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Studies on Sequence Distributions of Terpolyesters by High-Resolution Nuclear Magnetic Resonance

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ABSTRACT: NMR spectra of poly(ethylene terephthalate—sebacate—fumarate) and poly(ethylene terephthalate—sebacate—malonate) terpolyesters, which are obtained by ordinary molten-state polycondensation under reduced pressure, are studied. Ethylene glycol protons show six kinds of dyad sequences and their areas are measured by a curve resolver. Their relative intensities are in good accord with the calculated values for random (or Bernoullian) terpolymers. The relationships of three kinds of combination of two acid groups are plotted in the triangular coordinate system by normalizing the three kinds of dyad sequences. It is found that these three acid groups are randomly distributed.

KEY WORDS Sequence Distribution / NMR / Terpolymer / Polyester / Triangular Coordinate System / Curve Resolver / Poly(Ethylene Terephthalate—Sebacate—Fumarate) / Poly(Ethylene Terephthalate—Sebacate—Malonate) /

High-resolution nuclear magnetic resonance (NMR) is becoming an increasingly important tool in the study of sequence distributions in copolymers since its first application was demonstrated by Ferguson,[1] and many vinyl copolymers have been studied. But as for condensation copolymers, there are only a few reports about their sequence distributions by NMR.[2-5]

The authors[2] studied the sequence distributions of many kinds of copolyesters prepared by ordinary molten-state polycondensation from ethylene glycol and dimethyl esters of dicarboxylic acids, and found many of them were random (or Bernoullian) copolymers from their ethylene glycol proton resonance. The transesterification reaction between two kinds of homopolyesters was also studied and it was found that random (or Bernoullian) copolyesters were formed by this reaction.[2,6]

As found in our binary copolyester, glycol units are sensitive to the linking acid groups and show three kinds of linkages in glycol units, A—E—A, A—E—B (or B—E—A), and B—E—B, where A and B represent acid groups and E glycol units.

In terpolyesters prepared from ethylene glycol and three kinds of acids, six kinds of linkages, A—E—A, A—E—B (or B—E—A), A—E—C (or C—E—A), B—E—B, B—E—C (or C—E—B), and C—E—C, are found in their ethylene glycol proton resonance.[7]

In the present paper, the sequence distributions of many kinds of terpolyesters, prepared by ordinary molten-state polycondensation from ethylene glycol and dimethylesters of dicarboxylic acids, are studied by NMR spectra.

EXPERIMENTAL

Poly(ethylene terephthalate—sebacate—fumarate), PET/S/F, and poly(ethylene terephthalate—sebacate—malonate), PET/S/M, were prepared from ethylene glycol and dimethyl esters of the corresponding acids by ordinary molten-state polycondensation under reduced pressure at 195°C. Binary copolyesters and homopolyesters were also prepared from the corresponding dimethyl esters.

NMR spectra were measured in chloroform solution (0.05 g/m*l*) at 70°C with Varian A-60 and HA-100 spectrometers and the spectra were resolved by a du Pont 310 Curve Resolver.

RESULTS AND DISCUSSION

When we make a terpolymer from A, B, and C comonomers, it has 9 kinds of dyad sequence, A—A, A—B, A—C, B—A, B—B, B—C, C—A, C—B, and C—C, and in the case of terpolyesters consisting of three kinds of acids and ethylene glycol, they have six dyad sequences, A—E—A, A—E—B (or B—E—A), A—E—C (or C—E—A), B—E—B, B—E—C (or C—E—B), and C—E—C, where A, B, C represent acid groups and E ethylene glycol units.

In Figure 1, 60-MHz NMR spectra of PET/S/F terpolyesters are shown and ethylene glycol protons have six resonance peaks. The binary copolymers, PET/S, PES/F, and PEF/T, show three resonance peaks in the ethylene glycol region, and the homopolymers, PET, PES, and PEF have one peak, respectively. Therefore, these six peaks in PET/S/F terpolyesters can be assigned to T—E—T, T—E—F (or F—E—T), T—E—S (or S—E—T), F—E—F, S—E—F (or F—E—S), and S—E—S linkages from the low field, considering the NMR spectra of binary copolymers and homopolymers. These assignments are summarized in Table I.

NMR spectra of PET/S/M terpolyesters were also shown in Figure 2 and six resonance peaks in ethylene glycol protons were assigned in Table II.

These six peaks in ethylene glycol protons of PET/S/F were resolved with a du Pont 310 Curve Resolver, overlapping six Lorentzian curves as shown in Figure 3. PET/S/M terpolyesters are

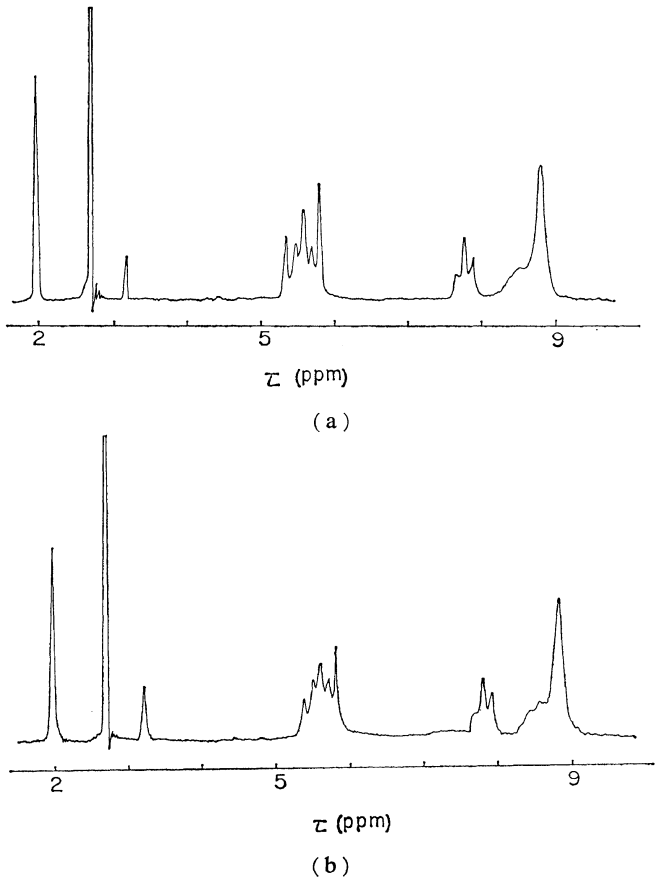


Figure 1. 60-MHz NMR spectra of PET/S/F terpolymers ((a) 40/40/20 and (b) 35/35/30) in chloroform at 70°C.

Table I. Assignments of ethylene glycol proton signals in PET/S/F terpolymers

T—E—T	5.38 ppm
T—E—F	5.50
T—E—S	5.60
F—E—F	5.61
S—E—F	5.72
S—E—S	5.82

Table II. Assignments of ethylene glycol proton signals in PET/S/M terpolymers

T—E—T	5.38 ppm
T—E—M	5.55
T—E—S	5.60
M—E—M	5.72
M—E—S	5.77
S—E—S	5.82

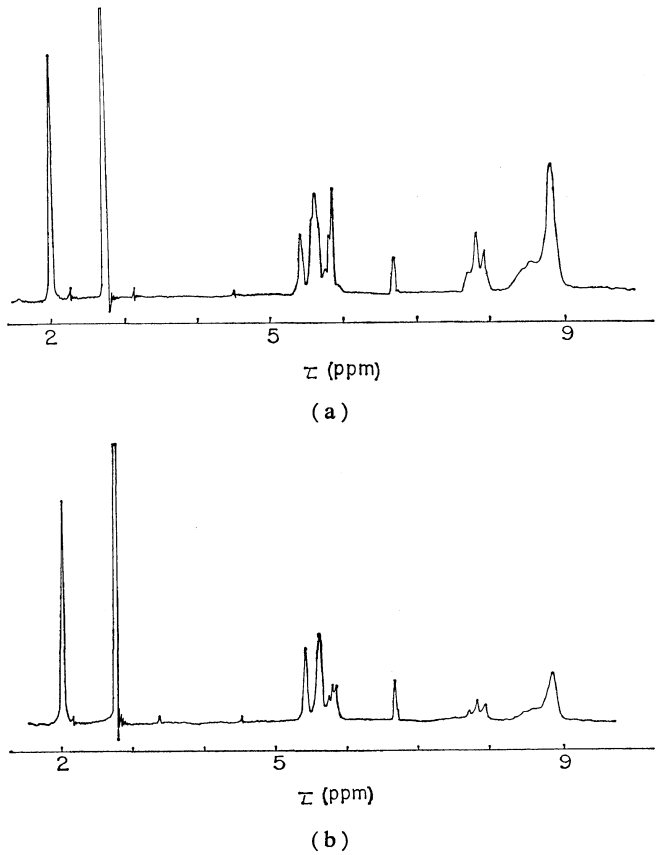


Figure 2. 60-MHz NMR spectra of PET/S/M terpolymers ((a) 40/40/20 and (b) 50/20/30) in chloroform at 70°C.

also resolved in Figure 4, and the area of each peak was measured by the integrator.

From these values of six peaks, the degree of randomness of the terpolymers can be discussed. Molar fractions of terephthalate (P_T), sebacate (P_S), and fumarate (P_F) are obtained from the intensities of the six kinds of signals in ethylene glycol protons by eq 1, 2, and 3, as well as from their relative intensities of aromatic protons of terephthalate, methylene protons of sebacate, and methine protons of fumarate.

$$P_T = P_{T-E-T} + 1/2P_{T-E-S} + 1/2P_{T-E-F} \quad (1)$$

$$P_S = P_{S-E-S} + 1/2P_{T-E-S} + 1/2P_{S-E-F} \quad (2)$$

$$P_F = P_{F-E-F} + 1/2P_{T-E-F} + 1/2P_{S-E-F} \quad (3)$$

where P_{T-E-T}, P_{T-E-S}, P_{T-E-F}, P_{S-E-S}, P_{S-E-F}, and P_{F-E-F} represent the proportions of the integrated intensities of the corresponding

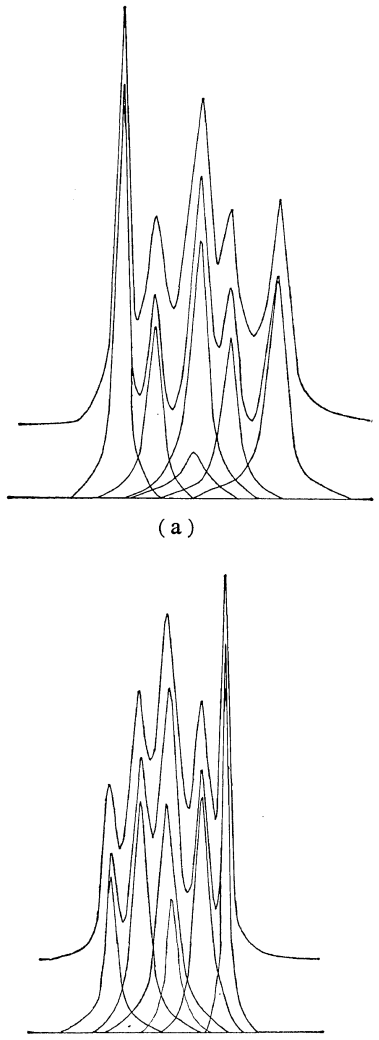


Figure 3. Ethylene glycol proton resonance spectra of PET/S/F terpolymers ((a) 40/40/20 and (b) 35/35/30); upper, observed spectra; middle, synthesized spectra; lower, six Lorentzian curves.

peaks of ethylene glycol protons.

The probability of finding a T unit next to an S unit in PET/S/F terpolyester can be obtained by eq 4,

$$P_{ST} = \frac{1/2P_{S-E-T}}{P_{S-E-S} + 1/2P_{S-E-T} + 1/2P_{S-E-T}} = \frac{P_{S-E-T}}{2P_S} \quad (4)$$

Similarly, P_{TS}, P_{TF}, P_{FT}, P_{SF}, and P_{FS} can be

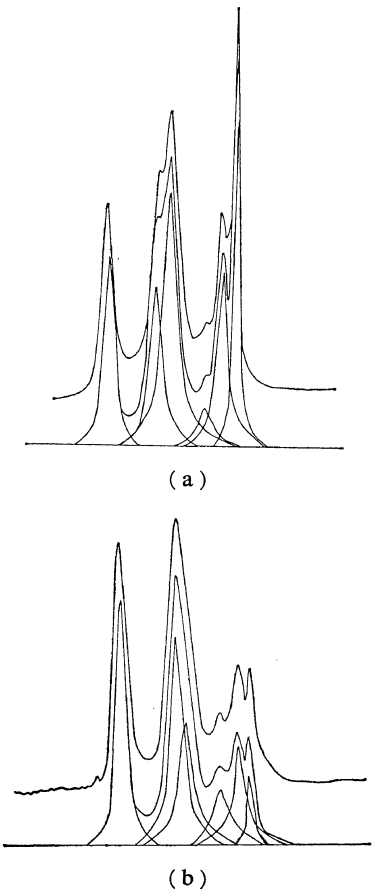


Figure 4. Ethylene glycol proton resonance spectra of PET/S/M terpolymers ((a) 40/40/20 and (b) 50/20/30); upper, observed spectra; middle, synthesized spectra; lower, six Lorentzian curves.

obtained by eq 5—9,

$$P_{TS} = \frac{P_{T-E-S}}{2P_T} \quad (5)$$

$$P_{TF} = \frac{P_{T-E-F}}{2P_T} \quad (6)$$

$$P_{FT} = \frac{P_{F-E-T}}{2P_F} \quad (7)$$

$$P_{SF} = \frac{P_{S-E-F}}{2P_S} \quad (8)$$

$$P_{FS} = \frac{P_{F-E-S}}{2P_F} \quad (9)$$

And the degree of randomness is defined by eq 10,

$$B = P_{ST} + P_{TS} + P_{TF} + P_{FT} + P_{SF} + P_{FS} \quad (10)$$

In the case of a random (or Bernoullian) terpolymer, where $P_{ST} = P_{FT} = P_T$, $P_{TS} = P_{FS} = P_S$, and $P_{TF} = P_{SF} = P_F$, B can be written in eq 11,

$$B = 2(P_T + P_S + P_F) = 2 \quad (11)$$

So a random terpolymer takes 2 as the value of B.

These values are shown in Table III. The same calculations were applied to PET/S/M terpolyesters and are shown in Table IV. The calculated values of six dyad distributions, assuming random (or Bernoullian) distribution of three acid groups, are also shown in the Tables and the measured values are in good accord with the calculated values. B takes almost 2, which means these acid units are randomly distributed in these terpolyesters.

The degree of randomness can also be evaluated by other methods.[8-10] Chujo[8] proposed the quantity $\Delta\varepsilon$ to classify the polymerization mechanism, and in the same way the degree of randomness is obtained by eq. 12, for PET/S copolymer,

$$R = \ln \frac{P_{TT} \cdot P_{SS}}{P_{TS} \cdot P_{ST}} = \ln \frac{(1 - P_{TS})(1 - P_{ST})}{P_{TS} \cdot P_{ST}} \quad (12)$$

In the random (or Bernoullian) copolymer, where $P_{TS} = P_S$, and $P_{ST} = P_T$, or $P_{T-E-S} = 2P_T \cdot P_S$, R takes 0. In an alternative copolymer, R takes $-\infty$ and it becomes larger according to the increase in block parts of the copolymers. For PET/S/F terpolymer R can be obtained by eq 13,

$$R = \ln \left(\frac{P_{TT} \cdot P_{SS}}{P_{TS} \cdot P_{ST}} \times \frac{P_{TT} \cdot P_{FF}}{P_{TF} \cdot P_{FT}} \times \frac{P_{SS} \cdot P_{FF}}{P_{SF} \cdot P_{FS}} \right)$$
$$= \ln \frac{(1 - P_{TS} - P_{TF})(1 - P_{SF} - P_{ST})}{P_{TS} \cdot P_{ST}} \times \frac{(1 - P_{TS} - P_{TF})(1 - P_{FS} - P_{FT})}{P_{TF} \cdot P_{FT}}$$

Table III. Sequence distributions in PET/S/F with various terpolymerization ratios[a]

Sample	Feed ratios, T/S/F	T—E—T, %	T—E—F, %	T—E—S, %	F—E—F, %	S—E—F, %	S—E—S, %	B
1	45/45/10	20.45 (20.25)	9.09 (9.00)	40.90 (40.50)	1.13 (1.00)	8.52 (9.00)	19.88 (20.25)	1.986
2	45/10/45	19.51 (20.25)	38.09 (40.50)	11.15 (9.00)	19.51 (20.25)	10.53 (9.00)	1.21 (1.00)	2.011
3	10/45/45	1.33 (1.00)	9.69 (9.00)	10.03 (9.00)	19.39 (20.25)	39.46 (40.50)	20.06 (20.25)	1.991
4	40/40/20	15.18 (16.00)	15.82 (16.00)	32.91 (32.00)	3.79 (4.00)	15.82 (16.00)	16.45 (16.00)	2.019
5	40/20/40	16.12 (16.00)	31.72 (32.00)	15.59 (16.00)	15.85 (16.00)	16.12 (16.00)	4.56 (4.00)	1.970
6	20/40/40	4.01 (4.00)	15.66 (16.00)	16.46 (16.00)	16.05 (16.00)	31.72 (32.00)	16.05 (16.00)	1.996
7	35/35/30	12.82 (12.25)	20.94 (21.00)	25.91 (24.50)	6.80 (9.00)	20.41 (21.00)	13.08 (12.25)	2.037
8	35/30/35	12.01 (12.25)	23.72 (24.50)	22.22 (21.00)	12.31 (12.25)	22.22 (21.00)	7.50 (9.00)	2.053
9	30/35/35	6.96 (9.00)	20.88 (21.00)	21.51 (21.00)	12.66 (12.25)	25.32 (24.50)	12.66 (12.25)	2.048
10	20/20/60	3.97 (4.00)	23.35 (24.00)	8.33 (8.00)	35.34 (36.00)	24.62 (24.00)	4.36 (4.00)	1.995
11	20/60/20	4.03 (4.00)	8.87 (8.00)	23.38 (24.00)	4.03 (4.00)	23.79 (24.00)	35.88 (36.00)	1.997
12	60/20/20	35.86 (36.00)	23.36 (24.00)	23.64 (24.00)	4.07 (4.00)	8.69 (8.00)	4.34 (4.00)	1.983
13	33.3/33.3/33.3	11.32 (11.11)	21.90 (22.22)	22.25 (22.22)	10.95 (11.11)	22.62 (22.22)	10.95 (11.11)	2.003

[a] Calculated values for random terpolymers are given in parenthesis.

Table IV. Sequence distributions in PET/S/M with various terpolymerization ratios[a]

Sample	Feed ratios, T/S/M	T—E—T, %	T—E—M, %	T—E—S, %	M—E—M, %	M—E—S, %	S—E—S, %	*B*
A	40/40/20	15.87 (16.00)	15.81 (16.00)	32.33 (32.00)	3.90 (4.00)	15.87 (16.00)	16.19 (16.00)	2.003
B	35/35/30	11.00 (12.25)	22.13 (21.00)	26.13 (24.50)	7.68 (9.00)	21.90 (21.00)	11.14 (12.25)	2.109
C	30/30/40	8.75 (9.00)	23.60 (24.00)	17.76 (18.00)	15.81 (16.00)	24.81 (24.00)	9.24 (9.00)	2.004
D	45/45/10	20.39 (20.25)	9.48 (9.00)	39.84 (40.50)	0.95 (1.00)	9.01 (9.00)	20.30 (20.25)	2.000
E	30/20/50	9.12 (9.00)	28.61 (30.00)	12.57 (12.00)	23.89 (25.00)	21.38 (20.00)	4.41 (4.00)	1.998
F	50/30/20	24.64 (25.00)	19.43 (20.00)	30.33 (30.00)	4.26 (4.00)	12.32 (12.00)	9.00 (9.00)	1.994
G	50/20/30	25.35 (25.00)	29.09 (30.00)	19.78 (20.00)	8.72 (9.00)	12.88 (12.00)	4.15 (4.00)	1.994
H	20/50/30	4.33 (4.00)	11.93 (12.00)	20.50 (20.00)	8.18 (9.00)	30.02 (30.00)	25.02 (25.00)	2.012
I	30/50/20	9.67 (9.00)	12.44 (12.00)	29.49 (30.00)	3.68 (4.00)	20.27 (20.00)	24.42 (25.00)	2.007

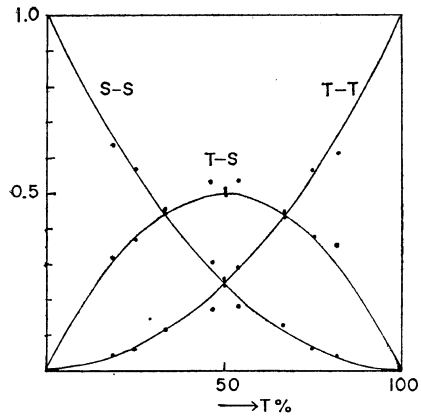
[a] Calculated values for random terpolymers are given in parenthesis.

Table V. Linkage probabilities and degree of randomness in PET/S/F with various terpolymerization ratios

Sample	Feed ratios, T/S/F	P_{ST}	P_{TS}	P_{TF}	P_{FT}	P_{SF}	P_{FS}	*R*
1	45/45/10	0.458	0.449	0.100	0.456	0.095	0.428	ln 1.431
2	45/10/45	0.462	0.126	0.432	0.434	0.437	0.120	ln 0.701
3	10/45/45	0.112	0.448	0.432	0.111	0.440	0.448	ln 1.252
4	40/40/20	0.403	0.416	0.200	0.403	0.194	0.403	ln 0.854
5	40/20/40	0.381	0.196	0.398	0.399	0.394	0.202	ln 1.564
6	20/40/40	0.205	0.410	0.390	0.197	0.395	0.399	ln 1.025
7	35/35/30	0.357	0.357	0.289	0.381	0.282	0.371	ln 0.684
8	35/30/35	0.374	0.318	0.338	0.335	0.374	0.314	ln 0.591
9	30/35/35	0.298	0.382	0.371	0.292	0.351	0.354	ln 0.614
10	20/20/60	0.200	0.210	0.588	0.197	0.592	0.208	ln 1.103
11	20/60/20	0.197	0.580	0.220	0.217	0.200	0.583	ln 0.917
12	60/20/20	0.577	0.200	0.197	0.581	0.212	0.216	ln 1.103
13	33.3/33.3/33.3	0.333	0.333	0.327	0.330	0.339	0.341	ln 1.009

Table VI. Linkage probabilities and degree of randomness in PET/S/M with various terpolymerization ratios

Sample	Feed ratios, T/S/M	P_{ST}	P_{TS}	P_{TM}	P_{MT}	S_{SM}	P_{MS}	*R*
A	40/40/20	0.401	0.404	0.198	0.401	0.197	0.402	ln 0.975
B	35/35/30	0.371	0.372	0.315	0.372	0.311	0.368	ln 0.366
C	30/30/40	0.291	0.301	0.401	0.294	0.407	0.310	ln 0.981
D	45/45/10	0.445	0.442	0.105	0.465	0.101	0.442	ln 0.836
E	30/20/50	0.294	0.211	0.482	0.293	0.499	0.219	ln 0.992
F	50/30/20	0.500	0.306	0.196	0.483	0.203	0.306	ln 1.085
G	50/20/30	0.483	0.199	0.292	0.489	0.314	0.217	ln 0.992
H	20/50/30	0.205	0.498	0.290	0.204	0.300	0.515	ln 0.940
I	30/50/20	0.299	0.482	0.203	0.311	0.206	0.506	ln 0.872



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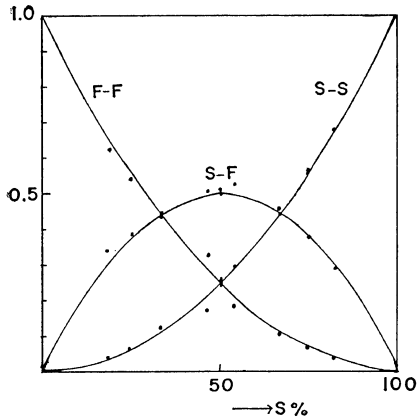

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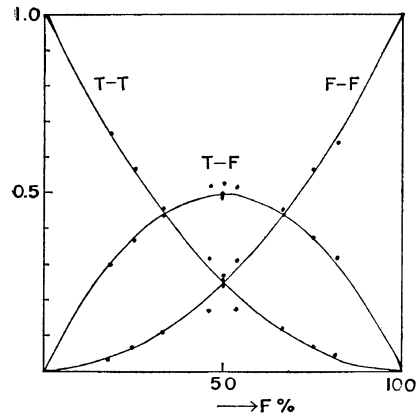

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Figure 5. Relationships between ((a) P_T and P_{T-E-T}, P_{T-E-S}, P_{S-E-S}; (b) P_S and P_{S-E-S}, P_{S-E-F}, P_{F-E-F}; (c) P_F and P_{F-E-F}, P_{F-E-T}, P_{T-E-T}) in PET/S/F terpolymers.

$$\times \frac{(1-P_{ST}-P_{SF})(1-P_{FS}-P_{FT})}{P_{SF}\cdot P_{FS}} \qquad (13)$$

In the case of a random (or Bernoullian) terpolymer, where $P_{TS}=P_{FS}=P_S$, $P_{TF}=P_{SF}=P_F$, and $P_{FT}=P_{ST}=P_T$, R takes 0. These values are obtained for PET/S/F terpolymers as shown in Table V, and for PET/S/M terpolymers in Table VI. These tables also show that these terpolymers are in random (or Bernoullian) distribution.

This can be seen more clearly in Figures 5 and 6. In Figure 5 a, distributions of terephthalate and sebacate are shown by normalizing

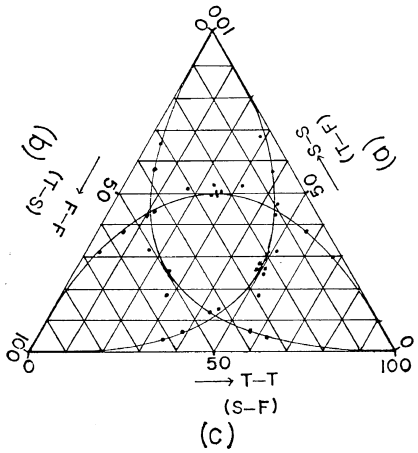
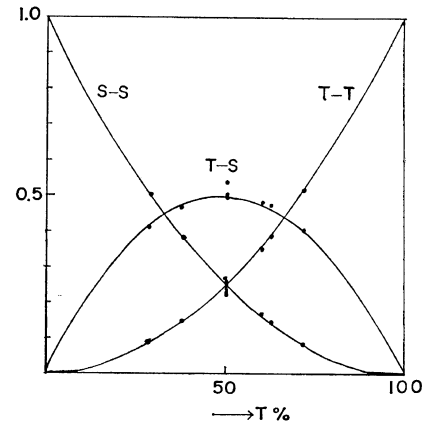


Figure 6. Relationships between ((a) P_{T-E-T}, P_{T-E-S}, and P_{S-E-S}; (b) P_{S-E-S}, P_{S-E-F}, and P_{F-E-F}; (c) P_{F-E-F}, P_{F-E-T}, and P_{T-E-T}) in PET/S/F terpolymers in a triangular coordinate system.



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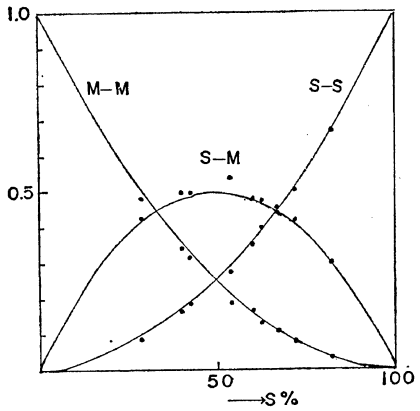

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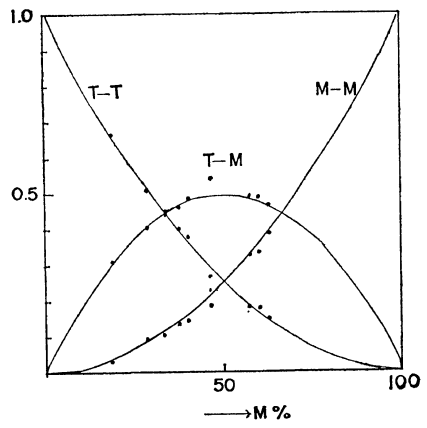

(c)

Figure 7. Relationships between ((a)P_T and P_{T-E-T}, P_{T-E-S}, P_{S-E-S}; (b) P_S and P_{S-E-S}, P_{S-E-M}, P_{M-E-M}; (c) P_M and P_{M-E-M}, P_{M-E-T}, P_{T-E-T}) in PET/S/M terpolymers.

P_{T-E-T}, P_{T-E-S}, and P_{S-E-S}. T and S are found in random (or Bernoullian) distribution. Similar relationships of sebacate and fumarate are shown in Figure 5 b by normalizing P_{S-E-S}, P_{S-E-F}, and P_{F-E-F}, and those of fumarate and terephthalate in Figure 5 c, where P_{F-E-F}, P_{F-E-T}, and P_{T-E-T} are normalized. Solid curves in these Figures mean random (or Bernoullian) distributions of these acid groups. These relationships are also shown in Figure 6 with the triangular coordinate system, where relationships between P_{T-E-T}, P_{T-E-S}, and P_{S-E-S} (a), and those of P_{S-E-S}, P_{S-E-F}, and P_{F-E-F} (b), and

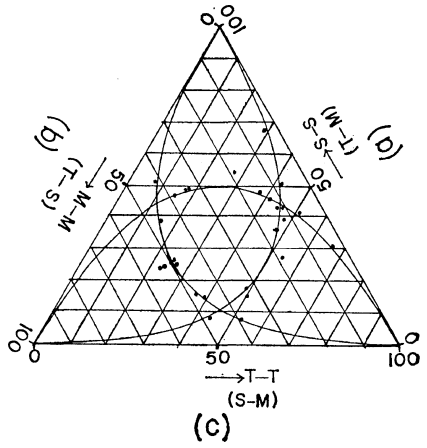

Figure 8. Relationships between ((a) P_{T-E-T}, P_{T-E-S}, and P_{S-E-S}; (b) P_{S-E-S}, P_{S-E-M}, and P_{M-E-M}; (c) P_{M-E-M}, P_{M-E-T}, and P_{T-E-T}) in PET/S/M terpolymers in a triangular coordinate system.

those of P_{F-E-F}, P_{F-E-T}, and P_{T-E-T} (c), are shown, the solid curves meaning random (or Bernoullian) distributions of terephthalate and sebacate, sebacate and fumarate, and fumarate and terephthalate, respectively. From these figures, it is quite clear that terephthalate, sebacate, and fumarate are in random (or Bernoullian) distributions in these terpolyesters.

Similar relationships of PET/S/M are plotted in Figures 7 and 8 by normalizing P_{T-E-T}, P_{T-E-S}, and P_{S-E-S} (Figure 7 a), P_{S-E-S}, P_{S-E-M}, and P_{M-E-M} (Figure 7 b), and P_{M-E-M}, P_{M-E-T}, and P_{T-E-T} (Figure 7 c). These figures clearly show that terephthalate, sebacate, and malonate are randomly distributed in these terpolyesters.

It is quite useful to plot in the triangular coordinate system in studying the sequence distribution of terpolymers.

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