Ethylene–Propylene Copolymerization Mechanism Based on the Sequence Distributions Determined by ^{13}C NMR Spectra

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ABSTRACT: The ethylene–propylene (E–P) copolymerization mechanism with heterogeneous Ziegler–Natta catalytic systems was investigated on the basis of the sequence distributions in ethylene–propylene (E–P) copolymers determined by ^{13}C NMR spectra. As the statistical models for the copolymerization mechanism, both single-site and two-site models, where the copolymerization proceeds under the control of Bernoullian or first-order Markovian statistics at catalytic sites, were used to predict the sequence distributions. By comparisons between the observed and predicted sequence distributions it is indicated that the observed sequence distributions in E–P copolymers are satisfactorily predicted by the two-site model (model MM), in which the copolymerization proceeds according to first-order Markovian statistics at the two different sites. The E–P copolymerization mechanism was described reasonably by using the optimized values of the parameters of model MM. Further, it is confirmed that the heterogeneous Ziegler–Natta catalytic systems have a two-site nature in which one site predominantly polymerizes ethylene and the other site predominantly polymerizes propylene.

Introduction

The sequence distribution in ethylene–propylene (E–P) copolymer is one of the important factors determining the mechanical properties of E–P copolymer. ^{13}C NMR is the most powerful analytical method to evaluate the dyad and triad sequence distributions in E–P copolymer.[1–6] Many studies[5,7–13] have been performed to obtain information on the nature of E–P copolymerization mechanism with heterogeneous Zieglar–Natta catalytic systems based on the sequence distributions determined by ^{13}C NMR spectra. Detailed investigation on the E–P copolymerization mechanism is very important to control the sequence distributions in products. A number of authors[5,7,8] have attempted to describe the E–P copolymerization mechanism using a first-order Markovian statistical model in which a single catalytic site was assumed. Cheng[9] found that a first-order Markovian model is appropriate for the description of sequence distributions observed in four polymers, while a second-order Markovian model gives better fits for the ones observed in two other polymers. The statistical validities of the low-order Markovian models are not stated in the analyses of these E–P copolymerization mechanisms.

An apparent discrepancy, beyond experimental error, has been found between the calculated and observed fractions of E-centered triads by Kakugo et al.[5] They suggested that multiple active sites are present: at one site ethylene preferentially polymerizes and at the other site less ethylene polymerizes. Similar results have been observed in E–P copolymers prepared with a silica-supported $MgCl_2/TiCl_4$ catalyst by Doi et al.[7] The observed PPP, PEP, EPE, and EEE triads were slightly larger than those predicted by a first-order Markovian model, and, in contrast, the observed PPE and PEE triads were smaller. Doi et al.[7] suggested that two types of active sites are present in the catalyst, one site producing a random or moderately alternating copolymer and the other giving a block copolymer. Two-site heterogeneous Ziegler–Natta catalytic systems have already been confirmed in propylene homopolymerization.[14–16] At one site propylene polymerization proceeds under the control of a symmetric Bernoullian model (meso- or racemo-select), and at the other site polymerization obeys an asymmetric Bernoullian model (dextro- or levo-select).

Recently, Ross[10–12] proposed a multisite statistical model for the E–P copolymerization mechanism in which each site is statistically independent and obeys a Bernoullian statistical model. In the second paper, Ross[11] showed that the observed data of Kakugo et al.[5] are consistent with this model, assuming the presence of two sites. Ross[12] further developed this model by taking into account the effect of catalytic heterogeneity on copolymer sequence distribution and found that the calculated triad sequence distributions fitted well to the observed ones. Cozewith[13] also demonstrated that a two-site model with a product of monomer reactivity ratios $(r_1r_2)_i$ equal to 1 is an adequate model for the data of Kakugo et al.[5] However, this model is not completely adequate, since the sum of the squares of the deviations between the predicted and observed sequence distributions in Doi's copolymers[7] was too large to confirm the validity of the statistical model.

In this paper, various statistical models are examined to predict the observed sequence distributions in E–P copolymers. One- and two-site models with first-order Markovian and Bernoullian statistics are investigated. The validity of the best-fit model is tested by the tetrad sequence distribution obtained in this work. The copolymerization mechanism with heterogeneous Ziegler–Natta catalytic systems will be described by using the optimized values of the model parameters.

Experimental Section

E–P Copolymers. The ethylene–propylene copolymer with a low ethylene content, designated PE, was polymerized with a stereoregular Ziegler–Natta catalytic system, δ-$TiCl_3/Et_2AlCl$, and was a generous gift from Tokuyama Soda Co. Ltd. The polymerization was performed at 60 °C in the presence of hydrogen in a slurry process. The solvent of this process was propylene monomer containing a small amount of ethylene. The monomer composition was kept constant during polymerization. From ^{13}C NMR, it was confirmed that this sample does not contain any detectable amounts of head-to-head and tail-to-tail propylene units, referring to the study of regioirregularity in the chain.[17,18] The sequence distribution data of Kakugo's,[5] Doi's,[7] and Cozewith's[13] copolymers were used in this study. The catalytic systems and the polymerization conditions of these copolymers were as follows:

1. **Kakugo's Copolymers.**[5] Kakugo's copolymers were polymerized at 60 °C for 2 h under atmospheric pressure with the δ-$TiCl_3/Et_2AlCl$ catalytic system. Heptane dried on a molecular sieve 13× was used as the polymerization medium. In all polymerization runs, the monomer composition did not change during polymerization.

2. **Doi's Copolymers.**[7] Doi's copolymers were polymerized at 45 °C for 45 min under a constant pressure (ethylene + propylene = 400 Torr) in a conventional gas circulation system[19] with

Table I
Observed and Predicted Triad Sequence Distributions in Copolymers C, E, and G by Kakugo et al.[5]

sample	triad	model	PPP	PPE	EPE	PEE	PEE	EEE
C	obsd		0.67	0.17	0.02	0.07	0.03	0.04
	calcd	M	0.687	0.163	0.010	0.061	0.062	0.016
	calcd	B	0.614	0.217	0.019	0.108	0.038	0.003
E	obsd		0.50	0.21	0.04	0.10	0.07	0.08
	calcd	M	0.496	0.228	0.026	0.079	0.123	0.048
	calcd	B	0.422	0.281	0.047	0.141	0.094	0.016
G	obsd		0.07	0.13	0.09	0.07	0.16	0.49
	calcd	M	0.060	0.139	0.080	0.031	0.237	0.452
	calcd	B	0.022	0.113	0.145	0.056	0.290	0.373

Table II
Cozewith's Analyses[13] for the Data of Kakugo et al.[5] by the Two-Species Model

		E-site		P-site
sample	mol % ethylene	f_1[a]	mol % ethylene	mol % ethylene
H	75	0.599	91.9	49.6
G	72	0.458	96.7	51.1
B	53	0.323	92.2	34.3
F	49	0.304	87.9	31.8
E	25	0.123	84.1	16.7
D	22	0.137	76.9	13.3
C	15	0.055	88.2	10.7
A	13	0.042	89.0	11.0

[a] Mole fraction of the copolymer polymerized at E-site.

a silica-supported MgCl$_2$/TiCl$_4$–Et$_3$Al catalytic system. The monomer concentration in the feed is shown as follows:

run no.	propylene content in feed mol %
1	66
2	75
3	81
4	85
5	90

3. Cozewith's Copolymers.[13] Cozewith's copolymers were polymerized under 510 kPa in *n*-hexane solvent in a continuous-flow stirred reactor. The catalytic system used is shown as follows:

sample	catalyst	cocatalyst
1	TiCl$_3$/$^1/_3$AlCl$_3$[a]	Et$_3$Al
2	Ti/Me/THF[b]	Et$_3$Al
3	Ti–MgR$_2$[c]	Et$_2$AlCl
4	Ti/Mg[d]	Et$_3$Al
5	Ti/Mg(OR)$_2$[e]	(*i*-Bu)$_2$AlCl
6	Ti/MgCl$_2$/EHA[f]	(*i*-Bu)$_2$AlCl
7	Ti/MgCl$_2$/EHA[f]	Et$_2$AlCl

[a] Stauffer AA. [b] TiCl$_3$/MgCl$_2$/tetrahydrofuran complex. [c] TiCl$_4$ reduced by di-*n*-hexylmagnesium. [d] Ti supported on MgCl$_2$. [e] TiCl$_4$/Mg, ethyl hexanoate soluble complex, [Mg]/[Ti] = 7. [f] TiCl$_4$/MgCl$_2$, ethylhexyl alcohol soluble complex, [Mg]/[Ti] = 7.

NMR Measurement. The ^{13}C NMR spectrum was recorded at 120 °C on a JEOL GSX-270 spectrometer at 67.8 MHz. The sample solutions, in a 10-mm-o.d. glass tube, were prepared to *o*-dichlorobenzene (90 vol %)/benzene-d_6 (10 vol %) to give 0.1 g of polymer/cm^3 of solvent. Benzene-d_6 provided the signal for the ^{2}H NMR internal lock. In all measurements broad band noise decoupling was used to remove ^{13}C–^{1}H couplings, the pulse angle was 90°, and 10 000 free induction decays were stored in 32K data points by using a spectral window of 10 000 Hz. Hexamethyldisiloxane was used as an internal reference (2.03 ppm downfield from the resonance of tetramethylsilane). For the quantitative measurements, the pulse repetition time was 15 s, which is more than 5 times as long as the spin–lattice relaxation time of the methyl carbons of 2.5 s at 135 °C.[20] The sequence distribution in the sample PE was determined by the method proposed by Kakugo et al.[5]

Results and Discussion

Statistical Models. Single-Site Models. 1. Model M. As shown in Table I, a first-order Markovian model (model M) provides good fits for the P-centered triad sequence distributions obtained by Kakugo et al.,[5] while this model provides larger values for PEE triad and smaller values for EEE triad. This indicates the existence of a second site which preferentially polymerizes ethylene, since the larger values of the observed EEE triad correspond to the existence of the longer ethylene sequences than that predicted by a first-order Markovian model. The parameters of model M are p_{11} and p_{22}, which are probabilities of ethylene and propylene adding to ethylene- and propylene-ended chains, respectively. (In general, p_{mn} means the probability of an *n*-monomer- adding to a *m*-monomer-ended chain, where 1 and 2 represent ethylene and propylene units, respectively.) The probabilities p_{12} and p_{21} are expressed by 1-p_{11} and 1-p_{22}, respectively.

2. Model B. As shown in Table I, a Bernoullian statistical model (model B) is not applicable to predict the sequence distributions in copolymers C, E, and G observed by Kakugo et al. Ross[12] also showed that a Bernoullian model is inadequate to predict the sequence distribution in Kakugo's copolymer C. The parameters of model B is the probability p_1 of ethylene adding to a chain end. The probability p_2 of propylene adding to a chain end is expressed by 1-p_1.

Two-Site Models. 1. Model BB. As reported by Cozewith,[13] a two-site model (model BB) with a product of monomer reactivity ratios $(r_1r_2)_i$ equal to 1.0 (Bernoullian model) is an adequate model to predict the data of Kakugo's copolymers. The values of PPE/PEP and PEE/EPE ratios equal to 2.0 predicted by this model correspond with the observed values in Kakugo's copolymers, which are nearly equal to 2.0. Observed data from Kakugo et al.[5] are as follows:

sample	A	B	C	D	E	F	G	H
PEE/EPE	1.40	1.56	1.50	2.00	1.75	1.88	1.78	1.55
PEP/PEP	2.00	1.82	2.43	1.80	2.10	1.91	1.86	2.00

Cozewith[13] reported that model BB gives better fits also for the data of Doi's copolymers[7] and that model M cannot provide adequate fits. Further, as shown in Table II, Cozewith's analyses indicate that the catalyst for Doi's copolymers has two sites: one site (E-site) polymerizes ethylene preferentially, and the other site (P-site) polymerizes propylene preferentially. However, the observed values of the PEE/EPE and PPE/PEP ratios in Doi's copolymers are smaller than 2.0, as follows:

sample	1	2	3	4	5
PEE/EPE	1.50	1.39	1.82	1.73	1.64
PPE/PEP	1.25	1.73	1.45	1.39	1.75

The low values of the PEE/EPE and the PPE/EPE ratios indicate that neither the two-site nor the multi-site model with r_1r_2 equal to 1 is adequate to predict the observed sequence distributions. The values of the PEE/EPE and PPE/EPE ratios predicted by model BB are 2.0, which are far from the observed values. Most of the deviations between the observed sequence distributions and those predicted by model BB arise from the inconsistencies mentioned above. The parameters of model BB are the respective probabilities p_1 at two different sites and the mole fraction of the copolymer produced at one of the two sites. The optimization of the parameters of model BB was performed by the nonlinear least-squares routine based on the algorithm proposed by Marquardt.[21]

2. Models BM, MB, and MM. It is assumed that the inconsistencies between the observed values of the PEE/EPE and PPE/EPE ratios in Doi's copolymers and those predicted by model BB are attributable to the difference between the Bernoullian and low-order Markovian statistics of the copolymerization mechanism at catalytic sites. Based on this assumption, we modify model BB by introducing first-order Markovian statistics to one of the two sites or to both sites. Models BM and MB are versions of model BB modified by introducing first-order Markovian statistics to the E-site and P-site, respectively. The parameters of model BM (model MB) are the probability p_1 at the P-site (E-site), the probabilities p_{11} and p_{22} at the E-site (P-site), and the mole fraction f_p of the copolymer produced at the P-site. Model MM is a two-site model in which the copolymerization mechanism obeys the respective first-order Markovian statistics at two different sites. The parameters of model MM are the respective probabilities p_{11} and p_{22} at P- and E-sites and the mole fraction f_p of the copolymer produced at the P-site. The optimization of the parameters of these models was performed by the nonlinear least-squares routine using the optimized values of the parameters of model BB as the initial values of the parameters of models MB, BM, and MM.

Validity of the Statistical Models. Cozewith[13] assumed that a sum of the squares of the deviations between the calculated and observed sequence distributions of less than 10×10^{-4} is an indication that a given model adequately represents the copolymerization process. We also use this statistical criteria to estimate the validity of the statistical models. In Table III are shown the observed sequence distributions in Kakugo's E–P copolymers and those observed in this work with the calculated results by five statistical models. Four two-site models predict the sequence distributions with the small deviations from the observed ones, and model M provides less satisfactory fits for the observed data. For the observed sequence distributions in the copolymers with a low ethylene content, all two-site models provide good fits. Further, there exist no significant differences among the sequence distributions predicted by four two-site models. The fits for those in the samples A and E given by four two-site models are identical. The sum of the squares of the deviations between the observed sequence distributions and the predicted ones by models BB and BM becomes larger as the ethylene content of the copolymer increases, as shown in the data of the samples B, G, and H. Models MM and MB in which the copolymerization mechanism obeys first-order Markovian statistics at the P-site do not show such a tendency and provide good fits for the data of all samples. The reason for these results should arise from the difference of the copolymerization mechanism between first-order Markovian and Bernoullian statistics at the P-site. Thus, at least the P-site has the character of first-order Markovian statistics.

In Table IV are shown the observed sequence distributions in Doi's copolymers with the calculated results by five statistical models. For the observed data on sample 2, the nonlinear least-square routine applied by using model BB failed to converge, as shown by the large sum of the squares of the deviations between the observed sequence distribution and the predicted one by model BB. For the observed data on the other samples, the fits provided by model BB are much improved in comparison with those provided by the single-site first-order Markovian model (model M). However, the sum of the squares of the deviations between the observed sequence distribution in each sample and the predicted one by model BB is too large to give satisfactory fits. Models BM and MB provide better fits for the data with the relatively small sum of the squares of the deviations, but the fit quality was not improved sufficiently by introducing first-order Markovian statistics to one of the two sites. Only model MM, in which the copolymerization mechanism obeys the respective first-order Markovian statistics at both sites, provides satisfactory fits. Thus the two sites in the catalytic system for Doi's copolymers have a character of first-order Markovian statistics. From the analyses of the copolymers mentioned above, it is suggested that model MM is an appropriate statistical model to describe the E–P copolymerization mechanism with the heterogeneous Ziegler–Natta catalytic systems, since the observed sequence distributions in Kakugo's and Doi's copolymers are satisfactorily predicted by model MM. As shown in Table V, the predicted values of the PPE/PEP and the PEE/EPE ratios indicate good agreements with the observed ones.

In Table VI are shown the optimized values of the parameters in model MM. The two-site nature for the catalytic systems of Kakugo's and Doi's copolymers in which one site prefers to polymerize ethylene and the other site prefers to polymerize propylene is confirmed from the optimized values of the parameters. For the data of Kakugo's copolymers A and E, the optimized values of the parameters p_{11} and p_{22} of model MM at two different sites are same as those of the parameters p_1 and p_2 of model BB, respectively, because model BB, whose parameters p_1 and p_2 at two different sites are used as the initial values of the parameters of model MM, provides satisfactory fits for the data of copolymers A and E. Since the parameters p_1 and p_2 of a Bernoullian statistical model satisfy the equation $p_1 + p_2 = 1$, the optimized values of the parameters p_{11} and p_{22} satisfy the equation $p_{11} + p_{22} = 1$, as shown in Table IV. For the data of the other Kakugo copolymers, the optimized values of the parameters of model MM are close to those of model BB, since the values of $p_{11} + p_{22}$ are nearly equal to 1.0. This suggests that the copolymerization mechanism with two different sites obey approximately the respective Bernoullian statistics in the catalytic system for Kakugo's copolymers. In Figure 1A are shown the dependences of the ethylene mole fractions of the copolymers produced at P- and E-sites predicted by model MM on the ethylene mole fractions of the whole polymers (E_w). The predicted mole fractions are abbreviated to E_p and E_e, respectively. According to first-order Markovian statistics, E_p and E_e are equal to the respective probabilities p_1 of ethylene adding to a chain end at P- and E-sites. The value of p_1 is calculated from the equation

$$p_1 = p_{21}/(p_{12} + p_{21})$$

The two-site catalytic systems for Kakugo and Doi copolymers indicate that at P-sites propylene polymerizes predominantly to produce copolymers with a low ethylene content and at E-sites ethylene polymerizes predominantly to produce copolymers with a high ethylene content. In Figure 1B are shown the dependences of the mole fractions (f_p) of the copolymers produced at the P-site predicted by model MM on the ethylene mole fractions (E_w) of the

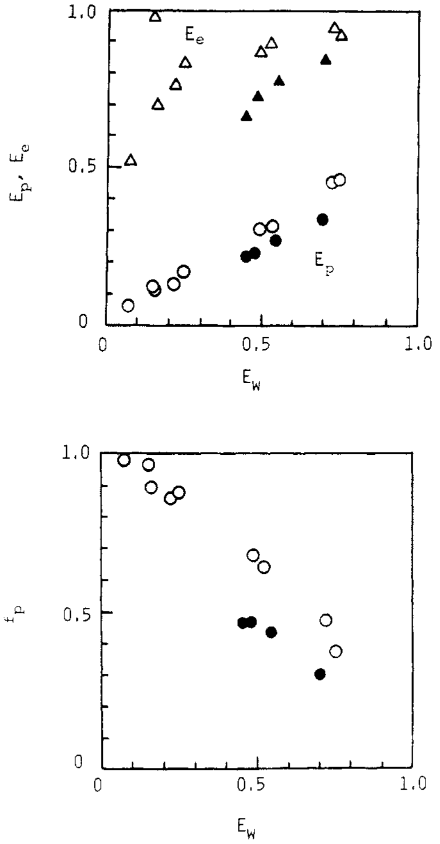

Figure 1. (A, Top) Dependences of the ethylene mole fractions of the polymers produced at P- and E-sites on the ethylene mole fractions (E_w) of the whole polymers, where the ethylene mole fractions are abbreviated to E_p (P-site) and E_e (E-site), respectively: (○) predicted ethylene mole fraction of the polymer produced at a P-site for Kakugo's data; (●) predicted ethylene mole fraction of the polymer at a P-site for Doi's data; (△) predicted ethylene mole fraction of the polymer produced at an E-site for Kakugo's data; (▲) predicted ethylene mole fraction of the polymer produced at an E-site for Doi's data. (B, Bottom) Dependence of the mole fraction (f_p) of the polymer produced at a P-site on the ethylene mole fraction (E_w) of the whole polymer: (○) predicted mole fraction of the polymer produced at a P-site for Kakugo's data; (●) predicted mole fraction of the polymer produced at a P-site for Doi's data.

whole polymers. The value of f_p decreases increasing value of E_w. This suggests that the propagation rate of the ethylene at the E-site is not equal to that at the P-site. Probably the former would be much larger than the latter, since the increase of the copolymerized ethylene unit at the E-site would be larger than that at the P-site with the increase of E_w.

In parts A and B of Figure 2 the probabilities p_{11} and p_{22} predicted by model MM are plotted versus the predicted ethylene mole fractions (E_p and E_e) of the copolymers produced at P- and E-sites. In the figure, two broken lines express the case of model BB in which the copolymerization mechanism is described by Bernoullian statistics at the two different sites. That is, the probabilities p_{11} and p_{22} satisfy the equation $p_{11} = 1 - p_{22} = p_1 = 1 - p_2$ at P- and E-sites. The deviations of p_{11} and p_{22} from the Bernoullian statistics at both sites are schematically represented by the differences between the plotted values of p_{11} and p_{22} predicted by model MM and the respective broken lines at definite values of E_p (in Figure 2A) and E_e (in Figure 2B). Except for the predicted values for the observed data of the sample C, it is recognized that the values of p_{11} and p_{22} at both sites predicted by model MM are close to those of model BB in the catalytic system for Kakugo's copolymers. At both sites, the

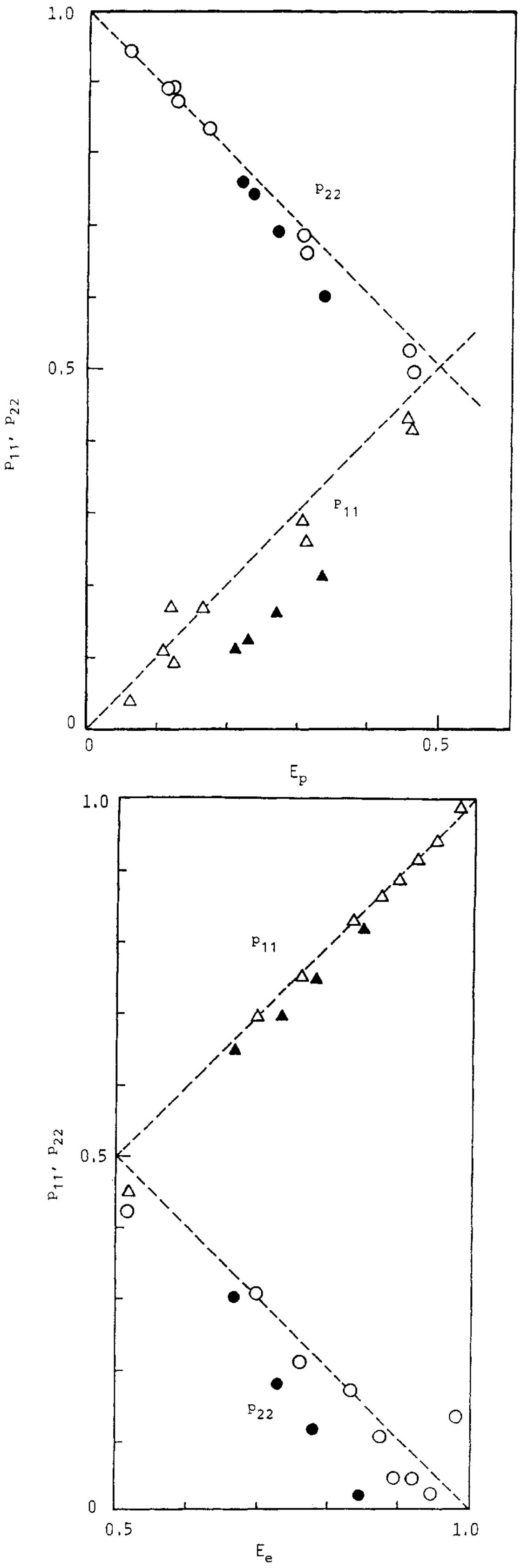

Figure 2. (A, Top) Dependences of the probabilities p_{11} and p_{22} on the ethylene mole fractions (E_p) of the polymers produced at a P-site: (○) p_{22} predicted for Kakugo's data; (●) p_{22} predicted for Doi's data; (△) p_{11} predicted for Kakugo's data; (▲) p_{11} predicted for Doi's data. Broken lines indicate that the copolymerization mechanism obeys a Bernoullian statistical model. (B, Bottom) Dependences of the probabilities p_{11} and p_{22} on the ethylene mole fraction (E_e) of the polymers produced at an E-site: (○) p_{22} predicted for Kakugo's data; (●) p_{22} predicted for Doi's data; (△) p_{11} predicted for Kakugo's data; (△) p_{11} predicted for Doi's data. Broken lines indicate that the copolymerization mechanism obeys a Bernoullian statistical model.

Table III
Triad Comonomer Sequence Distributions in Ethylene–Propylene Copolymers Observed by Kakugo et al.[5] and Predicted by One- and Two-Site Models[a]

sample		PPP	PPE	EPE	PEP	PEE	EEE	SS[b]/10^{-4}
PE	obsd	0.813	0.111	0.007	0.057	0.010	0.002	
	calcd (M)	0.810	0.116	0.004	0.056	0.013	0.001	0.54
	calcd (BB)	0.813	0.112	0.006	0.056	0.011	0.003	0.05
	calcd (BM)	0.813	0.112	0.006	0.056	0.011	0.003	0.05
	calcd (MB)	0.813	0.111	0.007	0.057	0.010	0.002	0.0
	calcd (MM)	0.813	0.111	0.007	0.057	0.010	0.002	0.0
A	obsd	0.63	0.17	0.03	0.08	0.05	0.04	
	calcd (M)	0.652	0.176	0.012	0.063	0.075	0.023	20.47
	calcd (BB)	0.633	0.169	0.025	0.085	0.051	0.037	0.70
	calcd (BM)	0.633	0.169	0.025	0.085	0.051	0.037	0.70
	calcd (MB)	0.633	0.169	0.025	0.085	0.051	0.037	0.70
	calcd (MM)	0.633	0.169	0.025	0.085	0.051	0.037	0.70
C	obsd	0.67	0.17	0.02	0.07	0.03	0.04	
	calcd (M)	0.687	0.163	0.010	0.061	0.062	0.016	18.79
	calcd (BB)	0.675	0.165	0.014	0.083	0.029	0.034	2.92
	calcd (BM)	0.675	0.168	0.011	0.079	0.032	0.035	2.20
	calcd (MB)	0.675	0.168	0.011	0.079	0.032	0.035	2.20
	calcd (MM)	0.675	0.168	0.011	0.079	0.032	0.035	2.20
D	obsd	0.57	0.18	0.03	0.10	0.06	0.06	
	calcd (M)	0.558	0.202	0.020	0.071	0.106	0.037	42.14
	calcd (BB)	0.568	0.184	0.031	0.092	0.062	0.063	0.98
	calcd (BM)	0.568	0.184	0.031	0.092	0.062	0.063	0.98
	calcd (MB)	0.567	0.181	0.035	0.095	0.059	0.063	0.70
	calcd (MM)	0.567	0.181	0.035	0.095	0.059	0.063	0.70
E	obsd	0.50	0.21	0.04	0.10	0.07	0.08	
	calcd (M)	0.496	0.228	0.026	0.079	0.123	0.048	48.10
	calcd (BB)	0.503	0.209	0.035	0.105	0.071	0.077	0.70
	calcd (BM)	0.503	0.209	0.035	0.105	0.071	0.077	0.70
	calcd (MB)	0.503	0.209	0.035	0.105	0.071	0.077	0.70
	calcd (MM)	0.503	0.209	0.035	0.105	0.071	0.077	0.70
F	obsd	0.22	0.21	0.08	0.11	0.15	0.23	
	calcd (M)	0.213	0.233	0.063	0.066	0.228	0.196	100.43
	calcd (BB)	0.221	0.213	0.076	0.106	0.153	0.231	1.41
	calcd (BM)	0.221	0.213	0.077	0.106	0.153	0.231	1.34
	calcd (MB)	0.220	0.210	0.080	0.110	0.150	0.230	0.0
	calcd (MM)	0.220	0.210	0.080	0.110	0.150	0.230	0.0
B	obsd	0.19	0.20	0.09	0.11	0.14	0.27	
	calcd (M)	0.190	0.221	0.064	0.053	0.233	0.234	143.11
	calcd (BB)	0.195	0.208	0.075	0.104	0.149	0.269	4.32
	calcd (BM)	0.195	0.207	0.075	0.104	0.150	0.269	4.32
	calcd (MB)	0.193	0.199	0.085	0.115	0.141	0.267	0.70
	calcd (MM)	0.193	0.199	0.085	0.115	0.141	0.267	0.70
G	obsd	0.07	0.13	0.09	0.07	0.16	0.49	
	calcd (M)	0.060	0.139	0.080	0.031	0.237	0.452	91.75
	calcd (BB)	0.071	0.132	0.081	0.066	0.163	0.488	2.14
	calcd (BM)	0.071	0.132	0.081	0.066	0.163	0.488	2.14
	calcd (MB)	0.070	0.128	0.086	0.071	0.159	0.487	0.31
	calcd (MM)	0.070	0.128	0.086	0.071	0.159	0.487	0.31
H	obsd	0.04	0.10	0.11	0.05	0.17	0.52	
	calcd (M)	0.040	0.120	0.084	0.028	0.228	0.496	55.0
	calcd (BB)	0.050	0.107	0.091	0.054	0.182	0.517	6.39
	calcd (BM)	0.050	0.107	0.091	0.054	0.182	0.516	6.40
	calcd (MB)	0.048	0.099	0.100	0.063	0.174	0.515	3.75
	calcd (MM)	0.048	0.099	0.100	0.063	0.174	0.515	3.75

[a] Samples: PE observed in this work; A, D, E, F, B, and G observed by Kakugo et al. The results calculated by models M, BB, BM, MB, and MM are abbreviated M, BB, BM, MB, and MM. [b] Sum of the squares of the deviations.

deviations of p_{11} and p_{22} predicted by model MM for Doi's copolymers from the Bernoullian statistics are larger than those for Kakugo's copolymers. The copolymerization mechanism of the catalytic system for Doi's copolymers has a distinct character of first-order Markovian statistics, while that for Kakugo's copolymers is explained well by model BB. As for the data of Doi's copolymers, it is confirmed that a two-site nature is an intrinsic character of his catalytic system regardless of the monomer feed ratio (E/P), referring to the monomer feed compositions presented in the paper by Doi et al.[7] Perhaps a similar description would be applicable to the catalytic system for Kakugo's copolymers.

In Table VII are shown the values of the r_1r_2 product at the two different sites in the catalytic systems for Kakugo's and Doi's copolymers predicted by model MM. The r_1r_2 products were calculated from the equation

$$r_1r_2 = (p_{11}p_{22})/(p_{12}p_{21})$$

From the values of the r_1r_2 product, the P-site for Kakugo's copolymers produces random or moderately alternating copolymers and the P-site for Doi's copolymers produces moderately alternating copolymers. Assuming that the ethylene/propylene monomer feed ratio E/P is constant at each site during the copolymerization, the values of r_1 and r_2 at the two sites in the catalytic system for Doi's copolymers were calculated from the equations

$$r_1 = p_{11}/p_{12}(\mathrm{E/P})$$

$$r_2 = p_{22}(\mathrm{E/P})/p_{21}$$

Table IV
Triad Sequence Distributions in Ethylene–Propylene Copolymers Observed by Doi et al.[7] and Predicted by One- and Two-Site Models[a]

sample		PPP	PPE	EPE	PEP	PEE	EEE	SS[b]/10^{-4}
1	obsd	0.07	0.10	0.14	0.08	0.21	0.40	
	calcd (M)	0.048	0.144	0.108	0.046	0.267	0.386	80.45
	calcd (BB)	0.076	0.118	0.115	0.059	0.229	0.403	18.41
	calcd (BM)	0.077	0.112	0.120	0.060	0.231	0.400	12.94
	calcd (MB)	0.074	0.119	0.115	0.061	0.227	0.403	16.61
	calcd (MM)	0.071	0.100	0.138	0.082	0.210	0.399	0.10
2	obsd	0.08	0.19	0.13	0.11	0.18	0.31	
	calcd (M)	0.100	0.200	0.100	0.067	0.267	0.267	126.67
	calcd (BB)	0.063	0.182	0.143	0.091	0.286	0.235	177.4
3	obsd	0.15	0.16	0.11	0.13	0.20	0.25	
	calcd (M)	0.139	0.222	0.093	0.076	0.260	0.210	123.7
	calcd (BB)	0.154	0.177	0.109	0.089	0.217	0.254	22.92
	calcd (BM)	0.155	0.170	0.115	0.090	0.219	0.250	17.51
	calcd (MB)	0.150	0.179	0.110	0.094	0.213	0.254	18.42
	calcd (MM)	0.150	0.160	0.110	0.130	0.200	0.250	0.0
4	obsd	0.21	0.18	0.11	0.13	0.19	0.18	
	calcd (M)	0.185	0.250	0.089	0.096	0.238	0.141	109.47
	calcd (BB)	0.207	0.198	0.102	0.099	0.203	0.191	16.08
	calcd (BM)	0.207	0.191	0.108	0.101	0.206	0.186	12.67
	calcd (MB)	0.204	0.200	0.103	0.103	0.199	0.191	14.16
	calcd (MM)	0.203	0.182	0.121	0.119	0.188	0.187	3.48
5	obsd	0.23	0.21	0.11	0.12	0.18	0.15	
	calcd (M)	0.210	0.260	0.080	0.098	0.224	0.128	67.04
	calcd (BB)	0.234	0.220	0.095	0.110	0.190	0.151	5.42
	calcd (BM)	0.234	0.216	0.099	0.111	0.192	0.148	3.82
	calcd (MB)	0.231	0.221	0.096	0.113	0.187	0.152	4.20
	calcd (MM)	0.231	0.210	0.108	0.122	0.180	0.149	0.10

[a] Models M, BB, BM, MB, and MM are abbreviated M, BB, BM, MB, and MM, respectively. [b] Sum of the squares of the deviations.

Table V
Observed Values of the PPE/PEP and PEE/EPE Ratios in Doi's Copolymers and Those Predicted by Model MM

sample		1	2	3	4	5
PEE/EPE	obsd	1.50	1.39	1.82	1.73	1.64
	calcd	1.52		1.82	1.55	1.67
PPE/PEP	obsd	1.25	1.73	1.45	1.39	1.75
	calcd	1.22		1.45	1.53	1.72

Table VI
Optimized Values of the Parameters of Model MM

sample[a]	ethylene mole fraction	f_p[b]	P-site		E-site	
			p_{22}	p_{11}	p_{22}	p_{11}
PE	0.070	0.979	0.939	0.041	0.418	0.454
C	0.150	0.967	0.889	0.163	0.134	0.984
A	0.160	0.892	0.890	0.110	0.306	0.694
D	0.220	0.855	0.870	0.092	0.206	0.750
E	0.250	0.872	0.832	0.168	0.170	0.830
F	0.490	0.676	0.685	0.288	0.105	0.868
B	0.525	0.637	0.663	0.254	0.042	0.886
G	0.720	0.466	0.524	0.430	0.022	0.942
H	0.750	0.368	0.495	0.413	0.0045	0.914
1	0.30	0.298	0.600	0.212	0.021	0.817
3	0.45	0.427	0.689	0.162	0.117	0.746
4	0.52	0.472	0.739	0.126	0.179	0.694
5	0.55	0.473	0.761	0.114	0.300	0.648

[a] PE, sample of this work; A–H, Kakugo's copolymers;[5] 1, 3–5, Doi's copolymers.[7] [b] Mole fraction of copolymer produced at P-site.

The calculated results are shown in Table VII. At the E-site, the values of r_1 are much larger than those of r_2, although the r_1r_2 products are smaller than 1.0. Thus, the E-site produces a block copolymer containing long E-sequences. This explanation for the silica-supported catalyst corresponds well with the copolymerization mechanism suggested by Doi et al.[7]

Concerning the character of the E-site in the catalyst for Doi's copolymers, Ti^{2+} species should be taken into consideration, since the reduction of Ti^{3+} species on the catalyst surface with the Et_3Al can occur in the copolymerization.[22] The schemes for the reduction of the transition metals are as follows:

$$[TiCl_3] + Et_3Al \rightarrow [TiCl_2Et] + Et_2AlCl$$

$$[TiCl_2Et] \rightarrow [TiCl_2] + C_2H_6 + C_2H_4$$

Soga et al.[23] have suggested that the Ti^{2+} site is only active for the ethylene propagation reaction. Assuming the best applicability of model MM to the E–P copolymerization mechanism, we propose that the E-site changes during copolymerization from Ti^{3+} to Ti^{2+} species. If the character of the site did not change in the copolymerization period, the values of r_1 and r_2 at the two sites would be constant even when the monomer feed ratio (E/P) varies. The values of r_1 and r_2 at the E-site vary with E/P, while they are constant at the P-site. This indicates that the E-site is not stable in the copolymerization. Further, the existence of Ti^{2+} species permits the production of the block copolymers containing long ethylene sequences at the E-site.

In Table VIII is shown the tetrad sequence distribution in the E–P copolymer with a low ethylene content (sample PE), prepared with δ-$TiCl_3/Et_2AlCl$ catalyst. The tetrad sequence distribution was determined on the basis of the assignments by Ray et al.[2] and by using the relationship EEEE = EEE − ($^1/_2$)PEEE. The relative areas of the peaks were evaluated accurately by the curve resolution method.[24] The tetrad sequence distribution is predicted by model MM with a small sum of the squares of the deviations from the observed one. This also confirms the validity of model MM. The observed value of the EPPE/PEEP ratio and that predicted by model MM is not equal to 1.0, while model BB gives 1.0. Thus, neither the two-site nor the multisite model with $(r_1r_2)_i$ equal to 1.0 is applicable to the E–P copolymerization mechanism strictly, although model BB provides good fits for the triad sequence distributions of E–P copolymers with a low ethylene content.

Table VII
Values of r_1, r_2, and r_1r_2 Product Predicted by Using Model MM

sample[a]	ethylene mole fraction	P-site r_1	P-site r_2	P-site r_1r_2	E-site r_1	E-site r_2	E-site r_1r_2
PE	0.070			0.658			0.597
C	0.150			1.560			9.516
A	0.160			1.000			1.000
D	0.220			0.678			0.778
E	0.250			1.0000			1.000
F	0.490			0.880			0.771
B	0.525			0.670			0.341
G	0.720			0.830			0.365
H	0.750			0.690			0.048
1	0.700	0.79	0.51	0.403	8.50	0.011	0.094
3	0.550	0.82	0.53	0.428	12.40	0.031	0.389
4	0.480	0.86	0.48	0.408	13.50	0.037	0.494
5	0.450	1.13	0.41	0.410	16.20	0.049	0.789

[a] PE, sample of this work; A–H, Kakugo's copolymers;[5] 1, 3–5, Doi's copolymers.[7]

Table VIII
Observed and Predicted Tetrad Sequence Distributions in Sample PE

sequence	obsd	calcd (M)	calcd (MM)
PPPP	0.771	0.756	0.762
PPPE	0.091	0.109	0.101
EPPE	0.006	0.004	0.005
PPEP + EPEP	0.114	0.111	0.114
PPEE + EPEE	0.011	0.013	0.010
PEEP	0.004	0.007	0.004
PEEE	0.002	0.001	0.003
EEEE	0.001	0.000	0.001
SS[a]/10^{-4}		5.770	1.840
EPPE/PEEP	1.50	0.571	1.25

[a] Sum of the squares of the deviations.

in Table IX are shown the analyses using model MM for Cozewith's copolymers prepared with titanium-based catalysts. Except for the observed sequence distribution of sample 6, model MM provides good fits for the observed data. The optimized values of the parameters reveal a two-site nature of the catalytic systems.

In the ethylene–propylene copolymerization with heterogeneous Ziegler–Natta catalytic systems, the gel effect[25] should be taken into consideration. Since the polymerization rate of ethylene is much faster than that of propylene, relative monomer concentrations of ethylene and propylene change rapidly at the catalytic sites owing to the occurrence of ethylene starvation. This leads to the heterogeneity of the E–P copolymers, as if they are polymerized at the many different sites. Thus, the heterogeneous catalytic systems should exhibit an apparent multiplicity of the sites (site multiplicity) due to the gel effect. However, it is impossible and unnecessary to examine a more complex model with a parameter of this apparent site multiplicity, because the number of the parameters becomes too large to be optimized from the respective fractions of triad sequences and because model MM provides a good fit to the sequence distribution data without such a parameter. Thus, the catalytic sites of heterogeneous Ziegler–Natta catalytic systems, which contain the apparent site multiplicity due to the gel effect, are characterized as the two types of sites, E and P. We considered that the optimized conditional probabilities at E- and P-sites represent the mean values of those at multiple sites apparently arisen from the gel effect. Furthermore, the "two-site" model (model MM) provides good fits to the sequence distribution data of various copolymers, although these copolymers were polymerized with different catalytic systems under different polymerization conditions. This means that the existence of two sites is an intrinsic characteristic of heterogeneous Ziegler–Natta catalytic systems. Therefore, it is concluded that the two-site model in which copolymerization proceeds under the control of the respective first-order Markovian statistics at the two different sites is applicable to the ethylene–propylene copolymerization mechanism with the titanium-based heterogeneous Ziegler–Natta catalytic systems.

Conclusions

The observed sequence distributions in ethylene–propylene copolymers prepared with heterogeneous Ziegler–Natta catalytic systems are predicted satisfactorily by the two-site model (model MM), in which copolymerization obeys first-order Markovian statistics at two different sites. The optimized values of the parameters of model MM fit reasonably such an ethylene–propylene copolymerization mechanism. Model MM can elucidate the difference in the statistical character of the copolymerization mechanism among the various catalytic systems, e.g., between the δ-$TiCl_3/Et_2AlCl$ system and the silica-supported $MgCl_2/TiCl_4$-Et_3Al system. The deviations of the conditional probabilities p_{11} and p_{22} for the copolymers prepared with $MgCl_2/TiCl_4$-Et_3Al system from Bernoullian

Table IX
Analyses of the Sequence Distributions in Cozewith's[13] Copolymers by Model MM

sample	ethylene content, mol %	f_P[a]	P-site p_{22}	P-site p_{11}	E-site p_{22}	E-site p_{11}	model MM SS[c]/10^{-4}	model BB[b] SS[c]/10^{-4}
1	62.9	0.321	0.714	0.100	0.093	0.298	4.64	54
2	62.1	0.248	0.722	0.073	0.152	0.704	1.06	29
3	65.1	0.288	0.581	0.207	0.147	0.724	4.39	28
4	62.9	0.220	0.774	0.087	0.180	0.719	0.28	19
5	63.4	0.201	0.785	0.093	0.156	0.709	1.74	25
6	64.9	0.255	0.746	0.003	0.024	0.748	13.74	52
7	62.4	0.267	0.686	0.093	0.118	0.347	4.55	35

[a] Mole fraction of the copolymer produced at P-site. [b] Analyses by Cozewith via Bernoullian–Bernoullian two-site model. [c] Sum of the squares of the deviations.

statistics are larger than those for the copolymers prepared with the δ-$TiCl_3/Et_2AlCl$ system. Furthermore, a two-site mechanism, in which one site (P-site) polymerizes propylene predominantly and the other site (E-site) polymerizes ethylene predominantly, is confirmed in the catalytic systems used for Kakugo's and Doi's copolymers. In the catalytic system for Doi's copolymers, the P-site produces random or moderately alternating copolymer and the E-site produces block copolymers containing long ethylene sequences. The applicability of model MM is verified by the analyses of Cozewith's copolymers prepared with various titanium-based catalytic systems. Therefore, it is concluded on the basis of the sequence distributions determined by ^{13}C NMR spectra that model MM is appropriate to describe the ethylene–propylene copolymerization mechanism with heterogeneous Ziegler–Natta catalytic systems, as far as it is concerned with the analyzed sequence distribution data of E–P copolymers in this study.

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Registry No. E, 74-85-1; P, 115-07-1; (E)(P) (copolymer), 9010-79-1.

References and Notes

(1) Wilkes, C. E.; Carman, C. J.; Harrington, R. A. *J. Polym. Sci., Polym. Symp.* **1973**, *43*, 237.
(2) Ray, G. J.; Johnson, P. E.; Knox, J. R. *Macromolecules* **1977**, *10*, 773.
(3) Randall, J. C. *Macromolecules* **1978**, *11*, 33.
(4) Smith, W. V. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1573, 1587.
(5) Kakugo, M.; Naito, Y.; Mizunuma, K.; Miyatke, T. *Macromolecules* **1982**, *15*, 1150.
(6) Cheng, H. N. *Macromolecules* **1984**, *17*, 1950.
(7) Doi, Y.; Ohnishi, R.; Soga, K. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 169.
(8) Soga, K.; Shiono, T.; Doi, Y. *Polym. Bull. (Berlin)* **1983**, *10*, 168.
(9) Cheng, H. N. *Anal. Chem.* **1982**, *54*, 1828.
(10) Ross, J. F. *J. Macromol. Sci., Chem.* **1984**, *A21*(4), 453.
(11) Ross, J. F. Presented at the International Symposium on Transition Metal Catalyzed Polymerization, Akron, OH, June 16, 1986; paper 60.
(12) Ross, J. F. *J. Macromol. Sci., Chem.* **1987**, *A24*(2), 211.
(13) Cozewith, C. *Macromolecules* **1987**, *20*, 1237.
(14) Zhu, S. N.; Yang, X. Z.; Chûjô, R. *Polym. J. (Tokyo)* **1983**, *15*, 859.
(15) Inoue, Y.; Itabashi, Y.; Chûjô, R.; Doi, Y. *Polymer* **1984**, *25*, 1640.
(16) Hayashi, T.; Inoue, Y.; Chûjô, R.; Asakura, T. *Polymer* **1988**, *29*, 138.
(17) Asakura, T.; Nishiyama, Y.; Doi, Y. *Macromolecules* **1987**, *20*, 616.
(18) Zambelli, A.; Locatelli, P.; Bajo, G. *Macromolecules* **1977**, *10*, 773.
(19) Soga, K.; Ohnishi, R.; Sano, T. *Polym. Bull. (Berlin)* **1982**, *7*, 547.
(20) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1693.
(21) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.
(22) Kissin, Y. V. *Isospecific Polymerization of Olefins*; Springer-Verlag: New York, 1985; Chapter II.
(23) Soga, K.; Sano, T.; Ohnishi, R. *Polym. Bull. (Berlin)* **1981**, *4*, 157.
(24) Randall, J. C. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 2083.
(25) Lukach, C. A.; Spurlin, H. M. *Copolymerization*; Ham, G. E., Ed.; Interscience: New York, 1964.

Three-Dimensional Structure of Main-Chain Liquid-Crystalline Copolymers. 1. Cylindrically Averaged Intensity Transforms of Single Chains

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ABSTRACT: As a first step in our X-ray analysis of the three-dimensional structure of wholly aromatic main-chain liquid-crystalline copolyesters, this paper describes calculation of the cylindrically averaged transforms of single chains. Attention is focused on the copolyesters prepared from *p*-hydroxybenzoic acid (HBA) of 2-hydroxy-6-naphthoic acid (HNA). Previous analyses of the aperiodic meridional intensity distribution have shown that these copolymers consist of arrays of parallel chains of completely random comonomer sequence. Nevertheless, the X-ray fiber diagrams contain equatorial and off-equatorial Bragg maxima, which point to the existence of three-dimensional order. The cylindrically averaged transforms are calculated by an extension of the one-dimensional model used previously, when the chain is treated as a one-dimensional paracrystal with random coordination statistics for the two monomers. It is found that a dimer repeat must be assumed in order to generate the intense layer line that occurs between the equator and the first meridional maximum. The chain is treated as a random array of the four possible dimers with a fixed conformation but with limited conformational correlation between successive dimer units. Good agreement is obtained when the dimers have conformations analogous to those of poly(*p*-benzamide) and poly(*p*-phenyleneterephthalamide), and analysis of the chain packing is necessary to decide between the various possibilities.

Introduction

The solid-state structure of liquid-crystalline polymers has stimulated much interest and research in recent years.[1–3] In particular, there has been extensive study of a group of wholly aromatic random copolyesters, which are thermotropic main-chain liquid-crystalline polymers with applications as high-strength fibers and high-performance moldings. The bulk properties of these copolymers show a high sensitivity to relatively small changes in the chemical structure and proportions of the monomer components.[4] In addition, the excellent mechanical properties of these systems appear to correlate with the development of three-dimensional crystalline order, which develops on cooling after processing from the melt and which increases on thermal treatment.[5]

Previous papers from this laboratory have described X-ray analyses of the structure of wholly aromatic thermotropic copolyesters and also of an analogous lyotropic