Markovian Statistics for Finite Chains: Characterization of End Group Structures and Initiation, Chain Propagation, and Chain-Transfer Probabilities in Poly(ethylene-*co*-propylene)

James C. Randall*

Corporate Research Laboratories, Exxon Research & Engineering Company, Route 22 East, Annandale, New Jersey 08801

Steven P. Rucker

Corporate Research Laboratories, Exxon Research & Engineering Company, 1900 East Linden Avenue, Linden, New Jersey 07036

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ABSTRACT: Poly(ethylene-*co*-1-olefin)s produced with metallocene catalyst systems usually have one aliphatic and one olefinic end group per copolymer chain. Four unique beginning and ending sequences, EE, EP, PE, and PP, for poly(ethylene-*co*-propylene) have been characterized both structurally and quantitatively from ^{13}C NMR data. A complete triad sequence distribution, which included all possible end group triads, was obtained and compared to a corresponding first-order Markovian statistical analysis, modified for chain-initiating and chain-terminating events. Chain-transfer reactions were observed to be sequence-dependent and occur in the order, $^{T}P_{PP} \cong {}^{T}P_{EP} \gg {}^{T}P_{PE} \cong {}^{T}P_{EE}$. The observed close similarities of the experimental triad distributions to those for corresponding first-order Markovian systems permitted a method to be developed for determining the concentrations of PE versus EE initiating sequences, which cannot be distinguished directly by ^{13}C NMR. This statistical approach led to the important conclusion that initiating units were almost exclusively propyl, irrespective of ethylene mole fractions between 0.48 and 0.69.

Introduction

Ethylene–1-olefin copolymers produced with metallocene catalysts have narrow compositional and molecular weight distributions. Typically, there is one olefinic and one saturated end group per chain. The former are produced by chain-transfer reactions involving possible β-hydride eliminations, β-hydride transfers to ethylene, or metalations followed by rearrangements.[1,2] The saturated end groups form following hydrogen transfer during initiation.[3] In contrast to the uniform sequence distributions observed for the main chain, the end groups may be structurally complex with a number of different types being present; namely, vinyl, branched vinyl, and di- and trisubstituted double bonds. The end group structures not only depend upon the precise mechanisms for initiation and chain transfer, but also upon the initial and final sequences of comonomer additions.

There are four unique beginning and ending diad sequences for an ethylene–propylene copolymer, that is, PP, EP, PE, and EE. A singular type of chain-transfer step that creates olefinic end groups would produce only four types of end groups. Each competing mechanism would produce another four end groups. A further structural complication occurs for penultimate propylene units, which can have configurational isomerism, that is, either *meso* or *racemic*. Such an effect may be manifested by subtle line splittings among the resonances observed for the PP and PE diads. Four kinds of olefinic end groups were identified from a fairly complex olefinic region containing a number of weak resonances. Of these, only two types were major, as will be discussed later. Three types of saturated end groups, again with only two being major, were identified in the present copolymers of ethylene and propylene. (The chains beginning with EE and PE produce similar linear structures.) These numbers alone indicate that there is only one mechanism for initiation and no significant variations in the chain-transfer chemistry for termination.

The present investigation was undertaken to develop a systematic approach to the structural analysis of ethylene–propylene copolymers. Determinations of the comonomer composition and distribution, end group types, and amounts and molecular weight are desired. A technique that provides abundant structural information for such analyses is carbon-13 nuclear magnetic resonance spectroscopy (NMR). The ^{13}C NMR methods for determination of the comonomer amounts and triad sequence distributions are well established for the ethylene–1-olefin copolymers ranging from ethylene–propylene to ethylene–1-octene.[4]

Carbon-13 NMR can also be used to identify, and to measure, the amounts of the various kinds of end groups. Once this is accomplished, a number average molecular weight can be computed easily. In previously published ^{13}C NMR analyses of ethylene–1-olefin copolymers, molecular weights were sufficiently high that the end group content did not enter into the analyses of sequence distributions and comonomer contents. The present copolymers have number average molecular weights between 700 and 1700; consequently the types and concentrations of end groups must be taken into consideration when performing any type of structural analysis. Once the end groups are identified and measured quantitatively, it is only natural that the distribution of comonomers as terminal units should be compared to the distribution of comonomers within the main chain. This is best accomplished by determining the statistical behaviors of the main chain and end group comonomer distributions. In the present study of ethylene–propylene copolymers, a first-order Markovian fit was obtained for the complete triad sequence distributions for four different types of saturated and for four different types of olefinic end groups.

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* Present address and author to whom all correspondence should be addressed: Baytown Polymers Center, 5200 Bayway Drive, Baytown, TX 77522.

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The Markovian probabilities for chain propagation could be compared directly with the Markovian probabilities for initiation and termination.

It was observed that the probabilities for initiation occurred in the following order for the chain-beginning diads:

$$P_{IP} >>> P_{IE}$$

and the probabilities for chain transfer were

$${}^{T}P_{PP} \cong {}^{T}P_{EP} \gg {}^{T}P_{PE} \cong {}^{T}P_{EE}$$

Both of the above sets of probabilities were independent of composition, in contrast to the probabilities for chain propagation, which were markedly dependent upon composition. At a mole fraction of ethylene of [E] = 0.48,

$$P_{EP} \cong P_{PE} > P_{PP} \cong P_{EE}$$

At [E] = 0.55,

$$P_{PE} > P_{EP} > P_{EE} > P_{PP}$$

and, at [E] = 0.69,

$$P_{PE} > P_{EE} \gg P_{EP} > P_{PP}$$

In addition to NMR experimental methods for data acquisition, this study also gives predicted results from first-order Markovian statistical models, which are compared with experimental data for both the complete copolymer triad sequence distributions and end group diad distributions.

Experimental Section

The three poly(ethylene-*co*-propylene) copolymers examined in this study ranged in molecular weight (M_n) from 700 to 1700 and in composition from 0.48 to 0.69 mole fraction of ethylene. An amount of 1.5 g of polymer dissolved readily in 3.5 g of deuteriated chloroform used as an NMR lock solvent. Relaxation times up to ~15 s for quaternary olefinic carbons require longer recycle delays for quantitative acquisitions than those for corresponding high molecular weight copolymers. To this end, a paramagnetic relaxation agent, $Cr(acac)_3$ (chromium acetylacetonate), was added to the lock solvent, at a concentration of 15 mg/mL. The relaxation agent shortens the necessary recycle delay period to 3–5 s, as opposed to the 1–1.5 min necessary for an undoped sample. The $Cr(acac)_3$ broadens the resonance lines slightly, but not enough to outweigh its benefits.

Spectra were acquired at a carbon Larmor frequency of 100 MHz on a JEOL GSX-400 spectrometer. The number of scans necessary for sufficient signal to noise ranged from approximately 4000, for a polymer molecular weight of 700, to 12 000, for a polymer molecular weight of 2000. Spectra were acquired with inverse gated decoupling to avoid nuclear Overhauser enhancement (NOE) effects, which would skew the quantitative analysis. Time domain free induction decays (FIDs) of 32K points were Fourier transformed to give 32K point spectra.

Review of First-Order Markovian Statistics for Infinite Chains

A review of the base case for high molecular weight copolymers (infinite chains) for first-order Markovian statistical analyses would be helpful in establishing a framework for the necessary modifications to the statistics for analyses of low molecular copolymers (finite chains), which require an accountability for initiation and termination reactions. Up to this point, Markovian statistics have been applied experimentally to data from copolymers of sufficient molecular weight that an omission of end groups created no significant errors in analyses of sequence distributions and comonomer mole fractions. There are excellent literature references available if the reader wants a thorough background in the application of Markovian statistics to "infinite chains".[5-7]

Price introduced the concept of Markovian statistics for finite chains and developed a framework for free radical copolymers.[8] Some information about the initiating and terminating copolymerization mechanisms must be known to define appropriately the Markovian transition probabilities for initiation and termination for finite chains. As pointed out by Price, Markovian statistics developed for finite chains from free radical copolymerizations cannot be applied directly to copolymers produced by other copolymerization mechanisms. Some modifications are needed primarily because of differences in terminating reactions. Chain transfer is extremely important in Ziegler–Natta polymerizations. It is also important to reduce any application of Markovian statistics for finite chains to practice through an experimental evaluation.

An important property of Markovian analyses is that the statistics reflect only the probabilities of going from initial to final states. They do not provide information about the pathways through which the final state was obtained. There are four basic first-order Markov transition probabilities for the four possible adjoining pairs of monomer units (diads) in a copolymer chain. In a Markov diad, the first unit is called the initial state and the second unit is called the final state. With the exception of the end groups, a diad description requires that each unit in a copolymer chain serve as both an initial state and a final state. For a copolymer chain, there are only two possibilities for an initial state and, likewise, only two possibilities for a final state. (The statistical treatments that follow will be derived using symbols for poly(ethylene-*co*-propylene), although they apply to any copolymer chain.)

initial state	add	final state	transition probability
E	E	E	P_{EE}
E	P	P	P_{EP}
P	E	E	P_{PE}
P	P	P	P_{PP}

Accordingly, the above four transition probabilities must be related as follows:

$$P_{EE} + P_{EP} = 1 \tag{1}$$

$$P_{PE} + P_{PP} = 1 \tag{2}$$

Equations 1 and 2 describe the options for propagation only; as will be seen later, additional terms are required when the end groups represent a significant, observable fraction of the chain composition.

A first-order Markovian system reduces to zero order, or Bernoullian, when

$$P_{EE} = P_{PE} = {}^{0}P_{E} = \text{mole fraction of "E"}$$

and

$$P_{EP} = P_{PP} = {}^{0}P_{P} = \text{mole fraction of "P"}$$

which demonstrates that chain propagation for Bernoullian copolymer systems is independent of the identity of the initial state. As a consequence of eqs 1 and 2, Bernoullian statistical analyses are defined with only one independent variable and first-order Markov analyses are defined with two independent variables.

To describe a sequence of any length in a first-order Markovian statistical scheme, it is necessary to define the probability for finding the first unit of the sequence. The subsequent units are defined by the appropriate transition probabilities. The following additional definitions are necessary:

${}^{1}P_{\mathrm{P}}$ = probability of finding a P unit at any location in a copolymer chain

${}^{1}P_{\mathrm{E}}$ = probability of finding a E unit at any location in a copolymer chain

and

$${}^{1}P_{\mathrm{P}} + {}^{1}P_{\mathrm{E}} = 1$$

In terms of transition probabilities, the probability of finding either a P or E unit anywhere in a copolymer chain follows from the consideration that the preceding unit can only be an E or P. Therefore,

$${}^{1}P_{\mathrm{P}} = {}^{1}P_{\mathrm{P}}P_{\mathrm{PP}} + {}^{1}P_{\mathrm{E}}P_{\mathrm{EP}} \tag{3}$$

$${}^{1}P_{\mathrm{E}} = {}^{1}P_{\mathrm{P}}P_{\mathrm{PE}} + {}^{1}P_{\mathrm{E}}P_{\mathrm{EE}} \tag{4}$$

Solving gives

$${}^{1}P_{\mathrm{P}} = \text{mole fraction of P} = P_{\mathrm{EP}}/(P_{\mathrm{EP}} + P_{\mathrm{PE}}) \tag{5}$$

$${}^{1}P_{\mathrm{E}} = \text{mole fraction of E} = P_{\mathrm{PE}}/(P_{\mathrm{EP}} + P_{\mathrm{PE}}) \tag{6}$$

A sequence of any length in a copolymer chain can now be defined in terms of only two transition probabilities. The first-order Markov description for a complete, normalized triad distribution is given below:

$$[\mathrm{EEE}] = {}^{1}P_{\mathrm{E}}P_{\mathrm{EE}}P_{\mathrm{EE}} = \frac{P_{\mathrm{PE}}(1 - P_{\mathrm{EP}})^{2}}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} \tag{7}$$

$$[\mathrm{EEP} + \mathrm{PEE}] = {}^{1}P_{\mathrm{E}}P_{\mathrm{EE}}P_{\mathrm{EP}} + {}^{1}P_{\mathrm{P}}P_{\mathrm{PE}}P_{\mathrm{EE}} = \frac{2P_{\mathrm{PE}}P_{\mathrm{EP}}(1 - P_{\mathrm{EP}})}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} \tag{8}$$

$$[\mathrm{PEP}] = {}^{1}P_{\mathrm{P}}P_{\mathrm{PE}}P_{\mathrm{EP}} = \frac{P_{\mathrm{PE}}P_{\mathrm{EP}}^{2}}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} \tag{9}$$

$$[\mathrm{EPE}] = {}^{1}P_{\mathrm{E}}P_{\mathrm{EP}}P_{\mathrm{PE}} = \frac{P_{\mathrm{PE}}^{2}P_{\mathrm{EP}}}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} \tag{10}$$

$$[\mathrm{PPE} + \mathrm{EPP}] = {}^{1}P_{\mathrm{P}}P_{\mathrm{PP}}P_{\mathrm{PE}} + {}^{1}P_{\mathrm{E}}P_{\mathrm{EP}}P_{\mathrm{PP}} = \frac{2P_{\mathrm{PE}}P_{\mathrm{EP}}(1 - P_{\mathrm{PE}})}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} \tag{11}$$

$$[\mathrm{PPP}] = {}^{1}P_{\mathrm{P}}P_{\mathrm{PP}}P_{\mathrm{PP}} = \frac{P_{\mathrm{EP}}(1 - P_{\mathrm{PE}})^{2}}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} \tag{12}$$

Note that the E- and P-centered triads sum independently as follows:

$$[\mathrm{EEE}] + [\mathrm{EEP} + \mathrm{PEE}] + [\mathrm{PEP}] = \frac{P_{\mathrm{PE}}}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} = [\mathrm{E}] \tag{13}$$

$$[\mathrm{EPE}] + [\mathrm{PPE} + \mathrm{EPP}] + [\mathrm{PPP}] = \frac{P_{\mathrm{EP}}}{(P_{\mathrm{EP}} + P_{\mathrm{PE}})} = [\mathrm{P}] \tag{14}$$

and, of course, the six triads sum to unity. These latter relationships appear trivial but can be helpful when testing experimental data for the best trial values for the transition probabilities. A computer program can be used effectively to narrow the choice of values for the transition probabilities, as will be seen later.

Development of First-Order Markovian Statistics for Finite Chains

Up to this point in the discussion, we have reviewed a copolymer statistical description that has been defined and used for over 30 years. Equations 1–4 were derived for infinite chains, with no consideration given to the end groups. Relatively low molecular weight copolymers pose a unique situation. Molecular weights in a range of 500–3000 can be achieved through chain-transfer reactions that occur with a sufficient frequency that both the termination option and the probabilities for initiation should be considered when defining any Markovian statistical distribution.

The present study develops the necessary modifications for a first-order Markovian statistical description for copolymers produced by Ziegler–Natta copolymerizations, which require Markovian probabilities for initiation and chain transfer. Initiation only occurs once per copolymer chain, but chain transfer is one of the options for each monomer adding to a growing copolymer chain. For chain transfer, four additional transition probabilities are required:

${}^{\mathrm{T}}P_{\mathrm{PP}}$ = probability that chain transfer occurs immediately following an addition of a P unit to a preceding P unit

${}^{\mathrm{T}}P_{\mathrm{PE}}$ = probability that chain transfer occurs immediately following an addition of an E unit to a preceding P unit

${}^{\mathrm{T}}P_{\mathrm{EP}}$ = probability that chain transfer occurs immediately following an addition of a P unit to a preceding E unit

${}^{\mathrm{T}}P_{\mathrm{EE}}$ = probability that chain transfer occurs immediately following an addition of an E unit to a preceding E unit

It is best to define the chain-transfer probabilities in terms of the first-order Markovian model as shown above. If the chain-transfer reactions actually do not depend upon the identity of the preceding unit, the system will automatically reduce to Bernoullian when

$${}^{\mathrm{T}}P_{\mathrm{EE}} = {}^{\mathrm{T}}P_{\mathrm{PE}}$$

and

$${}^{\mathrm{T}}P_{\mathrm{EP}} = {}^{\mathrm{T}}P_{\mathrm{PP}}$$

Chain initiation must also be considered when describing any order of Markovian statistics for finite chains. Either monomer unit can initiate a new chain at a vacant catalyst site at any time during copolymerization. Only two probabilities are required to describe the initiating sequence of events.

P_{IE} = probability that an incoming E unit adds to a vacant catalyst site and begins growth of a new copolymer chain

P_{IP} = probability that an incoming P unit adds to a vacant catalyst site and begins growth of a new copolymer chain

The symbols P_{IE} and P_{IP} (rather than ${}^IP_E$ and ${}^IP_E$) were chosen to avoid confusion with ${}^1P_E$ and ${}^1P_P$.

Although initiation is an option for an incoming monomer unit, it is not an option for a growing copolymer chain because initiation can only occur once per chain. Chain transfer also only occurs once per chain, but chain transfer and propagation are still the only two options possible at each step in the growth of a copolymer chain. Therefore, eqs 1 and 2 become

$$P_{EE} + P_{EP} + {}^TP_{EE} + {}^TP_{EP} = 1 \tag{15}$$

$$P_{PE} + P_{PP} + {}^TP_{PE} + {}^TP_{PP} = 1 \tag{16}$$

Price derived an equation in the same form as eqs 15 and 16 in his development of first-order Markovian statistics for finite chains for free radically produced copolymers.[8] His transition probability was for termination as opposed to chain transfer.

Markovian statistical results are normally compared to experimental data that represents an "average" chain, which has been gathered from a sample of, hopefully, largely redundant copolymer chains. Initiation and chain transfer still occur only once per "average" chain, although these events will be normalized over the various possibilities for initiation and chain transfer. The average chain, therefore, will have a normalized distribution of end groups over the possibilities for the entire assembly of chains. Markovian statistics, as applied to the average chain, will yield probabilities for initiation and chain transfer that reflect the events that occur over the distribution of chains. It should also be noted that the initial chain unit is inherently included in the transition probabilities, P_{EE}, P_{EP} and P_{PP}, P_{PE}, because the probability, for example, that a propylene unit adds to a chain ending in ethylene, P_{EP}, includes the possibility that the chain ending in ethylene has only one unit, which serves as the initial state.

As is similar to the description for infinite chains, the probabilities for finding a given unit at any position, *after the initiator unit*, in a finite copolymer chain is

$${}^1P_P = {}^1P_PP_{PP} + {}^1P_EP_{EP} + {}^1P_P{}^TP_P + {}^1P_E{}^TP_{EP} \tag{17}$$

$${}^1P_E = {}^1P_PP_{PE} + {}^1P_EP_{EE} + {}^1P_P{}^TP_{PE} + {}^1P_E{}^TP_{EE} \tag{18}$$

and, after appropriate substitutions, become

$${}^1P_P = \frac{P_{EP} + {}^TP_{EP}}{(P_{EP} + P_{PE} + {}^TP_{EP} + {}^TP_{PE})} \tag{19}$$

$${}^1P_E = \frac{P_{PE} + {}^TP_{PE}}{(P_{EP} + P_{PE} + {}^TP_{EP} + {}^TP_{PE})} \tag{20}$$

For the reasons stated previously, the above probabilities for finding a P or E unit do not contain any probability for initiation. This is not true for a triad distribution where initiation must be included to account for the first triad in the copolymer chain. A Markovian description of a triad distribution for a finite chain, which includes both initiation and termination, is given below:

$$[\mathrm{EEE}] = P_{IE}P_{EE}P_{EE} + P_{IE}P_{EE}{}^TP_{EE} + {}^1P_EP_{EE}P_{EE} + {}^1P_EP_{EE}{}^TP_{EE} \tag{21}$$

$$[\mathrm{EEP}] = P_{IE}P_{EE}P_{EP} + P_{IE}P_{EE}{}^TP_{EP} + {}^1P_EP_{EE}P_{EP} + {}^1P_EP_{EE}{}^TP_{EP} \tag{22}$$

$$[\mathrm{PEE}] = P_{IP}P_{PE}P_{EE} + P_{IP}P_{PE}{}^TP_{EE} + {}^1P_PP_{PE}P_{EE} + {}^1P_PP_{PE}{}^TP_{EE} \tag{23}$$

$$[\mathrm{PEP}] = P_{IP}P_{PE}P_{EP} + P_{IP}P_{PE}{}^TP_{EP} + {}^1P_PP_{PE}P_{EP} + {}^1P_PP_{PE}{}^TP_{EP} \tag{24}$$

$$[\mathrm{EPE}] = P_{IE}P_{EP}P_{PE} + P_{IE}P_{EP}{}^TP_{PE} + {}^1P_EP_{EP}P_{PE} + {}^1P_EP_{EP}{}^TP_{PE} \tag{25}$$

$$[\mathrm{PPE}] = P_{IP}P_{PP}P_{PE} + P_{IP}P_{PP}{}^TP_{PE} + {}^1P_PP_{PP}P_{PE} + {}^1P_PP_{PP}{}^TP_{PE} \tag{26}$$

$$[\mathrm{EPP}] = P_{IE}P_{EP}P_{PP} + P_{IE}P_{EP}{}^TP_{PP} + {}^1P_EP_{EP}P_{PP} + {}^1P_EP_{EP}{}^TP_{PP} \tag{27}$$

$$[\mathrm{PPP}] = P_{IP}P_{PP}P_{PP} + P_{IP}P_{PP}{}^TP_{PP} + {}^1P_PP_{PP}P_{PP} + {}^1P_PP_{PP}{}^TP_{PP} \tag{28}$$

For an infinite chain, EEP = PEE and EPP = PPE. As can be seen above, these equalities may not hold for a finite chain, which may have different E/P populations for the end groups than for the interior chain sequences. After appropriate substitution of eqs 15 and 16 into the above triad equations, the following first-order Markov description is obtained for those copolymers where end group options are important:

$$[\mathrm{EEE}] = ({}^1P_E + P_{IE})(1 - P_{EP} - {}^TP_{EE} - {}^TP_{EP})^2 + ({}^1P_E + P_{IE}){}^TP_{EE}(1 - P_{EP} - {}^TP_{EE} - {}^TP_{EP}) \tag{29}$$

$$[\mathrm{EEP}] = ({}^1P_E + P_{IE})P_{EP}(1 - P_{EP} - {}^TP_{EE} - {}^TP_{EP}) + ({}^1P_E + P_{IE}){}^TP_{EP}(1 - P_{EP} - {}^TP_{EE} - {}^TP_{EP}) \tag{30}$$

$$[\mathrm{PEE}] = ({}^1P_P + P_{IP})P_{PE}(1 - P_{EP} - {}^TP_{EE} - {}^TP_{EP}) + ({}^1P_P + P_{IP})P_{PE}{}^TP_{EE} \tag{31}$$

$$[\mathrm{PEP}] = ({}^1P_P + P_{IP})P_{PE}P_{EP} + ({}^1P_P + P_{IP})P_{PE}{}^TP_{EP} \tag{32}$$

$$[\mathrm{EPE}] = ({}^1P_E + P_{IE})P_{EP}P_{PE} + ({}^1P_E + P_{IE})P_{EP}{}^TP_{PE} \tag{33}$$

$$[\mathrm{EPP}] = ({}^1P_E + P_{IE})P_{EP}(1 - P_{PE} - {}^TP_{PP} - {}^TP_{PE}) + ({}^1P_E + P_{IE})P_{EP}{}^TP_{PP} \tag{34}$$

$$[\mathrm{PPE}] = ({}^1P_P + P_{IP})P_{PE}(1 - P_{PE} - {}^TP_{PP} - {}^TP_{PE}) + ({}^1P_P + P_{IP}){}^TP_{PE}(1 - P_{PE} - {}^TP_{PP} - {}^TP_{PE}) \tag{35}$$

$$[\mathrm{PPP}] = ({}^1P_P + P_{IP})(1 - P_{PE} - {}^TP_{PP} - {}^TP_{PE})^2 + ({}^1P_P + P_{IP}){}^TP_{PP}(1 - P_{PE} - {}^TP_{PP} - {}^TP_{PE}) \tag{36}$$

After expanding and summing eqs 29–36, the following

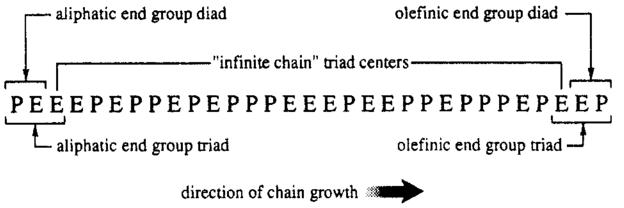

Figure 1. Model copolymer chain depicting end group diads and triads.

result is obtained:

$$\begin{aligned}&[\mathrm{EEE}] + [\mathrm{EEP}] + [\mathrm{PEE}] + [\mathrm{PEP}] + [\mathrm{EPE}] + [\mathrm{PPE}] + [\mathrm{EPP}] + [\mathrm{PPP}] \\ &= {}^1P_\mathrm{E} + {}^1P_\mathrm{P} - {}^1P_\mathrm{E}({}^\mathrm{T}P_\mathrm{EE}) - {}^1P_\mathrm{E}({}^\mathrm{T}P_\mathrm{EP}) - {}^1P_\mathrm{P}({}^\mathrm{T}P_\mathrm{PE}) - {}^1P_\mathrm{P}({}^\mathrm{T}P_\mathrm{PP}) + P_\mathrm{IE}P_\mathrm{EE} + P_\mathrm{IE}P_\mathrm{EP} + P_\mathrm{IP}P_\mathrm{PE} + P_\mathrm{IP}P_\mathrm{PP} \quad (37)\end{aligned}$$

$$= {}^1P_\mathrm{E} + {}^1P_\mathrm{P} = 1 \quad (38)$$

which, in eq 37, is the sum of the respective probabilities of finding P and E units minus the concentrations of the four terminal diads and plus the concentrations of the four initiating diads. Since the sum of the concentrations of the initiating diads must be the same as the sum of the concentrations of the terminating diads, these terms cancel in eq 37. Equation 38 demonstrates that when chain transfer and initiation are introduced into a Markovian statistical description of a *triad* distribution, the E- and P-centered triads still sum to the total probabilities for finding a P and an E unit, which is unity. This result is analogous to that for infinite chains, with the exception that the probability of finding either a P unit or an E unit is not the same as the respective mole fractions. The triad distribution does not include either the initial or final copolymer units, which are parts of diads, not triads. By definition, the central unit of a triad must have two neighbors. Diads are more complicated. Each unit of a copolymer chain is part of two diads, an initial state for one and a final state for the preceding diad. The mole fractions must include the initial and final unit contributions, but the definition of the probabilities for finding either an E unit or a P unit in a triad description inherently does not include the initial or final units of the copolymer chain, as shown in Figure 1.

When performing Markov statistical analyses on experimental triad distributions determined from NMR data of low molecular weight copolymers, resonances from the initial and terminal *diad* units in the chain must be located and excluded from the triad analysis. By contrast, steps must be taken to ensure that concentrations of the *end group triads* are included in a complete triad distribution for comparison with a calculated Markovian triad distribution. It should be noted in each of the Markovian triad equations 21–28 that independent terms exist for both the first and last *triads* of the copolymer chain.

The independent diad end group concentrations are still important because they can be used directly to determine values for P_IE and P_IP, and ${}^\mathrm{T}P_\mathrm{EE}$, ${}^\mathrm{T}P_\mathrm{EP}$, ${}^\mathrm{T}P_\mathrm{PE}$, ${}^\mathrm{T}P_\mathrm{PP}$, which are needed to calculate the overall triad distribution. Also, the diad concentrations can be used to determine concentrations for the end group triads, as shown below:

$$[\mathrm{EEE}]_\mathrm{t} = [\mathrm{E}][\mathrm{EE}]_\mathrm{t} = {}^1P_\mathrm{E}P_\mathrm{EE}({}^\mathrm{T}P_\mathrm{EE}) \quad (39)$$

$$[\mathrm{EEP}]_\mathrm{t} = [\mathrm{E}][\mathrm{EP}]_\mathrm{t} = {}^1P_\mathrm{E}P_\mathrm{EE}({}^\mathrm{T}P_\mathrm{EP}) \quad (40)$$

$$[\mathrm{PEE}]_\mathrm{t} = [\mathrm{P}][\mathrm{EE}]_\mathrm{t} = {}^1P_\mathrm{P}P_\mathrm{PE}({}^\mathrm{T}P_\mathrm{EE}) \quad (41)$$

$$[\mathrm{PEP}]_\mathrm{t} = [\mathrm{P}][\mathrm{EP}]_\mathrm{t} = {}^1P_\mathrm{P}P_\mathrm{PE}({}^\mathrm{T}P_\mathrm{EP}) \quad (42)$$

$$[\mathrm{EPE}]_\mathrm{t} = [\mathrm{E}][\mathrm{PE}]_\mathrm{t} = {}^1P_\mathrm{E}P_\mathrm{EP}({}^\mathrm{T}P_\mathrm{PE}) \quad (43)$$

$$[\mathrm{EPP}]_\mathrm{t} = [\mathrm{E}][\mathrm{PP}]_\mathrm{t} = {}^1P_\mathrm{E}P_\mathrm{EP}({}^\mathrm{T}P_\mathrm{PP}) \quad (44)$$

$$[\mathrm{PPE}]_\mathrm{t} = [\mathrm{P}][\mathrm{PE}]_\mathrm{t} = {}^1P_\mathrm{P}P_\mathrm{PP}({}^\mathrm{T}P_\mathrm{PE}) \quad (45)$$

$$[\mathrm{PPP}]_\mathrm{t} = [\mathrm{P}][\mathrm{PP}]_\mathrm{t} = {}^1P_\mathrm{P}P_\mathrm{PP}({}^\mathrm{T}P_\mathrm{PP}) \quad (46)$$

and

$$[\mathrm{EEE}]_\mathrm{i} = [\mathrm{EE}]_\mathrm{i}[\mathrm{E}] = P_\mathrm{IE}(P_\mathrm{EE})^2 \quad (47)$$

$$[\mathrm{EEP}]_\mathrm{i} = [\mathrm{EE}]_\mathrm{i}[\mathrm{P}] = P_\mathrm{IE}P_\mathrm{EE}P_\mathrm{EP} \quad (48)$$

$$[\mathrm{PEE}]_\mathrm{i} = [\mathrm{PE}]_\mathrm{i}[\mathrm{E}] = P_\mathrm{IP}P_\mathrm{PE}P_\mathrm{EE} \quad (49)$$

$$[\mathrm{PEP}]_\mathrm{i} = [\mathrm{PE}]_\mathrm{i}[\mathrm{P}] = P_\mathrm{IP}P_\mathrm{PE}P_\mathrm{EP} \quad (50)$$

$$[\mathrm{EPE}]_\mathrm{i} = [\mathrm{EP}]_\mathrm{i}[\mathrm{E}] = P_\mathrm{IE}P_\mathrm{EP}P_\mathrm{PE} \quad (51)$$

$$[\mathrm{EPP}]_\mathrm{i} = [\mathrm{EP}]_\mathrm{i}[\mathrm{P}] = P_\mathrm{IE}P_\mathrm{EP}P_\mathrm{PP} \quad (52)$$

$$[\mathrm{PPE}]_\mathrm{i} = [\mathrm{PP}]_\mathrm{i}[\mathrm{E}] = P_\mathrm{IP}P_\mathrm{PP}P_\mathrm{PE} \quad (53)$$

$$[\mathrm{PPP}]_\mathrm{i} = [\mathrm{PP}]_\mathrm{i}[\mathrm{P}] = P_\mathrm{IP}{P_\mathrm{PP}}^2 \quad (54)$$

First-order Markovian analyses, where each of the above types of conditional probabilities are obtained, will be performed on low molecular weight copolymers of ethylene and propylene.

Finally, it is instructive to examine the first-order Markovian description for finite chains as applied to a diad distribution:

$$[\mathrm{EE}] = P_\mathrm{IE}P_\mathrm{EE} + P_\mathrm{IE}{}^\mathrm{T}P_\mathrm{EE} + {}^1P_\mathrm{E}P_\mathrm{EE} + {}^1P_\mathrm{E}{}^\mathrm{T}P_\mathrm{EE} \quad (55)$$

$$[\mathrm{EP}] = P_\mathrm{IE}P_\mathrm{EP} + P_\mathrm{IE}{}^\mathrm{T}P_\mathrm{EP} + {}^1P_\mathrm{E}P_\mathrm{EP} + {}^1P_\mathrm{E}{}^\mathrm{T}P_\mathrm{EP} \quad (56)$$

$$[\mathrm{PE}] = P_\mathrm{IP}P_\mathrm{PE} + P_\mathrm{IP}{}^\mathrm{T}P_\mathrm{PE} + {}^1P_\mathrm{P}P_\mathrm{PE} + {}^1P_\mathrm{P}{}^\mathrm{T}P_\mathrm{PE} \quad (57)$$

$$[\mathrm{PP}] = P_\mathrm{IP}P_\mathrm{PP} + P_\mathrm{IP}{}^\mathrm{T}P_\mathrm{PP} + {}^1P_\mathrm{P}P_\mathrm{PP} + {}^1P_\mathrm{P}{}^\mathrm{T}P_\mathrm{PP} \quad (58)$$

After substituting for P_EE and P_PP using eqs 15 and 16, respectively, the following result is obtained for the sum of the four diads:

$$[\mathrm{EE}] + [\mathrm{EP}] + [\mathrm{PE}] + [\mathrm{PP}] = {}^1P_\mathrm{E} + {}^1P_\mathrm{P} + P_\mathrm{IE} + P_\mathrm{IP} = [\mathrm{E}] + [\mathrm{P}] = 1 \quad (59)$$

Because the end groups are parts of diads, the four possible diads sum to the mole fractions of E and P, which is unity.

^{13}C NMR End Group Resonance Assignments and Quantitative Method for the Triad and Diad Distributions

Quantitative methods for triad sequence distributions in poly(ethylene-*co*-propylene) have been developed from resonance assignments in ^{13}C NMR spectra.[4,9,10] A complete ^{13}C NMR spectrum at 100 MHz of a poly(ethylene-*co*-propylene) is shown in Figure 2a. The expanded aliphatic and olefinic regions are also shown in

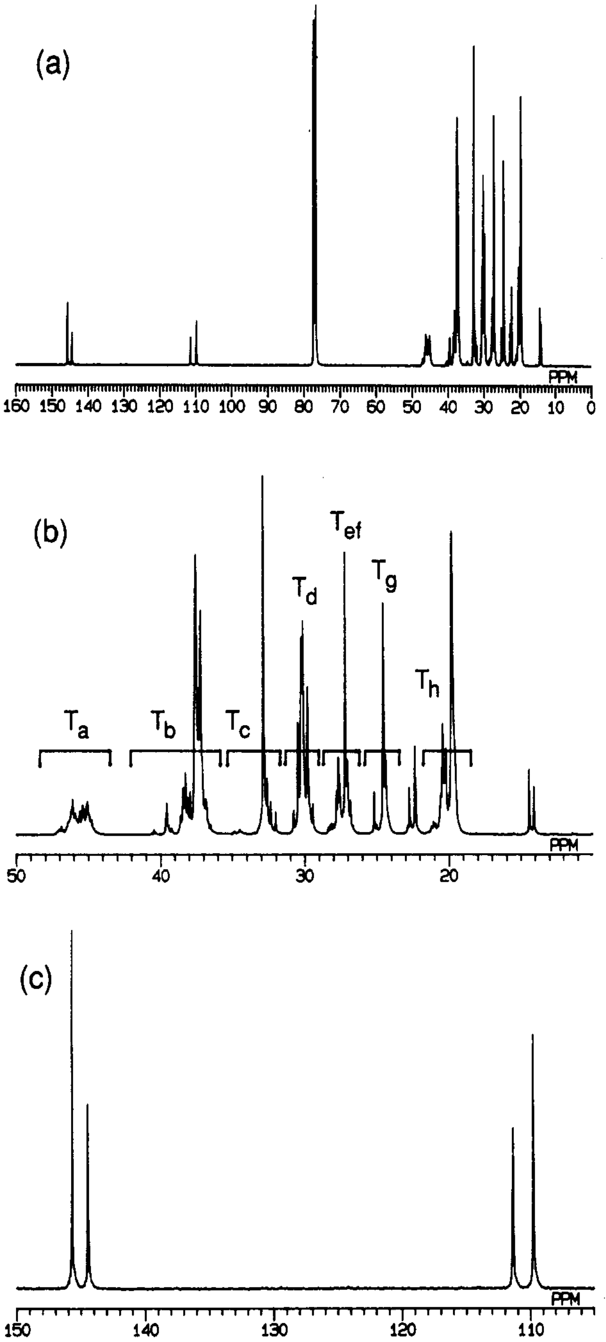

Figure 2. ^{13}C NMR spectrum of polymer C: (a) full spectrum, (b) aliphatic region, and (c) olefinic region.

Figure 2, parts b and c, respectively. The method chosen for this study utilizes a series of easily measurable, broad spectral regions from which various triad concentrations are readily extracted.[4] These spectral regions, as defined for triad sequence distributions for infinite chains, that is, when end groups are not taken into account, are given in Table 1.[4] End group contributions to each of the regions listed in Table 1 are given in Table 2 and illustrated in Figures 3 and 4 for terminating and initiating diads, respectively, although the regions have been expanded slightly over those in Table 1 to accommodate all of the end group diad contributions.

Table 1. ^{13}**C NMR Spectral Regions and Corresponding Triad Equations for Poly(ethylene-*co*-propylene)**[1] **(End Group Contributions Not Included)**

region	spectral range (ppm)	triad equations
a	45–48	$T_{\rm a} = k({\rm PPP} + {}^{1}/_{2}({\rm PPE} + {\rm EPP}))$
b	36–42	$T_{\rm b} = k({\rm PEP} + {}^{1}/_{2}({\rm PEE} + {\rm EEP}) + {\rm EPE} + {}^{1}/_{2}({\rm PPE} + {\rm EPP}))$
c	32–36	$T_{\rm c} = k({\rm EPE})$
d	29.5–32	$T_{\rm d} = k(2{\rm EEE} + ({\rm PPE} + {\rm EPP}) + {}^{1}/_{2}({\rm PEE} + {\rm EEP}))$
e + f	27–29.5	$T_{\rm e} + T_{\rm f} = k({\rm PPP} + ({\rm PEE} + {\rm EEP}))$
g	24–25	$T_{\rm g} = k({\rm PEP})$
h	19–22	$T_{\rm h} = k({\rm PPP} + ({\rm PPE} + {\rm EPP}) + {\rm EPE})$

Table 2. ^{13}**C NMR Spectral Regions and Corresponding Triad Equations for Poly(ethylene-*co*-propylene) with Contributions from End Group Diads and Triads**

area	triad + diad equations	eq no.
$T_{\rm a}$	$= k({\rm PPP} + {}^{1}/_{2}({\rm PPE} + {\rm EPP}) + {\rm PP_t} + {\rm PPP_i} + {\rm PEP_i})$	(60)
$T_{\rm b}$	$= k({\rm PEP} + {}^{1}/_{2}({\rm PEE} + {\rm EEP}) + {\rm EPE} + {}^{1}/_{2}({\rm PPE} + {\rm EPP}) + {\rm EP_t} + {\rm PE_t} + {\rm PP_i} + {\rm EPP_i} + {\rm PPE_i} + {\rm PEE_i} + {\rm EEP_i})$	(61)
$T_{\rm c}$	$= k({\rm EPE} + {\rm EPE_t} + {\rm EE_t} + {\rm EPP_i} + {\rm PE_i} + {\rm EEE_i} + {\rm EEP_i})$	(62)
$T_{\rm d}$	$= k(2{\rm EEE} + ({\rm PPE} + {\rm EPP}) + {}^{1}/_{2}({\rm PEE} + {\rm EEP}) + {\rm EPP_t} + {\rm PPE_t} + {\rm EEE_t} + {\rm PPP_i} + 2{\rm EPE_i} + {\rm EE_i} + {\rm EP_i} + {\rm PEP_i})$	(63)
$T_{\rm e} + {\rm T_f}$	$= k({\rm PPP} + ({\rm PEE} + {\rm EEP}) + {\rm EEP_t} + {\rm PPP_t} + {\rm PEE_t} + {\rm PPE_i})$	(64)
$T_{\rm g}$	$= k({\rm PEP} + {\rm PEP_t})$	(65)
$T_{\rm h}$	$= k({\rm PPP} + ({\rm PPE} + {\rm EPP}) + {\rm EPE} + {\rm PP_t} + {\rm PE_t} + 2{\rm PP_i} + {\rm EP_i})$	(66)
T_{144}	$= k({\rm PP_t})$	(67)
T_{111}	$= k({\rm PP_t})$	(68)
T_{146}	$= k({\rm EP_t})$	(69)
T_{110}	$= k({\rm EP_t})$	(70)
T_{139}	$= k({\rm EE_t})$	(71)
T_{114}	$= k({\rm EE_t})$	(72)
T_{137}	$= k({\rm PE_t})$	(73)
T_{115}	$= k({\rm PE_t})$	(74)
$T_{14.2}$	$= k({\rm PE_i} + {\rm EE_i})$	(75)
$T_{14.5}$	$= k({\rm PP_i})$	(76)
$T_{11.4}$	$= k({\rm EP_i})$	(77)
$T_{22.9}$	$= k({\rm EP_t} + {\rm PP_t} + {\rm PE_i} + {\rm EE_i})$	(78)

The task remaining is to determine experimentally each of the four initiating and terminating diad concentrations. Molecular weights were sufficiently high in the earlier referenced studies to preclude end group contributions from consideration when establishing the quantitative method for the triad distribution. Chemical shift assignments for the various carbons in the olefinic terminal diads are given in Figure 3 for the resonances shown in Figure 2c. There is no serious overlap among the olefinic carbon resonances from the terminating diads. In addition, there are two olefinic carbon resonances for each type of terminating end group diad, which leads to an overdetermination and increased accuracy in a direct and independent analysis of the four terminating end group diad concentrations. Similarly, assignments for the aliphatic diads comprising the initiating sequences are given in Figure 4. There are some overlap problems in the determination of the initiating end group diad concentrations. Methyl resonances from the PP and EP diads can be observed independently while the ^{13}C NMR resonances for the methyl and initial methylene groups for the EE and PE diads are not resolved at 100 MHz.

Because of chemical shift sensitivities, it is also necessary to examine structurally each of the possible end group triads when assigning chemical shifts for the end group diads. The identity of the repeat unit three units from the end of the chain is shown in parentheses in both Figures 3 and 4. The aliphatic carbons from each type of terminating diads, which overlap with the main chain triad resonances, are assigned to the appropriate spectral regions listed in Table 1. The olefinic carbon resonances, as well as the aliphatic diad carbon resonances that can be

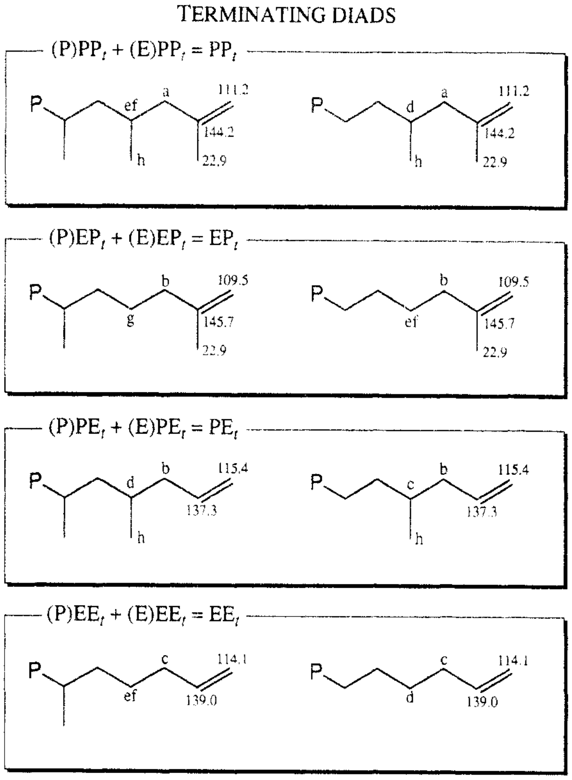

Figure 3. Structures and ^{13}C NMR spectral assignments for the olefinic end groups (terminating diad sequences) of poly(ethylene-*co*-propylene). P denotes the polymer chain, and polymerization occurs from left to right.

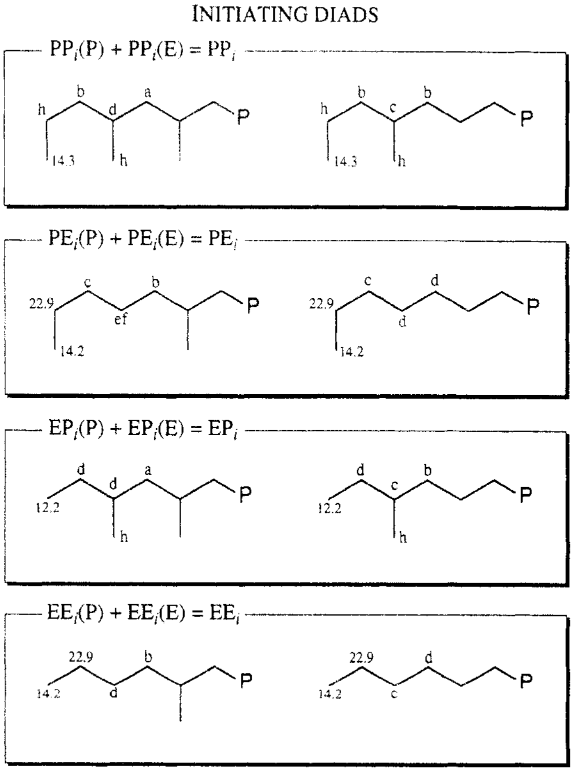

Figure 4. Structures and ^{13}C NMR spectral assignments for the aliphatic end groups (initiating diad sequences) of poly(ethylene-*co*-propylene). P denotes the polymer chain, and polymerization occurs from left to right.

identified free of spectral overlap with the main chain resonances, are identified by their chemical shift (ppm).

After the end group diads have been identified and concentrations determined, the mole fractions of E and P can be used to determine the concentration of each of the end group *triads*, as shown in Figures 3 and 4 and eqs 39–54. This will become important later when the complete triad distribution is needed for the first-order Markovian statistical analysis.

The assignments in Figure 4 for the initiating diads are the same as those previously reported by Cheng.[11] The total end group assignments, given in Figures 3 and 4 for the various end group diads, are used to modify the triad equations previously given for infinite chains (Table 1) to produce those for finite chains, given in Table 2. Again, it should be noted in Figure 4 and Table 2 that the methyl and initial methylene carbon resonances for the EE and PE initiating sequences have similar chemical shifts, that is, 14.1 and 22.9 ppm, respectively. The two types of methyl and methylene carbon resonances are not resolved at 100 MHz, although it is possible to distinguish the methyl resonances of PE(P) and EE(P) at 125 MHz.[12] There are differences in structural environments and in subsequent chemical shifts for those carbons in the second unit of the EE and PE diads, but a least-squares determination cannot be made without some initial value for the NMR area of either the EE diad or PE diad.

Concentrations for six of the eight end group diads can be determined directly from the ^{13}C NMR data and introduced into the revised equations in Table 2 for regions A–H. The overlap between the respective methyl and methylene resonances for EE and PE initiating diads must be resolved before contributions from these diads can be introduced into the area definitions for regions A–H.

Markovian statistics can be utilized to resolve the overlap between the EE and PE end group carbon resonances. The sum of EE_ik + PE_ik NMR integrated areas is determined experimentally. (k is the spectral area for one carbon.) The problem is how to distribute the observed sum between EE_ik and PE_ik. Any arbitrary value for PE_ik between zero and the observed sum for EE_ik + PE_ik removes the singularity of the matrix and permits a least-squares analysis to be performed. An iterative approach was adopted where PE_ik is set initially to zero and varied incrementally to the full value of the observed sum, EE_ik + PE_ik. A least-squares result for the complete triad and diad set, as well as the best first-order Markovian fit, was obtained for each iterative value of PE_ik. The closest agreement between the Markovian fit and the observed triad, diad distribution was used to establish the best value of PE_ik. This also identifies the best Markovian fit as well as the optimum triad and diad distributions.

Before examining experimental ^{13}C NMR data from an ethylene–propylene copolymer, it may be instructive to examine a model system to test the iterative procedure for determining the relative EE and PE diad concentrations. The model selected is Bernoullian with all eight triads having equal concentrations of 5 per chain. The diad end group concentrations were also set equal, which would be 0.25 for each type per chain.

EP model

$$PPP = PPE = EPP = EPE = 5$$

$$EEE = EEP = PEE = PEP = 5$$

$$PP_t = PE_t = EP_t = EE_t = 0.25$$

$$PP_i = PE_i = EP_i = EE_i = 0.25$$

A flowchart describing the calculations for a Microsoft Excel spreadsheet for a typical poly(ethylene-*co*-propylene) is given in Figure 5. The above values chosen for the EP model were used to calculate each of the NMR areas, which were inserted into the spreadsheet. As expected,

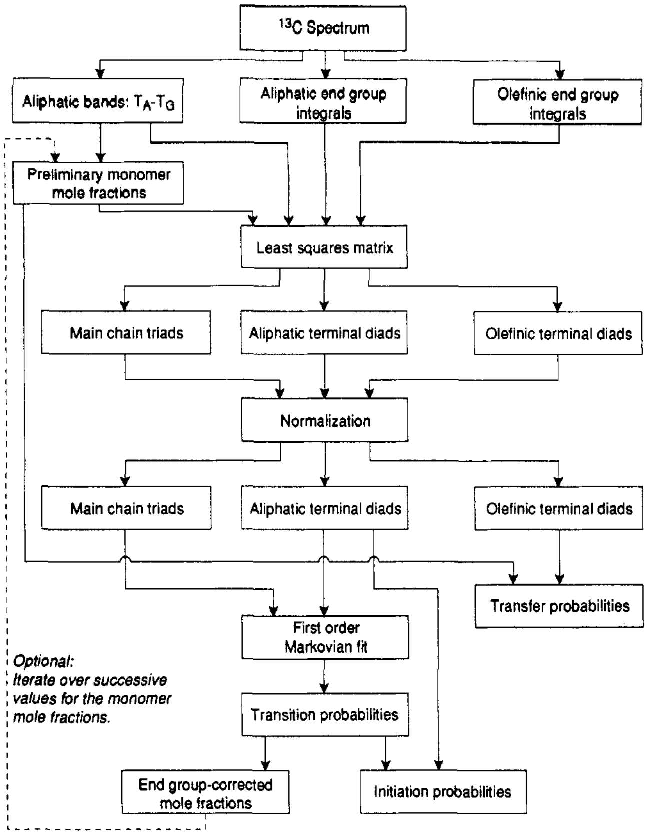

Figure 5. Flowchart outlining the calculations of the Microsoft Excel spreadsheet.

the resulting least-squares result and Markovian fit were perfect. The next step was to reexamine a range of $\mathrm{PE_i}k$ NMR intensities between 0.0 and 0.5, the sum of $\mathrm{EE_i}k + \mathrm{PE_i}k$. Experimental vs calculated values for the mole fractions $[\mathrm{EE}]_\mathrm{i}$, $[\mathrm{PE}]_\mathrm{i}$, $[\mathrm{PP}]_\mathrm{i}$, and $[\mathrm{EP}]_\mathrm{i}$ were obtained for each selected value of $\mathrm{PE_i}k$. The results, which demonstrate that a perfect Markovian fit was obtained for a value of $\mathrm{PE_i}k$ of 0.250, are given below:

NMR area for $\mathrm{PE_i}k$	calculated mole fractions				first-order Markov mole fractions			
	$[\mathrm{PP}]_\mathrm{i}$	$[\mathrm{EP}]_\mathrm{i}$	$[\mathrm{PE}]_\mathrm{i}$	$[\mathrm{EE}]_\mathrm{i}$	$[\mathrm{PP}]_\mathrm{i}$	$[\mathrm{EP}]_\mathrm{i}$	$[\mathrm{PE}]_\mathrm{i}$	$[\mathrm{EE}]_\mathrm{i}$
0.000	0.006	0.006	0.000	0.012	0.003	0.009	0.003	0.009
0.100	0.006	0.006	0.002	0.010	0.004	0.008	0.004	0.008
0.200	0.006	0.006	0.005	0.007	0.006	0.005	0.006	0.005
0.225	0.006	0.006	0.005	0.005	0.006	0.006	0.006	0.006
0.250	0.006	0.006	0.006	0.006	0.006	0.006	0.006	0.006
0.400	0.006	0.006	0.010	0.020	0.008	0.004	0.008	0.004

From these results, it is clear that iterations over the possible range of values for $\mathrm{PE_i}k$ and an identification of the minimum difference between calculated and first-order Markov mole fractions for the initiating diads will lead to the best values for the experimental input for $\mathrm{EE_i}k$ and $\mathrm{PE_i}k$.

Experimental data for three poly(ethylene-*co*-propylene)s, obtained from integration of the previously described NMR spectral regions, are given in Table 3. $\mathrm{PE_i}k$ was obtained iteratively by the procedure described above, which yielded values of 0.48, 1.00, and 1.10 for polymers A, B, and C, respectively. Linear regression results were calculated using Excel spreadsheets in accord with the flowchart are shown in Figure 5. (The spreadsheets were derived from the simultaneous equations given in Table 2.) The least-squares results for the ethylene–propylene copolymers are listed in Table 4. Satisfactory standard errors of estimates were obtained from the least-squares analyses for the complete set of triads and diads. The triad distributions from the spreadsheets were then corrected for the end group triads using the diad end group concentrations and the mole fractions [E] and [P]. The final normalized experimental results are listed in Table 5. First-order Markovian statistical analyses were performed iteratively. Final "fits" were obtained after minimizing the difference between calculated and observed triad distributions. The calculated results, which gave the lowest standard deviations between experimental and calculated triad distributions, are given in Table 5. The standard deviations are also included in Table 5. Finally, the transition probabilities, which gave the calculated Markovian triad and diad distributions closest to those observed experimentally, are given in Table 6.

Table 3. ^{13}C NMR Spectral Integral Areas (mm) for Typical Poly(ethylene-*co*-propylene)s[a]

polymer A	polymer B	polymer C
	Main Chain Triads	
$T_\mathrm{a} = 4.90$	10.40	9.50
$T_\mathrm{b} = 30.10$	32.40	34.00
$T_\mathrm{c} = 12.90$	12.20	12.00
$T_\mathrm{d} = 49.60$	30.00	21.00
$T_\mathrm{ef} = 20.80$	19.20	15.00
$T_\mathrm{g} = 5.90$	9.20	10.50
$T_\mathrm{h} = 19.80$	26.70	27.50
	Olefinic End Groups	
$T_{144} = 0.19$	0.83	1.13
$T_{111} = 0.21$	0.93	1.04
$T_{146} = 0.48$	1.01	1.47
$T_{110} = 0.49$	1.06	1.56
$T_{139} = 0.02$	0.04	0.01
$T_{114} = 0.03$	0.05	0.01
$T_{137} = 0.02$	0.07	0.01
$T_{115} = 0.02$	0.06	0.01
	Aliphatic End Groups	
$T_{14.1} = 0.52$	1.20	1.33
$T_{11.4} = 0.02$	0.05	0.05
$T_{22.9} = 1.20$	3.90	3.50
$T_{14.4} = 0.18$	1.10	1.23

[a] The fractional values were obtained after integrating on an expanded scale, and dividing by the scale factor.

Table 4. Triad and End Group Diad Fractions (mm) Calculated by a Least-Squares Regression of the Experimental Data in Table 3[a]

	sample					
	polymer A		polymer B		polymer C	
triad/diad	NMR area	std error	NMR area	std error	NMR area	std error
$[\mathrm{PPP}]k$	2.42	0.04	5.40	0.42	2.95	0.39
$[\mathrm{EPP}]k$	4.51	0.08	7.70	0.78	10.37	0.74
$[\mathrm{EPE}]k$	12.23	0.04	10.33	0.39	10.35	0.35
$[\mathrm{PEP}]k$	5.73	0.02	8.55	0.24	9.59	0.22
$[\mathrm{PEE}]k$	17.82	0.04	12.17	0.40	10.18	0.37
$[\mathrm{EEE}]k$	17.63	0.05	6.93	0.51	1.65	0.47
$[\mathrm{EP}]_\mathrm{t}k$	0.48	0.02	1.17	0.16	1.45	0.14
$[\mathrm{PP}]_\mathrm{t}k$	0.20	0.02	1.01	0.16	1.02	0.14
$[\mathrm{PE}]_\mathrm{t}k$	0.02	0.02	0.08	0.17	0.03	0.16
$[\mathrm{EE}]_\mathrm{t}k$	0.02	0.02	0.03	0.17	0.00	0.16
$[\mathrm{EP}]_\mathrm{i}k$	0.02	0.02	0.02	0.24	0.01	0.22
$[\mathrm{PP}]_\mathrm{i}k$	0.19	0.02	1.13	0.24	1.27	0.22
$[\mathrm{PE}]_\mathrm{i}k$	0.48	0.02	1.00	0.24	1.10	0.22
$[\mathrm{EE}]_\mathrm{i}k$	0.03	0.03	0.41	0.31	0.02	0.22

[a] k is the NMR integrated area for one carbon per average molecule.

Discussion of Results

The three poly(ethylene-*co*-propylene)s selected for this study can be characterized as having predominantly only

Table 5. Observed and Calculated First-Order Markov Triad and Diad Distributions for a Series of Poly(ethylene-*co*-propylene)s

	sample					
	polymer A		polymer B		polymer C	
triad/diad	obsvd	Markov	obsvd	Markov	obsvd	Markov
[PPP]	0.041	0.013	0.115	0.070	0.083	0.078
[PPE]	0.039	0.051	0.078	0.106	0.116	0.122
[EPP]	0.039	0.049	0.077	0.111	0.114	0.118
[EPE]	0.198	0.190	0.187	0.169	0.208	0.183
[PEP]	0.098	0.095	0.171	0.161	0.218	0.238
[EEP]	0.150	0.157	0.124	0.137	0.116	0.103
[PEE]	0.150	0.167	0.119	0.135	0.112	0.108
[EEE]	0.286	0.278	0.129	0.115	0.033	0.047
$[EP]_t$	0.008	0.008	0.021	0.021	0.029	0.029
$[PP]_t$	0.003	0.003	0.108	0.018	0.020	0.020
$[PE]_t$	0.000	0.000	0.001	0.001	0.001	0.001
$[EE]_t$	0.000	0.000	0.001	0.001	0.000	0.000
$[EP]_i$	0.000	0.000	0.000	0.004	0.000	0.000
$[PP]_i$	0.003	0.003	0.020	0.014	0.025	0.017
$[PE]_i$	0.008	0.009	0.018	0.024	0.022	0.030
$[EE]_i$	0.001	0.001	0.007	0.004	0.000	0.000
total E	0.685	0.698	0.552	0.554	0.480	0.497
std dev		0.010		0.018		0.010

one aliphatic end group and one olefinic end group. A least-squares approach was not needed to determine the total end group concentrations because they could be determined directly and accurately. It was gratifying to note that the least-squares results over the entire ^{13}C NMR spectrum yielded end group concentrations close to those observed directly. This can be seen by comparing the linear regression results in Table 4 with the experimental results in Table 3 for the various end groups. There is little doubt that linear regression analyses for the triad and diad distributions offer the best approach for treating the observed resonance areas experimentally.

The value of the Markovian analyses is that they offer a reference point for comparing observed structural trends in the experimental data. The ethylene mole fractions are 0.69, 0.55, and 0.48, respectively, and the experimental triad data closely follow that observed for first-order Markovian systems. The advantage of obtaining a Markovian distribution that closely resembles the observed data is that the Markovian parameters allow any sequence of any length to be calculated.

The definitions for the Markovian probabilities for initiation and termination intrinsically correct for composition, whereas the observed end group diad concentrations do reflect the overall E/P composition and can be misinterpreted if compositional effects are not considered. This point is illustrated below for polymer B, [E] = 0.55:

$$[PP]_t = 0.017 \qquad {}^{T}P_{PP} = 0.037$$

$$[EP]_t = 0.020 \qquad {}^{T}P_{EP} = 0.037$$

$$[PE]_t = 0.001 \qquad {}^{T}P_{PE} = 0.003$$

$$[EE]_t = 0.001 \qquad {}^{T}P_{EE} = 0.001$$

$$[PP]_i = 0.017 \qquad P_{IP} = 0.37$$

$$[PE]_i = 0.018$$

$$[EP]_i = 0.000 \qquad P_{IE} = 0.003$$

$$[EE]_i = 0.002$$

Table 6. First-Order Markov Transition Probabilities for Initiation, Propagation, and Termination for a Series of Poly(ethylene-*co*-propylene)s

	sample		
	polymer A	polymer B	polymer C
	Transition Probabilities for Propagation		
PP	0.195	0.356	0.352
EP	0.350	0.505	0.627
PE	0.793	0.600	0.607
EE	0.638	0.456	0.313
	Transition Probabilities for Initiation		
E	0.001	0.008	0.001
P	0.011	0.040	0.049
	Transition Probabilities for Termination		
EP	0.012	0.039	0.061
EE	0.001	0.001	0.000
PE	0.001	0.003	0.001
PP	0.010	0.040	0.039

The probabilities for initiation in an overall ethylene mole fraction range of 0.48–0.69 showed a strong preference for the initiating unit to be propyl. Propyl units are favored over ethyl by a 10:1 to 50:1 ratio. This result likely arises from a propylene initating unit, but consideration must also be given for ethylene initiation accompanied by a methyl addition. A corresponding study of butene initiating sequences, presently underway, will do a great deal to distinguish these two possibilities that lead to the same structural moiety.

The transfer probabilities for termination unequivocally establish the preference for transfer reactions involving propylene as the terminal unit. The probabilities for transfer involving EP and PP terminating sequences was favored from 10:1 to 60:1 over the corresponding PE and EE terminating sequences. The transfer probabilities were also essentially Bernoullian with no strong effect observed from the penultimate unit. In essence, the E/P copolymers prepared with these metallocene catalysts favor initiating and terminating propylene units in the ethylene mole fraction range of 0.48–0.69.

The transition probabilities for chain propagation define the chain architecture. The "cross" probabilities, that is, P_{PE} or P_{EP}, have the largest magnitudes within the set of four transition probabilities. The fact that the transition probabilities for propagation are E/P composition-dependent is the expected result. The surprising result is the lack of dependence upon composition for the chain-initiating and chain-terminating sequences.

In summary, a method has been developed for determining the detailed chain architecture of any E/P copolymer independently of choice of catalyst system. A determination of the concentrations and probability coefficients for initiating and terminating species has not been performed previously, probably because of a low interest in low molecular weight polyolefins historically.

It is possible to use the analytical approach presented in this report to establish relationships between catalyst recipes/polymerization conditions, and the structure of the resulting copolymers. Certainly, the development of methodology to characterize the initiating and terminating species can be used to increase our understanding of initiating and terminating reactions during copolymerization. Finally, the development of Markovian statistics for finite chains from Ziegler–Natta copolymerizations is new and can be used for any polymer or copolymer that meets the criteria for Markovian behavior.

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