Antepenultimate Reactivity Ratios
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NOTE

Antepenultimate Reactivity Ratios

It has been proposed that in copolymerizations exhibiting antepenultimate units effects [1], all sequences are reversible. This proposition is based on the principle [2] that a reaction will take that course which minimizes the production of entropy. Thus, in copolymerization the equivalence of reversed sequences would minimize a potentially important source of disorder.

To inspect this proposition a sequence is chosen "at random" and equated in occurrence to its mirror image:

$$P\{AABABBAA\} = P\{AABBABAA\} \tag{1}$$

It follows that

$$P\{AAB\}P_{aaba}\,P_{abab}\,P_{babb}\,P_{abba}\,P_{bbaa}$$

$$= P\{AAB\}P_{aabb}\,P_{abba}\,P_{bbab}\,P_{baba}\,P_{abaa} \tag{2}$$

$$P_{aaba}\,P_{abab}\,P_{babb}\,P_{abba}\,P_{bbaa} = P_{aabb}\,P_{abba}\,P_{bbab}\,P_{baba}\,P_{abaa} \tag{3}$$

Expressed as reactivity ratios we have

$$\left\{\frac{r_{aab}\,(A/B)}{1 + r_{aab}\,(A/B)}\right\} \left\{\frac{1}{1 + r_{aba}\,(A/B)}\right\} \left\{\frac{1}{1 + r_{bab}\,(A/B)}\right\} \left\{\frac{r_{bba}\,(A/B)}{1 + r_{bba}\,(A/B)}\right\}$$

$$= \left\{\frac{1}{1 + r_{aab}\,(A/B)}\right\} \left\{\frac{1}{1 + r_{bba}\,(A/B)}\right\} \left\{\frac{r_{bab}\,(A/B)}{1 + r_{bab}\,(A/B)}\right\} \left\{\frac{r_{aba}\,(A/B)}{1 + r_{aba}\,(A/B)}\right\} \tag{4}$$

[The practice is followed here of specifying reactivity ratios by letters indicating only the terminal sequence of the radical (reactive) chain. It is understood that unshown monomer A is compared in reactivity with unshown monomer B.]

Reducing we obtain

$$r_{aab} \, r_{bba} = r_{bab} \, r_{aba} \tag{5}$$

This key equation, expressed as it is in reactivity ratios, gives us a means of testing the equivalence of occurrence of reversed sequences in copolymer chains exhibiting antepenultimate unit effects, and, more important, the applicability of the Ham simplified antepenultimate copolymer equations.

Fortunately, two very important papers are being published by Pichot et al. [3] and Guillot et al. [4]. These papers offer for the first time experimental techniques applying Ham's simplified antepenultimate copolymer composition equations to the estimation of antepenultimate reactivity ratios. (The practice of estimating reactivity ratios with a composition equation which assumes sequence reversibility and then utilizing these reactivity ratios in another equation to test sequence reversibility will be questioned. It should be pointed out that a limiting procedure is used in estimating the reactivity ratios. It is regarded as highly unlikely to obtain agreement with Eq. 5 and not to have the antepenultimate equation apply. Of course, analyses of copolymer microstructure would give an independent check on the reactivity ratios.) Thus, in the system vinyl chloride(C)-vinyl acetate(Ac),

$$r_{AcCAc} = r_{CCAc} = r_{Ac} = 0.29 \qquad r_{CCC} = 1.67$$

$$r_{CAcC} = 2.20 \qquad r_{AcCC} = 4.60$$

$$r_{AcAcC} = 2.0$$

Substituting in Eq. (5) we have

$$r_{CCAc} \, r_{AcAcC} = r_{AcCAc} \, r_{CAcC}$$

$$0.29 \times 2.0 \cong 0.29 \times 2.20 \tag{6}$$

In the system vinylidene chloride(V)-vinyl acetate(Ac),

$$r_{Ac} = 0.07 \qquad r_{VVV} = 5.30 \qquad r_{AcVV} = 11.5$$

$$r_{AcAcV} = 8.0 \qquad r_{VAcV} = 6.0$$

Substitution in Eq. (5),

$$r_{VVAc}\ r_{AcAcV}\ =\ r_{AcVAc}\ r_{VAcV}$$

$$0.07 \times 8.0\ \cong\ 0.07 \times 6.0 \tag{7}$$

However, in the system vinyl chloride(C)-styrene(S),

$$r_{SSS}\ =\ 3.0 \qquad r_{CSS}\ =\ 20.00$$

$$r_{SCS}\ =\ 18.5 \qquad r_{CCS}\ =\ 2.7$$

$$r_C\ =\ 0.06$$

Substituting in Eq. (5),

$$r_{CCS}\ r_{SSC}\ =\ r_{SCS}\ r_{CSC}$$

$$2.7 \times 0.06 \cong 18.5 \times 0.06 \tag{8}$$

The reason for the lack of agreement in this instance is not known now. However, the sevenfold difference in r_{SCS} and r_{CCS} seems rather large for an antepenultimate effect.

The relatively good agreement in two of the three systems gives encouragement to the hypothesis of equivalence of occurrence of reversed sequences in copolymerizations exhibiting antepenultimate effects. Furthermore, the usefulness of Ham's simplified antepenultimate equations in estimation of reactivity ratios is confirmed.

These findings suggest that polymer chemists are on the threshold of a breakthrough in the understanding of neighboring unit effects not unlike that encountered 24 years ago with the confirmation of the usefulness of the Lewis-Mayo copolymer composition equation.

REFERENCES

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