Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ham, George E.(1975) 'Role of Triad Concentration in Glass Transition Temperatures of Copolymers', Journal of Macromolecular Science, Part A, 9: 3, 461 — 467
To link to this Article: DOI: 10.1080/00222337508065868
URL: http://dx.doi.org/10.1080/00222337508065868

J. MACROMOL. SCI.—CHEM., A9(3), pp. 461-467 (1975)

Role of Triad Concentration in Glass Transition Temperatures of Copolymers

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ABSTRACT

Equations are presented weighing the contribution of triad sequences to copolymer T_g's. Improved correlation is shown for acrylonitrile-methyl methacrylate copolymer and suggested for certain other systems.
Certain simplified correlations between T_g of random copolymers and T_{aa}, T_{bb}, and T_{ab} are presented.

The work of several scientists [1, 2] has established the desirability of assessing the individual contributions of the various diad sequences to the glass transition temperature of copolymers. In most instances agreement is substantially improved over that obtained with equations assuming simple additivity of the contribution of the individual monomer units.

The treatment of binary copolymers with regard to the contribution of various triad sequences to the glass transition temperature does not appear to have received serious consideration. Nevertheless, there are several binary copolymer systems whose glass transition behavior cannot be adequately explained by considering diads alone. This paper reports encouraging results on improving correlation between T_g behavior and binary copolymer composition by assessing the contributions of various triad sequences.

Figure 1 includes data on the T_g's of acrylonitrile-methyl methacrylate copolymers of various compositions as assembled by Barton [1] based on data from Beevers and White [3]. The heavy line indicates the theoretical curve obtained by Barton assuming the contribution of A-B sequences to T_g of copolymers. The curve is calculated assuming $T_{aa} = 108°$, $T_{bb} = 105°$, and $T_{ab} = 70°C$. Agreement is only modest, as can be seen. Deviations are particularly noticeable in the range of 50 to 80 mole % acrylonitrile.

Because of the mathematical complexities involved, the problem was first approached simplistically by assuming random copolymer distribution ($r_1r_2 = 1$, rather than $r_1r_2 = 0.18$ as observed experimentally).

Barton's equation was expanded to the form

$$T_g = n'_{aaa}T_{aaa} + n'_{bbb}T_{bbb} + n'_{aab}T_{aab} + n'_{baa}T_{baa} + n'_{abb}T_{abb} + n'_{bba}T_{bba} + n'_{aba}T_{aba} + n'_{bab}T_{bab} \qquad (1)$$

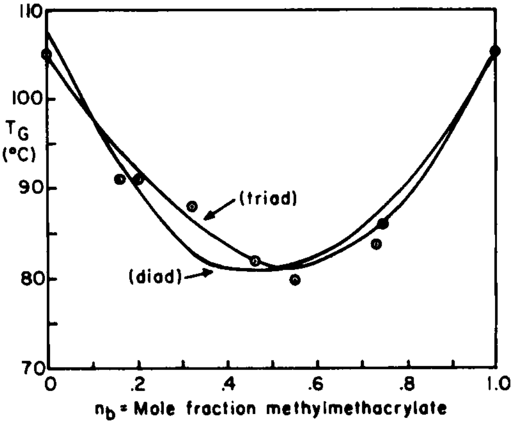

FIG. 1. Dependence of T_g on composition for acrylonitrile/methyl methacrylate copolymers. (⊙) Experimental data of Beevers and White [3]. Theory: (——) diad, (—) triad.

The question was simplified somewhat by assuming that sequence inversions would not affect T_g and that —ABA— and —BAB— sequences were equivalent in their contribution to T_g: e.g., T_{ab}.

$$T_g = n'_{aaa}T_{aaa} + n'_{bbb}T_{bbb} + (n'_{aab} + n'_{baa})T_{aab} + (n'_{abb} + n'_{bba})T_{abb} + (n'_{aba} + n'_{bab})T_{ab} \quad (2)$$

The following assumptions were made:

1. T_{aaa} and T_{bbb}, the glass transition temperatures of homo-triads of acrylonitrile and methyl methacrylate, were regarded as distinctive in contribution from other triads and taken as equal to the T_g's of homopolymers, 105 and 105°C.
2. T_{aab} and T_{baa} were assumed to be equal and not much lower in value than T_{aaa} because of interchain hydrogen bonding and dipole interaction.
3. T_{abb}, T_{bba}, T_{aba}, and T_{bab} were all taken to be equal in effect on T_g of copolymers. (Two methacrylate units together were not regarded as sufficient to increase T_g over that contributed by isolated units.)

The concentrations of all of the triads were calculated for copolymers in the sensitive glass transition temperature region as well as elsewhere, assuming random placement of units.

Good agreement was obtained for

$T_{aaa} = 105°C$

$T_{bbb} = 105°C$

$T_{aab} = T_{baa} = 89°C$

$T_{abb} = T_{bba} = 64°C$

$T_{aba} = T_{bab} = 64°C$

For example, copolymer T_g's of 85.5, 80, and 81°C. were obtained at $n_b = 1/3$, 1/2, and 2/3, respectively.

Of course, acrylonitrile-methyl methacrylate copolymers are not random ($r_1 r_2 = 0.18$), and, in fact, have a substantial alternating tendency. Accordingly, the following techniques were employed to calculate triad occurrence probabilities and to estimate more precisely the contribution of the various triads. Nevertheless, the above approach is recommended for the numerous copolymer systems wherein $r_1 r_2 = 1$ (of course, r_1 and r_2 can have any values as long as $r_1 r_2 = 1$).

Copolymer composition is related to monomer ratio by the following well-known equation:

$$\frac{a}{b} = \frac{r_1 x + 1}{r_2/x + 1} \tag{3}$$

The mole fraction of A and B in copolymer, n_a and n_b, respectively, are

$$n_a = \frac{a}{a+b} = \frac{r_1 x + 1}{r_1 x + r_2/x + 2} \tag{4}$$

$$n_b = \frac{b}{a+b} = \frac{r_2/x + 1}{r_1 x + r_2/x + 2} \tag{5}$$

The mole fraction of A diads, n_{aa}, is

$$n_{aa} = n_a P_{aa} = \frac{r_1 x + 1}{r_1 x + r_2/x + 2} \; \frac{r_1 x}{r_1 x + 1} = \frac{r_1 x}{r_1 x + r_2/x + 2} \tag{6}$$

The mole fraction of A triads, n_{aaa}, is

$$n_{aaa} = n_a P_{aa}^2 = \frac{r_1 x}{r_1 x + r_2/x + 2} \; \frac{r_1 x}{r_1 x + 1} \tag{7}$$

$$n_{aab} = n_a P_{aa} P_{ab} = \frac{r_1 x}{r_1 x + r_2/x + 2} \; \frac{1}{r_1 x + 1} \tag{8}$$

$$n_{ab} = n_a P_{ab} = \frac{r_1 x + 1}{r_1 x + r_2/x + 2} \; \frac{1}{r_1 x + 1} = \frac{1}{r_1 x + r_2/x + 2} \tag{9}$$

$$n_{aba} = n_a P_{ab} P_{ba} = \frac{1}{r_1 x + r_2/x + 2} \; \frac{1}{r_2/x + 1} \tag{10}$$

The mole fraction of B diads, n_{bb}, is

$$n_{bb} = n_b P_{bb} = \frac{r_2/x + 1}{r_1 x + r_2/x + 2} \; \frac{r_2/x}{r_2/x + 1} = \frac{r_2/x}{r_1 x + r_2/x + 2} \tag{11}$$

The mole fraction of B triads, n_{bbb}, is

$$n_{bbb} = n_b P_{bb}^2 = \frac{r_2/x}{r_1 x + r_2/x + 2} \; \frac{r_2/x}{r_2/x + 1} \tag{12}$$

$$n_{bba} = n_b P_{bb} P_{ba} = \frac{r_2/x}{(r_1 x + r_2/x + 2)\,(r_2/x + 1)} \tag{13}$$

Because of the equivalence of reversed sequences,

$$n_{ab} = n_{ba} \tag{14}$$

$$n_{aab} = n_{baa} \tag{15}$$

$$n_{abb} = n_{bba} \tag{16}$$

Triad concentrations of all possible types were calculated by the above techniques throughout the range, from 100 mole % acrylonitrile to 100 mole % methyl methacrylate. It was found that a good fit of the experimental curve relating copolymer T_g's to composition in the acrylonitrile-methyl methacrylate system was obtained with the following assignment of triad T_g values on substitution in Eq. (1) (see Fig. 1):

$T_{aaa} = 105°C$

$T_{bbb} = 105°C$

$T_{aab} = T_{baa} = 89°C$

$T_{abb} = T_{bba} = 75°C$

$T_{aba} = T_{bab} = 75°C$

The importance of taking precise sequence distribution into account is dramatically shown in this instance. The values of T_{abb}, T_{bba}, T_{aba}, and T_{bab} are all increased by 11°C over those estimated from the assumption of randomness.

It seems likely that similar analyses of the systems styrene-methyl methacrylate, vinylidene chloride-methyl acrylate, vinylidene chloride-ethyl acrylate, and styrene-butyl acrylate would lead to improved agreement over that obtained by merely weighing the effects of T_{aa}, T_{bb}, and T_{ab}.

Finally, for the numerous systems which obey the simpler Barton equation (weighing T_{aa}, T_{bb}, and T_{ab} alone), some further observations are in order.

1. Where T_{ab} is less than T_{aa} and T_{bb}, the copolymer T_g minimum for all copolymers (regardless of r_1r_2 values) must lie at equimolar copolymer (50 mole %/50 mole %).

2. Where T_{ab} is greater than T_{aa} and T_{bb}, the copolymer T_g maximum for all copolymers (regardless of r_1r_2 values) must lie at equimolar copolymer (50 mole %/50 mole %).

3. For random copolymers exhibiting maxima (and minima), the maximum (and minimum) T_g is related to T_{aa}, T_{bb}, and T_{ab} as follows:

$$T_{g_{\substack{max\\(min)}}} = \tfrac{1}{4}T_{aa} + \tfrac{1}{4}T_{bb} + \tfrac{1}{2}T_{ab} \tag{17}$$

In the system vinylidene chloride-methyl acrylate the experimental value for the maximum T_g of 315°K compares with a predicted value of 321°K. For the system vinylidene chloride-ethyl acrylate the experimental value of 300°K compares with a predicted value of 304°K.

4. There is no a priori requirement for alternation to generate a T_g maximum. However, many alternating systems generate T_g maxima.

5. For random copolymers exhibiting positive and negative deviations the T_g at equimolar copolymer is

$$T_{g(1/1)} = \tfrac{1}{4}T_{aa} + \tfrac{1}{4}T_{bb} + \tfrac{1}{2}T_{ab} \qquad (18)$$

In the system vinyl chloride-vinyl acetate the experimental (interpolated) value for $T_{g(1/1)}$ is 44°C compared with a predicted value of 42°C.

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Received for publication January 16, 1975