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Sequence Distribution in Terpolymers

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ABSTRACT

Factors influencing sequence distribution in terpolymers are examined. It is shown that the average sequence length of M_1 can be greater in a terpolymer than in the M_1/M_2 copolymer if $r_{13} > r_{12}$.

A matter of considerable importance is the influence of a third monomer on the sequence distribution in binary copolymers. Tosi [1] has pointed out, with accompanying proof, that the average sequence length in terpolymers is smaller than in the corresponding copolymers.

Thus the composition of the copolymer is

$$\frac{m_1}{m_2} = \frac{M_1}{M_2}\,\frac{r_{12}M_1 + M_2}{r_{21}M_2 + M_1} \tag{1}$$

The composition of the terpolymer, as far as the first two monomers are concerned, is

$$m_1 = \frac{M_1A}{M_1A + M_2B(r_{21}/r_{12}) + M_3C(r_{31}/r_{13})} \tag{2a}$$

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$$m_2 = \frac{M_2B(r_{21}/r_{12})}{M_1A + M_2B(r_{21}/r_{12}) + M_3C(r_{31}/r_{13})} \tag{2b}$$

where

$$A = M_1 + \frac{M_2}{r_{12}} + \frac{M_3}{r_{13}}$$

$$B = \frac{M_1}{r_{21}} + M_2 + \frac{M_3}{r_{23}}$$

$$C = \frac{M_1}{r_{31}} + \frac{M_2}{r_{32}} + M_3$$

The average sequence length of M_1 in the copolymer is

$$\bar{n}_1(c) = 1 + \frac{M_1}{M_2}r_{12} = 1 + \frac{M_1}{M_2/r_{12}} \tag{3}$$

For the same monomer in a terpolymer

$$\bar{n}_1(t) = 1 + \frac{M_1}{A - M_1} = 1 + \frac{M_1}{(M_2/r_{12}) + (M_3/r_{13})} \tag{4}$$

It follows that $\bar{n}_1(t) < \bar{n}_1(c)$.

It should be cautioned, however, that the result is only proven for the case of adding the third monomer to fixed amounts of two monomers, not to replacing a portion of one monomer with an equal amount of a third.

Two possibilities exist:

1. A portion of M_3 is used to replace some M_1 in an M_1/M_2 mixture. Thus the average sequence length of M_1 in the terpolymer

$$\bar{n}_1(t) = 1 + \frac{M_1 - M_3}{(M_2/r_{12}) + (M_3/r_{13})}$$

It is seen on comparison with Eq. (3) that $\bar{n}_1(t) < \bar{n}_1(c)$. For this the average sequence length reduction is more severe than for the Tosi case.

2. A portion of M_3 is used to replace some M_2 in an M_1/M_2 mixture. Thus the average sequence length of M_1 in the terpolymer

$$\bar{n}_1(t) = 1 + \frac{M_1}{[(M_2 - M_3)/r_{12}] + (M_3/r_{13})} \tag{5}$$

$$1 + \frac{M_1}{M_2/r_{12} - M_3/r_{12} + M_3/r_{13}}$$

This may be written

$$\bar{n}(t) = 1 + \frac{M_1}{M_2/r_{12} + M_3\left(\dfrac{1}{r_{13}} - \dfrac{1}{r_{12}}\right)}$$

It is seen by comparison with Eq. (3):

$$\text{If } \frac{1}{r_{13}} > \frac{1}{r_{12}}, \qquad \bar{n}_1(t) < \bar{n}_1(c)$$

$$\text{If } \frac{1}{r_{13}} < \frac{1}{r_{12}}, \qquad \bar{n}_1(t) > \bar{n}_1(c)$$

Thus, in this case the average sequence length of M_1 can actually be greater in a terpolymer than in the M_1/M_2 copolymer. Simply put, it is only necessary that M_1 sequences be more readily terminated by M_2 than by M_3, a condition arising from $r_{13} > r_{12}$.

Average sequence length in copolymers influences many important parameters, such as T_g, T_m, gas permeability, stiffness modulus, and elongation. It was of interest to determine the effect of different types of monomer M_3 on the sequence distribution in M_1/M_2 copolymers.

Styrene (M_1)-methyl methacrylate (M_2) was chosen as a base copolymer. As M_3, acrylonitrile, p-methylstyrene, and vinyl acetate were selected. For initial examination, 0.1 mol M_3 was added to 0.5 mol M_1 and 0.5 mol M_2.

TABLE 1. Effect of Varying M_3 in M_1/M_2 Combinations

M_3 = AN	M_3 = PMS	M_3 = VAc
r_{12} = 0.52	r_{12} = 0.52	r_{12} = 0.52
r_{21} = 0.46	r_{21} = 0.46	r_{21} = 0.46
r_{13} = 0.41	r_{13} = 0.83	r_{13} = 55
r_{31} = 0.04	r_{31} = 0.96	r_{31} = 0.01
r_{23} = 1.20	r_{23} = 0.405	r_{23} = 20
r_{32} = 0.15	r_{32} = 0.44	r_{32} = 0.015

			No M_3	M_3 = AN	M_3 = PMS	M_3 = VAc
0.5 M_1		$\bar{n}_1$	1.52	1.4148	1.4621	1.5190
	(0.1M_3)	$\bar{n}_2$	1.46	1.4272	1.3748	1.4579
0.5M_2		$\bar{n}_3$	-	1.0063	1.0603	1.0012
0.75M_1		$\bar{n}_1$	2.5600	2.0350	2.2474	2.5541
	(0.1M_3)	$\bar{n}_2$	1.1533	1.1459	1.1332	1.1529
0.25M_2		$\bar{n}_3$	-	1.0049	1.0741	1.0010
0.25M_1		$\bar{n}_1$	1.1733	1.1483	1.1600	1.1731
	(0.1M_3)	$\bar{n}_2$	2.38	2.1965	1.9489	2.3674
0.75M_2		$\bar{n}_3$	-	1.0089	1.0509	1.0013
0.5M_1		$\bar{n}_1$	1.52	1.4615	1.4893	1.5195
	(0.05M_3)	$\bar{n}_2$	1.46	1.4430	1.4130	1.4589
0.5M_2		$\bar{n}_3$	-	1.0032	1.0302	1.0006
0.75M_1		$\bar{n}_1$	2.56	2.2444	2.3863	2.5571
	(0.05M_3)	$\bar{n}_2$	1.1533	1.1495	1.1425	1.1530
0.25M_2		$\bar{n}_3$	-	1.0024	1.0371	1.0005

Average sequence lengths of M_1, M_2, and M_3, $\bar{n}_1$, $\bar{n}_2$, and $\bar{n}_3$, respectively, were determined by a computer program [2] and are given in Table 1.

It is seen that, at least for an equimolar mixture of styrene and methyl methacrylate, the addition of acrylonitrile, a strongly electron-withdrawing monomer, leads to the sharpest reduction in $\bar{n}_1$, the average sequence length of styrene units, from 1.52 to 1.4148.

TABLE 2. Effect of Vinylidene Chloride (M_3) on Sequence Distribution in Terpolymers

r_{12} = 0.53
r_{21} = 0.46
r_{13} = 2
r_{31} = 0.14
r_{23} = 2.53
r_{32} = 0.24

				M_3 = VCl_2
$0.5M_1$		$\bar{n}_1$	1.52	1.4943
	($0.1M_3$)	$\bar{n}_2$	1.46	1.4439
$0.5M_2$		$\bar{n}_3$	-	1.0177

p-Methylstyrene is intermediate in effectiveness, and vinyl actetate is least effective in reducing $\bar{n}_1$. p-Methylstyrene is an electron-rich monomer. Vinyl acetate probably has such a small effect on $\bar{n}_1$ because of its low reactivity with a growing styrene radical.

As might be expected, p-methylstyrene is more effective than AN in reducing $\bar{n}_2$, the average sequence length of MMA units. Again, VAc is poorly effective because of its low reactivity with MMA radicals.

As would be expected, $\bar{n}_3$, the average sequence length of M_3, is almost exactly 1 in all cases, indicating isolated M_3 units in all terpolymers. Still, $\bar{n}_3$ for p-methylstyrene is largest–1.0603, indicating highest reactivity with its own radical under sparse conditions.

A similar study was made at 0.75 M_1 and 0.25 M_2, but with the same level of M_3–0.1 mol as above. The same trends noted above were observed for $\bar{n}_1$, $\bar{n}_2$, and $\bar{n}_3$, albeit starting from a higher base–2.56 for $\bar{n}_1$ in an M_1/M_2 mixture and 1.1533 for $\bar{n}_2$.

Somewhat surprisingly, the same trends were observed at $0.25M_1$, $0.75M_2$, and $0.1M_3$. The strong alternating tendency of acrylonitrile with styrene or methyl methacrylate dominates sequence distribution, even at relatively high levels of MMA.

Noting the trends in sequence distribution at moderate levels of M_3 in M_1/M_2 copolymers, it was considered desirable to examine a lower level of M_3–0.05 mol. Similar trends as above were noted at 0.5/0.5 and 0.75/0.25 M_1/M_2; however, $\bar{n}_1$, $\bar{n}_2$, and $\bar{n}_3$ were considerably higher than at 0.1 mol M_3.

As expected, $\bar{n}_1$ was highest at 0.75 M_1, lower at $0.5M_1$, and least at 0.25 M_1. The trend for $\bar{n}_2$ was the reverse.

Finally, vinylidene chloride was examined as M_3 (0.1 mol) at M_1/M_2 = 0.5/0.5 (Table 2). Vinylidene chloride is known as almost unique in bridging the low reactivity of unconjugated and the high reactivity of conjugated monomers. It behaved as expected—its effectiveness in reducing $\bar{n}_1$ and $\bar{n}_2$ was greater than that of vinyl acetate, but less than that of acrylonitrile or p-methylstyrene.

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