

[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILLINOIS]

## A Study of the Ionization of Polystyrene Sulfonic Acid by Proton Magnetic Resonance<sup>1a</sup>

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RECEIVED SEPTEMBER 23, 1960

The chemical shift of the proton magnetic resonance in aqueous solutions of polystyrene sulfonic acid as a function of acid concentration has been measured. The magnitude of the slope of the straight line obtained in the customary plot of the chemical shift (in parts per million) *vs.* the stoichiometric mole fraction of acidic hydrogen is found to be  $11.5 \pm 0.3$ . This result is interpreted as indicating that the acid is completely ionized.

### I. Introduction

It is well known that the thermodynamic properties of linear polyelectrolytes, such as counterion activity<sup>2-7</sup> and osmotic pressure,<sup>8,9</sup> show values considerably smaller than those of the corresponding ideal solutions. This phenomenon has often been explained on the assumption that most or part of the counterions are associated in some manner with the polyion. In explaining other phenomena, such as conductivity,<sup>4b,8,10-12</sup> trans-

ference numbers,<sup>13,14</sup> electrophoresis,<sup>15,16</sup> Donnan membrane equilibrium,<sup>17-19</sup> potentiometric titration,<sup>20</sup> viscosity<sup>17,20,21</sup> and light scattering,<sup>22-24</sup> the idea of counterion binding also has been found useful. Unfortunately, the definition of the term ion binding (*e.g.*, association, fixation) is not

(1) (a) This research was supported jointly by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF49(638)-694, and by the National Institutes of Health. (b) On leave from the Department of Applied Chemistry, Nagoya University, Nagoya, Japan.

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(20) F. E. Harris and S. A. Rice, *J. Phys. Chem.*, **58**, 725, 733 (1954).

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(22) N. S. Schneider and P. Doty, *J. Phys. Chem.*, **58**, 762 (1954).

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