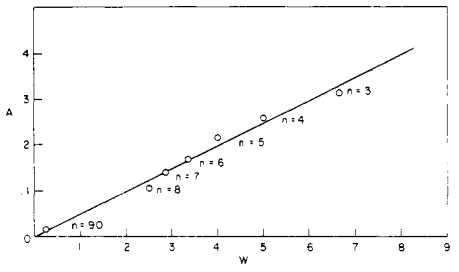

Figure 6. A plot of the ir absorbance (A) at 886 cm^{-1} *vs.* weight fraction (W) of CH_2CH_2OH in PEG.

tended (Figure 6). This band has been assigned to the *trans* conformation of the terminal $-CH_2CH_2OH$,[35] but we favor the assignment to the *gauche* conformation as suggested in the interpretation of the ethylene glycol spectrum.[33]

The weak band near 866 cm^{-1} is assigned to CH_2-CH_2OH groups which are not hydrogen bonded since it appears only in the spectra of oligomeric PEG in dilute benzene solutions which contain nonhydrogen bonded OH groups as shown by the appearance of a sharp band at 3600 cm^{-1} in the OH stretching region. The shift from 886 cm^{-1} to a lower frequency is to be expected when the hydrogen bonds are destroyed.[40]

The ir evidence of PEG in the crystalline form, the melt, and in benzene solutions indicated that (1) the conformation of the repeating unit in crystalline PEG is in the TGT form as previously suggested,[19,25,26] (2) in the melt or in benzene solution most of the ethylene groups in PEG remain in the *gauche* conformation, and the "disorder" of the polymer chain occurs mainly at the C–O bonds, (3) the conformations of the repeating unit of oligomeric PEG in benzene become more "disordered" in the dissociated state than in the associated form, and (4) the random conformations of PEG, which have been observed in the liquid state or in benzene solution, are greatly diminished in aqueous solution, with the appearance of relatively sharp bands at 844 and 2935 cm^{-1} corresponding to the perpendicular bands at 844 and 2950 cm^{-1} in the spectra of crystalline PEG.[19,25,26] We believe that the conformation of PEG in aqueous solution retains to a large degree the TGT sequence characteristic of crystalline PEB.

Finally, it should be pointed out that the nmr spin–lattice relaxation time (T_1) of PEG in aqueous solution is peculiarly short, only 0.65 sec at 35°.[15] The T_1 of PEG in methanol solution increases to 1.92 sec,[41] about three times that obtained in aqueous solution, whereas the viscosity of the methanol is only about 36% less than that of water. Conformational changes of PEG in aqueous solution could be involved to account for this peculiar difference. This is exactly consistent with what we have presently suggested for the special conformational structure of PEG in aqueous solution. Further work on nmr relaxation measurements is planned.

Acknowledgment. We would like to express our appreciation to Dr. Robert Ullman for valuable discussions, and to Miss S. J. Lignowski for some experimental help.

(40) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1958, p 96.

(41) K. J. Liu and J. E. Anderson, *Macromolecules*, **2**, 235 (1969).

Carbon-13 Nuclear Magnetic Resonance Analysis of Poly(propylene oxide)

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ABSTRACT: The white noise spin-decoupled, natural abundance ^{13}C nmr spectra of whole and fractionated poly(propylene oxide) have been obtained at 25.1 MHz. The spectra of the main-chain carbons are interpreted in terms of the structural and stereoregularities and defects in the chain backbone. The nmr analysis indicates that 89% of the crystalline fraction (mp 60°) and 49% of the noncrystalline fraction of this diethylzinc-catalyzed polymer consist of isotactic, structurally regular dyads.

The analysis of the chain structure of polymers by ^{13}C nmr has several advantages over analysis by ^1H nmr. First, all spin–spin interactions can be easily removed from the ^{13}C nmr spectrum by white noise heteronuclear decoupling techniques so that each nmr unique carbon produces just one line in the spectrum. Second, lines in the ^{13}C nmr spectrum are usually widely spaced because of the extensive range of relative ^{13}C chemical shifts. Finally, ^{13}C nmr resonances in polymers are not severely broadened by dipolar interactions because of the small ^{13}C nuclear magnetic moment. These advantages have already been demonstrated in the ^{13}C nmr determination of the monomer distribution in ethylene oxide–maleic anhydride copolymers.[1] The ^{13}C spectra were simple, well resolved, and provided information about both triads and pentads in the chain.

This paper reports the ^{13}C nmr analysis of the homopolymer of propylene oxide, $-[CH(CH_3)CH_2O]_x-$. Although the proton nmr analysis of this polymer is made intractable by small relative chemical shifts and over-

(1) J. Schaefer, *Macromolecules*, **2**, 210 (1969).

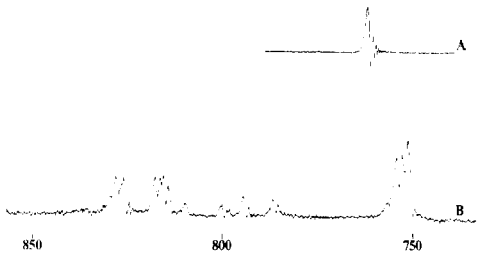

Figure 1. White noise spin-decoupled ^{13}C nmr spectra of chloroform solutions of (A) monopropylene glycol and (B) tripropylene glycol. Only the resonances from the methyl carbons are shown. Spectrum A is the accumulation of 100 scans and spectrum B of 1000 scans. The sweep rate for each scan was 2 Hz/sec. The numbers give the separation in hertz upfield from the spin-decoupled line of methanol at 40°. The magnetic field increases from right to left.

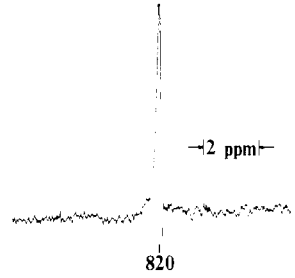

Figure 2. White noise spin-decoupled ^{13}C nmr spectrum of the methyl-carbon region of a chloroform solution of whole poly(propylene oxide). The spectrum is the accumulation of 2500 scans, each scan taken at a sweep rate of 5 Hz/sec. The number gives the separation in hertz upfield from the spin-decoupled line of methanol at 40°.

lapping spin–spin multiplets,[2] the ^{13}C nmr analysis is feasible. Both the structural and stereoisomerism of the chain can be determined by analysis of the ^{13}C nmr spectra of the carbons in the main chain.

Experimental Section

Natural abundance ^{13}C nmr spectra were obtained using a Varian HA-100 spectrometer, tuned to both 25.1 and 100 MHz, and coupled to a Varian C-1024 time-averaging computer.[1] Internal field–frequency stabilization of the spectrometer was provided by a lock signal from ^{13}C-enriched methanol included in the solvent. Both upper and lower side-band lock modes were used. The complications of proton–carbon spin–spin interactions were removed from the ^{13}C spectrum by white noise modulation of the 100-MHz channel.[3] Multiple-scan, low-power, frequency-swept spectra were obtained and accumulated by driving a voltage to frequency converter with the ramp voltage (reversed in sign) of the C-1024 operating in the internal trigger mode.

Poly(propylene oxide) was prepared using the heterogeneous catalyst diethylzinc in dipropylene glycol. A catalyst such as this is known to produce a polymer having some stereoregularity.[4] The resulting polymer was fractionated in two ways: first, by thermal precipitation from a 3% by weight acetone solution at −20°, and, second, by extraction with acetone at room temperature. The crystalline, or precipitated material from the first fractionation procedure had a melting point of 60° and ΔH melt = 11.0 cal/g, both values determined by differential scanning calorimetry. This material also had $\bar{M}_w$ = 30,000 and $\bar{M}_n$ = 9000 as determined by a gel permeation chromatographic analysis based on poly(methyl methaycrylate) as a calibration standard. The crystalline poly(propylene oxide) fraction consisted of about 15% of the whole polymer.

Polymer samples for nmr analysis were prepared from 10% (by weight) solutions of the whole polymer or its various fractions in $CDCl_3$ containing about 15% (by volume) ^{13}C-enriched methanol. Commercial propylene glycol and tripropylene glycol samples for nmr analysis were prepared from 50% (by volume) solutions in the same mixed solvent. The latter two materials served as low molecular weight analogs of poly(propylene oxide).

Results and Discussion

The white noise spin-decoupled, natural abundance ^{13}C nmr spectra of the methyl-carbon region of mono- and tripropylene glycol, $HOCH(CH_3)CH_2OH$ and $HO[CH(CH_3)CH_2O]_3H$, are shown in Figures 1A and 1B, respectively. The spectrum of the monopropylene glycol has only one line corresponding to the single nmr unique methyl carbon of that system, while the spectrum of the tripropylene glycol has on the order of 20 lines corresponding to the large number of structural (head-to-head, head-to-tail, etc.) and stereoisomers known to be present in this material.[5]

The spectrum of the methyl-carbon region of the whole poly(propylene oxide) is shown in Figure 2. Only a single line is observed. Apparently detectable structural and steric information about the polymer is not transmitted to the side groups of this chain, at least not to the extent information about the structural and steric differences of the low molecular weight triglycol are transmitted to the glycol methyl carbons.

The main-chain ^{13}C nmr spectra of the glycols are shown in Figures 3 and 4. Spectra of this region must

Figure 3. White noise spin-decoupled ^{13}C nmr spectrum of the main-chain carbons of monopropylene glycol. The spectrum is the accumulation of 25 scans, each scan taken at a sweep rate of 2 Hz/sec. The numbers give the separation in hertz downfield from the spin-decoupled line of methanol at 40°. The magnetic field increases from left to right.

(2) K. C. Ramey and N. D. Field, *J. Polym. Sci., Part B*, **2**, 461 (1964); H. Tani, N. Oguni, and S. Watanabe, *ibid., Part B*, **6**, 577 (1968).

(3) R. R. Ernst, *J. Chem. Phys.*, **45**, 3845 (1966).

(4) S. L. Aggarwal, L. Marker, W. L. Kollar, and R. Geroch, paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964; *Polym. Preprints*, **5**, 1136 (1964).

(5) J. Schaefer, R. J. Katnik, and R. J. Kern, *Macromolecules*, **1**, 101 (1968).

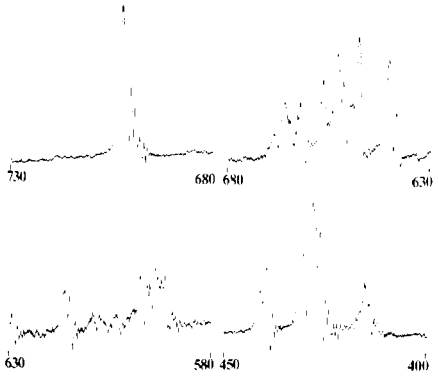

Figure 4. White noise spin-decoupled ^{13}C nmr spectrum of the main-chain carbons of tripropylene glycol. The spectrum was taken in four parts and each part is the accumulation of 2500 scans, each scan taken at a sweep rate of 2 Hz/sec. The numbers give the separation in hertz downfield from the spin-decoupled line of methanol at 40°. The recorder gain for the parts of the spectrum between 730 and 680 Hz and between 450 and 400 Hz have been reduced by a factor of 2. The magnetic field increases from left to right. Expanded scale versions of the lowest field part of the spectrum indicate that the lines following the very intense, low-field line are real.

be interpreted in terms of resonances arising from both methine and methylene main-chain carbons. Two of a possible two lines are observed in the monopropylene glycol spectrum and about 50 of a possible 90 lines are observed in the tripropylene glycol spectrum. The range of relative main-chain triglycol carbon chemical shifts is on the order of 300 Hz or roughly four times the range of methyl-carbon chemical shifts in the same system. This improved sensitivity of the main-chain carbon chemical shift to structural and stereoisomerism in the glycols leads to the hope that the same situation may prevail for the polymer.

This is, in fact, the case. Figure 5 shows the main-chain carbon nmr spectrum of whole poly(propylene oxide), revealing seven major lines. By moving the center of the white noise decoupling irradiation band

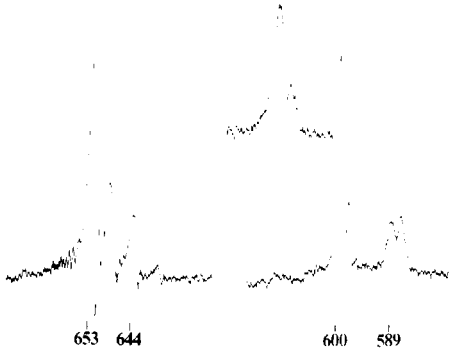

Figure 5. White noise spin-decoupled ^{13}C nmr spectrum of the main-chain carbons of a chloroform solution of whole poly(propylene oxide). The spectrum is the accumulation of 2500 scans, each scan taken at a sweep rate of 2 Hz/sec. The numbers give the separation in hertz downfield from the spin-decoupled line of methanol at 40°. The insert shows the line at 600 Hz in an expanded version at a sweep rate of 1 Hz/sec and approximately 1000 scans. The magnetic field increases from left to right.

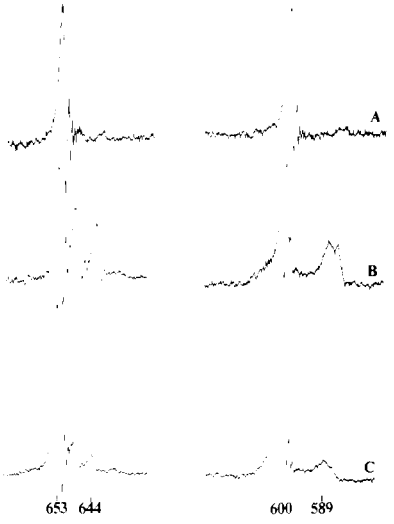

Figure 6. White noise spin-decoupled ^{13}C nmr spectra of chloroform solutions of (A) the thermally precipitated crystalline fraction, (B) the noncrystalline fraction, and (C) the room-temperature, acetone-extracted, insoluble fraction of poly(propylene oxide). Each spectrum is the accumulation of 2500 scans, each scan taken at a sweep rate of 2 Hz/sec. The concentrations of the solutions were not all identical. The numbers give the separation in hertz downfield from the spin-decoupled line of methanol at 40°. The magnetic field increases from left to right.

off-resonance about 300 Hz, the various lines in the two regions of the polymer main-chain spectrum can be identified as arising from either methine or methylene carbons. All of the low-field carbon resonances are broadened by the same amount and considerably less than the lines in the high-field grouping. When the same experiment is performed on monopropylene glycol the low-field line (known to arise from the methine carbon, spin coupled to only one proton[6]) is also broadened less than the high-field line. Thus, the polymer low-field lines can be assigned to methine carbons and the high-field lines to methylene carbons.

The spectra of various fractions of the whole poly(propylene oxide) are shown in Figure 6. The thermally precipitated or crystalline fraction has a main-chain carbon nmr spectrum which essentially consists of only two lines (Figure 6A). From earlier X-ray analysis, it is known that catalysts such as diethylzinc which was used to produce this polymer have a tendency to generate a crystalline fraction of structurally regular, isotactic chains.[4] Thus, it is apparent that qualtatively the lines 653 and 600 Hz downfield from the methanol resonance (which belong to methine and methylene carbons, respectively) give an indication of this isotactic, structurally regular content of the chain, while the remaining lines in the spectrum indicate the presence of either structural or steric defects.

Several consistent, quantitative interpretations of these main-chain ^{13}C nmr spectra of poly(propylene oxide) can be made in terms of either dyads or triads in the chain. Some of these interpretations attribute the many observed lines in the spectrum primarily to steric defects in the chain, some to structural defects, and

(6) See, for example, P. C. Lauterbur, *Ann. N. Y. Acad. Sci.*, 70, 841 (1958).

TABLE I
LINE ASSIGNMENTS FOR THE MAIN-CHAIN ^{13}C NMR SPECTRUM OF POLY(PROPYLENE OXIDE)

Structural sequence[a,b]	Carbon	Tacticity	Line position[c] (Hz at 25.1 MHz)
A*A*A*, A*A**A*	Methine	Iso-, hetero, and syndiotactic	653
A*A*A, A**A**A*	Methine	Iso and heterotactic	
(A)*A**A, A**A*(A*) A***A*(A), (A*)*A**A	Methine	Isotactic	648
A*A*A, A**A**A*	Methine	Syndiotactic	
(A)*A**A, A**A*(A*) A***A*(A), (A*)*A**A	Methine	Syndiotactic	644
AA, A*A*	Methylene	Isotactic	600
AA, A*A*	Methylene	Syndiotactic	599
AA*	Methylene	Isotactic	589
AA*	Methylene	Syndiotactic	587

[a] A = $-CH(CH_3)CH_2O-$; A* = $-CH_2CH(CH_3)O-$. [b] Units within parentheses may be either A or A*. Thus AA(A), for example, defines a structural dyad rather than triad. [c] As measured downfield from the spin-decoupled line of $^{13}CH_3OH$ at 40°. Accuracy is ±1 Hz.

some to a combination of both. Each of the interpretations can be made to satisfy the obvious restrictions that the number of methine carbons equals the number of methylene carbons, that the number of head-to-head structural defects equals the number of tail-to-tail structural defects, and that the defects in the chain, in general, give rise to the higher field lines of both methine and methylene regions.

A reasonable choice between these interpretations can be made by a consideration of the tripropylene glycol main-chain spectrum. The low-field part of this spectrum is due to methine carbons in the central unit of the triglycol, an assignment which can be made on the basis of off-resonance irradiation experiments and comparison of the relative intensities of the lines in the complete spectrum. The stereo- and structural isomer distributions of this sample of tripropylene glycol have been analyzed before.[5] All of the possible isomers are present. No impurities are present. While the stereoisomer distribution in the mixture has not been determined in as great detail as the structural isomer distribution, the available evidence indicates that it is close to random. If it is assumed that differences in the steric environments are *dominant* in determining the central methine ^{13}C chemical shift differences, the methine carbon spectrum must be interpreted in terms of triads. Under this assumption, however, the ^{13}C nmr line 703 Hz downfield from the methanol resonance, which accounts for 65% of the central methine-region intensity, cannot be assigned to any triad sequence, because none of any of the possible steric environments are present in relative concentrations approaching 65%. Thus structural environments must be important in determining relative methine chemical shifts.

The structural isomer distribution of the triglycol consists of a nonrandom mixture of the four possible isomers with AAA*, AA*A*, where A is $-CH(CH_3)-CH_2O-$ and A* is $-CH_2CH(CH_3)O-$, the most abundant (50%), AAA, A*A*A* the next most abundant (25%), and the other two isomers together the least abundant (25% for the sum). Thus, 75% of the central methine carbons of the triglycol have a local head-to-tail structural environment of $-OCH_2CH(CH_3)OCH_2-$ and the remaining 25% have a local head-to-head structural environment of $-OCH_2CH(CH_3)OCH(CH_3)CH_2O-$. The lowest field, intense triglycol methine carbon resonance is apparently related to the former kind of structure while, for the most part, the complicated higher field region is related to the latter.

TABLE II
RELATIVE CONCENTRATIONS OF DYADS IN WHOLE AND FRACTIONATED POLY(PROPYLENE OXIDE)

Polymer	Structural sequence	Tacticity	Relative concn[a]
Whole	AA, A*A*	Isotactic	0.57
	AA, A*A*	Syndiotactic	0.11
	A*A	Iso-plus syndiotactic	0.17
	AA*	Iso-plus syndiotactic	0.15
Crystalline (thermally precipitated)	AA, A*A*	Isotactic	0.89
	AA, A*A*	Syndiotactic	0.00
	A*A	Iso-plus syndiotactic	0.06
	AA*	Iso-plus syndiotactic	0.05
Noncrystalline	AA, A*A*	Isotactic	0.49
	AA, A*A*	Syndiotactic	0.13
	A*A	Iso-plus syndiotactic	0.20
	AA*	Iso-plus syndiotactic	0.18
Crystalline (acetone-extracted insoluble)	AA, A*A*	Isotactic	0.75
	AA, A*A*	Syndiotactic	0.05
	A*A	Iso-plus syndiotactic	0.10
	AA*	Iso-plus syndiotactic	0.10

[a] Estimated accuracy is ±0.02.

Different steric environments are responsible for multiple lines from each of these two types of carbons. In order for the nmr interpretation of the methine region (with its lowest field line constituting 65% of the total intensity) to be consistent with the known 75% relative concentration of the head-to-tail structure, part of the group of higher field lines is assigned to one of the stereoisomers of this head-to-tail structure. Since the stereoisomer distribution is close to random, the contribution must be due to a stereoisomer of a structural triad rather than dyad. (Otherwise, the remaining low-field intensity could account for no more than about half of 75%, or 40% of the total methine region rather than the observed 65%.) Thus, some but not all of the possible methine carbons in A*A*A*, A*A**A* are distinguished from A*A*A, A**A**A*. However, exactly which of these carbons is responsible for the higher field resonance is not known. The remaining high-field lines

are assigned to stereoisomers of the head-to-head structure and the low-field line to stereoisomers of head-to-tail containing structures.

The main-chain methine ^{13}C nmr spectrum of poly(propylene oxide) is very similar to the corresponding triglycol spectrum and is interpreted in the same way. That is, the polymer spectrum is interpreted in terms of dyads and triads of units in the chain with the relative chemical shifts determined both by structural and steric differences within these sequences. The regularity in the chain is reflected for the most part by the line at lowest field and the defects by the higher field lines. The line assignments are given in Table I. Just as for the triglycol spectrum, the choice of the structural triad assigned to the higher field group of lines (648 Hz) is arbitrary.

The main features of the methylene region of the polymer ^{13}C nmr spectrum can be interpreted exclusively in terms of structural dyads in the chain with steric differences having a minor but observable effect on the spectrum. These line assignments are also presented in Table I. The relative concentrations of sequences in all the spectra for both methine and methylene regions are consistent with the restrictions on the relative numbers of head-to-head and tail-to-tail structural defects. These values are presented in Table II.

Frequently, analysis of the diastereosequence or structural sequence probabilities will yield information about the mechanism of the polymerization. An elaborate statistical analysis of the ^{13}C nmr observed sequence concentrations is not justified because this polymer actually may be a sum of several different polymers generated by several different types of catalytic sites associated with the heterogeneous diethylzinc catalyst. Thus, sequence distributions cannot be reliably analyzed by a reasonable Markoffian scheme and insufficient information is available for a non-Markoffian analysis.

However, one qualitatively interesting comparison can still be made. The direct determination of the degree of steric purity of the crystalline poly(propylene oxide) fraction by ^{13}C nmr is in agreement with the predictions made by Aggarwal[4] using a modified version of a crystallization theory of Flory.[7] Aggarwal calculated head-to-tail isotactic dyad concentrations of 99 and 96% for polymers having melting points of 75 and 66°, respectively, so that the observed structurally regular, isotactic dyad concentration of 89% for a polymer with a melting point of 60° seems fairly reasonable.

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Nuclear Magnetic Resonance–Analog Computer Method for "Block Styrene"

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ABSTRACT: A method is described for determining "block styrene" in copolymers by using an analog computer to resolve overlapped aromatic proton nmr peaks. The method was applied to emulsion butadiene–styrene copolymers. It was shown that styrene sequences as small as two or three units are included in the "block styrene" determination. This technique should prove useful in obtaining sequence distribution information in most copolymer systems or in tacticity studies in which the resolution of overlapped peaks is important.

It was previously shown[1] that nmr composition analysis of some *n*-butyllithium-catalyzed butadiene–styrene copolymers yielded "block styrene" values in agreement with the chemical method[2] which uses osmium tetroxide for chain degradation. The question of how long the styrene sequences must be before nmr can detect them as "block styrene" was unanswered, although it was suggested that sequences as small as two or three might be observed. This paper describes a "block styrene" method which employs an analog computer to resolve the overlapped aromatic peaks of the styrene portion of nmr spectra. By use of a monomer sequence distribution computer program written by Harwood,[3] it was established that this method includes styrene sequences as short as two to three units in its "block styrene" determination.

Experimental Section

The emulsion butadiene–styrene copolymers were prepared at 50° with a common recipe. The copolymer solution concentration was 10% (weight/volume) in carbon tetrachloride or in hexachlorobutadiene. A small amount of tetramethylsilane was added as internal reference for nmr.

The 60-MHz nmr spectra were run at 28° with a Varian Model DA-60-IL spectrometer. The curve analysis was accomplished with an E.A.I. TR-48 analog computer

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(3) H. J. Harwood, *J. Polym. Sci., Part C*, 37 (1968).