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Structural Isomer Distribution in Linear Copolymers of Propylene Oxide[1]

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ABSTRACT: The 220-MHz nmr spectra of the methyl and vinyl regions of propylene oxide–maleic anhydride (PO–MA) and propylene oxide–citraconic anhydride (PO–CA) copolymers have been obtained and interpreted in terms of triads of monomers in the chain. PO units have a sense of direction in the PO–MA chain and this structural isomerism (head to head, head to tail, etc.) is observed. In PO–CA copolymers both monomers have a sense of direction. The four possible ways of combining PO and CA units by pairs are all observed. This nmr analysis of the copolymers has established that the structural isomer distribution of PO around MA and CA is random. This result, in view of the pronounced nonrandomness of the structural isomerism within closed runs of two PO units and randomness within closed runs of three PO units in the chain (as determined by glpc, mass and nmr techniques), eliminates any reasonable single chain propagation mechanism which involves control by monomers in the completed chain.

A study of the monomer distribution in propylene oxide–maleic anhydride (PO–MA) copolymers formed by a variety of homogeneous catalysts was possible by a combination of nmr analysis of the copolymer and glpc analysis of the glycol ethers resulting from hydrolysis of the copolymer.[2] These analyses demonstrated the need for high-order Markoffian statistics to describe the main features of the monomer distribution.

Since PO has a sense of direction when it enters the chain, a study of the structural isomer distribution may provide some insight into the question of the mechanism of the copolymerization. This paper will describe the use of nmr spectroscopy and glpc in determining the structural isomer distribution in PO–MA and in propylene oxide–citraconic anhydride (PO–CA) copolymers. In the latter both monomers have a sense of direction as they enter the chain since replacing a vinyl proton with a vinyl methyl changes MA to CA.

Experimental Section

Hydrolysis of PO–MA and PO–CA copolymers produces glycol ethers, the relative concentrations of which give the runs of PO in the chain. (Procedures for synthesis and hydrolysis of the copolymers are in ref 2.)

A glpc column was prepared by dissolving mercuric chloride in methanol to which dichloromethane and Carbowax 20M were added. The mixture was stirred until homogeneous. Chromosorb CL (60–80 mesh) was added and the solvent removed by evaporation. The dry packing material was tapped into a 0.25 in. × 10 ft piece of copper tubing and conditioned overnight at 200°. Chromatograms of the dimer and trimer of di- and tripropylene glycol ethers were obtained isothermally at 200° from an F & M Model 720 chromatograph. Fractions of the glycol ethers were collected at the exit of the chromatograph in 2-mm (o.d.) glass capillary tubing, coiled to increase trapping efficiency. Relative concentrations of the fractions were estimated from simulated chromatograms using a Du Pont 310 curve resolver.

Nmr spectra were obtained from 10% by weight solutions of polymer in $CDCl_3$ using a Varian A-60 spectrometer (60 MHz), a Varian HA-100 spectrometer (100 MHz), and a Varian superconducting magnet spectrometer (220 MHz).

Mass spectra were obtained from a Consolidated Electronics Corp. spectrometer (CEC 21-103-C) under standard operating conditions.

Results

1. Glpc, Mass, and Nmr Analyses of the Hydrolyzed Copolymer. By using a HgCl/Carbowax 20M glpc column the dimer and trimer (which represent *closed* runs of two and three PO units in the chain, respectively) of the glycol ethers obtained from hydrolysis of the copolymers can be resolved into structural and, in some cases, stereochemical isomers.

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[1] Parts of this paper were read at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[2] R. J. Kern and J. Schaefer, *J. Amer. Chem. Soc.*, 89, 6 (1967).

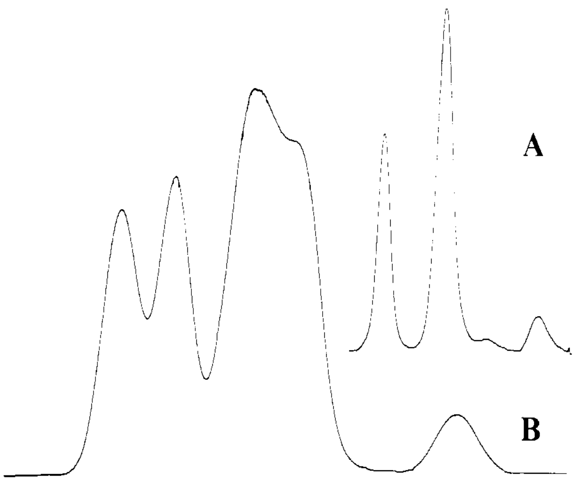

Figure 1. Chromatograms of the glycol ethers obtained by hydrolysis of the high-conversion PO–MA copolymer made from $SnCl_4$ and a comonomer charge ratio of 3:1: (A) dimer, (B) trimer. Order of elution is left to right.

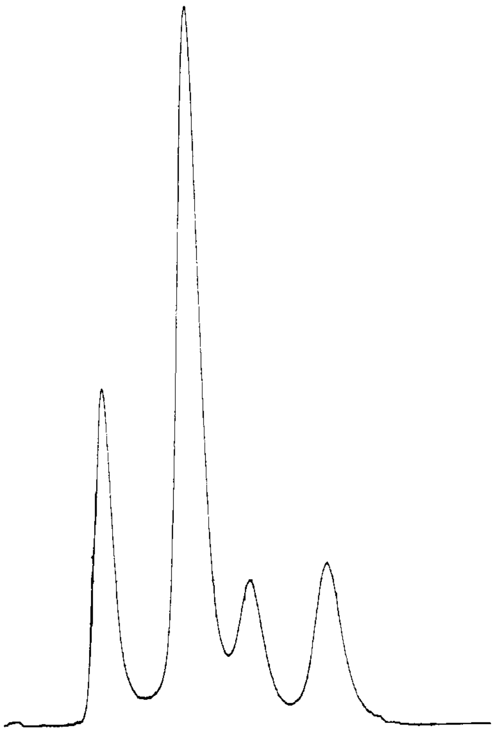

Figure 2. Chromatogram of the dipropylene glycol obtained from hydrolysis of the low-conversion PO–MA copolymer made from $SnCl_4$ and a comonomer charge ratio of 3:1.

Figures 1–3 contain typical chromatograms showing the dimer separated into four and the trimer into five fractions. The separated fractions were examined by nmr and mass techniques which allowed the structural configurational assignments of isomers given in Table I.

The nmr methyl region spectrum of glpc dimer fraction 2 (in order of elution) consists of eight lines (Figure 4) and can be definitely assigned to the four nmr unique methyls of the sum of the *dd,ll* and *dl,ld* pairs of AA, A*A*. (One methyl gives rise to two lines due to spin–spin coupling.) These stereo pairs are not present in equal concentrations. Methyl region spectra of glpc dimer fractions 1, 3, and 4 consist of a single doublet.

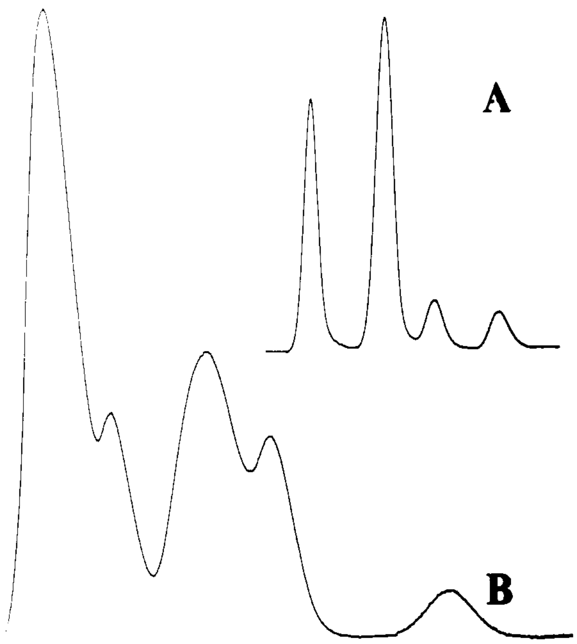

Figure 3. Chromatograms of commercial polypropylene glycols: (A) dimer, (B) trimer.

Table I

Structural Isomer Designations of the Dimer and Trimer of Polypropylene Glycol[a]

AA*	Tail–tail
AA,	Tail–head
A*A*	Head–tail
A*A	Head–head
AAA*	Tail–head, tail–tail
AA*A*	Tail–tail, head–tail
A*AA*	Head–head, tail–tail
AA*A	Tail–tail, head–head
A*AA	Head–head, tail–head
A*A*A	Head–tail, head–head
AAA	Tail–head, tail–head
A*A*A*	Head–tail, head–tail

[a] A = $-CH(CH_3)CH_2O-$; A* = $-CH_2CH(CH_3)O-$.

The mass spectra of the four dimer fractions show relative intensities of the peak at *m/e* 103 (parent ion minus $-CH_2OH$)[3a] of 0.6, 14.2, 15.6, and 16.2, respectively, when expressed as Σ_{28}. This indicates that dimer fraction 1 is AA* which alone has no terminal $-CH_2OH$ group. Thus, dimer fractions 3 and 4 are the *dd,ll* and *dl,ld* pairs of A*A, respectively. These assignments were confirmed by examining the nmr spectra of the trichloroacetyl isocyanate derivatives of each dimer fraction to determine the relative numbers of protons adjacent to primary and secondary hydroxyls.[3b]

The methyl region nmr spectra of the glpc trimer fractions are too complicated to interpret reliably. Nmr spectra of the trichloroacetyl isocyanate derivatives of the trimer fractions indicate fraction 1 has no $-CH_2OH$ groups, fraction 5 has no $-CH(CH_3)OH$ groups, fractions 2 and 3 have equal numbers of both, and fraction 4 has mostly $-CH(CH_3)OH$ groups. These results positively assign trimer fractions 1 and 5

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(3) (a) K. Bieman, "Mass Spectrometry," McGraw Hill Book Co., Inc., New York, N. Y., 1967, p 86; (b) V. W. Goodlett, *Anal. Chem.*, 37, 431 (1965).

TABLE II
STRUCTURAL ISOMER DISTRIBUTION IN THE DIMER AND TRIMER OF POLYPROPYLENE GLYCOL DETERMINED BY GLPC ANALYSIS

Copolymer	Catalyst	AA*[e,f]	AA, A*A*	A*A	AAA* AA*A*	A*AA*, AA*A + A*AA, A*A*A	AAA, A*A*A*
PO–MA	SnCl$_4$[a]	0.30	0.61	0.09	0.20	0.50	0.30
PO–MA	SbCl$_5$[b]	0.32	0.60	0.08	0.19	0.53	0.28
PO–MA	BF$_3$	0.24	0.65	0.11	0.24	0.48	0.28
PO–CA	Et$_2$Zn	0.32	0.62	0.06	0.24	0.47	0.29
Commercial polypropylene glycol[c]	Acid	0.36	0.51	0.13	0.50	0.25	0.25
PO–MA	SnCl$_4$[d]	0.21	0.52	0.27	0.24	0.53	0.23

[a] High conversion (77%). [b] High and low conversion isomer distributions are the same. [c] Dow Chemical Co. [d] Low conversion (2%). [e] For a system that was completely random entries in the six columns would read 0.25, 0.50, 0.25, 0.25, 0.50 and 0.25, respectively. [f] Estimated error is ±0.01. Concentrations were determined using a Du Pont 310 curve resolver.

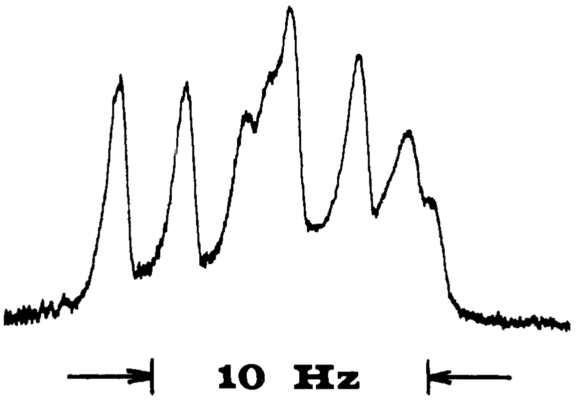

Figure 4. Methyl region spectrum (100 MHz) of the second glpc fraction of the dimer of commercial polypropylene glycol in CDCl$_3$. Magnetic field increases left to right.

to AAA*,AA*A* and A*AA,A*A*A, respectively. This is consistent with the mass spectral peak intensities for the five trimer fractions at m/e 161 (parent ion minus –CH$_2$OH) of 0.14, 1.35, 1.59, 2.03, and 2.83, respectively.

Definitive assignments of trimer fractions 2, 3, and 4 were not possible. Fortunately, none of the conclusions to be presented is affected since for all the copolymer systems studied these three peaks are about equal in intensity. The assignments were made by using the above nmr and mass results and making the very reasonable assumptions that the retention factors (and so order of elution) for the trimer are analogous to the dimer and that the only stereoisomers which can be separated belong to head–head structures. The spacing between glpc fractions 2 and 4 equals the spacing between fractions 4 and 5. Thus trimer fraction 2 is assigned to one stereo pair of A*AA*,AA*A, fraction 3 to AAA,A*A*A*, and fraction 4 to the sum of one stereo pair each of A*AA*,AA*A and A*AA,-A*A*A (with the concentration of the latter being greater as required by the nmr count of –CH(CH$_3$)OH groups for fraction 4). Since the relative concentrations of the stereo pairs are not equal and accurate determination of the actual ratio is not feasible for the rather poorly resolved trimer fraction 4, the concentrations of the structural isomers of the trimer have been summed as in Table II.

The features to note about the distributions in Table II are that for the SnCl$_4$-, SbCl$_5$-, BF$_3$- and Et$_2$Zn-catalyzed high-conversion copolymers and the SbCl$_5$-catalyzed low-conversion copolymer the dimer is distinctly nonrandom (with A*A as little as one-fourth that of the random 25%) while the trimer is very close to random.[4] In the commercial acid-catalyzed polypropylene glycol both dimer and trimer are distinctly nonrandom. In the low-conversion SnCl$_4$-catalyzed copolymer both dimer and trimer are random.

2. Nmr Analysis of the Copolymer. By hydrolyzing the copolymer the head to tail sense of direction that PO units had with respect to MA is lost. However, this information about the chain is contained in both the methyl and vinyl ^{1}H spectra. The 220-MHz methyl region spectrum of SnCl$_4$-catalyzed PO–MA is shown in Figure 5. The spectrum can be interpreted in terms of four PO methyl doublets (doublets due to spin–spin coupling) arising from the three triads, BAB (lines 1 and 2), BAA,AAB (lines 3 and 4, and lines 5 and 6), and AAA (lines 7 and 8). A is defined above and B = –COCH:CHCOO–. The two pairs of doublets for BAA,AAB triads result from structural isomerism within that triad. Lines 3 and 4 can be assigned[2] to BA(A),(A)A*B and lines 5 and 6 to BA*(A),(A)AB where the chain is counted left to right, linking oxygens are always on the right-hand side of a monomer and the parentheses around a monomer indicate it can have either sense of direction. B units never occur in runs longer than one.[2] These assignments have been given earlier by considering the 100-MHz spectrum; how-

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(4) Because A*AA*,AA*A was not determined separately from A*AA,A*A*A the concentration of one of these structural configurations could be significantly higher than the other making the over-all trimer distribution nonrandom. Even assuming this situation, the fact remains that in the copolymers, A*A sequences are far less frequent in the dimer than expected on a random basis. In the trimer there is no bias against A*A sequences. Thus, the nature of the distribution for dimer and trimer in the copolymer is distinctly different whether or not the trimer distribution is random. (By examining the nmr spectrum of the trichloroacetyl isocyanate derivative of the entire trimer mixture the total concentrations of primary and secondary hydroxyls were determined. This result, combined with the nmr and mass analyses of the individual glpc fractions reported in the text, showed that the trimer structural isomer distribution was random for the Et$_2$Zn-catalyzed copolymer. This experiment was not performed for copolymers produced by other catalyst systems.)

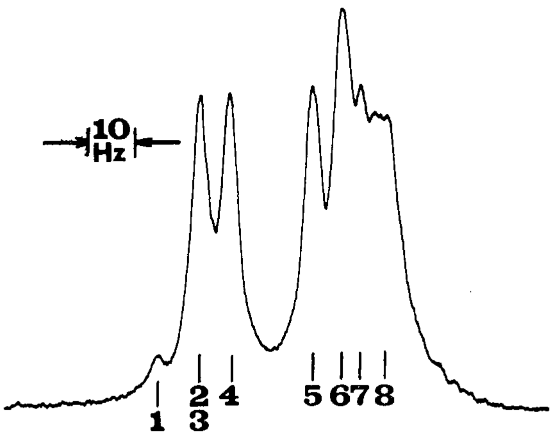

Figure 5. Methyl region spectrum (220 MHz) of SnCl-catalyzed high-conversion PO–MA copolymer. Line assignments are given in the text.

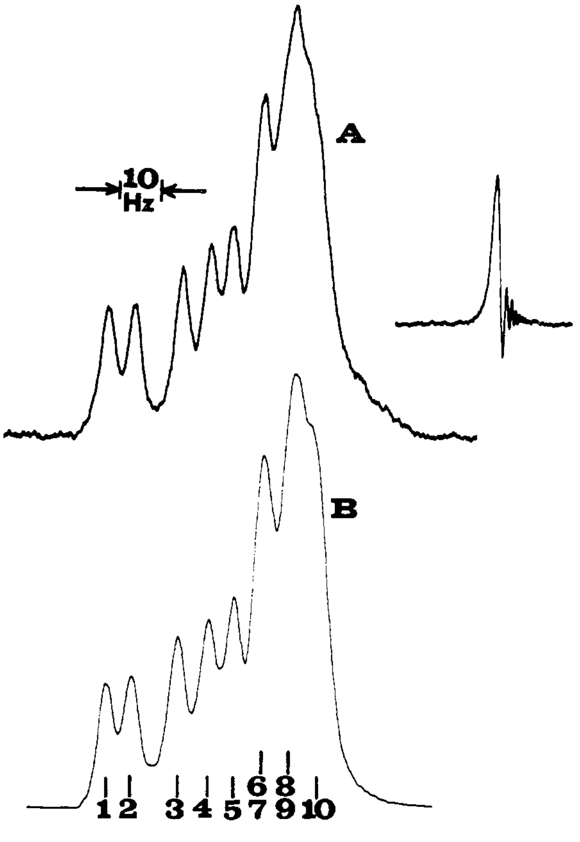

Figure 6. (A) PO methyl region spectrum (220 MHz) of Et$_2$Zn-catalyzed high-conversion PO–CA copolymer. The internal standard TMS is shown in the insert. (B) Ten-channel simulation of the spectrum in A made with a Du Pont 310 curve resolver. Line assignments are given in Table III.

Table III

Line Assignments of the 200-MHz Nmr Methyl Region Spectrum of Propylene Oxide–Citraconic Anhydride Copolymer

Line number	Relative intensity[a]	Sequence[b]
1	0.060	BA(A),(A)A*B*
2	0.065	
3	0.095	B*A(A),(A)A*B
4	0.085	
5	0.090	BA*(A),(A)AB*
6	0.080	
7	0.070	B*A*(A),(A)AB
8	0.080	
9[c]	0.190	(A)(A)(A)
10	0.190	

[a] Using these intensities the mole fraction of A in the copolymer is calculated as 0.76. (Experimental value is 0.76.) Estimated error of line intensity is ±0.01. [b] Definitions of A,A*,B and B* are given in the text. Monomers in parentheses can have either sense of direction. [c] Line 9 is actually at the same or slightly lower field than line 8.

ever, the higher frequency spectrum has two advantages. First, the beginnings of resolution of structural isomerism of (A)(*A*)(A) triads can be seen indicating that a study of this distribution in poly(propylene oxide) may be feasible at 220 MHz while it is not at 100 MHz. Second, the relative intensities of the pair of lines 3 and 4 can be seen to be essentially equal to the intensities of the pair of lines 5 and 6 by inspection (compare lines 4 and 5) without recourse to elaborate curve fitting techniques. Thus, the head and tail distribution of PO relative to MA is random in (B)(A),(A)(B) sequences.

The 220-MHz PO methyl region spectrum of the copolymer PO–CA catalyzed by Et$_2$Zn is shown in Figure 6A. This spectrum can be interpreted in terms of five pairs of PO doublets. The highest field pair, lines 9 and 10, corresponds to (A)(*A*)(A) triads. The other four pairs correspond to the four distinguishable ways of combining A, A*, B, and B* in the (A)(B),(B)(A) part of (A)(*A*)(B),(B)(*A*)(A) sequences where now B = $-COC(CH_3):CHCOO-$ and B* = $-COCH:C(CH_3)COO-$. (There are virtually no (B)(A)(B) sequences in this copolymer which consists mostly of runs of three (A) units.[5]) These assignments are given in Table III. Figure 6B is a ten-channel simulation of the spectrum made with a Du Pont 310 curve resolver. In the simulation, the intensities of lines within a spin doublet were made as equal as possible and the coupling constants of all the doublets were assumed to be equal. The agreement of observed and simulated spectra confirms the interpretation (as does the prediction of composition of the copolymer made from the relative concentrations of triads given in Table III). The chemical shifts of lines 1 and 2 and of lines 5 and 6 are similar to the chemical shifts of PO–MA B*A*(A) and B*A**(A) lines, respectively. (Note that when referring to PO–MA copolymers B = MA, and when referring to PO–CA copolymers, B = CA.) Thus, the assignment of the PO–CA lines was tentatively made by assuming B (rather than B*) in PO–CA triads is like B in PO–MA triads.

The relative concentrations of all the nmr spectra observable head to head and head to tail combinations of A and B in PO–CA (B)(A),(A)(B) sequences are about equal (within experimental error) as seen from Table III.

The advantages of the high-frequency spectrum of the methyl region of PO–CA can be seen by comparison of

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[5] The relative concentrations of closed runs of propylene oxide, [B(A)$_N$B], for N = 1, . . . 6 are 0.021, 0.059, 0.691, 0.187, 0.033, and 0.009, respectively.

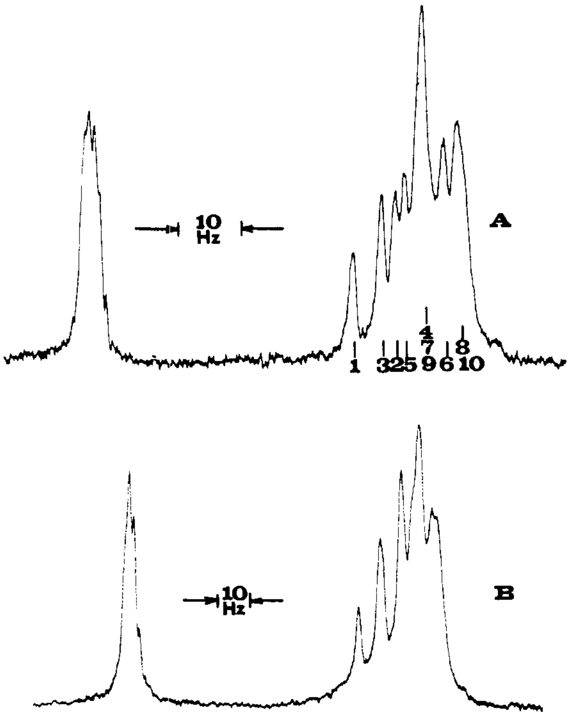

Figure 7. Methyl region spectra of Et_2Zn-catalyzed PO–CA copolymer: (A) 60 MHz and (B) 100 MHz. PO methyl lines are numbered as in Figure 6. The resonances at lower field are due to the CA vinyl methyl protons.

Figure 6 with spectra of the same copolymer taken at lower frequency shown in Figure 7A (60 MHz) and Figure 7B (100 MHz). The numbering of lines in Figure 7A corresponds to that of Figure 6. Because of the close superposition of two different doublets in these spectra, the concentrations of the five different triads *cannot* be determined uniquely at the lower frequencies. The increased line width of the 220-MHz spectrum of PO–CA compared to the 60-MHz spectrum (note the line width of the TMS signal included in Figure 6A) is related to the fact that each doublet represents more than one kind of nmr distinguishable triad (see Table III) and this multiplicity is more apparent at high frequency.

The vinyl region spectra of PO–MA and PO–CA copolymers obtained under a variety of conditions are shown in Figure 8. All of these spectra can be interpreted in terms of the three nmr distinguishable ways of forming (A)(*B*)(A) triads: A*(*B*)A; A*(*B*)A*,-A(*B*)A; and A(*B*)A*. The spectra show that for both copolymers the relative concentrations of these triads are close to the random 1:2:1 distribution. (None of the copolymers in this study contain large concentrations of closed runs of two PO units. Thus, the nonrandom (A)(A) distribution has only a minor effect on the (A)(*B*)(A) distribution.) The intensities of the three lines are easier to estimate from the high-frequency spectra, in which, because of the enhanced separation, no line appears as a shoulder of another and resonances not due to (A)(*B*)(A) triads[2] have been shifted to lower fields.

The increased line width of the PO–MA vinyl region lines at higher frequency, especially the central line (compare Figures 8d and e), is due in part to the multiplicity of triads (and perhaps pentads) each line represents and in part to the fact that the two vinyl protons of A*(*B*)A*,A(*B*)A triads are not equivalent. At 60 and 100 MHz the ratio of the chemical shift to coupling constant is small enough to produce only one line. At 220 MHz the observed line is considerably broadened although not resolved.

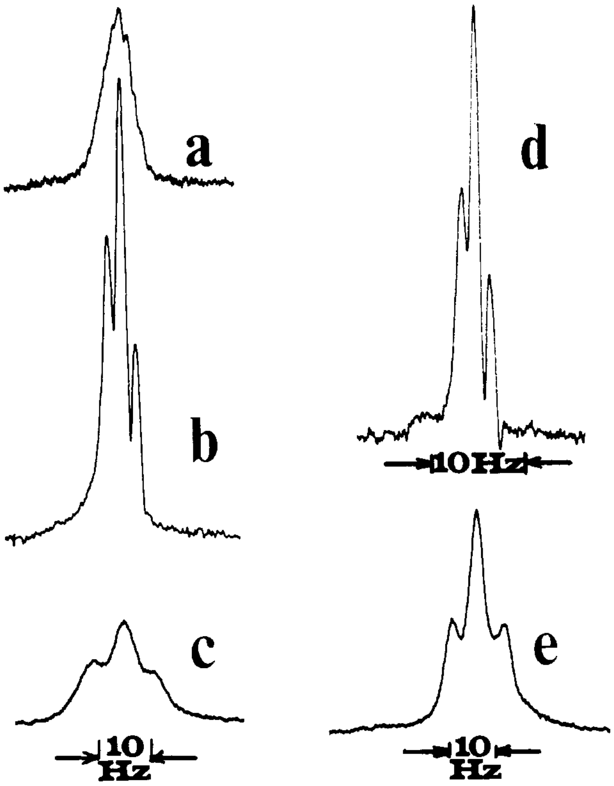

Figure 8. Vinyl region spectra of Et_2Zn-catalyzed PO–CA copolymer: (a) 100-MHz single resonance, (b) 100-MHz frequency swept double resonance in which the CA vinyl methyl protons are decoupled from the vinyl proton, (c) 220-MHz single resonance. Vinyl region spectra of $SnCl_4$-catalyzed PO–MA copolymer: (d) 60-MHz single resonance and (e) 220-MHz single resonance. Vinyl region spectra of $SbCl_5$, BF_3-catalyzed PO–MA copolymers are similar to those shown.

The relative concentrations of the nmr observable head and tail combinations of A and B in high- and low-conversion copolymers produced by all of the catalysts are the same.

Discussion

A study of the monomer distribution in low-conversion PO–MA copolymers indicated a description by third-order Markoffian statistics was satisfactory.[2,6] However, detailed analysis of the relative concentrations of long runs of PO in high-conversion PO–MA copolymers[6] demonstrated that the observed small deviations from a third-order Markoffian description of the monomer distributions could be described by assuming that the observed distribution is actually a sum of *at least* two different third-order Markoffian distributions, associated with two different types of catalysts (I and II). Furthermore, analysis of low-conversion PO–MA

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(6) J. Schaefer, R. J. Katnik, and R. J. Kern, *J. Amer. Chem. Soc.*, in press.

indicated that in the early stages of copolymerization, chains from catalyst I were highly favored but that the high-conversion material contained chains formed mostly, but not exclusively, from catalyst II.[7]

These conclusions are in agreement with the results of the isomer distribution analysis. In the low-conversion $SnCl_4$-catalyzed PO–MA copolymer both (A)(A) and (A)(A)(A) isomer distributions are random, consistent with being generated by one catalyst producing a random isomer distribution within all runs of PO. (Recall that (A)(A) and (A)(A)(A) refer to closed runs of two and three A units, respectively.) In the high-conversion $SnCl_4$-catalyzed material distinctly nonrandom (A)(A) but random (A)(A)(A) isomer distributions are observed consistent with this copolymer being generated predominantly by a second catalyst (a chemically modified version of the first) producing nonrandom (A)(A) and random (A)(A)(A) isomer distributions.

In both high- and low-conversion $SbCl_5$-catalyzed material distinctly nonrandom (A)(A) but random (A)(A)(A) isomer distributions are observed and no additional evidence for the presence of two distinct catalyst types is contained in this result.

The nonrandom dimer isomer distributions and random trimer isomer distributions produced by the second $SnCl_4$ catalyst type and both $SbCl_5$ catalyst types are not consistent with a mechanism in which PO units add to a single growing chain type, one at a time. In order to explain the distribution data this way, the structural isomeric addition probabilities for adding to a chain ending with (B)(A)(A) must be different from those for adding to a chain ending with (B) and with (B)(A). Furthermore they must be different in just such a way that the net results are the dissimilar (A)(A) and (A)(A)(A) structural isomer distributions (in which head to head sequences are infrequent in the former but not in the latter) and random (B)(A),(A)(B) and (A)(B)(A) structural isomer distributions. The constraints are not consistent with any *simple* model of control of propagation of a single chain type by monomers within the completed chain.[8]

Dissimilar (A)(A) and (A)(A)(A) isomer distributions generated by the same catalyst type and in the same chain can be explained by assuming that different, independent species or states of this catalyst type are formed by various numbers of unreacted monomers coordinated in reaction spheres by the catalyst to the growing chain end. These states are connected by propagation steps of the chain. That is, the catalyst coordinates a group of monomers, one unit at a time, arranges them, adds them to the chain, coordinates a different group of monomers, etc. Within these different spheres some of the steric or electronic requirements present in the formation of a (B)(A)(A)(B) sequence may be absent in the formation of a (B)(A)(A)(A)(B) sequence so that the dimer and trimer isomer distributions need not be related and can be dissimilar.

The presence of different states of one catalyst type is reasonable since, during the early part of the polymerization period, chains are being generated by a third-order Markoffian mechanism as established by analysis of the monomer distribution. (Any monomer distribution which can be described in terms of one Markoffian distribution is defined as generated by one catalyst type.) Several species or states of varying reactivity of this catalyst must be present in order to explain how, for example, BAAAB sequences form more frequently than BAAB or BAB sequences.

Unfortunately, whether the monomer distribution produced in the later part of the polymerization period is homogeneous from chain to chain (*i.e.*, whether there really is only one predominant type of propagating chain and one predominant type of catalyst) has not yet been established. The high-conversion material may be a sum of more than two distributions. Thus, the dissimilar dimer and trimer isomer distributions do not constitute a proof that monomers are coordinated and arranged before entering the chain.

Acknowledgment. The authors wish to thank Varian Associates, Palo Alto, Calif., for providing them with access to the superconducting magnet nmr spectrometer system.

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(7) A multiplicity of chain types is not present for the Et_2Zn catalyst system which produces a monomer distribution which can be described as one third-order Markoffian distribution (see ref 5).

(8) Consider the acid-catalyzed commercial dimer and trimer of polypropylene glycol, which are formed by one at a time monomer additions and in which chain end control of propagation is probably operating. The nature of the nonrandomness is preserved in this system.