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Sequence Distribution-Glass Transition Effects. II. Alkyl Methacrylate/Vinyl Chloride Copolymers

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Sequence Distribution-Glass Transition Effects. II. Alkyl Methacrylate/Vinyl Chloride Copolymers

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ABSTRACT

The glass transition temperatures of cyclized and uncyclized alkyl methacrylate/vinyl chloride copolymers have been measured and found to differ from values predicted using conventional glass transition prediction relationships. An additive relationship was developed that relates the sequence distribution of the copolymer to the polymer glass transition temperature. Using this relationship, good agreement between experimental and sequence distribution predicted glass transitions was found.

INTRODUCTION

A number of properties of copolymers and terpolymers have been shown to be influenced by the sequence distribution of the polymer. These properties not only include the polymer's NMR, UV, and IR spectra, but also such properties as thermal stability, oxidative stability, and enzymatic degradation [1]. In a previous paper [2]

we derived general equations for relating polymer sequence distributions to the property of glass transition temperature and verified these relationships experimentally using a series of butyl methacrylate/vinyl chloride copolymers.

This work [3] utilizes the general concept proposed in our first paper that large deviations in polymer glass transitions can be obtained by changing the steric and/or polar relationships of one monomer unit with its adjacent monomer units through varying the sequence distribution of the polymer. Sequence distribution-glass transition effects are reported for methyl methacrylate/vinyl chloride, cyclized methyl methacrylate/vinyl chloride, and cyclized butyl methacrylate/vinyl chloride polymers.

EXPERIMENTAL

Preparation of Polymers

The preparation of methyl methacrylate/vinyl chloride [4] (MMA/VCl) and butyl methacrylate/vinyl chloride (BMA/VCl) [2] copolymers was discussed in detail in previous papers. With one exception, all polymers were prepared in 2-butanone at 55°C from freshly distilled monomers which contained 0.4 wt% *t*-butyl peroxy pivalate as initiator. To provide a copolymer with higher molecular weight, BMA/VCl copolymer U-5 was prepared by a $K_2S_2O_8$ initiated emulsion system.

Conversions were kept below 10% in order to obtain uniform copolymers, and all polymers were isolated by pouring the polymerization mixture into a large excess of methanol. After several reprecipitations from 2-butanone or cyclohexanone into methanol, the polymers were dried in vacuo and copolymer compositions determined by C, H, and Cl analysis. Specific information on the preparation of MMA/VCl copolymers is given in Table 1, and the details of preparation of BMA/VCl copolymers previously presented [2] are repeated in Table 2.

Glass Transition Measurements

Glass transition temperatures of the polymers were measured using a Perkin Elmer DSC-1B Differential Scanning Calorimeter. An initial scan was made to produce a uniform thermal history in all polymers. The glass transition temperatures reported are the average of several additional scans at 10°C/min and were reproducible to $\pm 0.6^\circ\text{C}$.

TABLE 1. MMA/VCl Copolymer Preparation

| Sample No. | MMA (mole %) | | Conversion (%) | $[\eta]$ (dl/g) |
|------------|------------------|---------|----------------|-----------------|
| | Feed | Polymer | | |
| A-1 | 0.0 ^a | 0.0 | 8.0 | 0.52 |
| A-2 | 0.5 | 5.8 | 6.5 | 0.33 |
| A-3 | 2.5 | 25.1 | 6.7 | 0.38 |
| A-4 | 5.0 | 37.2 | 10.2 | 0.36 |
| A-5 | 6.0 | 44.6 | 6.4 | 0.36 |
| A-6 | 10.0 | 61.4 | 0.5 | 0.37 |
| A-7 | 15.0 | 69.8 | 2.0 | 0.34 |
| A-8 | 20.0 | 76.3 | 1.0 | 0.33 |
| A-9 | 100.0 | 100.0 | 29.0 | 0.42 |

^aPVC.

TABLE 2. BMA/VCl Copolymer Preparation

| Sample No. | BMA (mole %) | | Conversion (%) | $[\eta]$ (dl/g) |
|------------|------------------|---------|----------------|-----------------|
| | Feed | Polymer | | |
| U-1 | 0.0 ^a | 0.0 | 8.0 | 0.52 |
| U-2 | 1.5 | 13.0 | 9.9 | 0.36 |
| U-3 | 3.0 | 28.3 | 7.5 | 0.36 |
| U-4 | 6.0 | 45.7 | 8.0 | 0.34 |
| U-5 | 6.0 | 50.1 | 1.5 | 0.50 |
| U-6 | 9.0 | 60.1 | 1.5 | 0.33 |
| U-7 | 16.5 | 72.8 | 6.5 | 0.35 |
| U-8 | 100.0 | 100.0 | 3.5 | 0.59 |

^aPVC.

The literature often reports several different T_g 's for the same homopolymer. The reason for this is frequently ascribed to the T_g 's being obtained via different techniques. To add more validity to our DSC T_g measurements, we obtained T_g measurements on selected polymer samples using a DuPont Model 900 Differential Thermal Analyzer and both the expansion and penetration mode of a DuPont Model 941 Thermal Mechanical Analyzer. All three techniques provided T_g measurements with $\pm 1^\circ\text{C}$ of those obtained using the Perkin Elmer DSC-1B.

Intrinsic Viscosities

Intrinsic viscosities of polybutyl methacrylate, polymethyl methacrylate, and all copolymers were determined in 2-butanone at 25°C in a Ubbelohde dilution viscometer. Polyvinyl chloride's intrinsic viscosity was determined under the same conditions in cyclohexanone.

Cyclization Reactions

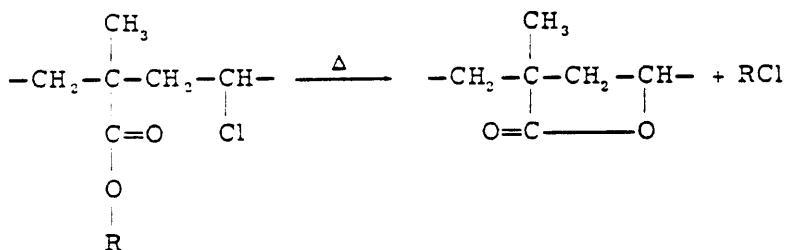
The cyclization of MMA/VCl and BMA/VCl copolymers was carried out by heating the copolymer to 200°C for 2 hr in glass tubes under high vacuum to insure the removal of all alkyl chloride. This time-temperature combination was found to be more than sufficient to promote cyclization to the maximum statistical extent possible [5].

THEORETICAL CONSIDERATIONS

Cyclization Reaction Predictions

Zutty and Welch [6] found that heating alkyl methacrylate/vinyl chloride copolymers to 150 to 200°C yields alkyl chloride (99.3% pure) and polymers containing γ -butyrolactone groups in their backbones.

Johnston and Harwood quantitatively studied this reaction in methyl methacrylate/vinyl halide copolymers [5] and terpolymers [7]. Their results indicated that the fraction of uncyclized alkyl methacrylate groups in a copolymer can accurately be predicted using Eq. (1) where $F_u(B)$ is the fraction



of uncyclized B units. A and B are the copolymer composition in mole per cent, and R is the run number.

$$F_u(B) = [\cosh (R^2/4AB)^{1/2} - (A/B)^{1/2} \sinh (R^2/4AB)^{1/2}]^2 \quad (1)$$

The run number [8] is defined as the average number of monomer sequences (runs) which occur per 100 monomer units in a copolymer and may be calculated from copolymer reactivity ratios (r_A, r_B) and monomer feeds (AF, BF) using Eq. (2).

$$R = \left[\frac{200}{2 + r_A \frac{AF}{BF} + r_B \frac{BF}{AF}} \right] \quad (2)$$

Reactivity ratios of 11.2/0.044 for MMA/VCl [5] and 13.5/0.05 for BMA/VCl [2] were used for all predictions in this work.

Copolymer T_g Predictions

The glass transition temperatures of copolymers are usually predicted by additive relations such as the Fox equation [9]:

$$\left(\frac{1}{T_{gP}} \right) = \left(\frac{W_A}{T_{gA}} \right) + \left(\frac{W_B}{T_{gB}} \right) \quad (3)$$

where T_{gP} is the T_g of a copolymer containing weight fraction W_A and W_B of the two monomer units A and B for which the homopolymers have glass transitions of T_{gA} and T_{gB} . The Fox and

other similar relationships do not take into consideration the effect of adjacent dissimilar monomer units on steric and energetic relations in the copolymer backbone and assume that the freedom of rotation and free volume contributed to a copolymer by a given monomer will be the same as it contributes to the homopolymer. As pointed out, this Fox type of relationship does not hold for all copolymers [2].

To accurately predict the glass transition temperature of many copolymers, it is necessary to take into consideration the sequence distribution of the polymer. Homopolymer T_g values hold for AA dyads in AB copolymers because the A units experience the same interactions as in A homopolymers. The formation of AB dyads results in new interactions and in many cases changes the T_g contribution of the A unit. Therefore, to obtain more accurate T_g predictions it is necessary to assign AB dyads and other sequence distributions their own T_g values.

The probabilities of having various linkages (P_{AB} , P_{AA}) may be calculated by computing the average run number (R) for a given copolymer composition (A,B) and using Eqs. (4) and (5)

$$P_{AB} = R/2A \quad (4)$$

$$P_{AA} = 1.0 - P_{AB} \quad (5)$$

Using these probabilities, an equation may be written to predict the copolymer glass transitions which takes into consideration the copolymer sequence distribution and AA, BB, and AB glass transition temperatures:

$$\left[\frac{1}{T_{gP}} \right] = \left[\frac{W_A P_{AA}}{T_{gAA}} + \frac{W_A P_{AB} + W_B P_{BA}}{T_{gAB}} + \frac{W_B P_{BB}}{T_{gBB}} \right] \quad (6)$$

T_{gP} is the T_g of a copolymer containing weight fraction W_A and W_B of two monomer units A and B which have the probabilities P_{AA} , P_{AB} , P_{BA} , and P_{BB} of having various linkages contributing T_g 's of T_{gAA} , $T_{gAB} = T_{gBA}$, and T_{gBB} to the copolymer.

For the majority of cases we have found that using a T_{gAB} value for

AB dyads is sufficient to predict sequence distribution- T_g effects in a series of copolymers. This assumes that one unlike neighbor will depress the copolymer T_g approximately as much as having a monomer unit between two unlike groups. Assigning a value of T_{gAB} to AB units therefore does not take into consideration such triads as BA*B, BA*A, or AA*B where A* may contribute different T_g 's to the copolymer. This assumption is not valid in all copolymer systems, and we have found some copolymers that exhibit strong triad- T_g effects. For these cases or in the case of terpolymers, Eq. (6) was expanded to meet the appropriate situation.

Cyclized Copolymer T_g Predictions

Cyclization of alkyl methacrylate/vinyl chloride copolymers usually results in the formation of an alkyl methacrylate/vinyl chloride/ γ -butyrolactone terpolymer with each of the three units having different T_g contributions. The exception to this would be copolymers containing such a small amount of monomer A that cyclization would utilize all of the A monomer and yield a γ -butyrolactone/B monomer copolymer. To predict sequence distribution- T_g effects in cyclized copolymers, the extent of cyclization as predicted by Eq. (1) as well as the T_g of the various sequence distributions in the terpolymer must be taken into consideration.

Cyclization can also change the steric/polar environment of the uncyclized monomer units. A M* (MMA) unit of a M/V (MMA/VCl) copolymer centered in a MVM*VM pentad may after cyclization be in a $\underline{M}V\underline{M}^*V\underline{M}$ pentad where $\underline{M}V$ is the γ -butyrolactone unit. The effect of having two rigid $\underline{M}V$ neighbors rather than two V neighbors may be to change the M* T_g contribution to the polymer. This same type of effect may be found in MM*VM tetrads where after cyclization there is approximately a 50% chance $\underline{M}M^*V\underline{M}$ may be formed and M* may have a different T_g than it would have in MM*M, in VM*V, or in $\underline{M}V\underline{M}^*V\underline{M}$. To take these factors into consideration we have made the assumption that the T_g contribution of M* in $\underline{M}M^*V\underline{M}$ would be equal to that of M* in MM*M and that M* in $\underline{M}V\underline{M}^*V\underline{M}$ would have a T_g equal to M* in VM*V. The T_g of M* in VM*V or of BMA in VCl-BMA-VCl was

calculated using Eq. (3), $T_{gP} = T_{gAB}$, $T_{gA} = T_{gPVC}$, W_A and $W_B =$ weight fraction of A and B in an AB dyad, and $T_{gB} = T_g$ of an isolated alkyl methacrylate group. Based on these approximations, Eq. (7) was derived:

$$\frac{1}{T_{gCP}} \cong \frac{AWCP}{T_{gAA}} + \frac{BWCP}{T_{gBB}} + \frac{IBWCP}{T_{gIB}} + \frac{CWCP}{T_{gCAB}} \quad (7)$$

T_{gCP} is the T_g of the cyclized polymer, AWCP is the weight fraction of A units left in the cyclized polymer, BWCP is the weight fraction of B units in the cyclized polymer that have not been reacted or isolated, IBWCP is the weight fraction of isolated B units not cyclized, CWCP is the weight fraction of γ -butyrolactone units in the cyclized polymer, $T_{gAA} = T_g$ of PVC, $T_{gBB} = T_g$ of alkyl methacrylate homopolymer, $T_{gIB} = T_g$ of an isolated alkyl methacrylate group, and T_{gCAB} is the T_g of a cyclized AB dyad or the T_g of the γ -butyrolactone group. The various weight fractions involved in Eq. (7) are calculated from Eq. (1) and the appropriate sequence distribution predictions. These calculations and all other calculations in this work are carried out using computer programs written for this purpose and an IBM 1130 computer.

RESULTS AND DISCUSSION

Sequence Distribution, T_g Values

T_{gAB} values have been determined by several techniques. One technique is to prepare an AB copolymer with a low B content. This copolymer would have most B units centered in ABA triads and a very low or negligible probability of BB. An experimental T_g (T_{gP}) would then be obtained and Eq. (6) used to solve for T_{gAB} . A second technique is to use the T_g 's of a series of copolymers, Eq. (6), and a computerized multiple regression analysis program to solve for T_{gAB} .

Using both of these techniques a $T_{g_{AB}}$ value for BMA-VCl of 12.6°C and a $T_{g_{AB}}$ value for MMA-VCl of 49.6°C were found. These values are lower than those expected from an additive relationship such as Eq. (3).

The $T_{g_{AB}}$ values for MMA/VCl and BMA/VCl are used, as discussed in the previous section, to calculate $T_{g_{IB}}$. $T_{g_{IB}}$ is used in Eq. (7) and is the T_g of an isolated alkyl methacrylate group. $T_{g_{IB}}$ for MMA is 34.6°C and $T_{g_{IB}}$ for BMA is -8.7°C.

To find the T_g of the γ -butyrolactone unit, we used much the same techniques. Copolymer A-2 contains 5.8 mole % MMA and would on cyclization form a γ -butyrolactone/VCl copolymer. Knowing the T_g of the cyclized polymer, the T_g of PVC, and the polymer composition, an equation similar to Eq. (3) was solved to yield $T_{g_{CAB}}$. $T_{g_{CAB}}$ is 148.9°C and is the T_g of a cyclized MMA-VCl dyad or the T_g of the γ -butyrolactone unit. Multiple regression analysis of the T_g data of all the cyclized MMA/VCl copolymers yields much the same value. These values and the other sequence distribution- T_g values are listed in Table 3.

Copolymer Glass Transitions

Table 4 compares experimental T_g 's of MMA/VCl copolymers with those predicted using Eq. (6), the sequence distribution T_g relationship, and the appropriate values from Table 3. Table 5 repeats the T_g data shown in our previous work for BMA/VCl copolymers [2]. For all copolymers better agreement between experimental and predicted T_g 's was found using the sequence distribution-glass transition relationship. The Fox relationship, Eq. (3), predicted T_g 's up to 14°C higher for the BMA/VCl copolymers and up to 24°C higher for the MMA/VCl copolymers than those experimentally found.

TABLE 3. Sequence Distribution, T_g Values

| Unit | Symbol | T_g ($^{\circ}\text{C}$) |
|--|---------------|------------------------------|
| MMA-MMA | $T_{g_{BB}}$ | 105.0 |
| BMA-BMA | $T_{g_{BB}}$ | 20.0 |
| VCl-VCl | $T_{g_{AA}}$ | 77.0 |
| VCl-MMA | $T_{g_{AB}}$ | 49.6 |
| VCl-BMA | $T_{g_{AB}}$ | 12.6 |
| $\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}-\text{CH}_2-\text{CH}- \\ \quad \quad \\ \text{O}=\text{C} \quad \quad \text{O} \end{array}$ | $T_{g_{CAB}}$ | 148.9 |
| $\text{M}-\text{V}-\text{MMA}-\text{V}-\text{M}$ | $T_{g_{IB}}$ | 34.6 |
| $\text{B}-\text{V}-\text{BMA}-\text{V}-\text{B}$ | $T_{g_{IB}}$ | -8.7 |

Cyclized Copolymer Glass Transitions

Table 6 compares the experimental T_g 's of the cyclized MMA/VCl copolymers with those predicted using Eq. (7) and the appropriate values from Table 3. The agreement between predicted and experimental values is good considering the approximations involved in Eq. (7).

We obtained a value of $T_{g_{CAB}}$ or a T_g for the γ -butyrolactone unit of 148.9 $^{\circ}\text{C}$ in the study of the cyclized MMA/VCl copolymer system. As the same γ -butyrolactone unit is formed in the cyclization of BMA/VCl copolymers as in MMA/VCl copolymers, we should be able to use the same $T_{g_{CAB}}$ in both systems. Table 7

TABLE 4. MMA/VCl Copolymer Glass Transitions

| Sample No. | MMA (mole %) | T_g ($^{\circ}$ C) | | |
|------------|------------------|-----------------------|------------------------------------|------------------|
| | | Expt | Predicted | |
| | | | Sequence distribution ^a | Fox ^b |
| A-1 | 0.0 ^c | 77 | - | - |
| A-2 | 5.8 | 74 | 73 | 79 |
| A-3 | 25.1 | 65 | 65 | 86 |
| A-4 | 37.2 | 66 | 64 | 90 |
| A-5 | 44.6 | 68 | 66 | 93 |
| A-6 | 61.4 | 73 | 72 | 97 |
| A-7 | 69.8 | 73 | 77 | 99 |
| A-8 | 76.3 | 82 | 82 | 100 |
| A-9 | 100.0 | 105 | - | - |

^aPredicted using Eq. (6).^bPredicted using Eq. (3).

cPVC.

TABLE 5. BMA/VCl Copolymer Glass Transitions

| Sample No. | BMA (mole %) | T_g ($^{\circ}$ C) | | |
|------------|------------------|-----------------------|------------------------------------|------------------|
| | | Expt | Predicted | |
| | | | Sequence distribution ^a | Fox ^b |
| U-1 | 0.0 ^c | 77 | - | - |
| U-2 | 13.9 | 51 | 51 | 60 |
| U-3 | 28.3 | 36 | 35 | 48 |
| U-4 | 45.7 | 24 | 24 | 37 |
| U-5 | 50.2 | 21 | 22 | 35 |
| U-6 | 60.1 | 18 | 20 | 31 |
| U-7 | 72.8 | 21 | 19 | 27 |
| U-8 | 100.0 | 20 | - | - |

^aPredicted using Eq. (6).^bPredicted using Eq. (3).

cPVC.

TABLE 6. Cyclized MMA/VCl Glass Transitions

| Sample No. | MMA in original copolymer (mole %) | T_g ($^{\circ}$ C) | |
|------------|------------------------------------|-----------------------|------------------------|
| | | Expt | Predicted ^a |
| A-2-C | 5.8 | 84 | 84 |
| A-3-C | 25.1 | 106 | 106 |
| A-4-C | 37.2 | 114 | 117 |
| A-5-C | 44.6 | 118 | 123 |
| A-6-C | 61.4 | 113 | 115 |
| A-7-C | 69.8 | 116 | 118 |
| A-8-C | 76.3 | 106 | 109 |

^aPredicted using Eq. (7).

TABLE 7. Cyclized BMA/VCl Glass Transitions

| Sample No. | BMA in Original Copolymer (mole %) | T_g ($^{\circ}$ C) | |
|------------|------------------------------------|-----------------------|------------------------|
| | | Expt | Predicted ^a |
| U-2-C | 13.9 | 91 | 91 |
| U-3-C | 28.3 | 100 | 101 |
| U-4-C | 45.7 | 91 | 92 |
| U-5-C | 50.2 | 85 | 83 |
| U-6-C | 60.1 | 68 | 65 |
| U-7-C | 72.8 | 49 | 48 |

^aPredicted using Eq. (7).

compares the experimental T_g 's of cyclized BMA/VCl copolymers with those predicted using Eq. (7), the $T_{g_{CAB}}$ value from cyclized MMA/VCl, and other appropriate values from Table 3.

Figure 1 shows a plot of the MMA/VCl and cyclized MMA/VCl T_g data from Tables 4 and 6 vs the wt% methyl methacrylate in the uncyclized copolymer.

Figure 2 shows a plot of the BMA/VCl and cyclized BMA/VCl T_g data from Tables 5 and 7 vs the wt% butyl methacrylate in the

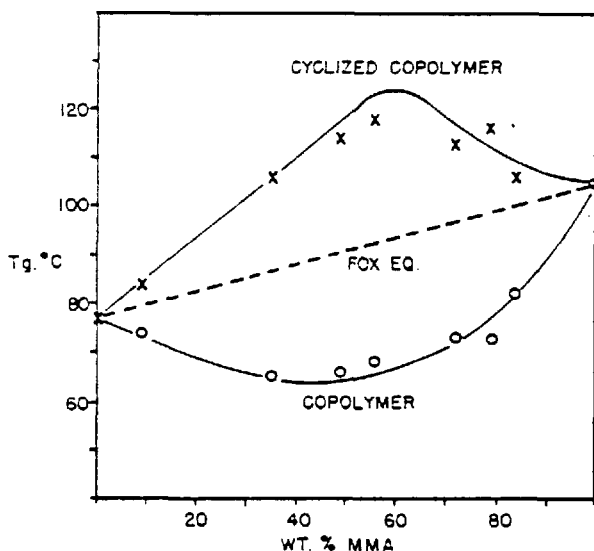


FIG. 1. The experimental and sequence distribution predicted T_g 's of MMA/VCl cyclized and uncyclized copolymers and the Fox equation predicted copolymer T_g 's vs the wt% MMA in the uncyclized copolymer.

uncyclized copolymer. The T_g of BMA/VCl copolymers increase up to 70°C upon cyclization and formation of the high T_g γ -butyrolactone unit.

Although our final results indicate that the T_g 's studied in this work are influenced by the sequence distribution of polymers, we were concerned at the beginning of this program that we were measuring a molecular weight- T_g depression effect. This concern developed because, as shown in Tables 2 and 3, the intrinsic viscosities of all of the copolymers prepared by solution polymerization were lower than the homopolymer intrinsic viscosities. A BMA/VCl copolymer (U-5) was prepared by emulsion polymerization to provide a sample with an intrinsic viscosity in the same range as the homopolymer values. The high molecular weight BMA/VCl copolymer experimental T_g agrees very well with values predicted from the sequence distribution- T_g relationship and falls in line with the other T_g values in the copolymer series. The experimental T_g 's of the three homopolymers also agree

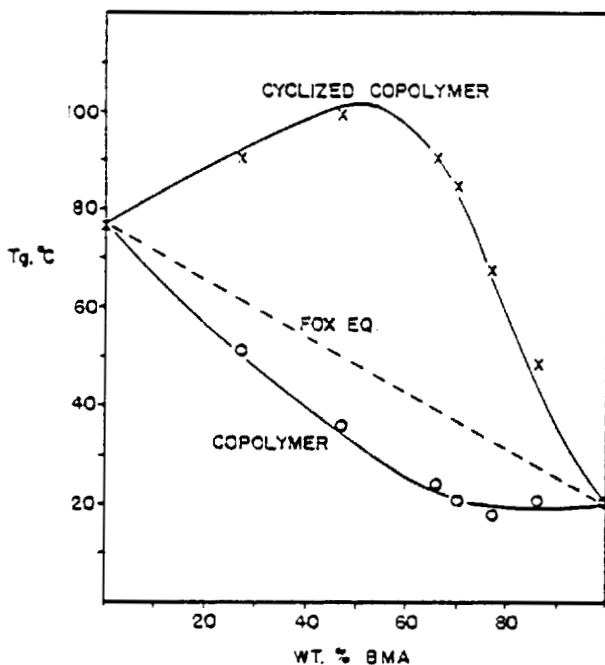


FIG. 2. The experimental and sequence distribution predicted T_g 's of BMA/VCl cyclized and uncyclized copolymers and the Fox equation predicted copolymer T_g 's vs the wt% BMA in the uncyclized copolymer.

well with literature values [10]. This indicates the solution polymerization prepared polymers do not exert a noticeable molecular weight depression effect on the T_g 's.

CONCLUSIONS

A definite correlation exists in some copolymers and terpolymer systems between sequence distribution and glass transition temperatures. The results obtained indicate that glass transition temperatures may be accurately predicted by taking into consideration the probabilities of having adjacent unlike monomer units and the glass transitions that they contribute to a polymer.

The sequence distribution-glass transition effects reported in this work are not confined to alkyl methacrylate-vinyl halide type systems.

These types of effects are found in a large number of copolymer and terpolymer systems, several of which we plan reporting on in the near future.

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