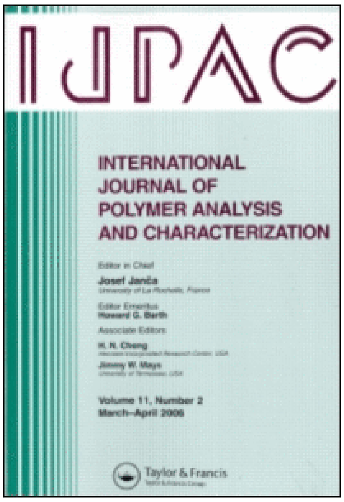

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^{13}C-NMR of Anionic Low-Molecular-Weight Stat-Poly(Ethylene Oxide-Co-Propylene Oxide): Correlation with Monte Carlo Simulation

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Low-molecular-weight stat-poly(ethylene oxide-co-propylene oxide) copolymers have been prepared by anionic way using a new heterogeneous catalytic process. After checking the reactivity ratios of the system, the new resonance peaks due to low-molecular-weight chains (end groups) have been assigned and the copolymers were fully characterized by ^{13}C-NMR in terms of triads centered in ethylene oxide units. Finally, signal areas have been successfully compared with computer simulation based on the Monte Carlo method, taking into account the chain length distribution resulting from anionic polymerization.

KEY WORDS Statistical anionic copolymerization; ^{13}C-NMR; Monte Carlo simulation

INTRODUCTION

Block copolymers of ethylene oxide (EO) and propylene oxide (PO) are well known for their applications as surfactants [1] and are commercially available. Physical properties such as solubility or critical micellar concentration depend on the hydrophilic–hydrophobic balance, which is controlled by the ratio of PEO/POP sequences. Statistical copolymers could emphasize these properties through controlling the microstructure of the polymer chains. Another interesting application is that of solid polymer electrolytes, [2] in which the insertion of small amounts of PO units in the backbone is expected to reduce highly the recrystallization of the PEO sequences and decrease the glass transition temperature. In all these cases, statistical tailor-made copolymers must be synthesized, in which the sequence distributions have to be well controlled to obtain the best balance between the EO and PO contents. To this aim, NMR analysis is a convenient technique for determining the intramolecular structure of copolymers.

Oxiranes polymers are usually obtained from anionic or anionic-coordinated initiators but statistical copolymers are scarcely reported. Commercial random copolymers are available but the synthesis conditions are not well defined.

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Alcoholates are well-known examples of the first class of initiators, but they generally require drastic reaction conditions. Particularly, strong basic medium can lead to secondary reactions when polymerizing PO, such as proton abstraction. Heatley et al. [3,4] reported the use of the alkali salt of 1-methoxy-2-propanol as initiator complexed or not with crown ethers to synthesize EO-PO copolymers. In that case, no structures due to secondary reactions were detected.

Anionic-coordinated initiators are versatile systems, although they display some drawbacks. In homogeneous systems, aluminium isopropoxide [5,6] leads to the clustering of the active centers. The high cost of the porphyrin aluminium, [7] as well as the remaining color, limit their use.

Anionic polymerizations can be carried out according to a stoichiometric mode in which there are as many polymer chains as initiator molecules. When adding a protic compound, such as an alcohol, reversible exchange reactions occur between the growing chain and the alcohol. It must be emphasized that any alcohol function can be involved in the transfer reactions, namely the initial alcohol molecules, as well as the polymer chain having already undergone the transfer reaction. Therefore, the final number of polymer chains is the sum of the initiator and alcohol molecules and the system becomes catalytic.

$$\langle DP \rangle = [\text{Monomer}]/[\text{Initiator} + \text{Alcohol}] \tag{1}$$

Both anionic and anionic-coordinated systems can be used in the catalytic mode. If the alcohol concentration is much higher than that of the initiator, which is the most usual case, the relation becomes

$$\langle DP \rangle = [\text{Monomer}]/[\text{Alcohol}] \tag{2}$$

The known starting monomer and alcohol concentrations and the degree of conversion allow the determination of the theoretical average degree of polymerization. This theoretical value can be correlated with ^{1}H-NMR spectroscopy results.

We have used a new patented heterogeneous catalytic system [8,9] to obtain easily and rapidly a large amount of statistical copolymers. The initiator is an aluminium alkoxyde supported on porous silica. This procedure avoids the clustering of the active centers so that the catalytic system is expected to have uniform activity. In addition, PO polymerizes without any transfer to monomer.

This paper first deals with the ^{13}C-NMR characterization of copolymers synthesized by using this new catalytic system. Owing to their low molecular weight, new resonance peaks appear which are due to the chain ends and the alcohol residue. This study has been focused mainly on the EO-centered triads. An incremental approach concerning neighboring effects on chemical shift values and model compounds have been used for the assignment of terminal EO-centered triads. Furthermore, each composite NMR signal area (each resonance includes contributions from carbons belonging to several distinct triads) was compared with Monte Carlo simulation. Since the triad distribution is related to the polymerization mechanism, it can be used to test the validity of the kinetic models. We have employed the Monte Carlo method to simulate the building of polymer chains with finite length since calculations based on the addition probabilities do not take into account the end groups.

EXPERIMENTAL

Random Copolymers

EO and PO copolymerizations have been carried out according to the process described in reference 8. The alcohol present initially is the 2-[2-butoxyethoxy]-ethanol. The reaction can be written as follows:

$$\mathrm{Bu(EO)_2OH} \xrightarrow{(n-2)\,\mathrm{EO}+\mathrm{m\ PO}} \mathrm{Bu(EO)}_n\mathrm{(PO)}_m\mathrm{OH}$$

The polymerizations were carried out in a 250-mL round-bottom flask containing the catalytic system and 2-[2-butoxyethoxy]ethanol (1.5 g, 0.0092 mole) in 100 mL of toluene. Ethylene oxide (20 mL, 0.4 mole) and propylene oxide (28 mL, 0.4 mole) are added at room temperature under vacuum. The reaction mixture was stirred at 50°C. After the appropriate time, the copolymers were carefully dried (under vacuum at 50°C) and weighted to determine the conversion degree.

NMR Spectra

^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AC250 spectrometer at 250 MHz and 62.9 MHz, respectively. Deuterochloroform was used as solvent and tetramethylsilane (TMS) as the internal standard. The temperature was 335 K. The concentration was about 30 wt% for ^{13}C-NMR. Spectra were obtained with a broad band/1H dual 5-mm probe over 2–4 h periods (750–1500 transients) with a 10-s recycle time to allow the complete relaxation. The pulse angle was 70° and 64 K data size. The data were processed without line broadening. The digital resolution was 0.005 ppm. Signal areas were determined by the Bruker linesim routine program.

No significant difference in integrated areas of methylenic carbons was observed between acquisition made under these conditions and that made in the absence of the nuclear Overhauser effect (N.O.E.); this experiment shows that all methylenic carbons have nearly identical nuclear Overhauser enhancement.

Simulation calculations were performed on a 80386 personal computer. The programs were written either in Quick Basic or Turbo Pascal. The details of the Monte Carlo algorithm are given elsewhere in this paper.

RESULTS AND DISCUSSION

Reactivity Ratios

The kinetic behavior of copolymerizations is usually treated according to the terminal model developed by Lewis and Mayo [10] for radical polymerizations. In

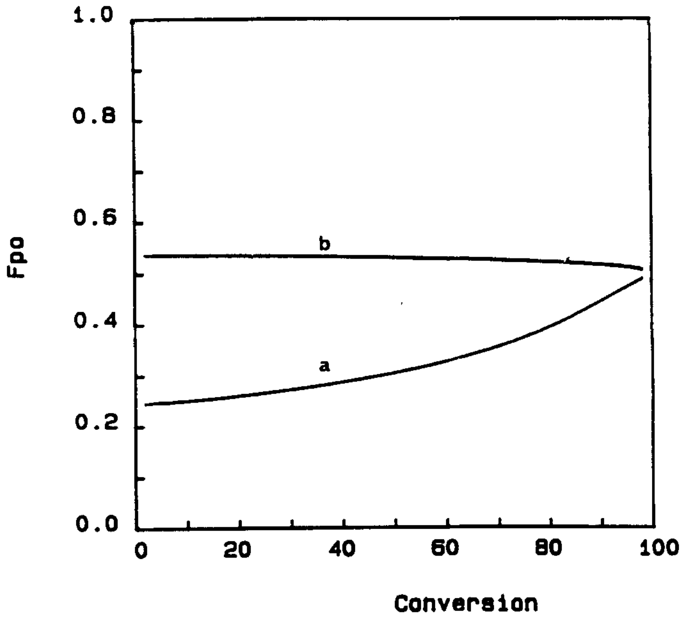


FIGURE 1 Average molar fraction of propylene oxide in the copolymer chains versus conversion for an equimolecular initial monomer mixture: (a) $r_{eo} = 3.00$, $r_{po} = 0.27$; (b) $r_{eo} = 0.3$, $r_{po} = 0.5$.

this model, both reactivity ratios are the pertinent parameters to describe the structure of the copolymers.

With porphyrin aluminium as initiator, Inoue [7] found $r_{eo} = 0.3$, and $r_{po} = 0.5$ while Heatley [3] found 3 and 0.3 for the same monomers with a usual anionic system. These two sets of values lead to copolymers, the microstructure of which are fundamentally different although starting from the same monomer mixture (Figure 1). In some cases, copolymers with the same overall chemical composition may have different microstructures.

It is worth highlighting the differences that exist between the radical and anionic modes and discussing the consequences on the average molecular weight and the polymer microstructure. In the first mode of polymerization, the lifetime of a macroradical is very short. The proportion of both monomers incorporated into the polymer chains formed during this time is around the same (d[EO]/d[PO] is constant) so that these polymer chains display the same composition. In addition, they have the same average molecular weight. Other chains obtained at another time will not have neither the same composition nor the same average molecular weight. In anionic polymerization, no termination reaction occurs (living polymerization). The lifetime of the polymer chains is that of the reaction and their number remains unchanged during the reaction. Since the proportion of monomers incorporated in each chain depends on the conversion degree, all the polymer chains must display the same composition shift.

Therefore, the question was to determine the reactivity ratios of our system before any characterization or simulation. The determination of both reactivity ratios involves usually the analysis of copolymers obtained at very low conversions, assuming the monomer composition in the feed remains unchanged during this

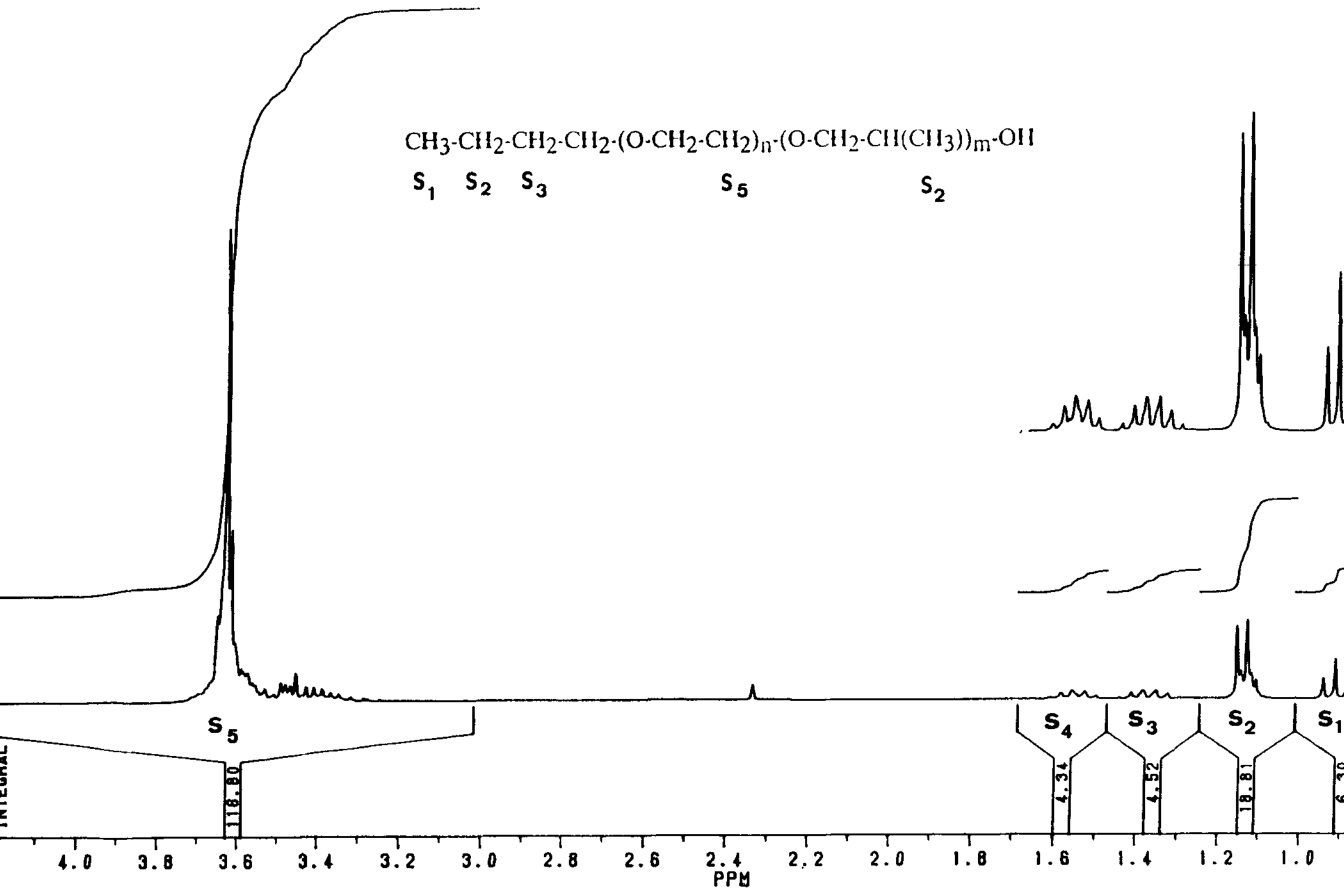


FIGURE 2 Typical proton-NMR spectrum (250 MHz) of a low-molecular weight co

time interval. Another method consists in following the evolution of the chemical composition of a copolymer during the reaction and to compare it with simulation calculation. Preliminary results showed that simulations performed with Heatley's reactivity ratios were in a good agreement with the first copolymers we prepared. According to the values of these reactivity ratios, the composition drift is important when starting from an equimolar mixture of monomers and can be determined easily. The copolymerization has been stopped at different degrees of conversion and the composition of the products determined by ^{1}H-NMR (Figure 2).

Resonances in the range δ 3.2–3.8 ppm are assigned to the methylene and methine protons of the EO and PO units and the bands around 1.15 ppm to the methyl protons of the PO units. The triplet at 0.910 ppm and bands centered at 1.370 and 1.555 ppm are assigned to the methyl and methylene groups of the initiator.

The values of n and m can be determined with good accuracy by ^{1}H-NMR if methylenic protons from the initiator can be measured separately (provided n and m values are not too high). The following equations can be used:

$$S_2 = 3mp$$

$$S_5 = (4n + 3m + 2)p$$

with

$$p = S_4/2 = S_3/2 = S_1/3 \text{ and } S_1 \text{ to } S_5 \text{ defined in Figure 2.}$$

Otherwise, NMR can only give the ratio n/m and the degree of conversion is required to get access to the individual values, assuming that all the alcohol molecules have reacted. For very short chains, the residual alcohol may be detected and its contents estimated by NMR.

The assumption of living copolymerization is confirmed by NMR. In addition, it is clearly shown that no secondary reaction occurs during the polymerization, such as proton elimination of the PO units.

Experimental values of the average molar fraction of propylene oxide in the copolymer $\langle F_{po} \rangle$ determined from ^{1}H-NMR vs. the conversion degree are plotted in Figure 3 and compared with the curves drawn from the numerical integration [11] of the copolymerization equation as presented previously. The best fitting has been obtained with the following values: $r_{eo} = 3.00$ and $r_{po} = 0.27$, very close to those found by Heatley, although the structure of the active centers are rather like the Inoue's system. The fit is good enough to prove the statistical nature of the polymerization and to exclude any contribution of block copolymerization.

^{13}C-NMR ASSIGNMENTS

^{13}C-NMR analysis is used to determine the triad occurrences along the polymer chains. Spectra of EO-PO copolymers have been first assigned by Whipple and Green [12] in terms of dyad sequences. Later on, Heatley [13] reported the results obtained at 75.5 MHz by using spectral editing techniques (DEPT) available on

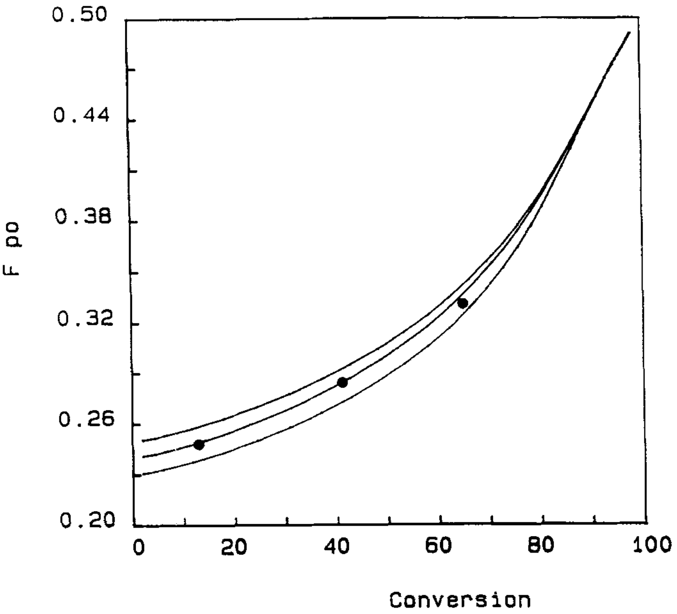


FIGURE 3 Experimental values of F_{po} (●) versus molar conversion with different reactivity ratios. The domain between the external curves shows how the copolymer composition may change for reactivity ratios, such as $2.8 < r_{eo} < 3.2$ and $0.2 < r_{po} < 0.3$. The continuous line inside this domain represents the composition drift calculated with $r_{eo} = 3.00$, $r_{po} = 0.27$.

modern spectrometers. He has shown that, when the inverted addition occurs in poly(propylene oxide), there is an overlapping of CH and CH_2 carbons resonances. Moreover, even without propylene oxide inversion, CH_2(E$\underline{P}$P) occurs in the CH (P$\underline{P}$P) region in EO-PO copolymers (See notation of triads below). He obtained CH and CH_2 subspectra which eliminate overlapping and made a complete analysis in terms of triads both E- and P-centered. Gronski [14] characterized ethylene oxide-propylene oxide adducts in order to determine the structure parameters of the polymer chains.

Small differences in chemical shifts values are generally obtained by different authors. They result from a high sensitivity of the chemical shifts to concentration, temperature, and solvents.

In this paper, we have focused our study on the distribution of triads centered in EO units. Owing to our polymerization mode and the low molecular weights, new peaks appear due to the end groups and the alcohol residue (Figure 4).

Model compounds and experimental incremental values deduced from the observed chemical shifts of all central E-centered triads allow the complete prediction of terminal E-centered triads chemical shifts on both ends of the polymer chain.

We used Heatley's notations to specify a particular carbon: EO and PO units are noted by E and P, respectively. The unit in which the examined carbon is located is underlined. In case of unsymmetrical sequences, the methylene groups of the EO units are not identical and are designed by *a* or *b* representing respectively the left- and the right-hand group in the sequence as written. An

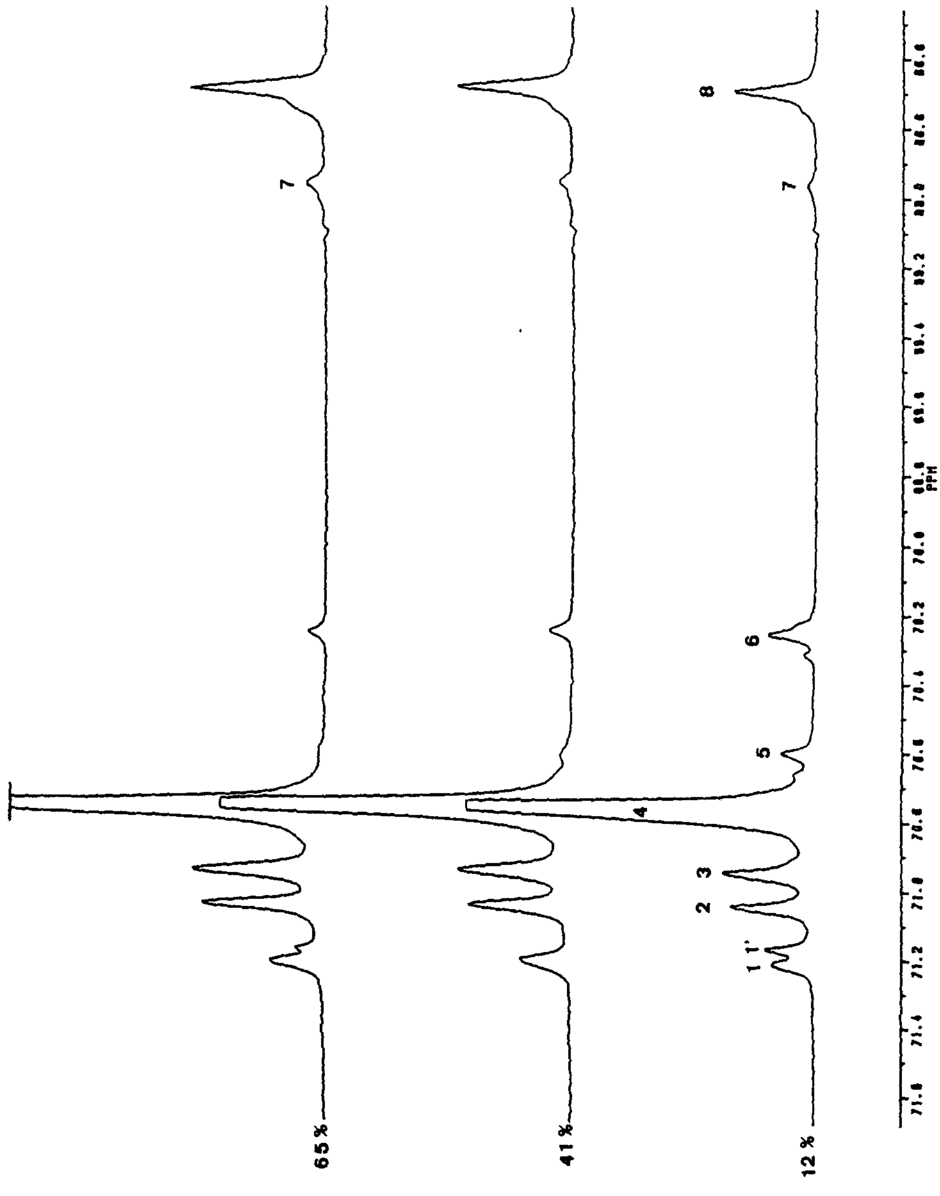


FIGURE 4 ^{13}C-NMR spectrum (62.9 MHz) of copolymers at different conversions (equimolar initial monomer mixture). Enlargement of resonance region of the *a*- and *b*- methylenic carbons belonging to E-centered triads.

TABLE 1

Assignments of ^{13}C-NMR peaks relative to the E-centered triads

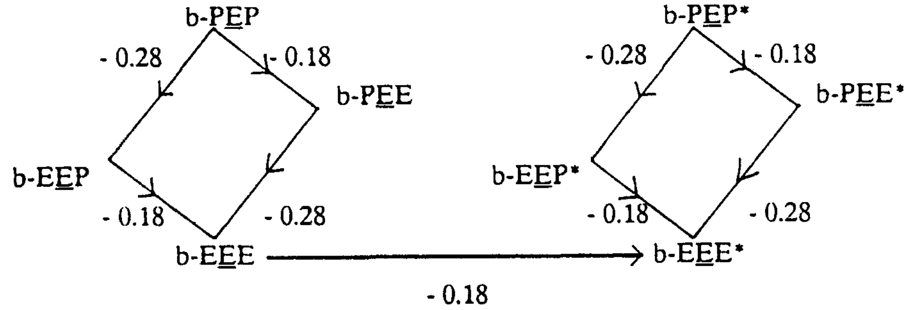
Peak	δ(ppm)	Central Triads	Terminal Triads
1	71.24	*b*-P$\underline{\mathrm{E}}$P	
1′	71.17		$\underline{\mathrm{I}}^1$EE
2	71.06	*b*-P$\underline{\mathrm{E}}$E	*b*-P$\underline{\mathrm{E}}$P*
3	70.96	*b*-E$\underline{\mathrm{E}}$P	
4	70.78	(*a*- + *b*-$\overleftarrow{\mathrm{P}}\underline{\mathrm{E}}\overrightarrow{\mathrm{P}}$) *a*-E$\underline{\mathrm{E}}$E + *b*-E$\underline{\mathrm{E}}$E *a*-E$\underline{\mathrm{E}}$P	*b*-P$\underline{\mathrm{E}}$E* *b*-I$\underline{\mathrm{E}}$E *a*-E$\underline{\mathrm{E}}$E* + *a*-E$\underline{\mathrm{E}}$P* + *b*-E$\underline{\mathrm{E}}$P*
5	70.61		*b*-E$\underline{\mathrm{E}}$E*
6	70.25		*a*-I$\underline{\mathrm{E}}$E
7	68.98		(*a*- + *b*-$\overrightarrow{\mathrm{P}}\underline{\mathrm{E}}\overleftarrow{\mathrm{P}}$)
8	68.70	*a*-P$\underline{\mathrm{E}}$E + *a*-P$\underline{\mathrm{E}}$P	*a*-P$\underline{\mathrm{E}}$E* + *a*-P$\underline{\mathrm{E}}$P*

asterisk designs an end unit. I represents the butoxy group of the initiator residue coming from the alcohol and bound in the polyether chain. I^1 represents the carbon atom bound to the oxygen atom. With this notation, the 2-[2-butoxy]ethanol used as initiator molecule will be represented as IEE*. Both carbon atoms of the internal ethoxy group will be noted as *a*-I$\underline{\mathrm{E}}$E* and *b*-I$\underline{\mathrm{E}}$E*, respectively.

From the observed δ values concerning *central* triads (Table 1), the incremental values Δ(δ) are deduced which correspond to the change in the chemical shift value of a given *a*- (or *b*-) carbon of the central E unit when one of the neighboring unit is changed from P to E. For example, $\Delta\delta = \delta_{b\text{-P}\underline{\mathrm{E}}\mathrm{P}} - \delta_{b\text{-E}\underline{\mathrm{E}}\mathrm{P}} = \delta_{b\text{-P}\underline{\mathrm{E}}\mathrm{E}} - \delta_{b\text{-E}\underline{\mathrm{E}}\mathrm{E}}$.

Considering the *b*-carbon of the central E unit, $(\Delta\delta)_1 = -0.28$ (δ effect) when the previous neighboring unit is changed from a P to a E unit, whatever the next unit (E or P). In the same way, we notice a $(\Delta\delta)_{1'} = -0.18$, (δ′ effect) when the following unit changes from P to E, whatever the previous unit (E or P) (left part of the Scheme I). These observations will be used for the assignments of some of the carbons of the terminal E-centered triads.

However, the *a*-carbon chemical shift of the central E unit is not modified by the nature of the following (E or P) unit ($\delta_{a\text{-P}\underline{\mathrm{E}}\mathrm{E}} = \delta_{a\text{-P}\underline{\mathrm{E}}\mathrm{P}} = 68.70$ and $\delta_{a\text{-E}\underline{\mathrm{E}}\mathrm{E}} = \delta_{a\text{-E}\underline{\mathrm{E}}\mathrm{P}} = 70.78$), and when the previous one changes from P to E, the change in chemical shift is $(\Delta\delta)_2 = \delta(4) - \delta(7) = 2.08$ (γ change). The same observations



SCHEME I Prediction of ^{13}C-NMR chemical shifts through an incremental approach.

are expected with the terminal units E* or P*. Consequently, the following assignments are proposed:

$$\delta_{a\text{-}\mathrm{E\underline{E}E^*}} = \delta_{a\text{-}\mathrm{E\underline{E}E}} = \text{peak } \#4$$

$$\delta_{a\text{-}\mathrm{E\underline{E}P^*}} = \delta_{a\text{-}\mathrm{E\underline{E}P}} = \text{peak } \#4$$

$$\delta_{a\text{-}\mathrm{P\underline{E}E^*}} = \delta_{a\text{-}\mathrm{P\underline{E}P^*}} = \delta_{a\text{-}\mathrm{P\underline{E}E}} = \delta_{a\text{-}\mathrm{P\underline{E}P}} = \text{peak } \#7$$

Two model compounds have been used for other useful assignments: 2-[2-butoxyethoxy]ethanol CH_3-CH_2-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH was used to precisely determine the δ value of $\underline{\mathrm{I}}^1$EE*, and *a*- and *b*-I$\underline{\mathrm{E}}$E* carbon atoms which were 71.28, 70.37 and 70.68, respectively. Notice that these peaks may allow the detection of some residual free alcohol. The *a*- and *b*- carbons from the last E* units are assigned at δ = 72.89 and 61.79, respectively.

Homo poly(ethylene oxide) prepared with the same initiator was used to assign δ values of $\underline{\mathrm{I}}^1$EE (δ = 71.17, peak #1′), *a*-I$\underline{\mathrm{E}}$E_(70.25, peak #6), *b*-E$\underline{\mathrm{E}}$E* (70.61, peak #5); *b*-I$\underline{\mathrm{E}}$E and *a*-E$\underline{\mathrm{E}}$E* are not separated from the *a*- and *b*-E$\underline{\mathrm{E}}$E at 70.78. Finally, the *a*- and *b*-carbon from the last E* unit are assigned at 72.84 and 61.80, respectively.

The difference observed in chemical shift between *b*-E$\underline{\mathrm{E}}$E (peak #4) and *b*-E$\underline{\mathrm{E}}$E* (peak #5) is used to assign the last *b*-E$\underline{\mathrm{E}}$P*, *b*-P$\underline{\mathrm{E}}$P* and *b*-P$\underline{\mathrm{E}}$E* carbons from E-centered triads, using the incremental values determined with the corresponding central triads (Scheme I). From this incremental approach, *b*-E$\underline{\mathrm{E}}$P* is expected to be included in peak #4, *b*-P$\underline{\mathrm{E}}$P* included in the peak #2 and *b*-P$\underline{\mathrm{E}}$E* was expected to be 70.88. In fact, this last resonance does not appear at the expected chemical shift, that is to say between peaks #3 and #4. Heatley [13] assigned this triad at the same chemical shift as that of *b*-E$\underline{\mathrm{E}}$P (peak #3) from the spectra obtained at ambient temperature in deuterated chloroform. We tested also the alternative assignment and compared the results with Monte-Carlo simulation. Table I gives the complete assignments of all carbons from both central and terminal E-centered triad.

Also included in this chemical shift range are some other resonances that are not relative to E-centered triads, particularly the *a*-PP$\underline{\mathrm{E}}$* which is expected in peak #3. Nevertheless, if considering the reactivity ratios and the composition of the feed used here, its relative intensity must be quite small, except at very high conversion.

It is worth noticing that the OP units described above are always oriented in the same direction. The peaks *a*- and *b*-$\vec{\mathrm{P}}\mathrm{E}\overleftarrow{\mathrm{P}}$ at 68.98 can be neglected; therefore the contribution of *a*- and *b*-$\overleftarrow{\mathrm{P}}\mathrm{E}\vec{\mathrm{P}}$ into peak #3 can also be neglected.

SIMULATION BY THE MONTE CARLO METHOD

Peak resonances are assigned to the triads centered in EO units. The correlation of NMR results with simulation calculation can be validated using both experimental results (peaks assignments, reactivity ratios) and theoretical kinetic schemes.

The number of instantaneous centered triads is usually deduced from the addition probabilities of any monomer on the growing polymer chains (see Appendix) and the average distributions obtained by integration over all the reaction. Nevertheless, since the end groups are not taken into account, these classical expressions are restricted to infinite chains and cannot be used here.

We have employed the Monte Carlo method to build up the polymer chains. Such an approach was already described by Mirabella [15] to simulate the compositional heterogeneity of copolymers synthesized by radical polymerization. All triads can then be deduced by "reading" the monomer units all along the polymer chain.

Simulation Algorithm

One of the main purposes of the simulation algorithm is to generate a large number of polymer chains so that the counting of the sequences can be considered as representative of the actual sample, but nevertheless smaller than the computer capacity. In addition, dealing with a too great number of polymer chains increases the calculation time. In our case, the polymer chains are built and the triads counted dynamically, that is, each new monomer addition on a growing chain leads to a new triad, the nature of which is analyzed and counted before proceeding to any new monomer addition. This procedure reduces highly the required memory since it is not necessary to store the composition of each polymer chain.

The algorithm can be simply described by the following steps:

1. Input variables are the number of alcohol and monomers (ethylene oxide and propylene oxide) molecules and the reactivity ratios. As stated above in the anionic case, the number of polymer chains is defined by the number of alcohol molecules. The ratio of monomer to alcohol numbers will define the degree of polymerization. The proportion of ethylene oxide and propylene oxide first added on the starting alcohol is assumed to depend on the monomer mixture (initiation step).
2. A polymer chain is chosen at random. The conditional probabilities of propagation on the last monomer unit are calculated according to a first-order Markov model (see Appendix) and the reaction of either EO or PO is selected depending on these probabilities.
3. Once the polymer chain contains at least three monomer units, the nature of the triad is determined and stored in the appropriate counter. The program loops on steps 2 and 3 until the complete consumption of the monomers. This simulation assumes that only regular head-to-tail addition takes place. The inversion placement of the PO units can be neglected because of the low content of PO units in the copolymer chains investigated here. This algorithm is suitable not only to determine the microstructures of polymer chains synthesized anionically, but also to simulate the kinetic behavior and to obtain the molecular weight distribution.

Results and Discussion

The number of monomer molecules considered in the simulation goes generally from 200,000 to 500,000 so that the experimental conditions (molar fraction of both monomers) are reproduced. The number of alcohol molecules is taken in order to obtain the desired degree of polymerization.

The simulation gives all the E-centered triads occurrence, both inside and at the ends of the polymer chains. The first E-centered triad is always IEE since all the polymer chains start with the diethoxybutanol, so that the analysis of the triads (step 3 of the algorithm) begins after the first monomer addition. The triads have been combined in order to reproduce the composite NMR peaks according to assignments given in Table I, keeping in mind that the simulation does not distinguish between the *a*- and *b*-carbon atoms of the E-centered unit while they are distinguishable by NMR. For example, the fraction of *a*-E$\underline{\text{E}}$E carbon atoms will be half the fraction of E$\underline{\text{E}}$E triads given by the simulation.

In the case of probabilities-based calculations (infinite chain lengths), the equations yielding the intensities of the NMR peaks would be:

$$I_1 = (b\text{-P}\underline{\text{E}}\text{P}) = 0.5.(\text{P}\underline{\text{E}}\text{P})$$

$$I_2 = (b\text{-P}\underline{\text{E}}\text{E}) = 0.5.(\text{P}\underline{\text{E}}\text{E}) = 0.5.(\text{E}\underline{\text{E}}\text{P})$$

$$I_3 = (b\text{-E}\underline{\text{E}}\text{P}) = I_2$$

$$I_4 = (a + b)\text{-}(\text{E}\underline{\text{E}}\text{E}) + (a\text{-E}\underline{\text{E}}\text{P}) = (\text{E}\underline{\text{E}}\text{E}) + 0.5.(\text{E}\underline{\text{E}}\text{P})$$

$$I_7 = (a\text{-P}\underline{\text{E}}\text{E}) + (b\text{-P}\underline{\text{E}}\text{E}) = 0.5.(\text{P}\underline{\text{E}}\text{E}) + 0.5.(\text{P}\overline{\text{E}}\text{P}) = I_1 + I_2.$$

Both I_5 and I_6 relative to chains ends are equal to zero.

Figures 5 and 6 show how some peak intensities may depend on the conversion and on the average chain length. Note that this simulation is not valid for radical copolymerization since the polymer chains formed at the beginning of the reaction, that is, at low conversion, are the longest ones.

Figure 5 depicts the variation of the intensity of the peak #4 [$I_4 = (a + b) -$ (E$\underline{\text{E}}$E) + (a-E$\underline{\text{E}}$P)] which is the most intense peak in the NMR spectrum. The probability model assumes that infinite chain lengths are formed even at low conversion. The intensity decreases with increasing conversion since ethylene oxide is the most reactive of both monomers and the proportion of propylene oxide increases in the monomer mixture. In our case, the chain lengths are short at the beginning of the reaction and increase with conversion. The proportion of E-centered triads first increases with the chain length and then decreases as above.

The evolution of two chain end triads, namely *b*-E$\underline{\text{E}}$E* (peak #5) and *a*-I$\underline{\text{E}}$E (peak #6) are shown in Figure 6. As expected, their intensity decreases with increasing conversion. The probability based model would give zero for these peaks.

Comparison with the NMR results are displayed in Table II. Overlapping peaks #1 and #1′ have been considered together. When the area of peak #5 is too small compared with that of peak #4 (case of the higher DP when the fraction of terminal triads *b*-E$\underline{\text{E}}$E* becomes negligible), they are both considered together.

The most important feature is good agreement between NMR results and Monte Carlo calculations, for validating both the assignments of the NMR peaks

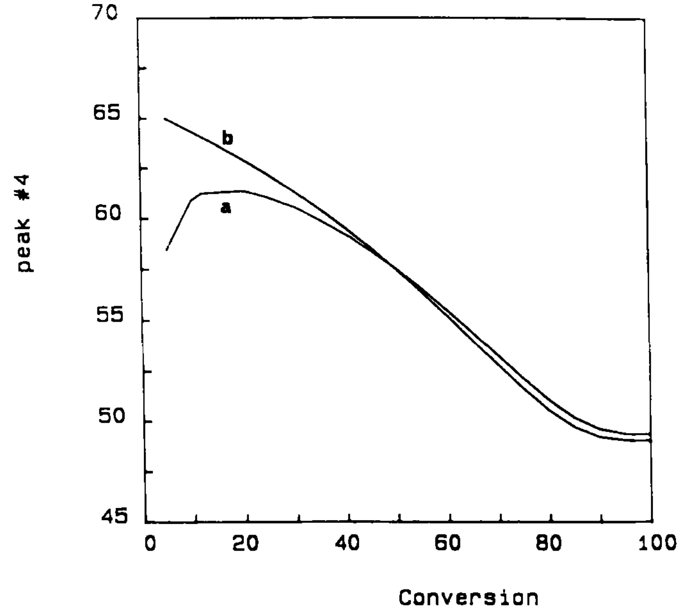


FIGURE 5 Simulation of the peak #4 intensity versus conversion from Monte Carlo method (a) and probability model (b).

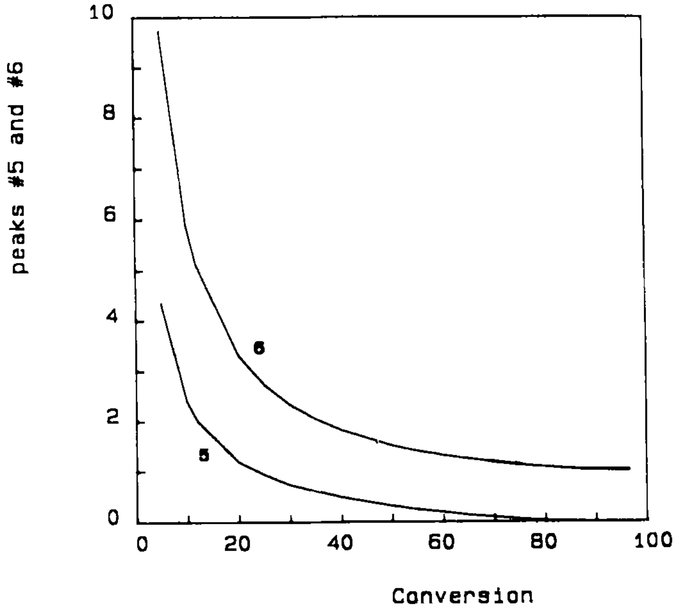


FIGURE 6 Simulation of the peak #5 (*b*-EEE*) and 6 (*a*-IEE) intensities versus conversion from the Monte Carlo method.

TABLE II

Experimental and simulation results. NMR: ^{13}C-NMR results.

Yield	12%			41%			65%		
DP	10			33			56		
Peaks	NMR	MC	P	NMR	MC	P	NMR	MC	P
1 + 1'	6.95	7.09	3.45	6.11	5.71	4.57	6.82	6.98	6.43
2	8.05	7.13	9.67	8.79	9.57	10.45	9.75	10.40	11.04
3	8.85	7.58	9.67	10.42	9.67	10.45	11.58	10.29	11.04
4	61.40	61.25	63.37	60.96	59.53	59.51	54.96	54.52	54.01
5	2.55	1.99	0.00						
6	4.50	5.06	0.00	2.07	1.99	0.00	1.18	1.38	0.00
7	7.70	10.24	13.12	11.62	13.75	15.02	13.39	16.35	17.47

MC: Monte Carlo method; P: probabilities of infinite length chains.

and the kinetic models from which the Monte Carlo algorithm has been constructed. It may be seen that the probability-based results are particularly wrong when dealing with short-length chains, since the terminal triads cannot be counted (hence the values 0.00 for the peaks #5 and #6). The difference becomes smaller when the chain lengths increase since the proportion of the chain ends in the triads occurrence decreases. This effect is clearly evidenced when the DP goes from 10 to 56. For this latter case, NMR, Monte Carlo, and probability results are in reasonable agreement.

APPENDIX

Calculation of the Number of Different E-centered Triads

Propagation mechanisms are usually described using a first-order Markov model in which the probability of adding a new monomer unit depends on the polymer chain end (i.e., the last added monomer).

Let us consider a unit E at the end of the polymer chain. The probability to obtain a diad EE will be P_{ee} and, consequently, the probability of occurrence of a diad EP will be $P_{ep} = 1 - P_{ee}$. Therefore, the number of diads EE formed in a small conversion range (instantaneous diads) will be equal to the number of units E multiplied by P_{ee}. (Owing to the composition drift, we have to consider only small ranges of conversion during which the composition remains constant.) In the same way, the number of instantaneous triads will be:

$$(\mathrm{EEE}) = (\mathrm{E}).(\mathrm{P}_{ee})^2$$

$$(\mathrm{EEP}) = (\mathrm{E}).\mathrm{P}_{ee}.\mathrm{P}_{ep} = (\mathrm{PEE})$$

$$(\mathrm{PEP}) = (\mathrm{P}).\mathrm{P}_{pe}.\mathrm{P}_{ep}.$$

where (E) and (P) are the instantaneous numbers of E and P units, respectively.

TABLE III

Classical simulation of the copolymerization. F_E is the E instantaneous molar fraction in the copolymer and $\langle F_E \rangle$ is the average molar fraction. The triads EEE, EEP and PEP are given in molar fraction (EEP = PEE).

Conv.	F_E	$\langle F_E \rangle$	EEE	EEP	PEP
10	0.739	0.749	0.547	0.192	0.068
20	0.715	0.738	0.530	0.198	0.074
30	0.684	0.725	0.512	0.203	0.082
40	0.645	0.710	0.491	0.209	0.091
65	0.471	0.656	0.430	0.221	0.129
95	0.011	0.526	0.382	0.218	0.183

NMR signals are proportional to the overall number of triads all along the chains. These values are obtained by summation of the instantaneous data over the conversion. For example, the summation of all the triads EEE will be given by

$$(\mathrm{EEE}) = \Sigma d[\mathrm{EO}].(P_{ee})^2$$

where d[EO] is the amount of EO reacted during a polymerization increment (taken here as 0.001 of the starting monomer concentration). Results are usually given in terms of E-centered triads fractions.

Table III reports the results of such a simulation for an equimolar monomer mixture and the following reactivity ratios: $r_{eo} = 3.00$, $r_{po} = 0.27$.

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