

Investigation of Ethylene/1-Octene Copolymerization Models by Carbon-13 NMR

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SYNOPSIS

Statistical reaction models have been used to fit C-NMR spectra for ethylene/1-octene copolymers and to describe the polymerization reaction probabilities. Ten models ranging in complexity from a one-site Bernoulli probability to multiple site second-order Markov systems were studied. Model parameters were determined by fitting the experimental integrations of replicated spectra using a maximum likelihood method. The best fit to the experimental NMR spectra was obtained with a two-site model, one site producing mainly high-density polymer following a Bernoulli probability model, while the second site allows more incorporation of octene following a chain-end controlled probability described by first-order Markov statistics. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Carbon-13 nuclear magnetic resonance (^{13}C -NMR) spectroscopy is used extensively to study the microstructure of polymers. It can be used to determine overall composition and the sequence distribution; if two or more polymers are present, it can provide a quantitative determination of the mixture composition.

The ordering of monomer units within a copolymer chain is a very sensitive probe of the propagation mechanism. For example, Hill et al.¹ conclusively demonstrated, on the basis of ^{13}C triad sequence distributions, that the free-radical copolymerization of styrene and acrylonitrile was best explained using the penultimate or second-order Markov model.

A more difficult situation can arise if the copolymer is a mixture resulting from the existence of different polymerization sites in the reaction medium. Even in this case, sequence distribution information can be used to discriminate between alternative polymerization models, and to determine the reaction parameters and relative amount of polymer formed at each site.²

This method has been previously applied to a number of polyolefin systems (e.g., ethylene/propylene³ and ethylene/1-butene⁴). For ethylene/1-octene copolymers, signals from carbons on the hexyl branches and along the main chain overlap

and complicate the NMR spectrum. Since the spectral peaks include contributions from all components of the mixture, interpretation of the data becomes complex.

Cheng has developed a systematic approach to analyzing such complex spectra.^{2,5,6} It involves computerized simultaneous fitting of all peaks in the spectrum with statistical irreversible propagation models. The reaction probability parameters resulting from a successful fit are then used to determine polymer composition and comonomer sequence distribution consistent with the entire spectrum.

The statistical models commonly used to describe copolymerization at a single catalyst site are the Bernoullian (B) and first- and second-order Markovian models (M1 and M2). These models differ by the extent of end chain control which is assumed to influence the polymerization reaction probabilities.

The second-order Markovian model (M2) is the most complex of the models. It assumes that the probabilities of adding each comonomer to a propagating chain depend on the previous two monomer units added. This model leads to eight propagation reactions and requires the determination of four independent reaction parameters. Using conventional notation where P_{ABC} is the probability of monomer "C" adding to a polymer chain ending with an "AB" sequence, we define the parameters for ethylene/1-octene copolymers as follows:

$$\alpha = P_{OOO} \quad \beta = P_{OEO} \quad \gamma = P_{EOO} \quad \delta = P_{EEO}$$

The four remaining dependent parameters are designated

$$\alpha' = P_{OOE} \quad \beta' = P_{OEE} \quad \gamma' = P_{EOE} \quad \delta' = P_{EEE}$$

such that $\alpha' = 1 - \alpha$, $\beta' = 1 - \beta$, $\gamma' = 1 - \gamma$, and $\delta' = 1 - \delta$.

The first-order Markovian model simplifies to two independent parameters by assuming only the terminal unit of the polymer chain influences reaction probability.

$$\alpha = P_{OO} \quad \beta = P_{EO}$$

These two probabilities and the corresponding dependent parameters (α' , β') describe four propagation reactions and are related to the traditional reactivity ratios of copolymerization (r_1 , octene; r_2 , ethylene) which have been so useful in increasing our knowledge of monomer reactivity.

$$\alpha = \frac{r_1}{r_1 + [E]/[O]} \quad \beta = \frac{[O]}{r_2[E] + [O]}$$

The Bernoullian model assumes no dependence of the reaction probability on the nature of the propagating chain and requires only a single reaction parameter.

$$\alpha = P_O \quad (\alpha' = 1 - \alpha = P_E)$$

This model corresponds to "ideal copolymerization" with statistically random reaction of the monomers (i.e., $r_1 r_2 = 1$).

With each model, theoretical expressions for the ^{13}C -NMR signal intensities for all spectral lines can be derived and compared with observed integrations to determine the fit parameters. For more than one catalyst site, weighted combinations of these models are used and total signal intensities are calculated by summation of individual site contributions.

$$I_T = \sum_{i=1}^n w_i I_i$$

We have applied this method of analysis to NMR spectra of ethylene/1-octene copolymers. The observed spectra have been fitted with each of the three models, assuming a single catalyst site, and with combinations of the models for two and three-site systems.

The method of maximum likelihood was used in this work to infer the best copolymerization model from a statistical basis. Fisher introduced the concept of maximum likelihood in the 1920s,⁷ although its application did not follow for several years. In recent times it has seen significant use in chemical process modelling.⁸

The least-squares method is still the most commonly used method of statistical estimation. It is the appropriate method when dealing with data for which the errors are independently and identically distributed. The method of maximum likelihood is a generalization of the least-squares method. It can be used when the errors are independent but not identically distributed, in which case it is equivalent to the weighted least-squares method; it can also be used when the errors are neither independent nor identically distributed. A comparison of the weighted least squares and maximum likelihood methods is given by Seber and Wild.⁹

EXPERIMENTAL

Three experimental ethylene/1-octene copolymer resins with different octene concentrations were analyzed. Homogeneous NMR samples were prepared by grinding 8 g of each resin and dissolving enough of the powders in 1,2,4-trichlorobenzene to give approximately 15 wt % concentrations. The samples were repeatedly heated and cooled in 5 mm o.d. NMR tubes to minimize the effects of thermal history.

Carbon-13 NMR spectra were obtained on a Bruker AC-F 200 spectrometer at 110°C using a 90 degree pulse, a pulse delay of 30 s, and complete broadband proton decoupling. For each sample, five blocks of 300 scans were recorded and saved separately.

RESULTS AND DISCUSSION

Modelling the NMR spectra required reduction of the data to a format which was compatible with the information provided by the reaction probability models. We chose to integrate nine regions in the spectra and to use the integration areas as the input for the model fitting. The integration ranges are indicated on a sample spectrum shown in Figure 1. These ranges are the same as those specified by de Pooter et al. for the determination of octene content in ethylene/1-octene copolymer.¹⁰ In this way, the analysis uses all spectral peaks except that for the terminal methyl groups CH_3 (1) at 14 ppm which has unreliable intensity resulting from a long spin-lattice relaxation time, T_1 .¹⁰

The spectra were transferred from the spectrometer to floppy disk and imported into Spectra Calc. The Spectra Calc software package permits easy manipulation of the spectral data. We wrote routines in Array Basic which operate within the Spectra Calc environment to extract the integration values to be fit by the models and to calculate normalized peak areas. The results are summarized in Table I.

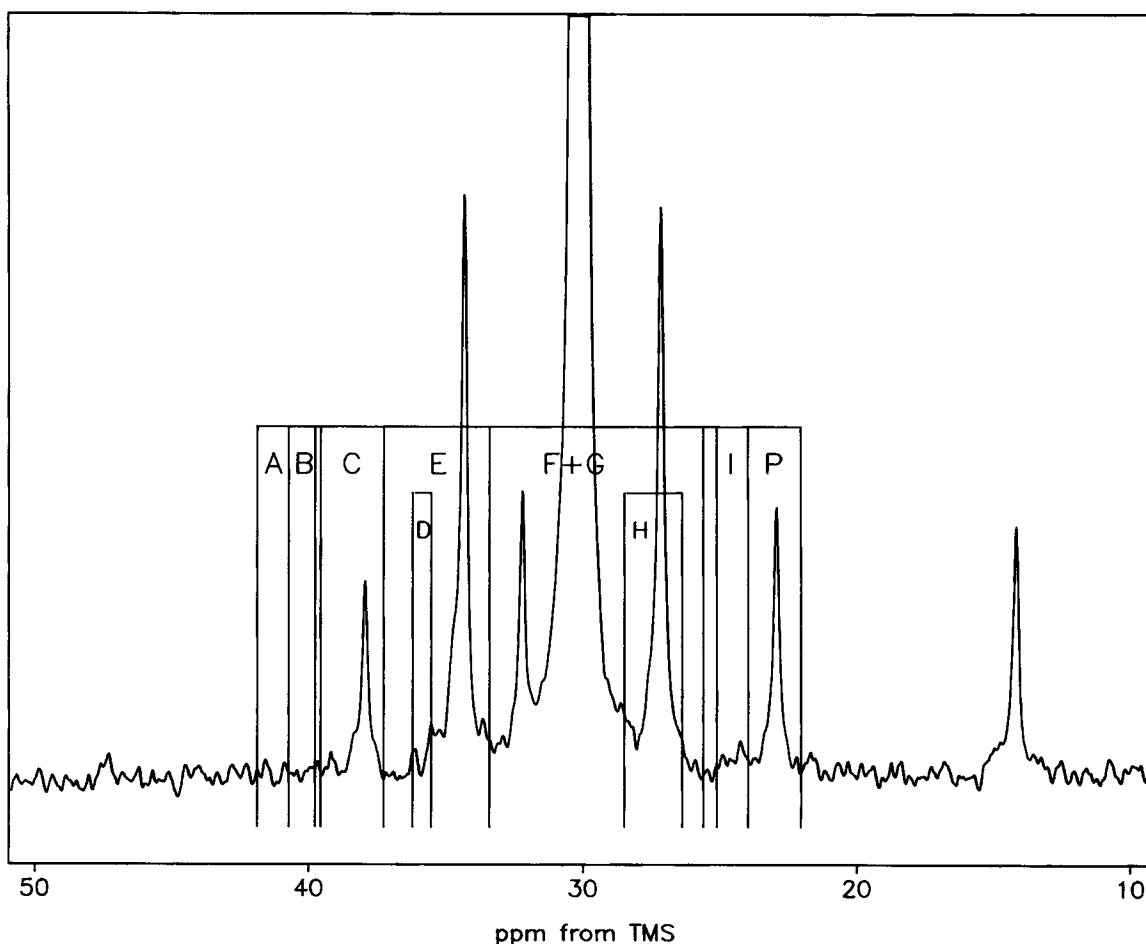


Figure 1 Carbon-13 NMR spectrum of sample A. Integration ranges indicated are used in the model fitting.

Sufficient spectral resolution to clearly distinguish the major peaks found in each of the integration ranges is required. However, moderate overlap at the base of the peaks does not appear to seriously affect the calculations. Fitting the spectra with a Lorentzian curve-fitting routine provided with Spectra Calc and using the fitted areas in our calculations gave similar results to those for which simple integration was used.

Chemical shift assignments for all observed signals of ethylene/1-octene copolymers are given in Table II along with the second-order Markovian expressions for their theoretical intensities. The assignments are designated by: "br" for branching methines; Greek letters " $\alpha, \beta, \gamma, \delta$ " corresponding to the number of carbons distant from the nearest branching methine in each direction along the polymer chain for methylenes on the chain; and " $\text{CH}_2(n)$ " for branch methylenes with n indicating position number from the terminal $\text{CH}_3(1)$. Triads and tetrads are specified when more than one signal arises from otherwise similarly designated species.

Intensity expressions for the simpler models can be derived by the substitutions $\gamma = \alpha, \delta = \beta$ for first-order Markov and $\delta = \gamma = \beta = \alpha$ for Bernoulli.

The observed integrations for each set of five spectra were fitted by ten different statistical models using the SimuSolv[®] (Dow Chemical Company) computer program. SimuSolv provides a simplex algorithm (Nelder-Mead Search) for iteration of the reaction probability parameters to optimize the fit. The expressions used to calculate NMR signal intensities for the integration ranges are derived from the second-order Markovian statistical model as given in Table II. Calculations are simplified for the Bernoullian and first-order Markovian models by equating the appropriate parameters. For models involving more than one catalytic site, weighted averages of the signals are calculated. The method of maximum likelihood¹¹ is used to determine the best fit parameters. The likelihood function is calculated from the difference between fitted and actual integrations for all peaks in the spectrum. In practice, the log of the likelihood function (LLF) is maxi-

Table I Normalized Integration Data for Five Spectra from Each of the Three Ethylene/1-Octene Copolymer Samples

Integration Range (ppm)	Normalized Area				
	1	2	3	4	5
Sample A					
41.75-40.50	.002865	.001257	-.00149	.001966	.001884
40.50-39.50	.003002	.000860	.000601	.004538	.003038
39.50-37.00	.031057	.033526	.028418	.035492	.033739
36.20-35.60	.004299	.002134	.003584	.004486	.004269
36.80-33.20	.103909	.098518	.107356	.110144	.112739
33.20-25.50	.811120	.816463	.820899	.802926	.808638
28.50-26.50	.095328	.092745	.099076	.091634	.093773
25.00-24.00	.008025	.007848	.006274	.008836	.003091
24.00-22.00	.040022	.041541	.037938	.036098	.036870
Sample B					
41.75-40.50	.003588	.001206	.004549	.002736	.005980
40.50-39.50	.004862	.005772	.005204	.000594	.004860
39.50-37.00	.026424	.024715	.024924	.020029	.027114
36.20-35.60	-.00041	.002028	.005118	.001374	.004008
36.80-33.20	.064334	.078351	.078110	.060235	.069813
33.20-25.50	.864246	.862640	.855461	.888083	.858468
28.50-26.50	.076686	.068307	.068991	.085698	.084579
25.00-24.00	.005283	.005322	.008951	.000819	.005333
24.00-22.00	.031263	.021994	.022801	.027505	.028432
Sample C					
41.75-40.50	.004515	.003367	.007516	.005512	.004094
40.50-39.50	.002761	.003602	.004847	.004226	.002036
39.50-37.00	.014019	.021253	.025530	.015450	.015644
36.20-35.60	.001742	.004206	.004070	.004520	.004324
36.80-33.20	.037677	.055692	.053968	.048221	.053656
33.20-25.50	.912192	.893467	.884622	.901219	.892342
28.50-26.50	.058611	.053306	.050351	.055684	.056472
25.00-24.00	.010608	.007859	.003827	.007526	.007914
24.00-22.00	.018229	.014759	.019690	.017846	.024314

mized to arrive at the most probable values of the parameters.

The analysis of multiple spectra for each copolymer is necessary to account for the errors in integrations which arise from noise in the spectra. Calculating the log likelihood function for a single spectrum assumes that the experimental values are without error. This results in a function which has a local maximum at each point where any variable or combination of variables is well fitted. Analysis of such a function to determine the absolute maximum is extremely difficult. When the error of the integrations is accounted for by using several data sets, the complexity of the log likelihood function is eliminated. The difference can be readily seen in Figure 2. The acquisition of multiple spectra can be achieved in the same period as a single spectrum

having superior signal/noise. The loss in signal for the individual spectra is more than compensated for by the ease of analysis and the ability to estimate the error in the NMR integrations.

The results from the fits are summarized in Table III. The models are numbered 0 to 9 and are defined by the accompanying combinations of B, M1, and M2. The same sequence of maximum log likelihood values appears in each data set. For each case, the poorest fits are given by models 0 and 1, which are the simple one-site B and M1 models. Obviously, the formation of the polymer is not governed by simple probability at a single catalyst site. The fits are only slightly improved for models 3 and 8, the multiple-site B/B and B/B/B models. The lack of improvement observed in going from model 3 to model 8 is strong evidence that the polymerization

Table II Chemical Shift Assignments for ^{13}C -NMR of Ethylene/1-Octene Copolymers and Corresponding Second-Order Markovian Expressions for Signal Intensities

δ/ppm	Assignment	2nd-Order Markovian	
13.99	CH_3 (1)	$(\alpha' + \gamma)\delta$	
22.83	CH_2 (2)	$(\alpha' + \gamma)\delta$	
24.60	$\beta\beta$ -OEO	$\alpha'\beta\delta$	
26.91	CH_2 (5)-OOO	$(\alpha' + \gamma)\delta$	
27.07	CH_2 (5)-OOE		
27.22	CH_2 (5)-EOE		
27.28	$\beta\delta$ -OEE		$2\alpha'\beta'\delta$
29.95	CH_2 (4), $\delta\delta$		$2\alpha'\beta'\delta' - \alpha'\beta'\delta\delta'$ $+ (\alpha' + \gamma)\delta$
30.46	$\gamma\delta$ -OEE	$2\alpha'\beta'\delta\delta'$	
30.98	$\gamma\gamma$ -OEEO	$\alpha'\beta'\delta^2$	
32.17	CH_2 (3)	$(\alpha' + \gamma)\delta$	
33.86	br-OOO	$\alpha\gamma\delta$	
34.56	CH_2 (6)-EOE, $\alpha\delta$ -EOEE	$2\alpha'\beta'\delta + \alpha'\gamma\delta$	
34.95	$\alpha\gamma$ -EOEO		
35.07	CH_2 (6)-OOE, $\alpha\delta$ -OOEE		
35.50	$\alpha\gamma$ -OOEO	$2\alpha'\beta\delta + 2\alpha'\gamma\delta$	
35.65	CH_2 (6)-OOO		
35.96	br-OOE	$2\alpha'\gamma\delta + \alpha\gamma\delta$	
38.22	br-EOE	$\alpha'\gamma'\delta$	
40.28	$\alpha\alpha$ -EOOE	$\alpha'^2\gamma\delta$	
40.96	$\alpha\alpha$ -OOOE	$2\alpha\alpha'\gamma\delta$	
41.47	$\alpha\alpha$ -OOOO	$\alpha^2\gamma\delta$	

Source: From Refs. 15, 16.

reaction involves some degree of end chain control.

The six models remaining all give log likelihood maxima significantly higher than the less complex models. In addition, there is very little difference among the values given by these remaining models. This suggests that the simplest of these is capable of explaining the intensities observed in the spectra, and no advantage is given by using more complex descriptions of the polymerization reaction. The models requiring the fewest fitting parameters are models 2, 4, and 5.

The maximum likelihood method provides a statistical discrimination between models. The difference in LLFs between one model and a more simplified model nested within it follows approximate chi-square statistics.¹² Specifically, for a three-parameter model, a difference in the LLF maxima of greater than 3.91 would imply that a fourth parameter made a significant improvement; therefore model 4, B/M1, is a real improvement over model 3, B/B. Similarly, a difference greater than 5.57

would be required to add a fifth parameter to the model; none of the more complex models makes an improvement of this order.

A number of studies have suggested the existence of two or more catalyst sites.¹³ The broad, multimodal, short-chain branching distribution of ethylene/1-alkene copolymers observed by TREF analysis also indicates multiple sites.¹⁴ Therefore, it is surprising initially to find that model 2, a one-site second-order Markovian probability model, is equally capable of explaining the observed spectra as any of the multiple-site models on the basis of maximum likelihood. However, the number of reaction probability parameters, four, is the same as for the equally well-fitting two-site models, 4 and 5. Given this, discriminating among these models requires closer inspection of the fits. The model 2 fitting parameters are given in Table IV. For all three copolymers, the value required for β (P_{OEO}) is substantially greater than δ (P_{EEO}). For this to be true, the presence of a hexyl branch at a carbon three bonds removed from the catalyst site must increase the probability of reaction with octene above that for a straight carbon chain. This effect is the opposite of what is expected on the basis of steric control, and there is little reason to believe it could be caused by an inductive electronic effect. While it is interesting that a one-site model could generate the observed NMR spectra of the copolymers, the model parameters cannot be rationalized in terms of a diffusion-limited catalyst site or an obvious reactivity difference between end chain types.

On the other hand, the two-site models give results which can be interpreted rationally. Models 4 and 5, B/M1 and M1/B, are equivalent. Both were fitted as a check on the symmetry of the signal intensity calculations and on the reproducibility of the fitting algorithm. Negligible differences in the maximum log likelihood values arise from the choice of initial parameters in the fits. The reaction probabilities and the site weighting parameters for model 4 which best fit the spectra of the three copolymers are given in Table V. In each case, the low values of α_1 suggest the existence of one type of catalyst site which preferentially reacts with ethylene and produces high-density polymer. The probability of octene reacting at this site increases with increasing overall octene content in the resin but remains small even for high concentrations of octene. The probability of octene reacting at the second site is much higher as given by the values of α_2 and β_2 . Also, the difference between these values for each copolymer indicates that $P_{\text{EO}} > P_{\text{OO}}$ for this site. Finally, the amount of polymer produced at each type of site is

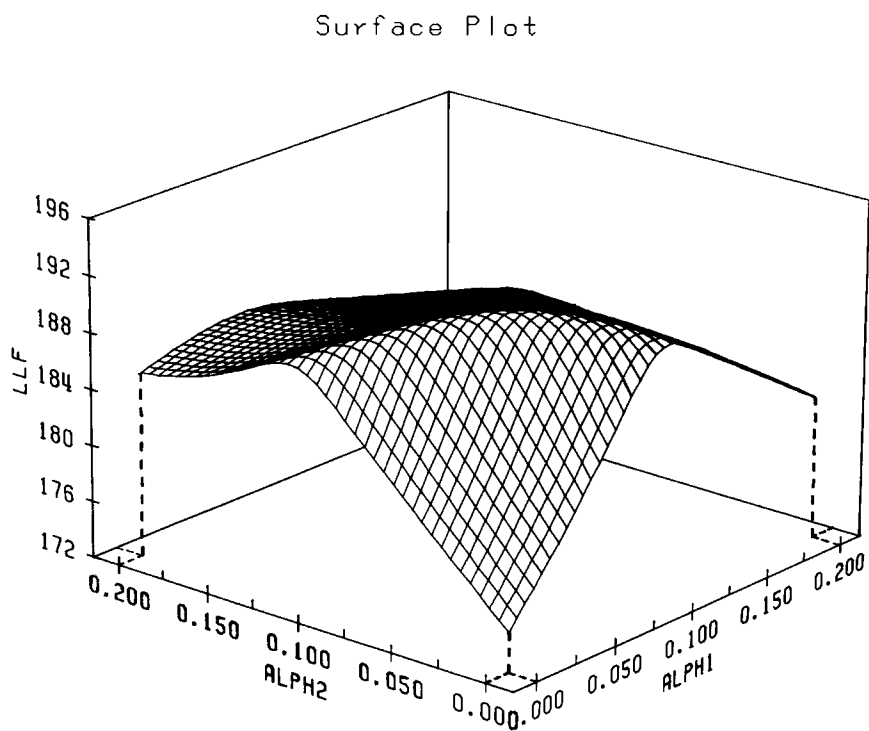
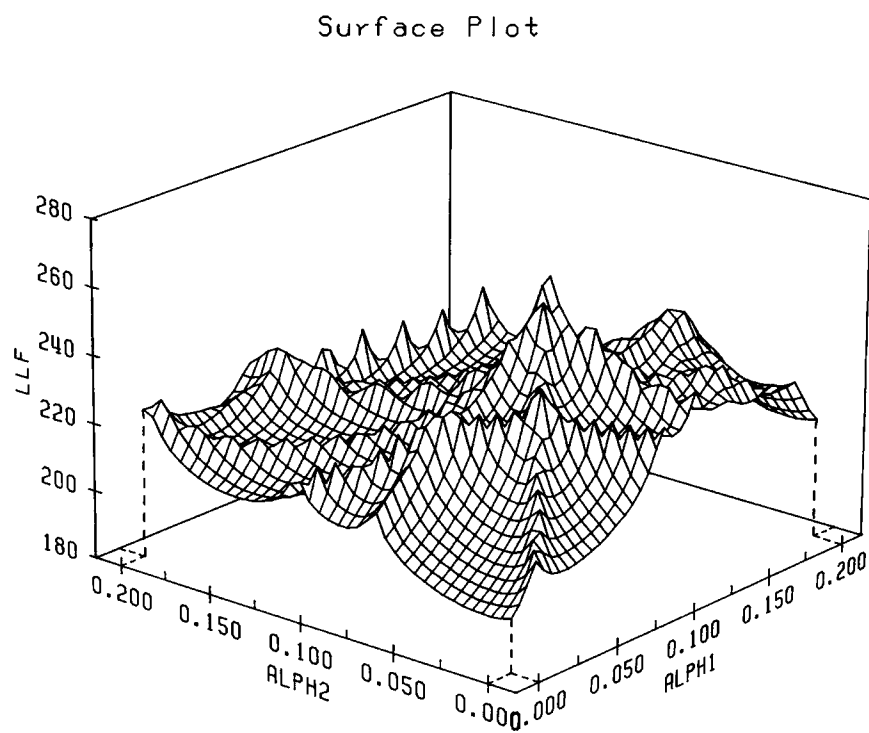


Figure 2 Surface plots of the log likelihood function for the fit of ^{13}C -NMR spectra of sample A by a two-site first-order Markovian model (M1/M1) using a single spectrum (top) and the same data analyzed as five individual spectra (bottom).

Table III Maximum Log Likelihood Valued for Various Reaction Models and Ethylene/Octene Copolymers

	Model	Par. #	Sample A	Sample B	Sample C
0	B	1	179.75	175.01	173.27
1	M1	2	182.39	175.78	181.41
2	M2	4	192.12	179.25	188.40
3	B/B	3	182.64	177.75	183.49
4	B/M1	4	192.32	179.25	188.15
5	M1/B	4	192.33	179.08	188.15
6	M1/M1	5	192.50	179.94	188.15
7	M2/M2	9	192.65	180.06	188.40
8	B/B/B	5	182.64	177.47	182.17
9	M1/M1/M1	8	192.50	180.07	188.65

B = Bernoulli, M1 = first-order Markov, M2 = second-order Markov; B/M1, e.g., refers to a two-site model, one of which obeys Bernoulli statistics and the other first-order Markov statistics.

also a function of overall octene concentration, as shown by the values of the parameter $WEIGH_1$.

A peak-by-peak analysis of the fit of the B/M1 model to each of the three sets of spectra was performed. Most of the fitted integration values fall within the 95% confidence intervals determined from the errors in experimental integration. The exceptions are only marginally outside the intervals and appear to be randomly distributed from sample to sample. The fit could likely be improved with greater spectral resolution or with error estimates for the fitted values.

The fit parameters of this two-site model are in keeping with the concept of a catalyst in which some of the sites have very limited opportunity to react with the larger octene monomer because of diffusion limitations while other more accessible sites react with octene with rates dependent on steric hindrance caused by the growing end chain. Whether this description of the catalyst is complete or the polymerization actually involves small contributions from other types of sites or more complex reaction control at the sites is not evident from our analysis. We see no significant improvement in fit for more

complicated models over the two-site B/M1 model. It may be possible to distinguish these cases with increased spectral signal/noise. It would also be useful to analyze fractionated samples of the copolymers in terms of the two-site model. For a physically realistic model, the reaction probability parameters must remain unchanged as the weighting parameter varies from fraction to fraction.

CONCLUSION

The ^{13}C -NMR spectra of ethylene/1-octene copolymers have been fitted with statistical reaction models ranging in complexity from single site Bernoullian probabilities to multiple site second-order Markovian systems. The spectral integration was found to be well simulated by a two-site system. The fit parameters suggest that one site produces mainly high-density polymer following a Bernoulli probability model, while the second site allows more incorporation of the octene comonomer following a chain-end controlled probability described by first-order Markovian statistics.

Table IV Best Fit Parameters for Model 2 (M2) With Ethylene/Octene Copolymers

Parameter	Sample A	Sample B	Sample C
α P_{OOO}	6.4485E-7	6.7470E-6	6.2002E-7
β P_{OEO}	0.20897	0.18027	0.28521
γ P_{EOO}	5.7199E-2	9.5128E-2	9.0438E-2
δ P_{EEO}	8.1986E-2	6.0057E-2	3.7726E-2

Table V Best Fit Parameters for Model 4 (B/M1) With Ethylene/Octene Copolymers

Parameter	Sample A	Sample B	Sample C
α_1	6.6083E-3	3.5085E-4	8.5378E-6
α_2	5.7515E-2	9.3374E-2	8.5779E-2
β_2	0.21308	0.18061	0.28600
$WEIGH_1$	0.55584	0.60094	0.81147

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