Numerical Results

Numerical results for three sets of statistical weight parameters are presented in Table III. These sets are the ones arbitrarily chosen in Flory's original work,[2] and they use the matrices in eq 2–4 with $\omega = 0$; i.e., the order of the **U** matrices is reduced to 2×2. For given sequence lengths m, the solution for the smallest chain length $x = m$ was computed by hand and is exact, solutions for longer chains were obtained by numerical methods, and values for infinite chains were obtained by successive squaring of $\hat{W}_q$. Values for $m = 2$ and 3 are identical with Flory's results.[2]

In general, the conformational partition function of a chain as a whole cannot be factorized into separate contributions from independent substructures.[18] This precludes adherence to any type of unidirectional statistics, e.g., of the Markoffian type, although a Bernoullian dyad distribution could be observed in the limit. Deviation of dyad distribution from these common statistics is demonstrated in Table III with the values of quantities often used in testing for given statistics. Testing for Bernoullian statistics is done with[21]

$$4f_{mm}f_{rr}/f_{mr}^2 \tag{21}$$

and with the *persistence ratio*, ρ[22]

$$\rho = 2f_m f_r/f_{mr} \tag{22}$$

where both quantities assume values of unity for Bernoullian dyad distributions. Compliance with a first-order Markoff scheme is checked with Ω[23]

$$\Omega = f_r f_{rrr}/f_{rr}^2 \tag{23}$$

that is unity for Bernoullian and first-order Markoffian statistics. Finally we tabulate values for a quantity

$$f_{mm}f_{mmmm}/f_{mmm}^2 \tag{24}$$

that is unity for Bernoullian and first-order and second-order Markoffian dyad distributions.[21] As is obvious from the numbers in Table III, none of these statistics is appropriate for the description of dyad distribution in vinyl chains at stereochemical equilibrium; the numbers approach unity close enough, however, to make experimental proof of the deviation from these types of statistics only possible in exceptional cases.

References and Notes

(1) Taken in part from the Habilitationsschrift submitted by the author to the ETH Zürich in 1979.
(2) Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 1798–1804.
(3) Clark, H. G. *J. Polym. Sci., Part C* **1968**, *16*, 3455–60.
(4) Williams, A. D.; Brauman, J. I.; Nelson, N. J.; Flory, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 4807–8.
(5) Williams, A. D.; Flory, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 3111–8.
(6) Flory, P. J.; Williams, A. D. *J. Am. Chem. Soc.* **1969**, *91*, 3118–21.
(7) Billups, W. E.; Kurtz, A. N. *J. Am. Chem. Soc.* **1968**, *90*, 1361–2.
(8) Flory, P. J.; Pickles, C. J. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 632–42.
(9) Suter, U. W.; Pucci, S.; Pino, P. *J. Am. Chem. Soc.* **1975**, *97*, 1018–23.
(10) Tien, C. F.; Hogen-Esch, T. E. *Macromolecules* **1976**, *9*, 871–2. *J. Am. Chem. Soc.* **1976**, *98*, 7109–10.
(11) Tien, C. F.; Hogen-Esch, T. E. *J. Polym. Sci., Polym. Lett. Ed.* **1978**, *16*, 297–302.
(12) Suter, U. W.; Schönhausen, U.; Pino, P., in preparation.
(13) Suter, U. W. Ph.D. Dissertation, ETH Zürich, 1973, pp 69–74.
(14) Listner, G. J. U.S. Patent 3 511 824, 1970. Stehling, F. C.; Knox, J. R. *Macromolecules* **1975**, *8*, 595–603. Prosser, T. H. U.S. Patent 4 105 837, 1976; French Patent 2 367 082, 1977 (to Hercules Inc., U.S.A.). Randall, J. C. "Polymer Sequence Determination, Carbon-13 NMR Method"; Academic Press: New York, 1977, pp 24–5.
(15) Shepherd, L.; Chen, T. K.; Harwood, H. J. *Polym. Bull.* **1979**, *1*, 445–50.
(16) Shepherd, L. Ph.D. Dissertation, University of Akron, 1979; *Diss. Abstr. Int. B* **1979**, *40*, 1201.
(17) Suter, U. W.; Neuenschwander, P. *Macromolecules*, following paper in this issue.
(18) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience: New York, 1969; Chapter 6.
(19) Flory, P. J.; Sundararajan, P. R.; DeBolt, L. C. *J. Am. Chem. Soc.* **1974**, *96*, 5015–24.
(20) Tse-Sun Chow In "Handbook of Applied Mathematics"; Pearson, C. E., Ed.; Van Nostrand: New York, 1974; pp 933–4.
(21) Bovey, F. A. "High Resolution NMR of Macromolecules"; Academic Press: New York, 1972; Chapter 8.
(22) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065–75. *J. Polym. Sci., Part A* **1963**, *1*, 3183–97.
(23) Coleman, B. D.; Fox, T. G.; Reinmöller, M. *J. Polym. Sci., Part B* **1966**, *4*, 1029–32.

Epimerization of Vinyl Polymers to Stereochemical Equilibrium. 2. Polypropylene[1]

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ABSTRACT: Isotactic polypropylene was epimerized to stereochemical equilibrium at 270 °C in the melt under a hydrogen atmosphere, using metallic palladium as catalyst. Equilibrium was reached practically without side reactions. The equilibrium frequencies of the various diastereomeric structures comprising five monomeric units (pentads) were measured by ^{13}C NMR spectroscopy and they were found to agree well with predictions based on a rotational isomeric state model with five states per main chain bond. Other investigated properties of the equilibrate are practically identical with those of so-called "atactic" polypropylene. ^{13}C spin–lattice relaxation times (T_1) were measured for all resolved lines in the spectrum. Relaxation times for the methyl pentad signals mmmm and rrrr were compared with the times obtained in isotactic and predominantly syndiotactic samples and were found to be different in the equilibrate and the stereoregular chains. Schilling and Tonelli's as well as Zambelli et al.'s hexad assignments for the methylene carbon bands were both found to agree reasonably well with the spectrum of the equilibrate.

Introduction

To date, polypropylene is the only vinyl polymer whose stereostructure can be experimentally determined unambiguously in terms of completely assigned pentads[2] and which, at the same time, can be epimerized apparently without side reactions.[3,4] For model compounds equilibrium epimerization has been reported.[5] A detailed conformational analysis has been carried out for this polymer.[6]

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Hence, polypropylene seems to be a promising candidate for an experimental test of epimerization equilibrium theory as generalized in the preceding paper,[7] hereafter called I. In this paper we will describe the epimerization of isotactic samples to stereochemical equilibrium and use the equilibrium polymers to test the theoretical predictions. We will then examine the properties of these samples. Finally, the ^{13}C NMR spectra of the equilibrium-epimerized polymers are used to test recent assignments of hexads in the methylene carbon resonance region by Tonelli et al. and Ferro et al.[8–11]

Experimental Part

Isotactic polypropylene was obtained with the Ziegler–Natta-type supported catalyst $TiCl_4/MgCl_2$/ethyl *p*-methylbenzoate/$Al(C_2H_5)_3$ in *n*-heptane at 60 °C. The fraction insoluble in boiling *n*-heptane was found to have a viscosity-average molecular weight $\bar{M}_\eta$ = 395 000, more than 95% isotactic dyads, and a $\bar{M}_w/\bar{M}_n$ (GPC) ratio of ca. 5 (details of procedures are given below). A sample of lower molecular weight was obtained from O. Piccolo and F. Francalanci of Montedison, Italy, that is characterized by $\bar{M}_\eta$ = 115 000 and (m) > 0.95.

Epimerization was carried out in the melt with metallic palladium on charcoal or on aluminum oxide (10% w/w). The type of support was found to have no discernible influence on the results. Equal weights of catalyst and polymer were ground together and, under an atmosphere of 13 bar of hydrogen, kept for the desired time at a temperature of 270 °C in open glass vials in a steel vessel. The reaction was stopped by cooling the steel vessel in ice, and polymer and catalyst were separated by extraction with boiling xylene. After precipitation with methanol the samples were fractionated with boiling solvents in the sequence acetone, ether, *n*-heptane.

360-MHz ^{1}H NMR spectra were measured on a Bruker HXS 360 spectrometer at 140 °C in *o*-dichlorobenzene-d_4 at concentrations of 1.6% (w/v). Hexamethyldisiloxane (HMDS) was used as internal reference. Thirty-six scans were accumulated with a pulse interval of 10 s. The FID was stored in 32K storage locations, using a spectral window of 4000 Hz.

22.63-MHz ^{13}C NMR spectra were measured on a Bruker WH 90 spectrometer at 140 °C in *o*-dichlorobenzene-d_4 at concentrations of 12% (w/v) with HMDS as internal reference. The FID was stored in 16K storage locations; the spectral width was 6000 Hz. Protons were decoupled by using the broad-band noise-decoupling technique. Signal intensities of the broad-band-decoupled spectra were compared with the intensities obtained with gated broad-band decoupling and the differences were used to estimate nuclear Overhauser effects (NOE). The pulse angle was 90° and a pulse interval of 10 s was used. Errors in the measured NOE values due to incomplete relaxation are estimated to be less than 3%.

Spin–lattice relaxation times, T_1, were measured by using the inversion–recovery pulse sequence (180°–τ–90°–τ_a–τ_d), τ_d being 10 s.[12] Experimental data were corrected for imperfect 90° pulse angle (originating in pulse signal offset) according to Gerhards.[13] Estimated confidence limits for the values of T_1 were ca. 5%.

Intrinsic viscosities were obtained in tetralin at 135 °C in Bischoff–Desreux viscosimeters, and the relationship [η] (mL/g) = $0.00124\bar{M}_\eta^{0.96}$ was used.[14] Precision in [η] was 1–2%.

Gel permeation chromatography was used to estimate $\bar{M}_w/\bar{M}_n$. Measurements were performed in 1,2,4-trichlorobenzene at 135 °C on a Knauer chromatograph with a set of columns that allows resolution of polystyrene standards for molecular weights in the range 4800–10 000 000. Correction of the relationship log $\bar{M}$-elution volume was made with the well-known "universal calibration technique", using the intrinsic viscosity-$\bar{M}$ relationships for polypropylene in 1,2,4-trichlorobenzene at 135 °C and for polystyrene under conditions of calibration (THF, 25 °C). Estimates of $\bar{M}_w/\bar{M}_n$ are probably accurate to ±1.

Results and Discussion

Epimerization. Characteristics of the polymers recovered from the epimerization mixtures after reaction times of a few hours were substantially changed from those of the isotactic starting material. The boiling *n*-heptane insoluble fraction quickly disappeared and the corresponding material was found to have been added to the boiling ether soluble fraction (containing usually the so-called "atactic" chains). Average molecular weights of the ether-soluble fraction were markedly smaller than the ones of the starting materials, but after only 1 day the molecular weights had assumed values that did not noticeably change anymore for more than 10 months. The pentad frequency distribution, however, obtained by ^{13}C NMR, still changed after the molecular weights had stabilized and did not settle on the apparent equilibrium values until much later. The "equilibrium" was reached within experimental limits before 52 days under the chosen conditions; some values are displayed in Table I.

Table I
Epimerization of Isotactic Polypropylene at 270 °C in the Melt with Palladium (10% w/w on Charcoal)

reaction time, days	$\bar{M}_\eta$	$(m)^a$	$\bar{M}_w/\bar{M}_n$	
		Sample A		
0	395 000	>0.95	~5	100% *n*-heptane insoluble
52	72 000	0.48	~4	100% ether soluble
171	72 000	0.48	~5	100% ether soluble
328	72 000	0.48	~5	100% ether soluble
		Sample B		
0	115 000	>0.95	*b*	100% *n*-heptane insoluble
63	70 000	0.48	*b*	100% ether soluble

[a] From pentad frequencies obtained from ^{13}C NMR spectra; precision is ca. ±0.01. [b] Not determined.

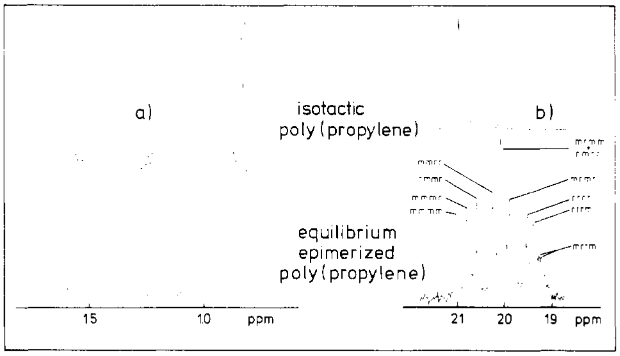

Figure 1. (a) 360-MHz ^{1}H NMR spectrum of the isotactic starting material and the polymer at stereochemical equilibrium after 171 days' reaction time. Spectra measured at 140 °C in *o*-DCB-d_4. (b) 22.6-MHz ^{13}C NMR spectrum of the same samples (140 °C in *o*-DCB-d_4). Only the methyl carbon region is displayed.

One polymer sample was separated from the catalyst after a reaction time of 52 days and treated with fresh catalyst for an additional 119 days. The ^{13}C NMR spectrum measured then could not be distinguished from the spectrum of other samples epimerized with the same catalyst for 52 days or more. It was assumed then that stereochemical equilibrium had been reached with reaction times of less than 52 days.

The ^{1}H resonance spectra and the methyl part of the ^{13}C resonance spectra of isotactic starting material ($\bar{M}_\eta$ = 395 000) and of a sample at stereochemical equilibrium are displayed in Figure 1. Assignment of the methyl carbon signals follows Zambelli et al.[2] The ^{13}C resonance spectra of epimerized samples were recorded under conditions that ensure quantitative linear relationships between spectral

Table II
Dyad Distribution at Stereochemical Equilibrium in Polypropylene at 270 °C

f_q	obsd[a]	calcd
f_{mmmm}	0.05	0.054
f_{mmmr}	0.11	0.116
f_{rmmr}	0.07	0.063
f_{mmrr}	0.11	0.124
f_{mmrm} f_{rmrr}	0.26	0.251
f_{rmrm}	0.12	0.127
f_{mrrm}	0.06	0.063
f_{mrrr}	0.15	0.132
f_{rrrr}	0.07	0.070
f_{mmm}	0.11[b]	0.112
f_{mmr}	0.25[b]	0.242
f_{mrm}	0.12[b]	0.123
f_{mrr}	0.24[b]	0.257
f_{rmr}	0.13[b]	0.130
f_{rrr}	0.15[b]	0.136
f_{mm}	0.23	0.233
f_{mr}	0.49	0.502
f_{rr}	0.28	0.265
f_{m}	0.48[b]	0.484

[a] From carbon resonance in the methyl region; precision ca. ±0.01. [b] Estimated from the experimental values for the pentads. It was assumed that the overlapping pentads mmrm and rmrr contributed to the common band in the same proportion as the calculated values for f_{mmrm} and f_{rmrr}.

intensity and frequency of occurrence of the observed pentads. Numerical resolution of the digital representation of the methyl part of these spectra into nine "Lorentzian" bands of the form

$$I = I_0(1 + 4[\nu - \nu_0]^2 b^{-2})^{-1} \qquad (1)$$

was performed with Fraser and Suzuki's algorithm.[15] I_0 is the peak intensity of the individual band and b is its "full width at half-height"; the integrated intensity of a band is, therefore, equal to $0.5\pi I_0 b$. The signals of the pentads mmrm and rmrr were treated as a single peak. Results thus obtained are tabulated in Table II.

Degradation reactions like the one that obviously is reducing the molecular weights of our polymers during the first hours of the epimerization reaction, apparently to a limit given by the experimental conditions (see Table I), were reported in 1955 by Natta, Pino, and Mazzanti;[16] they observed that the viscosity of solutions of isotactic polypropylene, at temperatures in the vicinity of the one employed here, is quickly reduced to a stable value. It has also been reported that, under reaction conditions similar to ours, this degradation stops at molecular weight averages that increase as hydrogen pressure increases.[4] The mechanisms of the chain-breaking reactions are subject to further study, as is the mechanism of the epimerization reaction that is unknown to date. For the purpose of this paper it is sufficient that stereochemical equilibrium is indeed reached with chains of considerable length ($\bar{x}_\eta \approx 1700$).

Comparison with Theory. Comparison of the experimental results with theory is facilitated by the fact that the epimerization equilibrium has been achieved in the molten state, and with a catalyst that is completely insoluble in the polymer phase. In this melt so-called Θ conditions must exist.[17] The conformational characteristics of polypropylene under conditions where all long-range effects are compensated (i.e., Θ conditions) are such that a five-state rotational isomeric state scheme can be employed.[6] When the matrices given in ref 6 are substituted into eq I-5 and I-9,[18] eq I-10 and I-18 yield the values of the equilibrium frequencies f_q of stereosequences q that are tabulated in Table II, calculated for $x \rightarrow \infty$. Agreement of these theoretical predictions with experiment is quite satisfactory, especially since no adjustable parameters are present in the model.

The agreement between calculation and experiment also supports the concept that the conformer populations in low molecular weight model compounds and in the polymer melt, ceteris paribus, are described by exactly the same model.

Properties of Equilibrium-Epimerized Polypropylene. The equilibrium-epimerized polypropylenes are probably, of all "atactic" samples known to date, the ones that are closest to an idealized polymer with equal numbers of meso and racemic dyads and a Bernoullian dyad distribution (even though they are clearly not *exactly* Bernoullian).[7] Their properties were investigated in order to determine if these samples would in any way distinguish themselves from the traditional "amorphous" polypropylenes, for which the dyad distribution statistics is complex and determined in most cases by the multitude of not identical kinetic processes involved in the polymerization reactions and by the fractionation process used to separate them from the isotactic polymers.

The macroscopic habitus is that of a perfectly colorless, clear rubbery substance. The glass transition temperature, T_g, was found to be −10 °C, the value usually found in conventional amorphous polypropylene. The infrared spectrum of a film also does not differ from the ones of the usual amorphous samples (a possible exception is a weak signal at 886 cm^{-1} that often can be observed in amorphous samples and that is completely absent in our equilibrate).

The equilibrium-epimerized polymer is with certainty statistically homogeneous; this should facilitate interpretation of experimental data for dynamic properties such as the spin-lattice relaxation time, T_1. ^{13}C spin-lattice relaxation was measured for isotactic samples [(m) > 0.95], for the equilibrium-epimerized polymers, and for a preferentially syndiotactic sample [(m) < 0.2] that was kindly provided by A. Zambelli and P. Locatelli. The methyl carbon band is well resolved into nine signals associated with individual pentads;[2] only two pentads overlap. Hence, NOE and T_1 could be measured for all but two pentads individually. The methine carbon band shows only little structure, and values were measured for the band as a whole. The methylene carbon band is resolved into signals not only from tetrads but also from hexads,[8-11] but these signals overlap to form only few well-separated domains (cf. seq.). We arbitrarily separated the region into four sections, A, B, C, and D, as indicated in Figure 2; values for NOE and T_1 were obtained for these sections. Experimental values are displayed in Table III.

The nuclear Overhauser effect is about the same for all samples and nuclei and assumes almost its maximal value. The ratio $T_1(\mathrm{CH})/T_1(\mathrm{CH_2})$ falls in the interval 1.6–1.9, indicating that the processes relevant to relaxation could be anisotropic motions of chain segments or that the distributions of correlation times could be unusually broad.[19,20] The values of T_1 are different in the isotactic and syndiotactic chains (this fact has already been reported for a few other polymers)[21,22] and are different for the differing stereochemical sequences in the atactic sample. It is interesting to note that also the mmmm pentads in atactic and isotactic chains show different T_1's, as do the rrrr pentads in atactic and syndiotactic chains. These

Table III
Spin–Lattice Relaxation Times of Carbon Nuclei in Equilibrium-Epimerized Polypropylene and Comparison with Isotactic and Syndiotactic Samples[a]

structural unit	stereosequence	T_1, s (NOE) equilibrium epimerized	isotactic	syndiotactic
CH_3	mmmm	2.87 (1.80)[b]	3.16 (1.85)	
	mmmr	3.07		
	rmmr	2.52		
	mmrr	2.79		
	mmrm rmrr	2.91		
	rmrm	2.86		
	mrrm	3.22		
	mrrr	2.93		
	rrrr	2.93		2.69 (1.89)
CH_2	A[c]	0.85 (2.04)[b]		
	B[c]	0.93		0.84 (1.89)
	C[c]	1.00	1.18 (2.00)	
	D[c]	1.00		
CH		1.62 (1.93)	2.12 (1.92)	1.49 (1.90)

[a] In o-dichlorobenzene-d_4 at 140 °C. [b] NOE for all signals was found to be identical within experimental limits. [c] The overlapping methylene carbon resonances were arbitrarily separated into four sections, A, B, C and D, as indicated in Figure 2. B contains rrrrr; C contains mmmmm.

differences clearly exceed the combined experimental errors. There is no straightforward interpretation of the variations in T_1; one can, however, deduce that the dynamic properties in solution are dependent on configurational sequences that are clearly longer than pentads; i.e., relaxation of a given nucleus depends on the configuration of chain segments more than two monomeric units away (along the chain).

All six tetrad and many hexad signals in the methylene carbon region of the ^{13}C NMR spectra have been unambiguously assigned through work recently published by two groups of researchers.[8-11] There is an astonishingly good agreement between the results obtained by both groups, but there are also some distinct differences. Since the equilibrium-epimerized polymer is an atactic polypropylene with unusual, but known, dyad distribution, we will compare its spectrum in what follows with the assignments made by both groups.

Figure 2 displays the methylene region of the spectrum of equilibrium-epimerized polymer. We estimated the equilibrium hexad frequencies for all hexads at 270 °C and obtained the following values: mmmmm, 0.026; mmmmr, 0.056; rmmmr, 0.030; mmmrm, 0.056; mmmrr, 0.061; rmmrm, 0.061; rmmrr, 0.064; mmrmm, 0.029; mmrmr, 0.062; rmrmr, 0.033; mmrrm, 0.060; mmrrr, 0.065; rmrrm, 0.065; rmrrr, 0.068; mrmrm, 0.030; mrmrr, 0.065; rrmrr, 0.034; mrrrm, 0.032; mrrrr, 0.068; rrrrr, 0.036. These values, together with Zambelli et al.'s[10] and Schilling and Tonelli's[11] relative chemical shift data for hexads at 140 °C (the calculated values for 140 °C were kindly provided by Dr. Tonelli) yielded the stick spectra and simulated spectra (with bands according to eq 1 for each hexad, $b = 0.1$ ppm) also included in Figure 2.

This approach is very crude; it assumes that all lines are of Lorentzian shape and of equal width, i.e., that the octad broadening of all hexads is identical. Despite this fact, both simulations reproduce the overall features of the experimental spectra quite well. The hexad spacing in the "triplet" associated with mrm (section D in Figure 2) is better reproduced by Schilling and Tonelli's data, but the lines associated with the rmr tetrad (section A in Figure 2) are better placed by Zambelli et al.'s calculations. Schilling and Tonelli clearly estimated mrmrm to be closer to mrmrr than it is. Their calculations, however, leave the fifth line from the low-field end of the spectrum, mrrrr, rather isolated, in agreement with the experimental spectrum, while Zambelli et al.'s results suggest that it should be at higher field, closer to rmmrm. The rest of section B, containing rrrrr and all lines of mmr, is estimated to have a similar shape by both groups, in essential agreement with the experiment. The predictions differ somewhat for section C, most dramatically in the position of mmmmm, although both estimates yield the location of the maximum amplitude very accurately. Schilling and Tonelli place the main band area on the high-field side of this maximum; Zambelli et al. place it on the low-field side. The experiment seems to indicate a line spacing between the two predictions.

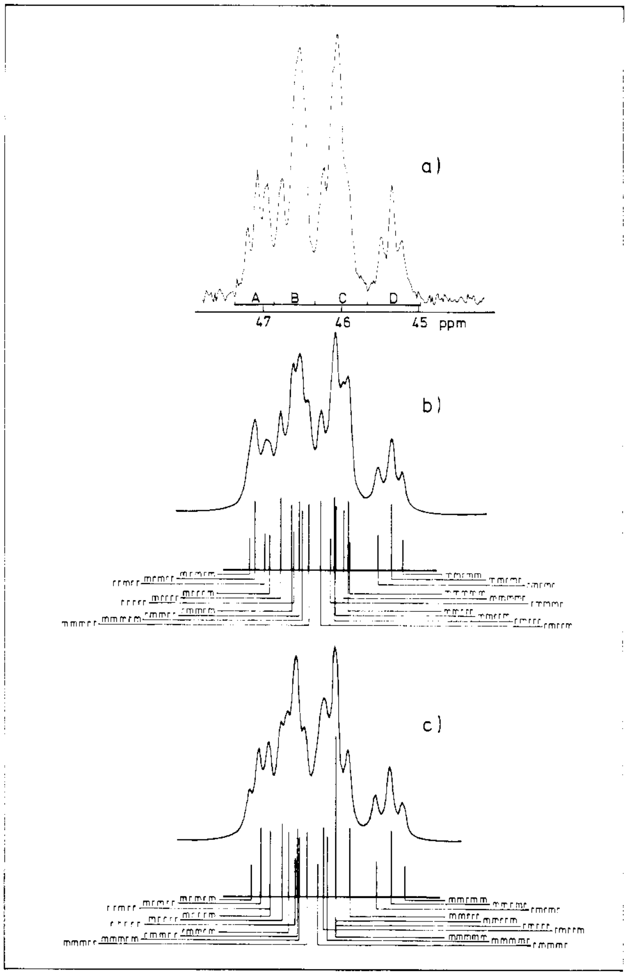

Figure 2. Methylene carbon region of the 22.6-MHz ^{13}C NMR spectrum of polypropylene at stereochemical equilibrium: (a) experimental spectrum; (b) prediction with Schilling and Tonelli's shift data; (c) prediction with Zambelli et al.'s shift data (see text for details). Sections A, B, C, and D refer to data in Table III.

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References and Notes

(1) Taken in part from the Habilitationsschrift submitted by U.W.S. to the ETH Zürich in 1979.
(2) Zambelli, A.; Locatelli, P.; Bajo, G.; Bovey, F. A. *Macromolecules* **1975**, *8*, 687-9.
(3) Suter, U. W. Ph.D. Dissertation, ETH Zürich, 1973, pp 69-74.
(4) Prosser, T. H. U.S. Patent 4 105 837, 1976; French Patent 2 367 082, 1977 (to Hercules Inc., U.S.A.). For other attempts to epimerize polypropylene see: Listner, G. J. U.S. Patent 3 511 824, 1970. Stehling, F. C.; Knox, J. R. *Macromolecules* **1975**, *8*, 595-603.
(5) Suter, U. W.; Pucci, S.; Pino, P. *J. Am. Chem. Soc.* **1975**, *97*, 1018-23.
(6) Suter, U. W.; Flory, P. J. *Macromolecules* **1975**, *8*, 765-76.
(7) Suter, U. W. *Macromolecules*, preceding paper in this issue.
(8) Tonelli, A. E. *Macromolecules* **1978**, *11*, 565-7.
(9) Ferro, D. R.; Zambelli, A.; Provasoli, A.; Locatelli, P.; Rigamonti, E. *Macromolecules* **1980**, *13*, 179-86.
(10) Zambelli, A.; Locatelli, P.; Provasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267-70.
(11) Schilling, F. C.; Tonelli, A. E. *Macromolecules* **1980**, *13*, 270-5.
(12) Levy, G. C.; Peat, I. R. *J. Magn. Reson.* **1975**, *18*, 500-21.
(13) Gerhards, G.; Dietrich, W. *J. Magn. Reson.* **1976**, *23*, 21-9.
(14) Kohn, E.; Schuurmans, H. J. L.; Cavender, J. V.; Mendelson, R. A. *J. Polym. Sci.* **1962**, *58*, 681-95.
(15) Fraser, R. D. B.; Suzuki, E. In "Spectral Analysis"; Blackburn, J. A., Ed.; Marcel Dekker: New York, 1970; pp 171-211.
(16) Natta, G.; Pino, P.; Mazzanti, G. *Chim. Ind.* **1955**, *37*, 927-32.
(17) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, N.Y., 1953; p 602.
(18) At 270 °C the rotational isomeric state model of ref 6 is characterized (for the purpose at hand) by the three statistical weight matrices

$$U''_m = \begin{bmatrix} 0 & 0.193 & 0 & 0.946 & 0 \\ 0.193 & 0 & 0 & 0 & 0.051 \\ 0 & 0 & 0 & 0.204 & 0.051 \\ 0.946 & 0 & 0.204 & 0 & 0 \\ 0 & 0.051 & 0.051 & 0 & 0 \end{bmatrix}$$

$$U''_r = \begin{bmatrix} 0.895 & 0 & 0.193 & 0 & 0 \\ 0 & 0 & 0 & 0.204 & 0.051 \\ 0.193 & 0 & 0 & 0 & 0.051 \\ 0 & 0.204 & 0 & 1 & 0 \\ 0 & 0.051 & 0.051 & 0 & 0 \end{bmatrix}$$

$$U' = \begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 0 & 0 & 1 \\ 1 & 1 & 1 & 1 & 0 \end{bmatrix}$$

(19) Schaefer, J. *Macromolecules* **1973**, *6*, 882-8.
(20) Schaefer, J.; Natusch, D. F. S.; *Macromolecules* **1972**, *5*, 416-27.
(21) Hatada, K.; Kitayama, T.; Ikamoto, Y.; Ohta, K.; Umemura, Y.; Yuki, H. *Makromol. Chem.* **1978**, *179*, 485-96.
(22) Lyerla, J. R., Jr.; Horikawa, T. T.; Johnson, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 2463-7.

Carbon-13 Nuclear Magnetic Resonance Study of the Hydrolysis of Bisphenol A Polycarbonate

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ABSTRACT: ^{13}C NMR is an effective tool for the identification and quantitative measurement of the products formed in the hydrolysis of bisphenol A polycarbonate. The polymer, without additives, was hydrolyzed in steam at 125 °C. As the hydrolysis proceeded, the formation of products was followed by ^{13}C NMR and gel permeation chromatography. The products formed were primarily bisphenol A, dimer, and higher oligomers. The polymer chain ends in the starting polycarbonate resin were identified as phenyl carbonate units. End group concentration was measured at each level of hydrolysis. The rates of formation of bisphenol A and dimer are compared to theoretically predicted values.

The degradation of polymers is a subject which has wide economic, technological, and scientific interest.[1-3] Cheng et al.[4] have shown ^{13}C NMR to be an investigative tool of great utility in attempting to understand the oxidative degradation of polyethylene. The results of that work demonstrate that by ^{13}C NMR one can unambiguously identify and measure the products formed as a function of the extent of oxidation. In this paper we wish to report the results of a ^{13}C NMR study of the hydrolytic degradation of bisphenol A polycarbonate (poly[bis(4-hydroxyphenyl-2,2-propanediyl) carbonate]). It is the purpose of this study to identify products which result from the hydrolysis of polycarbonate and to record their concentration as a function of the extent of hydrolysis. ^{13}C NMR is of particular value in this type of study because of its ability to identify unambiguously the products formed as the result of hydrolysis. Band overlap, which makes exact product identification difficult in infrared spectroscopy, is normally not a problem in ^{13}C NMR. In addition, with proper attention paid to spin-lattice relaxation times (T_1) and nuclear Overhauser enhancements (NOE),[5] ^{13}C NMR provides direct quantitative measurement of the various products formed.

A substantial effort has been made in recent years to elucidate the thermal and photooxidative degradation of polycarbonates.[6-9] This work has concentrated mainly on the effects of these degradation processes on the physical properties of the polymer and on the identification of volatile products. Few reports are available on the hydrolytic degradation of polycarbonate under conditions where significant thermal and photooxidative degradation do not occur. A recent study by Pryde and Hellman[10] is the first attempt to quantify rates of formation of bisphenol A upon hydrolysis. Gardner and Martin[11] have related the loss in mechanical properties to the degree of hydrolysis at fairly low temperatures (65-93 °C).

The hydrolysis of bisphenol A polycarbonate is generally presumed to follow the reaction of organic diaryl carbonates such as diphenyl carbonate. The reaction proceeds at an appreciable rate in neutral solution and is both acid and base catalyzed:[12]

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