If both of these contributions to the constant volume entropy of fusion are accounted for, then the entries in the third column of Table I, which should now be labeled $(\Delta S_u)_V$ instead of ΔS_{conf}, must each be increased by 0.6 to 1.6 eu/mol of backbone bonds. Since the total entropy of fusion of isotactic polypropylene is 1.5 eu/mol of backbone bonds, addition of 1.6 eu to the calculated conformational entropies in Table I leads to constant-volume entropies of fusion in excess of the total entropy of fusion. Even inclusion of the lower estimate (0.6 eu) of the combination of lattice exclusion and long-range disorder entropies to the conformational entropies results in constant volume entropies of fusion which exceed the experimental value (0.85–1.06 eu) for all values of E_τ and E_ω less than *ca.* 4.0–5.0 kcal/mol.

Hence, it appears that either the calculated segment length (five backbone bonds) is an overestimate and/or Starkweather and Boyd's[7] proposal of $R/2$–R eu/mol of backbone bonds for the magnitude of the long-range disorder contribution is excessive. More likely, we believe, is the possibility that both contributions tend to largely cancel each other, resulting in the validity of eq 2 and 3, which means in words that the constant-volume entropy of fusion is given by the gain in conformational entropy upon melting calculated for an isolated polymer chain. This belief is supported by the general agreement found[8] between the experimental constant volume entropies of fusion and the calculated changes in isolated chain conformational entropies for several polymers with widely differing chemical structures.

Consequently, the previously drawn conclusions that for isotactic polypropylene $E_\tau \geq 0.5$ and $E_\omega \geq 2.0$ kcal/mol, that isotactic vinyl polymers including polypropylene contain several per cent of racemic dyad placements, and that isotactic polypropylene is less flexible than polyethylene most probably remain valid.[27]

Acknowledgment. The author is grateful to the referees of this paper for their helpful comments and suggestions.

(27) NOTE ADDED IN PROOF. After completion of the present manuscript, papers by Heatley [F. Heatley, *Polymer* **13**, 218 (1972)] and Boyd and Breitling [R. H. Boyd and S. M. Breitling, *Macromolecules*, **5**, 279 (1972)], which modify the usual[11,15] three rotational isomeric state model of isotactic polypropylene, have appeared. This modification was achieved by employing semiempirical potential functions to locate the rotational minima and estimate their energies. Both Heatley and Boyd and Breitling conclude that for reasonable values of E_τ and E_w the dimensions and their temperature coefficient calculated from their models of isotactic polypropylene are in agreement with the experimental values, thus rendering unnecessary the contention[11,15,19–21] that all isotactic polypropylenes studied to date contain several per cent of racemic dyad placements. Heatley presents $E_\tau = 1250 \pm 500$ cal/mol and $E_w = 1950 \pm 100$ cal/mol as the appropriate energies to be used with his model. When these energies, together with Heatley's statistical weight matrix, are used to calculate the conformational or intramolecular contribution to the entropy and energy of melting, the following results are obtained: $\Delta S_{conf} = 1.43$–1.66 eu/mol of backbone bonds and $\Delta E_{conf} = 366$–407 cal/mol of backbone bonds. On the other hand, Boyd and Breitling conclude, as appropriate for isotactic polypropylene, $E_\tau = 600$ cal/mol and $E_w = 1300$ cal/mol. These energies lead to $\Delta S_{conf} = 1.80$ eu/mol of backbone bonds when inserted as Boltzmann factors into the statistical weight matrices developed by them. Both rotational isomeric state models lead to calculated intramolecular or conformational contributions to the entropy of fusion which equal or exceed the value of 1.5 eu/mol of backbone bonds measured[1] for the total entropy of fusion. In fact, the intramolecular or conformational contribution to the energy of fusion calculated from Boyd and Breitling's model exceeds the total measured[1] enthalpy of fusion (700 cal/mol of backbone bonds). Thus, we conclude that both of these rotational isomeric state models are incompatible with or fail to adequately describe the conformational characteristics of isotactic polypropylene as deduced from its fusion behavior.

The Poly(hydroxy-L-proline) Ring Conformation Determined by Proton Magnetic Resonance

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ABSTRACT: From a computer simulation of the 220-MHz spectrum of poly(hydroxy-L-proline), all ring vicinal couplings have been obtained. Using these couplings and a Karplus-type equation to estimate ring dihedral angles, it is found that the ring maintains a single nonplanar conformation in aqueous solution. This puckered conformation, having C_γ exo, is described by the angles $\chi_1 \approx -\chi_4 \approx -25°$, $\chi_2 \approx -\chi_3 \approx 45°$, $\varphi \approx 120°$. Prolyl and hydroxyprolyl conformations obtained previously are compared to this conformation, and discussion is provided of a possible interaction of the peptide backbone with the OH moiety, in a C_γ-exo Hyp ring.

Recently, prolyl ring conformations of cyclo(tri-Pro)[1,2] and poly(Pro)[3] have been obtained using Karplus-type equations[4–6] to relate ring dihedral angles to vicinal couplings, the latter determined by computer simulating nmr spectra obtained by 220 MHz. In the case of poly(Pro), the nmr analysis indicated that several conformations were in rapid equilibrium (on the nmr time scale), and it was concluded, on the basis of the nmr results, X-ray data,[7] and energy calculations,[8] that two C_γ puckered ring conformations (C_γ exo or endo

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(1) The following abbreviations are used in this paper: Pro for L-prolyl, Hyp for hydroxy-L-prolyl, Gly for glycyl, poly(Pro) and poly(Hyp) for the helical forms of these polymers having trans peptide bonds, X for any amino acid residue except Pro or Hyp, $|\varphi|$ for absolute value of φ, DP for degree of polymerization.

(2) C. M. Deber, D. A. Torchia, and E. R. Blout, *J. Amer. Chem. Soc.*, **93**, 4893 (1971).

(3) D. A. Torchia, *Macromolecules*, **4**, 440 (1971).

(4) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *ibid.*, **33**, 1842 (1960).

(5) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(6) M. Barfield and M. Karplus, *ibid.*, **91**, 1 (1969).

(7) R. Balasubramanian, A. V. Lakshminarayanan, M. N. Sabesan, G. Tegoni, K. Venkatesan, and G. N. Ramachandran, *Int. J. Protein Res.*, **2**, 303 (1970).

(8) G. N. Ramachandran, A. V. Lakshminarayanan, R. Balasubramanian, and G. Tegoni, *Biochim. Biophys. Acta*, **221**, 165 (1971).

relative to the C=O moiety) were the predominent solution conformations.

In the present investigation, the Hyp ring conformation of poly(Hyp) has been obtained from an analysis of the 220-MHz spectrum of the polypeptide. A determination of the solution structure of the poly(Hyp) ring is of interest since it allows comparison of the ring conformations of poly(Pro) and poly(Hyp). Also, the relative stabilities of polypeptide backbone conformations may depend upon the conformation of the Hyp ring. Differences in optical and hydrodynamic properties have been observed[9,10] for polypeptides having identical sequences, except that Pro is replaced by Hyp. It has been noted[10] that these differences may result from backbone–side-chain interactions involving the Hyp OH moiety, if the ring conformation is puckered with C_γ exo, as found for the amino acid hydroxy-L-proline, in the crystal[11] and in solution.[12,13]

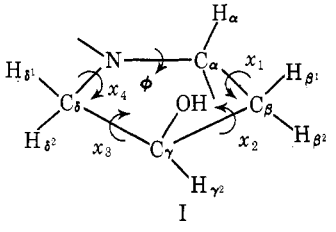
Experimental Section

Materials. The sample of poly(Hyp) used in this study was kindly provided by Professor Leo Mandelkern, and the configuration of the Hyp ring is that of the (trans) naturally occurring isomer. Comparison of intrinsic viscosity of this sample with that of the poly(Hyp) samples of known molecular weights indicates that DP $\approx$ 75.[14] D_2O (99.7 and 100.0%) was purchased from Diaprep, Inc. and *tert*-butyl alcohol-d_1 was obtained from Merck Sharpe and Dohme.

Methods. Nmr spectra were obtained using Varian HA-100 and HR-200 spectrometers. Homonuclear spin decoupling was accomplished using Muirhead D-890-B and General Radio 1107-A audiooscillators at 100 and 220 MHz, respectively. The *tert*-butyl resonance at τ 8.77 (relative to DSS in D_2O) of *tert*-butyl alcohol-d_1 was used as internal reference and (at 100 MHz) lock. The sample was prepared by lyophilizing a D_2O (99.7%) solution of poly(Hyp) in an nmr tube and then adding 100.0% D_2O to the tube in a drybox.

Results and Discussion

(1) Computer Simulation of the Poly(Hyp) Spectrum. The diagram (I) of a planar 4-hydroxy-L-proline ring ($\chi_i = 0°$, $i = 1$–4; $\varphi = 120°$) shows the designations of ring atoms and rotation angles used in this report.[15] The 220-MHz



I

spectrum of poly(Hyp), 25 mg/ml, in D_2O at 57° is shown in Figure 1a. As expected, the resonances sharpen on increasing the temperature and the line widths at 57° (*ca.* 5–6 Hz) are small enough so that the fine structure (due to spin–spin splittings) of the resonances is seen. Slight reduction in line widths (to *ca.* 4–5 Hz) is obtained on raising the temperature to 85°, but the small improvement in resolution is offset by

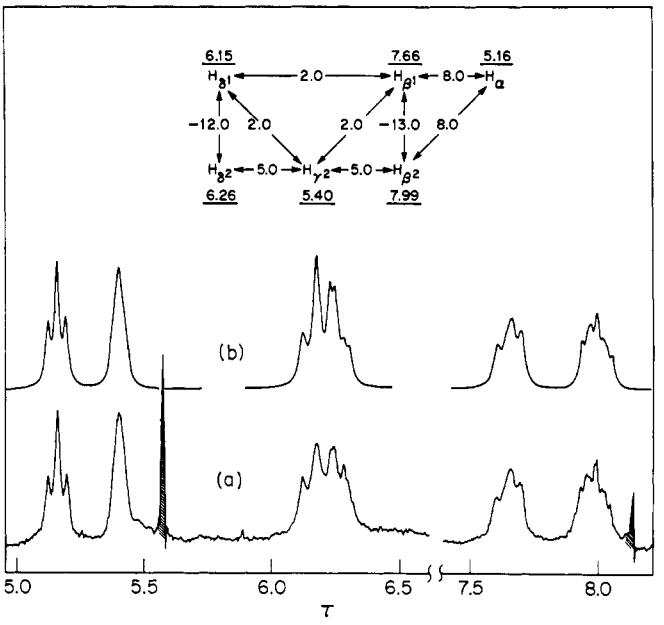


Figure 1. Comparison of 220-MHz spectra of poly(Hyp): (a) experimental spectrum at 57° in D_2O, shaded resonances, HDO at τ 5.57 and side band of *tert*-butyl alcohol-d_1 at τ 8.12; (b) computer-simulated spectrum. At top is a schematic summary of the coupling constants (hertz) and chemical shifts (underlined) used in the simulation. Line widths assumed in simulation, 5–6 Hz. Chemical shifts, τ units, measured from internal *tert*-butyl alcohol-d_1, at τ 8.77 relative to sodium 2,2-dimethyl-2-silapentane-5-sulfonate.

increasing overlap of the two $C_\delta H_2$ resonances. No changes in line widths were observed on reducing the concentration from 25 to 5 mg/ml at a fixed temperature.

In order to calculate the spectrum of the poly(Hyp) ring spin system, six chemical shifts, two geminal couplings, and six vicinal couplings are required as input data for the machine program. Four of the ring protons, H_α, H_γ, and the two H_β's give distinct resonances at τ 5.16, 5.40, 7.66, and 7.99, respectively, while the H_δ protons have overlapping resonances centered at τ 6.2. Assignment of the β and δ resonances is based on previous analyses[2,12,13] of Hyp spectra, while the H_α, H_γ assignments follow from spin-decoupling experiments at 100 MHz. Simultaneous irradiation of both $C_\beta H_2$ protons resulted in a singlet (*ca.* 5-H_z line width) at τ 5.16. By contrast, irradiation of both $C_\delta H_2$ protons had no effect on the τ 5.16 triplet.

An approximate value of the $C_\beta H_2$ geminal coupling was obtained from the $C_\beta H_2$ AB quartet which resulted on simultaneous irradiation of H_α and H_γ. Initial estimates of the $J_{\alpha\beta}$ and $J_{\beta\gamma}$ vicinal couplings were obtained from the fine structure of the H_α and H_β resonances. Approximate values of $|J_{\delta 1\delta 2}|$ and chemical shifts of individual H_δ protons were obtained from the measured center positions of the four broad lines of the $C_\delta H_2$ AB quartet, while values of the two $J_{\gamma\delta}$ vicinal couplings were estimated from the widths of the individual AB signals.

The initial values of chemical shifts and coupling constants thus obtained were adjusted until a satisfactory simulation, Figure 1b, was found. A chart at the top of Figure 1 summarizes the chemical shifts and coupling constants used to calculate the spectrum. The indicated specific assignments of the $H_{\delta 1}$, $H_{\delta 2}$ and $H_{\beta 1}$, $H_{\beta 2}$ resonances, and the inclusion of a single nonzero long-range coupling ($J_{\beta 1\delta 1} = 2$ Hz) are discussed as part of the conformational analysis to which we now turn.

(9) W. L. Mattice and L. Mandelkern, *Macromolecules*, **3**, 199 (1970).
(10) W. L. Mattice and L. Mandelkern, *Biochemistry*, **10**, 1926 (1971).
(11) J. Donohue and K. N. Trueblood, *Acta Crystallogr.*, **5**, 419 (1952).
(12) R. J. Abraham and K. A. McLaughlan, *Mol. Phys.*, **5**, 195 (1962).
(13) R. J. Abraham and K. A. McLaughlan, *ibid.*, **5**, 513 (1963).
(14) D. Rabenold and L. Mandelkern, private communication.
(15) For discussion of nomenclature, see J. T. Edsall, P. J. Flory, J. C. Kendrew, A. M. Liquori, G. Nemethy, G. N. Ramachandran, and H. A. Scheraga, *Biopolymers*, **4**, 121 (1966); *J. Biol. Chem.*, **241**, 1004 (1966); *J. Mol. Biol.*, **15**, 399 (1966).

TABLE I
COMPARISON OF HYDROXY-L-PROLINE AND POLY(HYP) RING VICINAL COUPLINGS[a]

Vicinal coupling	Amino acid value[b]	Poly(Hyp) value[c]
$J_{\alpha\beta 1}$	7.66	8.0
$J_{\alpha\beta 2}$	10.44	8.0
$J_{\beta 1\gamma 2}$	1.41	2.0
$J_{\beta 2\gamma 2}$	4.31	5.0
$J_{\gamma 2\delta 1}$	1.22	2.0
$J_{\gamma 2\delta 2}$	4.09	5.0
$J_{\beta 1\delta 1}$	1.6	2.0

[a] In hertz. [b] Reference 12. [c] Uncertainty ±1.0 Hz.

(2) Poly(Hyp) Ring Conformations. The vicinal couplings in the chart at the top of Figure 1 can be related to the dihedral angles, φ_d, involving the Hyp ring protons by a Karplus-type equation.

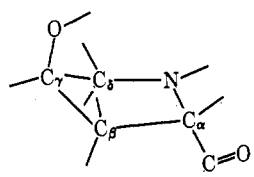
$$J_{H,H} = A\cos^2\varphi_d + B \qquad 0° \leq |\varphi_d| \leq 90°$$
$$J_{H,H} = A'\cos^2\varphi_d + B \qquad 90° \leq |\varphi_d| \leq 180° \qquad (1)$$

An analysis[1] of the spectrum of the Hyp protons of cyclo(Pro-Pro-Hyp) benzoate indicates that the following set of coefficients (in hertz) are appropriate for Hyp ring couplings.

$$(A, A', B) = (8.5, 10.5, 1.4)$$
for coupling not involving $H_{\gamma 2}$ (2)

$$(A, A', B) = (7.0, 9.0, 1.1)$$
for $H_{\gamma 2}$ couplings (3)

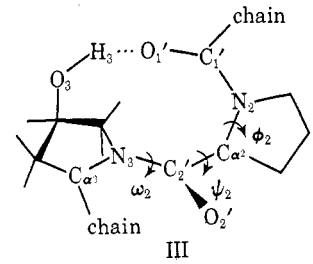
In using eq 1–3 and the couplings listed in Figure 1 to ascertain the ring conformation, we note first that all couplings involving $H_{\gamma 2}$ are ≤ 5 Hz, with two couplings having particularly small values of 2 Hz. These 2-Hz couplings are assigned to $J_{\beta 1\gamma 2}$ and $J_{\gamma 2\delta 1}$, since such small couplings require dihedral angles *ca.* 90 ± 20°, and if severe ring strain is to be avoided only protons above the Hyp ring plane (designated $H_{\beta 1}$,$H_{\delta 1}$ in I can make such large dihedral angles with $H_{\gamma 2}$. Hence, the 5-Hz couplings correspond to $J_{\beta 2\gamma 2}$ and $J_{\gamma 2\delta 2}$. These assignments in conjunction with eq 1–3 are consistent with a unique set of *dihedral angles* $|\varphi_d(\beta^1\gamma^2)| \approx |\varphi_d(\gamma^2\delta^1)| \approx 75°$, $|\varphi_d(\beta^2\gamma^2)| \approx |\varphi_d(\gamma^2\delta^2)| \approx 45°$, *i.e.*, an exo puckering of the Hyp ring at C_γ, with $\chi_2 \approx -\chi_3 \approx 45°$. In the C_γ puckered ring, $\chi_1 \approx -25°$ corresponding to $|\varphi_d(\alpha\beta^1)| \approx 25°$, $|\varphi_d(\alpha\beta^2)| \approx 145°$, respectively. These dihedral angles and eq 1–3 yield values of $J_{\alpha\beta 1} = 8.4$ Hz, $J_{\alpha\beta 2} = 8.5$ Hz, in good agreement with the experimental values of 8 Hz. Hence, the above considerations suggest a Hyp ring, puckered exo at C_γ, shown in II, defined by the dihedral angles ($\varphi \approx 120°$, $\chi_1 \approx -\chi_4 \approx -25°$, $\chi_2 \approx -\chi_3 \approx 45°$). These dihedral angles have uncertainties of ±10° due to uncertainties in the values of the coupling constants (see Table I).



(C_γ)exo
II

An interesting feature of II is its similarity to the conformation proposed[12,13] for 4-hydroxy-L-proline on the basis of a Karplus analysis of the amino acid spectrum. A comparison of the couplings obtained here and for the amino acid appears in Table I.[16] The small couplings involving $H_{\gamma 2}$ are an important feature of both spectra, since, as pointed out previously,[13] the presence of many ring conformations rapidly interconverting leads to average $H_{\gamma 2}$ couplings of 5–6 Hz. Hence, the observation of small $H_{\gamma 2}$ couplings is strong evidence that the C_γ-exo conformation (II) is the predominant poly(Hyp) ring conformation in aqueous solution.[17] By contrast, the poly(Pro) results[3,7,8] indicate that approximately equally populated C_γ-exo and C_γ-endo conformations are rapidly interconverting. Both C_γ-exo and C_γ-endo solid-state Pro ring conformations have also been reported,[7,18] whereas the ring conformation of crystalline hydroxy-L-proline has been determined[11] to be C_γ exo (with $\chi_2 = 17°$), while the solid-state poly(Hyp) X-ray data[19] are also consistent with a C_γ-exo ring conformation. Hence, the available data indicate that Pro C_γ-exo and C_γ-endo ring conformations have about equal energies, while the C_γ-exo conformation has lower energy in the Hyp ring.[20]

(3) Interaction of the Hyp Ring with the Peptide Backbone. Mattice and Mandelkern[10] have suggested that an interaction of the Hyp ring and the peptide backbone may occur in poly(Hyp-Gly), arguing that the low-temperature poly(Pro) type CD observed for poly(Hyp-Gly), but not for poly(Pro-Gly), might be due to ordered structure resulting from hydrogen bonding of a Hyp OH with the C=O moiety of the preceding Hyp residue. A portion of a poly(Hyp) chain, having an analogous OH···O=C hydrogen bond, is illustrated in III.



III

The residue rotation angles in conformation III have the values $\varphi_2 = \varphi_3 = 120°$, $\psi_2 = 280°$, $\omega_1 = \omega_2 = 0°$, (*i.e.*, trans peptide bonds), and the Hyp ring angles are those obtained from the nmr analysis. As noted previously,[10] models indicate that a strong OH···O=C hydrogen bond is obtained only if (a) the Hyp ring is significantly exo puckered at C_γ ($\chi_2 \gtrsim 30°$) and (b) the residue rotation angles assume the values $\varphi_2 \approx 120°$, $\psi_2 \approx 280°$. The O_3–O_1' distance is *ca.* ±0.3 Å of the optimum value,[21] 2.7–2.8 Å, when φ_2, ψ_2 are restricted to $\varphi_2 = 120 \pm 20°$, $\psi_2 = 280 \pm 10°$.

(16) It is seen in Table I that a single nonzero long-range coupling, $J_{\beta 1\delta 1}$ was used in simulating the spectra of the amino acid and poly(Hyp). In the case of the amino acid, the small line widths permitted direct measurement of $J_{\beta 1\delta 1}$, while inclusion of this coupling in the present case accounts, in part, for the observation that $H_{\beta 1}$ and the H_δ's have slightly broader lines than the other poly(Hyp) ring protons.

(17) After completing this manuscript, samples of poly(Hyp-Gly) and *tert*-Boc-Gly-Hyp-OH were obtained, and 220-mHz spectra of these compounds reveal that all Hyp ring couplings are in agreement (to within 1 Hz) with the poly(Hyp) values in Table I. These results support the view that the C_γ exo conformation is generally the predominant Hyp ring conformation in solution.

(18) Y. C. Leung and R. E. Marsh, *Acta Crystallogr.*, **11**, 17 (1958).

(19) V. Sasisekharan, *ibid.*, **12**, 897, 903 (1959).

(20) Hyp and Pro ring conformations not exhibiting C_γ puckering have been reported for cyclo(Pro-Pro-Hyp) benzoate and cyclo(tri-Pro), respectively. In both instances the rings were found to pucker at the ring nitrogen atom, due to the unusual peptide backbone structure resulting from steric constraints and planar cis peptide bonds.

(21) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman, San Francisco, Calif., 1960, p 282.

These φ, ψ values approximate those found for the helical forms of poly(Pro) and poly(Hyp), and the stabilizing side chain–backbone interaction depicted in III may account for the observation[9] that higher concentrations of $CaCl_2$ are required to disrupt the poly(Hyp) helix. It is stressed that this conclusion is tentative, since interaction of the OH and C=O moieties with water molecules or ions may be at least as strong as the proposed OH···O=C hydrogen bond. The nmr analysis shows only that the Hyp ring assumes the conformation required for formation of an intrachain hydrogen bond. Additional evidence that an increase in stability of helical polypeptide structure results on replacing Pro by Hyp is needed to (a) verify the presence of such bonds and (b) determine the extent that they stabilize, at least locally, a poly(Pro)-type chain conformation.[22]

Acknowledgments. I am grateful to Dr. D. Rabenold and Professor L. Mandelkern of the Florida State University for their gift of the molecular weight characterized sample of poly(Hyp) used in this work and to Mr. R. L. Kornegay of Bell Laboratories for providing the computer program used to simulate the spectrum. The poly(Hyp-Gly) sample was provided by Professor D. F. DeTar of the Florida State University while *tert*-Boc-Gly-Hyp-OH was obtained from Dr. C. M. Deber and Professor E. R. Blout of the Harvard Medical School.

(22) Evidence for Hyp ring–peptide backbone interactions in polypeptides of the form poly(Gly-X-Hyp) would be of particular interest with respect to the role of Hyp in collagen. Pro and Hyp residues in α_1 chains of rat skin collagen occur almost exclusively in triplets Gly-Pro-X and Gly-X-Hyp, respectively, where X is usually not Hyp or Pro.[23] Hence, it is possible for a Hyp residue in the third position to hydrogen bond to the preceding Gly C=O, and stabilize a poly(Pro) type local backbone conformation. It may be noted that in the native collagen molecule a Hyp residue on the second position of the triplet could not perform an analogous function, since the C=O of the third residue in the preceding triplet participates in an interchain hydrogen bond with a Gly NH.[23]

(23) W. Traub and K. A. Piez, *Advan. Protein Chem.*, **25**, 243 (1971).

Electron Spin Resonance in Crystallizable, High Molecular Weight Polyphenylacetylene[1a]

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ABSTRACT: The thermally activated paramagnetism which appears when crystalline polyphenylacetylene is annealed at successively higher temperatures is introduced irreversibly, if the temperature of the order–disorder transition at about 120° (T_c) is not exceeded. Upon cooling below the annealing temperature the esr signal intensity always displays a Curie dependence. A thorough search for triplet spectra was unsuccessful. It is suggested that the unpaired spins are diradicals which originate from π electrons released in the rupture of skeletal π bonds. Although the Curie dependence shows that the paramagnetism does not result from a lattice-independent electronic excitation, the diradicals can be viewed as pairs of "bond-alternation defects" which must have some mobility (Pople and Walmsley).

Studies of electron spin resonance (esr) in polyphenylacetylene prepared by thermal polymerization (PPA-T) and by transition metal catalysts (PPA-C) had established that the paramagnetism of this polymer cannot be associated with a chemical impurity, but must be intrinsic to the molecular structure.[2] The increase in the concentration of unpaired spins per unit sample weight (N_s) when freshly prepared PPA-C was heated represented a sharp contrast to the behavior of other conjugated polymers,[3,4] and the change in character of the temperature dependence of N_s near the temperature where X-ray diffraction indicated an order–disorder transition suggested that at least some of the paramagnetism was associated with irregular chain conformations. Whereas the former phenomenon, *i.e.*, the thermally activated paramagnetism, was consistent with an electronic excitation, the latter indicated the presence of what might be termed "conformational defects." The structural and dynamic aspects of the two phenomena appeared to be distinct and would, it seemed, have to be associated with different mechanisms of electronic conductivity.

The "bond-alternation defect" model of Pople and Walmsley,[5] which allows the rapid migration of an electronic excitation, provides perhaps the only mechanism capable of accounting for both electronic conductivity and a thermally activated paramagnetism in polyenes in terms of simple structural concepts. It seemed, initially, that this attractive model would have to be ruled out for PPA, if the paramagnetism were found to be wholly attributable to changes in the electronic properties of the ground state. In either case, it seemed important to determine whether the paramagnetism in PPA was associated with disordered molecules (conformational defects), with electronic excitations, or both, and, if possible, to obtain additional information about the structure of the centers of paramagnetism.

Experimental Section

The polymer samples used in this study had been obtained by Kern by polymerizing PPA in tetralin in the presence of a rhodium trichloride–lithium borohydride catalyst.[6] PPA prepared with other transition metal catalysts by Kern and also in this laboratory,

(1) (a) Based in part on the Master's thesis of G. M. Holob; (b) Department of Chemical Engineering; (c) Department of Chemistry.

(2) (a) P. Ehrlich, R. J. Kern, E. D. Pierron, and T. Provder, *J. Polym. Sci., Part B*, **5**, 911 (1967); (b) P. Ehrlich, *J. Macromol. Sci.-Phys.*, **2**, 153 (1968).

(3) A. A. Berlin, *J. Polym. Sci.*, **55**, 621 (1961).

(4) M. Nechtschein, *J. Polym. Sci., Part C*, **4**, 1367 (1965).

(5) J. A. Pople and S. H. Walmsley, *Mol. Phys.*, **5**, 15 (1962).

(6) R. J. Kern, *J. Polym. Sci., Part A-1*, **7**, 621 (1969).