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George E. Ham[a]
[a] G. E. Ham Associates, New York

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Role of Triad Concentration in Glass Transition Temperatures of Copolymers. II

GEORGE E. HAM

G. E. Ham Associates
284 Pine Road
Briarcliff Manor, New York 10510

ABSTRACT

Improved correlation between glass transition temperatures and copolymer composition was obtained in styrene-methyl methacrylate copolymers by assessing contributions of triad rather than diad concentrations. Contributions of ABA and BAB triads were found to be significantly different. Glass transition temperature minima as a function of copolymer composition were found to be related to the solubility parameters (and cohesive energy densities) of the parent homopolymers.

In the first paper in this series [1] there were presented equations for weighing the contribution of triad sequences to copolymer T_g's. Improved correlation was obtained for acrylonitrile-methyl methacrylate copolymers and suggested for certain other systems.

This paper illustrates the application of the technique to styrene-methyl methacrylate copolymers. Correlation is greatly improved over that obtained by Barton [2] where the contribution merely of diads was assessed.

T_g CORRELATIONS BASED ON ASSUMPTION OF RANDOM DISTRIBUTION OF SEQUENCES

In this copolymer system there is some tendency toward alternation ($r_1 = .48$, $r_2 = .46$). However, the great simplification possible in obtaining sequence distributions at various compositions assuming random distribution made it desirable to make preliminary T_g correlations based on that hypothesis.

As shown in Fig. 1 and confirmed in the original Beevers article [3], a minimum in T_g occurs at about 67 mole % styrene. As shown in Ref. 1, a minimum T_g where T_{ab} is less than T_{aa} and T_{bb} must occur at 50 mole % - 50 mole % copolymer. It follows that diad alone cannot explain the observed deviation.

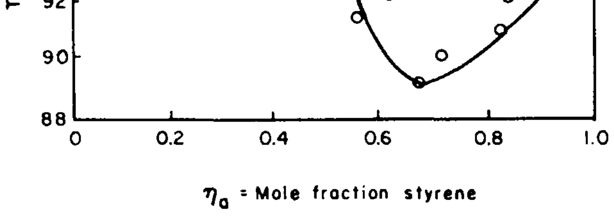


FIG. 1. Dependence of T_g on composition for styrene-methyl methacrylate copolymers. (○) Data from Ref. 3. (——) Theory, $T_{aab} = T_{baa} = T_{aba} = 83°C$; $T_{aaa} = 96°C$; $T_{bab} = T_{abb} = T_{bba} = T_{bbb} = 100°C$.

Using Eq. (1) from Ref. 1:

$$T_g = n_{aaa}{}'T_{aaa} + n_{bbb}{}'T_{bbb} + n_{aab}{}'T_{aab} + n_{baa}{}'T_{baa} +$$

$$n_{abb}{}'T_{abb} + n_{bba}{}'T_{bba} + n_{aba}{}'T_{aba} + n_{bab}{}'T_{bab}$$

it was ascertained that triad sequences containing two methyl methacrylate units and one styrene unit (ABB, BBA, and BAB) had to possess a T_g of the same order of magnitude as that of polymethyl methacrylate, otherwise the persistence of high T_g's to about 50 mole % styrene could not be explained.

Furthermore, the sharp drop in T_g's in the region of 50 to 80 mole % styrene required a low T_g contribution by triad sequences containing one methyl methacrylate and two styrene units (AAB, BAA, and ABA).

The closest fit to the experimental T_g's was obtained by the assignment of $T_{bbb} = T_{bba} = T_{abb} = T_{bab} = 100°C$, $T_{aba} = T_{baa} = T_{aab} = 78°C$, and $T_{aaa} = 96°C$.

Within the limitations of the "random" assumption, the precision is believed to be within ±1°C. For example, if $T_{aba} = T_{baa} = T_{aab}$ is assumed to be 80°C, copolymer T_g's in the range of 50 to 80 mole % styrene are increased by almost 1°C—well beyond experimental error.

In addition, if T_{bba}, T_{abb}, and T_{bab} are taken as less than T_{bbb}, the T_g of polymethyl methacrylate (100°C), the estimated copolymer T_g's fall well below the experimental values in the range of 0 to 50 mole % styrene.

Particularly interesting was the finding that the contribution of ABA and BAB sequences had to be separately assessed. Next-to-nearest neighbor methyl methacrylate units reinforce one another ($T_{bab} = 100°C$) when separated by styrene. The converse does not occur. Next-to-nearest neighbor styrene units do not reinforce one another ($T_{aba} = 78°C$) when separated by methyl methacrylate. All attempts to treat these sequences as equivalent led to poor fits quite unlike the results obtained in Ref. 1 with acrylonitrile-methyl methacrylate copolymers.

T_g CORRELATIONS BASED ON SEQUENCE DISTRIBUTIONS CALCULATED FROM REACTIVITY RATIOS

Actual sequence distributions of triads were calculated from reactivity ratios employing Eqs. (3) to (16) from Ref. 1. Typical values are shown in Table 1.

The same general conclusions concerning T_g contributions of various triads resulted as for the "random" case above, although the actual values obtained for $T_{aab} = T_{baa} = T_{aba}$ equaled 83°C instead of 78°C (Fig. 1).

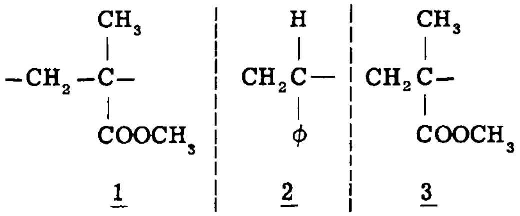
T_g CONTRIBUTIONS OF STYRENE (A)-METHYL METHACRYLATE (B) TRIADS

T_{aaa}	T_{aab}	T_{baa}	T_{aba}	T_{bab}	T_{abb}	T_{bba}	T_{bbb}
96	83	83	83	100	100	100	100

As in the "random" case, it was confirmed that ABA and BAB sequences give quite different contributions to the T_g of copolymers. This result could arise from dipole interaction or hydrogen bonding effects involving methyl methacrylate units at the 1 and 3 positions with appropriate groups in other chains.

TABLE 1. Sequence Distributions of Triads

n_a	n_{aaa}	n_{aab}	n_{baa}	n_{aba}	n_{bab}	n_{bba}	n_{abb}	n_{bbb}
1/3	.006	.039	.039	.12	.245	.16	.16	.221
1/2	.055	.113	.113	.233	.230	.107	.107	.0494
2/3	.209	.161	.161	.246	.124	.042	.042	.0075



$$-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}- \;\Big|\; CH_2\overset{\displaystyle H}{\underset{\displaystyle \phi}{C}}- \;\Big|\; CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle COOCH_3}{C}}-$$

The converse case involving styrene units at the 1 and 3 positions and methyl methacrylate at the 2 position does not appear to allow for as effective interaction with other chains.

It may be further speculated that π-bonding involving phenyl groups in polystyrene must occur—to the extent that it occurs—principally along a given chain, rather than involve phenyl groups of different chains to an important degree. The low contribution to T_g of copolymers by the sequences AAB, BAA, and ABA—relative to AAA—reinforce such a belief.

As pointed out above in the case of acrylonitrile-methyl methacrylate copolymers, $T_{aba} = T_{bab}$. Why this copolymer behavior is so different from styrene-methyl methacrylate is not known with certainty. That acrylonitrile units should be equivalent to methyl methacrylate units in ABA and BAB triads with regard to T_g contributions may arise from the accident that the smaller size of nitrile groups relative to carbomethoxy (and methyl) groups is just balanced by their greater polarity.

It is of interest to note that in the acrylonitrile-methyl methacrylate copolymers T_g is a minimum at 58 mole % methyl methacrylate compared with 58 mole % theoretical* and in the styrene-methyl methacrylate copolymers T_g is a minimum at approximately 1/3 mole fraction methyl methacrylate compared with 1/3 theoretical.†

The $T_{g(min)}$ in a copolymer system gives an indication of that composition where the associative effects of either component are

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*$T_{abb} = T_{bba} = T_{aba} = T_{bab} = 75°C$, well below the T_g contributions of other triads. The methyl methacrylate content of such triads is 58.3 mole % and must coincide with the T_g minimum for experimental acrylonitrile-methyl methacrylate copolymers.

†$T_{aab} = T_{baa} = T_{aba} = 83°C$, well below T_g contributions of other triads. The methyl methacrylate content of such triads is 1/3 mole fraction and must coincide with the T_g minimum for experimental styrene-methyl methacrylate copolymers.

just balanced by those of the other. Thus, this point occurs on the high methyl methacrylate side in acrylonitrile-methyl methacrylate copolymers and on the low methyl methacrylate side in styrene-methyl methacrylate copolymers.

It is proposed that a correlation exists between the cohesive energy density (and the solubility parameter, δ) of homopolymers A and B and the copolymer composition at $T_{g(min)}$ of A-B copolymers, designated $n_{(min)}$. This correlation is

$$n_{(min)} = a/b = \delta b/\delta a$$

Thus, substituting the reported [4] solubility parameters for polystyrene (9.3 ± 1.3) and polymethyl methacrylate (10.8 ± 1.2) in the above equation one obtains

$$n_{(min)} = 10.8/9.3 = 1.16$$

compared with 2.0 for the actual mole ratio at $T_{g(min)}$ in the system styrene-methyl methacrylate.

Similarly, substituting reported solubility parameters for polyacrylonitrile (12.8) and polymethyl methacrylate (10.8 ± 1.2), one obtains

$$n_{(min)} = 10.8/12.8 = 0.845$$

compared with 0.715 for the actual mole ratio at $T_{g(min)}$ in the system acrylonitrile-methyl methacrylate. There is some evidence that the solubility parameter for polyacrylonitrile may be higher than 12.8, which would lead to improved correlation.

Even better correlation is obtained if actual cohesion energy densities are used in place of solubility parameters in

$$n_{(min)} = a/b = e_b/e_a$$

For styrene-methyl methacrylate,

$$n_{(min)} = 117/86.5 = 1.35$$

compared with 2.0 for the actual mole ratio at $T_{g(min)}$.

For acrylonitrile-methyl methacrylate, substituting actual cohesive energy densities in

$$n_{(min)} = 117/164 = 0.714$$

compared with 0.715 for the actual mole ratio at $T_{g(min)}$.

The improved correlation observed between cohesive energy density ratios rather than solubility parameter ratios and $T_{g(min)}$ might be expected, since these systems are compatible copolymer mixtures rather than solvent polymer mixtures or homopolymer mixtures which are much more risky systems for predictions concerning mutual solubility.

Just how general is the indicated approach to assessing cohesive energy densities from the ratio of components at $T_{g(min)}$ could not be immediately assessed because of the sparcity of data about suitable systems. Most copolymer systems do not possess the T_g minima which are required if the equations given above are to be used.

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