Structure of Anionic Poly(2-phenylbutadiene)

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ABSTRACT: The anionic solution polymerization of 2-phenylbutadiene and the influence of various polar modifiers on the microstructure of the resulting polymers were investigated. Although polar modifiers increase the vinyl content of these polymers, there is an upper limit of about 50% vinyl repeat units which can be obtained. The reason for such a limit is the high steric hindrance associated with 1,2 structural units forcing them to alternate with 1,4 units during polymerization. Intramolecular cyclization reactions involving 3,4 structural units occur during the polymerization of 2-phenylbutadiene in polar media. This has been verified by examination of the mass spectra of the ozonolysis products of polymers prepared in tetrahydrofuran using hexamethylphosphoramide modifier. Poly(2-phenylbutadienes) containing about 50% vinyl repeat units were molded with peroxide curing agents at various temperatures. Degradation reactions are much more prevalent during peroxide molding of these polymers than the expected cross-linking reaction.

Although some studies have been done on the preparation of poly(phenylbutadienes) by various techniques,[1-4] little information is available on the anionic solution polymerization of these monomers. In this study we have investigated the anionic solution polymerization of 2-phenylbutadiene and the influence of various polar modifiers on the microstructure of the resulting polymers. The 1,2, 3,4, and 1,4 contents of these polymers were examined by infrared and nuclear magnetic resonance spectroscopy. Ozonolysis of the polymers combined with mass spectra of the ozonides was used to study the presence of cyclic structures.

Polybutadiene, particularly when it contains a high proportion of 1,2 repeat units, can be cross-linked efficiently with peroxide catalyst to obtain hard thermosetting resins.[5] We have also investigated the peroxide curability of poly(2-phenylbutadiene) and found that it behaves much differently during peroxide cure than its polybutadiene analogs. The experimental results of both the microstructure and curing studies will be presented and discussed.

Experimental Section

Reagents. 2-Phenylbutadiene was prepared according to the method of Marvel and Woolford.[6] The distilled monomer was stored over calcium hydride at −30° and used as needed.

Tetrahydrofuran (THF), cyclohexane, methoxybenzene (anisole), and triethylene glycol dimethyl ether (triglyme) were purified by distillation in the presence of sodium metal. The latter was distilled at 103° (10 mm). Hexamethylphosphoramide (HMPA) and tetramethylethylenediamine (TMEDA) were distilled from calcium hydride. The HMPA was distilled at 98–100° (6 mm).

Dicumyl peroxide (98% active) was obtained from Hercules Inc., while benzoyl peroxide was obtained from Matheson Coleman and Bell. Both were used without further purification. A solution of butyllithium was obtained from Lithium Corp. of America. Analysis of this initiator was accomplished using the Gilman double titration procedure.[7,8]

Polymerization. 2-Phenylbutadiene was anionically polymerized with butyllithium under a variety of conditions. In a typical run, 4 g of monomer was added to a 3:1 volume ratio of cyclohexane and anisole. The appropriate amount of butyllithium was then added and polymerization was allowed to proceed for 2 hr at room temperature. All subsequent homopolymerizations were run in THF containing various polar modifiers at −78° for 1.5 hr. Conversion was always quantitative.

Compounding and Molding. The homopolymers were compounded by dissolving in chloroform containing the prescribed amount of peroxide. The chloroform was removed under vacuum and the dried resins were molded at the desired temperature through ten half-lives of the particular peroxide.[9]

Polymer Characterization. Nmr spectra were measured at 60 MHz for all polymers in CCl_4 at room temperature to investigate microstructure and copolymer composition. Peak areas of signals for aromatic protons as well as for terminal and nonterminal olefinic protons were determined and analyzed according to the method of Senn.[10a] Infrared spectra were measured on a Perkin-Elmer 337 grating infrared spectrophotometer. The polymers were examined as films cast from chloroform solution. All films were of 1.3-mil thickness.

Molecular weight measurements were made on a Mechrolab Model 502 high-speed membrane osmometer and on a Mechrolab Model 302 vapor-phase osmometer. The vapor-phase osmometer was used on all samples with molecular weights less than 15,000 g/mol. Intrinsic viscosities were measured in toluene at 25°.

An AEI Model MS12 mass spectrometer recorded the mass spectra of the ozonized polymers. An ionizing electron energy of 14 eV and an ion source temperature of 200° were used to obtain the parent peaks for most major components. Parent peaks of the cyclic fragments were obtained at 70 eV and 300° because of their low volatility.

Ozonolysis was carried out according to the method of Beroza and Bierl.[10b]

Results and Discussion

Preparation and Characterization of Polymers. Polymerization conditions as well as some of the characteristics of the homopolymers examined are listed in Table I. Figure 1 illustrates the infrared spectra of two of the samples listed in Table I. The sharp band at 867 cm^{-1} has been ascribed totally to the 3,4 structural unit, while the band at 1007 cm^{-1} is characteristic of the 1,2 structural unit.[4] The band of moderate intensity at 913 cm^{-1} also characterizes the 1,2 structural unit; however, this last band is interfered with by a band inherent to the polymer which Smets[4] has shown to remain even after bromine saturation.

(1) J. K. Stille and E. D. Vessel, *J. Polym. Sci.*, **49**, 419 (1961).
(2) A. Z. Shikhmamedbekova and S. I. Sodykh-Zada, *Azerb. Khim. Zh.*, 73 (1962).
(3) P. de Radzitzki and G. Smets, *Bull. Soc. Chim. Belg.*, **62**, 320 (1953).
(4) P. de Radzitzki, M. C. de Wilde, and G. Smets, *J. Polym. Sci.*, **13**, 477 (1954).
(5) W. L. Hergenrother, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **11**, 834 (1970).
(6) C. S. Marvel and R. G. Woolford, *J. Org. Chem.*, **23**, 1658 (1968).
(7) H. Gilman, *et al.*, *J. Amer. Chem. Soc.*, **66**, 1515 (1944).
(8) H. Gilman, *et al.*, *ibid.*, **83**, 4089 (1961).
(9) G. E. Mapstone, *Chem. Proc.*, **26**, 347 (1963).
(10) (a) W. L. Senn, Jr., *Anal. Chim. Acta*, **29**, 505 (1963); (b) M. Beroza and B. A. Bierl, *Anal. Chem.*, **39**, 1131 (1967).

TABLE I
POLYMERIZATION OF 2-PHENYLBUTADIENE

Sample no.	Solvent	Catalyst, modifier	Modifier/ catalyst, mol ratio	Polym time, min	Polym temp, °C	$[\eta]$, dl/g
1	Cyclohexane–anisole[a]	BuLi, none	0	120	25	0.09
2	THF	BuLi, none	0	90	−78	0.26
3	THF	BuLi, triglyme	50	90	−78	0.16
4	THF	BuLi, HMPA	50	90	−78	0.48

[a] 75:25 volume ratio of cyclohexane to anisole. The polymer was insoluble in pure hydrocarbons.

TABLE II
MICROSTRUCTURE OF POLY(2-PHENYLBUTADIENE)

Sample no.	OD ratio[a]	3,4, %	Nmr ratio terminal/ nonterminal olefinic H	1,2, %	Total vinyl, %
1	1.06	7.4	0.16	0	7.4
2	0.72	5.0	0.94	40	45
3	0.76	5.3	1.02	43	48
4	0.75	5.2	1.10	47	52

[a] Optical density ratio of the 867-cm^{-1} band to the 1078-cm^{-1} band corrected for the base line at 815 cm^{-1}.

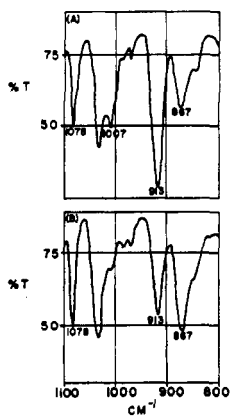


Figure 1. Infrared spectra of poly(2-phenylbutadiene): (A) polymer prepared in polar media, (B) polymer prepared in cyclohexane–anisole mixture.

For the polymer prepared in THF–HMPA solution, there is a band of moderate intensity at 1007 cm^{-1}. This band has essentially disappeared for the polymer prepared in the cyclohexane–anisole mixture. This indicates a much higher 1,2 content for the THF–HMPA polymer than for that prepared in cyclohexane–anisole. In addition, the band at 867 cm^{-1} for the THF–HMPA polymer has decreased slightly in intensity when compared with that of the cyclohexane–anisole polymer. This indicates that the 3,4 content of the polymer prepared in cyclohexane–anisole is slightly higher than that of the polymer prepared in the highly polar medium.

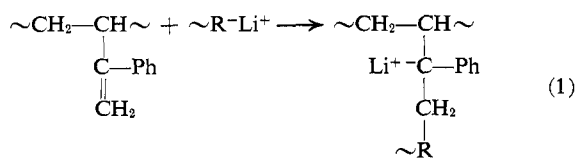
Table II characterizes the polymers listed in Table I according to microstructure. The numbers listed in the second column of Table II were determined directly from the infrared spectra. These values were used as a measure of the relative concentration of 3,4 structural units in the various polymers. The band at 1078 cm^{-1} is assigned to a monosubstituted benzene[11] and was used as an internal standard since it is unaffected by variations in olefinic microstructure. If it is assumed from the absence of an absorption band at 1007 cm^{-1} that the polymer prepared in cyclohexane–anisole (sample 1) contains no 1,2 structural units, then nmr analysis can be used to determine the actual 3,4 content of sample 1. This is accomplished by applying Senn's method[10a] for obtaining total vinyl microstructure from the ratio of terminal to nonterminal olefinic hydrogens (column 4). Actually, there is a small shoulder at 1007 cm^{-1} in the ir spectrum of sample 1, indicating a small amount of 1,2 structure. However, even if one assumes that the vinyl content of sample 1 is entirely composed of 1,2 units, the total vinyl content (column 6) as calculated by nmr becomes 7.9%. This is only 0.5% higher than the value which we obtained in Table II. Since it is obvious from the absorption band at 867 cm^{-1} that the vinyl content of sample 1 is largely composed of 3,4 units, the assumption that no 1,2 units exist in sample 1 leads to only a very small error. The 3,4 content of sample 1 provides a calibration of the optical density ratio so that the 3,4 contents (column 3) as well as total vinyl microstructures (column 6) can be calculated for all of the other polymers examined. The difference between total vinyl and 3,4 content is a measure of the 1,2 content of each polymer (column 5).

The polymerization of diene monomers in hydrocarbon–anisole mixtures has historically produced polydienes containing low vinyl contents.[12] Poly(2-phenylbutadiene) is no exception, as is seen from its low vinyl content listed in Table II. On the other hand, polar solvents such as THF and polar modifiers such as HMPA and triglyme traditionally produce polydienes containing a high proportion of vinyl units.[13–15] It can be seen from the data in Table II that regardless of polymerization conditions, about 50% vinyl content is the upper limit for vinyl microstructure in poly(2-phenylbutadiene). This can be explained, however, by the high steric hindrance associated with the 1,2 structural unit. This steric hindrance necessitates the alternation of 1,2 and 1,4 structural units.[4] It should be pointed out that the small quantity of vinyl microstructure in sample 1 of Table II is composed almost entirely of 3,4 structural units. A possible explanation of this is that at room temperature in a nonpolar medium such as cyclohexane–anisole, 1,2 growing anions, if formed, can readily convert to 1,4 structural units. The driving force for this conversion is the relief of steric

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Wiley, New York, N. Y., 1954, p 65.
(12) A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.*, **40**, 73 (1959).
(13) French Patent 1,388,577, Feb 5, 1965, Esso Research and Engineering Co.
(14) A. Kh. Bagdasaryan, B. A. Dolgoplosk, and V. M. Froloo, *Dokl. Akad. Nauk SSSR*, **185** (4), 860 (1969).
(15) British Patent 1,066,667, Phillips Petroleum Co.

hindrance obtained by the shifting of the 1,2 anion to an unhindered terminal carbon atom. Such a shift enables the terminal anions to associate in solution, behavior quite common for growing anions in nonpolar media.[16] No similar driving force exists with 3,4 structural units.

A further look at the nmr spectra shows that the ratio of olefinic hydrogens to aromatic hydrogens does not agree with that expected from the microstructures of those polymers prepared in polar media. These results are tabulated in Table III. The found values in column 6 were obtained directly from the nmr spectra, while the calculated values in column 5 were calculated from the microstructures determined simply by dividing column 6 by column 5. It is apparent from the above table that some residual unsaturation that should be present in the polymers prepared in polar media has been destroyed during polymerization. There are two likely possibilities that consume unsaturation during polymerization. Since the 3,4 repeat unit in poly(2-phenylbutadiene) is structurally similar to an α-methylstyrene unit, one would expect it to be vulnerable to anionic attack. If such attacks occur intermolecularly, carbon–carbon covalent bonds would be formed between adjacent polymer chains as shown in (1). Such reactions would quickly result in chemical cross-linking and subsequent gel. Since there was no evidence of even small quantities of gel in any of our polymers, this possibility must be ruled out. The alternative is the intramolecular cyclization of 3,4 structural units. The possibilities for intramolecular cyclization occur when a 3,4 structural unit is followed by a growing anion in any of the three structural configurations, *i.e.*, 1,2, 3,4, or 1,4. These possibilities are shown in Figure 2.



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The cyclization reaction shown in example V of Figure 2 is unlikely, since it results in the formation of a seven-membered ring VI. Both examples I and III, however, result in the formation of five-membered rings, a situation made possible by the close proximity of the growing anion and the 3,4 structural unit before ring closure. This makes these latter possibilities very real. If the intramolecular cyclization reactions postulated in Figure 2 do indeed occur, then one would expect a lower olefinic content for poly(2-phenylbutadienes) containing high concentrations of vinyl units than for 1,4-poly(2-phenylbutadienes). The results listed in Table III show this to be the case. In addition, since the cyclization reactions consume 3,4 structural units, it is not surprising that the measured vinyl content for all polymers prepared in polar media is largely composed of 1,2 structural units.

Ozonolysis of Poly(2-phenylbutadienes). In an effort to establish the presence of cyclic structures along the poly(2-phenylbutadiene) chains as well as to recheck the internal structure for alternation, ozonolysis of samples 1 and 4 in Table I was carried out and the ozonolysis products were examined by mass spectrometry. The ozonolysis of different structures of poly(2-phenylbutadienes), *i.e.*, variations in microstructure as well as head-to-tail and head-to-head additions, should give a variety of scission products as indicated in VII. Scission may occur at positions a, b, c, and d. For 1,4-poly(2-phenylbutadiene), R is simply a single bond. The other possibilities are R equal to a 1,2 or 3,4 structural unit. If cyclization occurs when a 3,4 unit is followed by the 1,2 configuration, R becomes II; however, if cyclization occurs when a 3,4 unit is followed by the 3,4 configuration, then R is IV. The various ozonides which could occur upon ozonolysis of structure VII are listed in Table IV. The first value for molecular weight listed in column 4 is characteristic of the aldehyde product obtained on reductive work-up of the ozonolysis products. The numbers in brackets refer to the various oxidative products obtained when the aldehydes are partially or totally oxidized. Although a reductive work-up was used in this study, conditions were such that partial or total oxidation of the ozonolysis products could have occurred before the mass spectra were obtained. The case of R equal to a 3,4 structural unit has been omitted in Table IV, since this sequence gives the same molecular weights as when R is a 1,2 unit. In addition, the cyclic structures shown in Table IV are those which occur from structure I of Figure 2. The cyclic structures possible from structure III of Figure 2 have also been omitted, since they have the same molecular weights as the cyclic structures listed.

(16) M. Morton, L. J. Fetters, and E. E. Bostick, *J. Polym. Sci., Part C*, No. 1, 311 (1963).

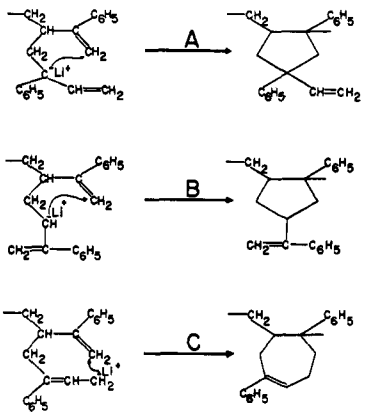

Figure 2. Intramolecular cyclization in poly(2-phenylbutadiene): (A) 3,4 unit (I) followed by 1,2 configuration (II), (B) 3,4 unit (III) followed by 3,4 configuration (IV), (C) 3,4 unit (V) followed by 1,4 configuration (VI).

TABLE III
OLEFINIC TO AROMATIC PROTON RATIOS FOR POLY(2-PHENYLBUTADIENE)

Sample no.	% microstructure 1,4	1,2	3,4	Nmr olefinic H/aromatic H Calcd	Found	% found
1	93	0	7.4	0.21	0.20	95
2	55	40	5.0	0.37	0.29	78
3	51	43	5.3	0.39	0.30	77
4	48	47	5.2	0.40	0.29	72

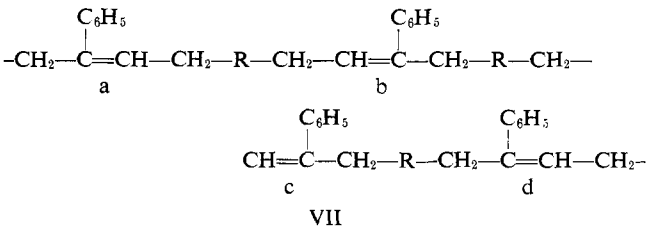

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TABLE IV
OZONOLYSIS PRODUCTS OF POLY(2-PHENYLBUTADIENES)

R	Bonds cleaved	Product obtained: No.	Product obtained: Structure	Mol wt of product, g/mol
	a and b	VIII	$OCH(CH_2)_2CHO$	86 [102] [118]
	b and c	IX	$O{=}C(C_6H_5)(CH_2)_2CHO$	162 [178]
	c and d	X	$O{=}C(C_6H_5)(CH_2)_2(C_6H_5)CO$	238
1,2 unit	a and b	XI	$OCH(CH_2)_2\underset{\displaystyle CHO}{\underset{\vert}{C}}(C_6H_5)CH_2CHO$	218 [234] [250] [266]
1,2 unit	b and c	XII	$O{=}\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}(CH_2)_2\underset{\displaystyle CHO}{\underset{\vert}{C}}(C_6H_5)CH_2CHO$	294 [310] [326]
1,2 unit	c and d	XIII	$O{=}\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}(CH_2)_2\underset{\displaystyle CHO}{\underset{\vert}{C}}(C_6H_5)CH_2\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}O$	370 [386]
Cyclic	a and b	XIV	$OCH(CH_2)_2CH(C_6H_5)CH_2CHO$ CH_2 CH_2 $C(C_6H_5)CHO$	348 [364] [380] [396]
Cyclic	b and c	XV	$O{=}\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}(CH_2)_2CH(C_6H_5)CH_2CHO$ CH_2 CH_2 $C(C_6H_5)CHO$	424 [440] [456]
Cyclic	c and d	XVI	$O{=}\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}(CH_2)_2CH(C_6H_5)CH_2\underset{\displaystyle C_6H_5}{\underset{\vert}{C}}{=}O$ CH_2 CH_2 $C(C_6H_5)CHO$	500 [516]

TABLE V
OZONOLYSIS OF 1,4 AND 50% VINYL
POLY(2-PHENYLBUTADIENES)

Sample no.	% microstructure 1,4	1,2	3,4	Mol wt obsd in mass spectra, g/mol
1	93	0	7.4	[178] 238 294
4	48	47	5.2	[178] [234] [250] 294 [310] 370 [364] [380] 424 500

The data obtained from the mass spectra of the ozonolysis products of samples 1 and 4 of Table I are listed in Table V. There were no P + 130 peaks observed in the entire spectra, indicating complete ozonolysis of the polymers.

The above data establish the presence of cyclic structures along the poly(2-phenylbutadiene) chain. In addition, they show the alternation of 1,4 and 1,2 structural units. The molecular weights [234] [250], 294 [310], and 370 (structures XI, XII, and XIII) observed for sample 4 are consistent with what one might expect from alternating 1,4 and 1,2 structural units in poly(2-penylbutadiene). The peaks at [364] [380], 424, and 500 (structures XIV, XV, and XVI) are representative of the cyclic structures discussed in Table IV. Molecular weights [178] and 238 (structures IX and X) for sample 1 are what one would expect for 1,4-poly(2-phenylbutadiene) containing head-to-tail and tail-to-tail linkages, respectively. The 86 [102] [118] peaks (structure VIII) corresponding to head-to-head linkages were difficult to observe. This structure must be present, since tail-to-tail linkages do not exist in the absence of head-to-head structures. The 238 peak, corresponding to tail-to-tail linkages, was detected only in high-voltage spectra. This detection was facilitated by the lack of interfering fragments in this region, a situation which did not exist in the 86 [102] [118] region. The weak peak at 294 (structure XII) can be explained by the small quantity of 3,4 structural units present in this polymer. The weak peak at molecular weight [178] in sample 4 indicates the presence of a small amount of 1,4–1,4 linkages. Peaks at 76 corresponding to carbon disulfide, the ozonolysis solvent, and 278 corresponding to triphenylphosphine oxide produced in the reductive work-up were also clearly identified. Although it is difficult to quantitatively assign a relative importance to each mass peak, it appears that the [178] peak was the major component in sample 1 while the 294 peak was the major component in sample 4.

TABLE VI
PEROXIDE TREATMENT OF POLY(2-PHENYLBUTADIENE)

Sample no.	Peroxide[a]	Molding temp, °C	Soluble material after molding, %	$\bar{M}_n$, g/mol × 10^{-3}	Nmr olefinic H/aromatic H
4	0			77	0.29
4A	1 (dicumyl)	135	80	25	0.25
4B	2 (dicumyl)	135	68	18	0.17
4C	6 (dicumyl)	177	50	1.3	0.17
4D	6 (benzoyl)	91	100	4.5	0.25

[a] Parts per hundred parts polymer.

Peroxide Treatment of Poly(2-phenylbutadiene). It is well established that polybutadienes containing a high proportion of 1,2 structural units can be peroxide cured to hard thermosetting resins.[5] The cross-linking reaction is of very high efficiency, presumably because it occurs *via* a chain polymerization type mechanism in which several double bonds are consumed by each peroxide molecule.[17] Table VI lists the results obtained when a poly(2-phenylbutadiene) containing about 50% vinyl units is molded with various amounts of peroxide.

Sample 4 was not molded, but is listed in Table VI as a control. The characterization data for this polymer are listed in Tables II and III. The numbers in the fourth column of Table VI were obtained by extracting the molded samples with hot toluene overnight. The molecular weight values in column five were measured on the soluble portions of the molded polymers. When dicumyl peroxide was employed, dramatic decreases in molecular weight with increasing peroxide loadings were observed. In addition, the concentration of olefinic protons decreased with increasing peroxide levels. When benzoyl peroxide was used, no gel was obtained after molding. However, decreases in both molecular weight and olefinic proton concentration were noted. These results indicate that polymer degradation occurs readily during the peroxide molding of poly(2-phenylbutadiene). This is in sharp contrast to the peroxide treatment of high vinyl polybutadiene, which produces highly cross-linked thermosetting resins.[5]

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(17) B. M. E. Van Der Hoff, *Ind. Eng. Chem., Prod. Res. Develop.*, 2 (4), 273 (1963).

Conformational Properties of Polypropylene[1]

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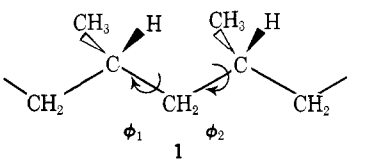
ABSTRACT: Conformational energy calculations have been carried out on 2,4,6-trimethylheptane as a model for polypropylene using energy minimization with all internal degrees of freedom allowed to participate. Previously developed energy functions were used. The conformational energies are well represented by a simple model (identical with one proposed by Flory, Mark, and Abe) with gauche main-chain interactions (E_g = 400 cal), skew methyl interactions (E_{SK} = 600 cal), and excess "pentane interference" interactions (E_ω = 1300 cal). The latter agrees well with both the experimental and our calculated value for the similar interaction in polyethylene. Calculations of characteristic ratio and its temperature coefficient are made over a range of values of E_ω (0–3000 cal) and over the complete range of tacticities (replication probability 0.0–1.0). The calculated characteristic ratios of isotactic and atactic polymer for the conformational energies deduced in our work are in good agreement with experimental values. We conclude that there is no necessity for assuming stereoirregularity in the isotactic form to obtain agreement with experiment for the characteristic ratio or its temperature coefficient. Profiles for the least energy path for bond rotation in the isotactic and syndiotactic forms were calculated.

The conformational properties of polypropylene have aroused considerable interest ever since the discovery of the stereospecific polymerization of propylene. Because of steric repulsions between methyl groups and methyl groups and the chain backbone, inspection of models leads to the expectation that there should be a marked preference for certain sequences of conformations of the skeletal bonds. For example, the isotactic form should prefer repeated TG sequences or repeated G′T sequences (see Table I) for bonds 1 and 2 of **1**. The syndiotactic form should prefer repeated



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TTTT, TTGG, or G′G′TT sequences for bonds 1, 2, 3, and 4 of **2**. These expectations are confirmed by the conformations in the crystalline forms of these polymers.[2,3] The degree

(1) Presented at the Meeting of the Division of Polymer Chemistry, American Chemical Society, April 9–14, 1972, Boston, Mass.

(2) G. Natta, P. Corradini, and P. Ganis, *Makromol. Chem.*, **39**, 238 (1960).

(3) G. Natta, P. Corradini, and P. Ganis, *J. Polym. Sci.*, **58**, 1191 (1962).