Effect of Large Polar Side Groups on the Glass Transition Temperature of Acrylic Copolymers

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ABSTRACT: The glass transition temperatures of poly[*N*-[4-(methacryloyloxy)phenyl]-2-(4-methoxyphenyl)-acetamide] (poly-O) and poly[*N*-[4-[[(4-methoxyphenyl)acetyl]oxy]phenyl]methacrylamide] (poly-A) are discussed on the basis of the structural characteristics of the corresponding monomeric units, taking into consideration that both O and A have the same substituents but functional groups with opposite orientation, in such a way that O is a methacrylic ester, whereas A is a methacrylamide. The variation of the T_gs of copolymers with hydroxyethyl methacrylate is discussed on the basis of treatments which consider the influence of the distribution of monomeric units on the T_gs of the copolymer samples, determining the T_gs of the corresponding alternating diads, T_{gOH} and T_{gAH}.

Introduction

The composition dependence of the glass transition temperature (T_g) of polymer mixtures and statistical, block, and graft copolymers has been studied experimentally for many systems, and the variation of T_g with the composition has been interpreted mainly with empirical expressions based on the free-volume theory suggested by Fox and Flory[1] or the entropic theory developed by Gibbs and Di Marzio.[2]

Recently, we have studied the microstructural characteristics of statistical copolymers prepared by the free radical copolymerization of *N*-[4-(methacryloyloxy)phenyl]-2-(4-methoxyphenyl)acetamide (O) and *N*-[4-[[(4-methoxyphenyl)acetyl]oxy]phenyl]methacrylamide (A) with 2-hydroxyethyl methacrylate (H).[3] One interesting structural characteristic of the monomers O and A is that both compounds are acrylic derivatives with the same elemental composition but a different distribution of the functional groups in the molecule (see Chart I). O is a methacrylic ester bearing a voluminous polar side group having an aminophenyl spacer group between the methacrylic ester and the 4-methoxyphenyl side residue. However, A is a methacrylamide derivative in which the aminophenyl spacer group has been rotated 180° with respect to the O molecule. This structural difference has profound consequences not only in the kinetics of the free radical polymerization[4] and copolymerization[3] of both monomers but also in the microstructural characteristics of the corresponding homopolymers and copolymers.[3,5,6]

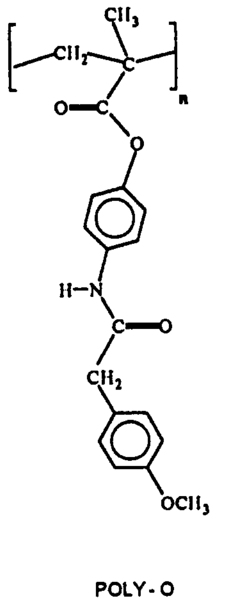
On the other hand, polymeric systems based on these monomers are of practical interest because of their properties as pharmacologically active compounds available for controlled delivery systems as well as for the targeting of specific drugs with antiinflammatory and analgesic properties.[5,6]

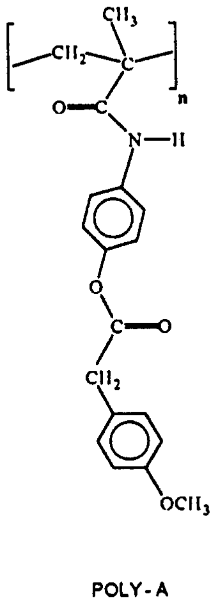
This paper deals with the study of the interesting thermal behavior of polymers and copolymers of O and A with 2-hydroxyethyl methacrylate in relation to the flexibility of the polymer and copolymer segments according to the structural characteristics of the corresponding acrylic side residues.

Experimental Section

Preparation of Monomers. *N*-[4-(Methacryloyloxy)phenyl]-2-(4-methoxyphenyl)acetamide (O) was synthesized in two steps as described elsewhere:[5] First, we prepared an intermediate derivative by the amidation reaction of (4-methoxyphenyl)acetic acid with 4-aminophenol. The monomer O was prepared by the reaction of this intermediate with methacryloyl chloride in aqueous sodium hydroxide solution at 0 °C.

Chart I


POLY-O


POLY-A

N-[4-[[(4-Methoxyphenyl)acetyl]oxy]phenyl]methacrylamide (A) was also synthesized in two steps:[6] The intermediate derivative was prepared by selective amidation reaction of 4-aminophenol with methacrylic anhydride at low temperature. Then we prepared the monomer A by the reaction of the intermediate with (4-methoxyphenyl)acetic acid. Both monomers were purified by fractional crystallization with methanol/water and by column chromatography (Kieselgel 60, Merck) using ethyl acetate as eluent, respectively. Other experimental details are given elsewhere.[5,6]

2-Hydroxyethyl methacrylate (H) (Hydron Europe Ltd.) containing <0.05 wt % of ethylene glycol dimethacrylate was distilled under a reduced pressure of nitrogen, and the fraction of bp 87–89 °C/0.5 mmHg was collected.

2,2′-Azobis(isobutyronitrile) (AIBN) was purified by fractional crystallization from methanol, mp = 104 °C.

N,N-Dimethylformamide (DMF) was dried over anhydrous magnesium sulfate for 2 days and then with phosphoric anhydride overnight. After drying, DMF was distilled under a reduced pressure of nitrogen. Other reagents were of extrapure grade and used without purification.

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Polymerization. Copolymerization reactions were carried out in DMF solution at 50 ± 0.1 °C in Pyrex glass ampules sealed off under high vacuum. Monomer and initiator concentrations were 1 and 1.5×10^{-2} mol/L, respectively. The sealed ampules were shaken vigorously and immersed in a water bath held at the required temperature of polymerization. After the proper reaction time, the ampules were removed from the bath and at once the contents were poured into a large excess of a 1:1 diethyl ether–chloroform mixture. The precipitated samples were washed with the precipitant mixture and dried under vacuum until a constant weight was attained.

The copolymers obtained from different mixtures of O or A and H were analyzed by ^{1}H-NMR spectroscopy with a Varian XLR-300 spectrometer (300-MHz). The spectra were recorded at 80 °C on 5% (w/v) DMSO-d_6 solutions.

Differential Scanning Calorimetry (DSC). Glass transition temperatures were determined with a Perkin-Elmer calorimeter. Measurements and calibration were carried out at heating rates of 4, 8, and 16 °C/min. The difference in T_g values obtained at the heating rates were $\leq 1\%$. T_g was taken as the extrapolated onset of the base line shift. Samples were prepared as compressed disks of 2-mm thickness and 4-mm diameter ($\simeq$20-mg weight).

The samples introduced into the aluminum pan were heated in the calorimeter at 500 K for 30 min and then quenched at room temperature previous to the run of measurement.

Results and Discussion

It is widely recognized that some of the factors which influence the T_g of polymers with side chains are the polarity, bulkiness, and the flexibility of the pendant units, and when a bulky phenyl substituent is attached to the main chain of a macromolecule, it can exert a dramatic influence on T_g.[7,8] For example, Krause et al.[9] in a pioneering work demonstrated that a dramatic decrease of T_g with respect to that of polystyrene is observed when the phenyl group is moved farther away from the polymer backbone by introducing spacer groups such as carbonyl, carboxyl ester, or oxyalkyl functions, which was interpreted considering the flexibilization of the side groups and the reduction of the steric hindrance which make easier the segmental cooperative motion of the polymer backbone.

Moreover, the relative position of specific functional groups such as carboxylic or ester functions in the side residues of polyvinyl chains has a noticeable effect on the T_g of the corresponding polymers. According to data reported by Giusti et al.,[8] poly(vinyl benzoate) and poly(vinyl phenyl ketone) present T_gs around 70 and 73 °C, whereas the T_g of poly(phenylacrylate) is sensibly lower, 55 °C (measured by refractometry)[8] or 50 °C (measured by DSC),[10] although poly(phenyl acrylate) and poly(vinyl benzoate) have the same functional side groups but with opposite orientation. The fact that poly(vinyl phenyl ketone) and poly(vinyl benzoate) have very similar T_gs is explained by Giusti et al.[8] by considering that in both polymers the carbonyl group is bonded directly to the phenyl ring and it could be considered that an oxygen atom between the polyvinyl backbone and the carbonyl group does not play an important role in the segmental mobility of the macromolecular main chain. However, if the oxygen is between the carbonyl group and the phenyl ring as in poly(phenyl acrylate), a noticeable increase in the flexibility of the main chain is observed.

The glass transition temperatures of the homopolymers poly-O and poly-A, determined by DSC under the experimental conditions indicated above, are 418 and 515 K, respectively (the structure of the repeating unit of poly-O and poly-A is shown in Chart I). These values are sensibly higher than that of poly(methyl methacrylate) (PMMA), T_g = 378 K,[11] prepared by free radical polymerization. This difference arises from the bulkiness and the strong polarity of the side substituents of poly-O and poly-A, in comparison to the less polar and relatively small methyl group of PMMA.

It is noteworthy that the T_g of the poly(methacrylamide) derivative poly-A is 97 K higher than that of the poly(methacrylic ester) poly-O. This great difference must be related to the higher stiffness of the methacrylamide side substituents compared to the corresponding methacrylic ester, probably because the C–N bond of the methacrylamide units has a partial double-bond character,[12] being linked directly to the macromolecular backbone (see Chart I), whereas in the case of the poly(methacrylic ester) poly-O the C–O ester bond has free rotation and its influence on the stiffness of chain segments is relatively small as mentioned above. A similar behavior has been reported for other substituted poly(methacrylamides) and poly(alkylacrylamides) in comparison with the corresponding poly(methacrylates) and poly(acrylates). For example, the glass transition temperature of poly[[4-(methoxycarbonyl)phenyl]methacrylamide] is 453 K, 74 K higher than that of poly[4-(methoxycarbonyl)phenyl methacrylate], T_g = 379 K,[9,11] and several poly(alkylacrylamides) present glass transition temperatures up to 130–140 K higher than the corresponding poly(alkyl acrylates).[11]

The monomers O and A are crystalline solids with melting points of 153 and 130 °C, respectively. However, the crystallization can be avoided by quenching the samples from the melt with liquid nitrogen. In this way it is possible to determine the glass transition temperature of these compounds, giving values of 265 K for A and 278 K for O. The glass transition temperature of low molecular weight compounds depends on the intermolecular interactions of individual molecules, exclusively, being controlled by the molar volume and dipolar connectivities, hydrogen bonds, and van der Waals interactions between molecules. The T_g values of these monomers are relatively high, indicating strong dipolar interactions between monomer molecules which correspond to the side substituents of the polymeric chains. It is important to stress the fact that the T_g of both compounds has a difference of only 13 °C as a consequence of the orientation of the aminophenoxy spacer group between the methacrylic and (*p*-methoxyphenyl)acetic residues. Therefore, the much higher difference between the T_g of the corresponding homopolymers might be related to the intramolecular interactions of neighboring units along the macromolecular chains together with the partial double-bond character of the methacrylamide residue.

Copolymer Composition Glass Transition Effect. The preparation of copolymers of O or A with hydroxyethyl methacrylate is of practical interest because it is possible to obtain biocompatible coatings with a hydrophobic/hydrophilic balance controlled by the average composition and the distribution of comonomeric units along the copolymer chains. Moreover, physical properties of biomedical interest such as the swelling behavior of coatings in hydrated or physiological media and the ability of film to adhere to biological substrates including natural and synthetic implants depend on the flexibility of macromolecular chains, which in addition is controlled not only by the average composition of copolymer systems but also by the distribution of comonomeric units along the copolymer chains.

In previous work we determined unequivocally the glass transition temperature of poly(hydroxyethyl methacrylate) (poly-H) as 358 K.[11,13] The difference between this value and the T_g of poly-O or poly-A permits the application of treatments that consider the variation of T_g of copolymer

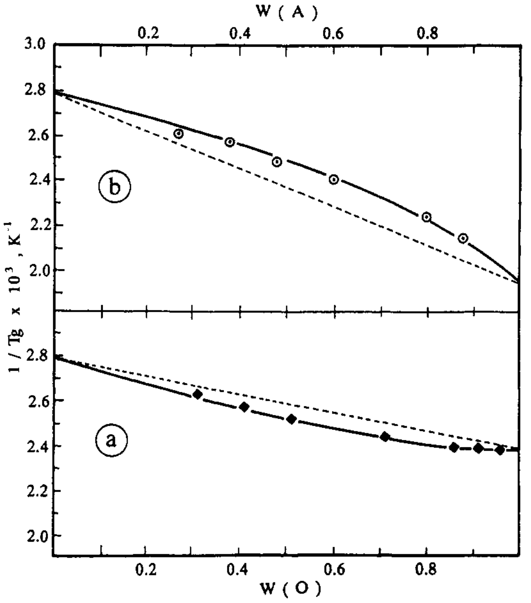

Figure 1. Application of the Fox treatment to the variation of the inverse of T_g with the weight-average fraction of O and A units of copolymers O–H and A–H prepared by free radical copolymerization at low conversion.

systems according to the distribution of comonomeric units along the macromolecular chains. Figure 1 shows the variation of the inverse of T_g with the average weight fraction of monomers, w(O) or w(A), in the copolymer chains. The straight lines connecting the values of the homopolymers correspond to the application of the well-known Fox equation[1] based on the free-volume theory. It is clear from this figure that the experimental points of the A–H copolymers deviate positively whereas those of the O–H copolymers deviate negatively with respect to the prediction of the Fox equation. This means that the T_gs of A–H copolymers are lower than the weight-average values of the T_gs of the corresponding homopolymers. However, the T_gs of O–H copolymers seem to be somewhat higher than the weight-average values of the T_gs of poly-O and poly-H. In both cases, the deviations are more noticeable for O-rich or A-rich copolymers.

Several reports in the literature[14–17] describe the strong effect of hydrogen-bonded polymer complexes on the glass transition temperature which give rise to considerable deviations with respect to the weight-average values of the T_gs of the parent homopolymers. Sometimes, the transition temperature of strong ionic complexes may exceed the value of the high-T_g component.[18] The presence of CONH, COO, and CH_3O polar groups in the side substituent of O and A units could explain the monotonic increase of the T_g of copolymers with respect to that of poly-H, but it is clear from Figure 1 that the relative position of the polar functional groups dramatically affects the T_g of the copolymers. Probably, the position of the amide gorup in O units is more favorable with respect to that of methacrylamide A units to form hydrogen bonds with neighboring units or even intermolecular interactions, giving rise to values of T_g for the copolymers higher than those corresponding exclusively to the weight-average contribution of the parent homopolymers.

Experimental values of the T_g of O–H and A–H together with statistical parameters for both systems are quoted in Tables I and II. The kinetic study of the free radical copolymerization of these systems has been described previously.[3] The reactivity ratios of monomers under the experimental conditions outlined in the Experimental Section were $r_A = 0.29$, $r_H = 1.47$ and $r_O = 1.49$, $r_H = 0.61$.

Table I. Average Molar Composition, Glass Transition Temperature, and Conditional Probability Data of O–H Copolymers Prepared by Free Radical Copolymerization in DMF Solution at 50 °C

F_O(feed)	f_O(cop)	conv (wt %)	T_g (K)	P_{OH}	P_{HO}
0.00	0.00		358	0.000	0.000
0.10	0.15	5.3	379	0.858	0.154
0.15	0.22	6.2	388	0.792	0.224
0.20	0.29	4.5	397	0.729	0.291
0.40	0.50	4.0	409	0.502	0.522
0.60	0.71	2.6	416	0.309	0.711
0.75	0.81	7.8	417	0.183	0.831
0.85	0.90	5.4	419	0.106	0.903
1.00	1.00		418	0.000	0.000

Table II. Average Molar Composition, Glass Transition Temperature, and Conditional Probability Data of A–H Copolymers Prepared by Free Radical Copolymerization in DMF Solution at 50 °C

F_A(feed)	f_A(cop)	conv (wt %)	T_g (K)	P_{AH}	P_{HA}
0.00	0.00		358	0.000	0.000
0.20	0.13	7.5	385	0.932	0.145
0.30	0.20	5.3	389	0.889	0.226
0.40	0.27	4.9	403	0.838	0.312
0.55	0.38	3.8	416	0.738	0.454
0.80	0.61	4.6	447	0.463	0.731
0.89	0.75	7.2	466	0.299	0.846
1.00	1.00		515	0.000	0.000

The copolymer samples were prepared at the conversions indicated in the third column of Tables I and II, in all cases the molecular weights were higher than 75 000.

The sequence distribution was predicted using the reactivity ratios by the application of statistical relations[19] considering that both copolymerization systems present a predominantly random distribution of the monomeric units in the copolymer chains:[20]

$$P_{12} = 1 - P_{11} = \frac{1}{1 + r_1 X}$$

$$P_{21} = 1 - P_{22} = \frac{1}{1 + r_2/X}$$

where P_{ij} ($i,j = 1,2$) are the conditional probabilities of the addition of monomer j to a growing chain ending in an active i radical and $X = [M_1]/[M_2]$, the composition of the monomer feed. The transition probabilities for the first-order Markovian model of copolymerization, P_{OH}, P_{HO} and P_{AH}, P_{HA} are collected in the fifth and sixth columns of Tables I and II, respectively.

Application of modern semiempirical methods for the prediction of the variation of T_g of random copolymer systems considers the variation with the average composition of the statistical parameter known as the "run number", defined by Harwood and Ritchey as the average number of monomer alternations in a copolymer per segment of 100 monomer units.[19]

$$R = \frac{200}{r_1 X + 2 + r_2/X} \tag{1}$$

where r_1 and r_2 are the reactivity ratios of the monomers of interest and X is the ratio of the molar concentration of the monomers in the feed. This parameter provides a useful picture of the sequence distribution in a copolymer chain and can be used to estimate the variation of the physical properties of copolymers with the composition. Figure 2 shows the variation of R with the O or A molar fraction in the monomer feed. The diagrams obtained for the systems are different in the sense that the copolymerization system O–H reaches a maximum value of $R \simeq 50$ for a molar fraction in the feed f(O) = 0.38 whereas the

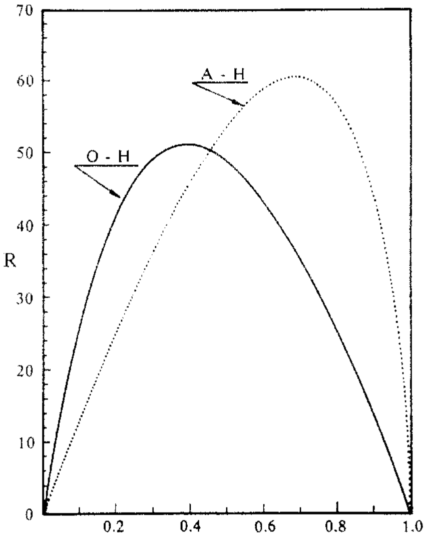

Figure 2. Variation of the "run number" of statistical copolymers O–H and A–H with the molar fraction of O and A monomers in the feed.

A–H system reaches a maximum $R \simeq 62$ for a molar fraction in the feed $f(\mathrm{A}) = 0.70$.

Although in pioneering studies it was considered that the variation of the T_g of random copolymer systems followed a single mixture rule like that suggested in the fifties by Fox[1] for compatible polymer blends, it has been widely demonstrated that in general the T_g of the copolymer systems is affected by the distribution function of monomers along the macromolecular chains. We have observed that, according to the experimental data shown in Figure 1, the systems studied in this work seem to follow the microstructural distribution model.

From a general point of view, in a copolymer formed from monomers 1 and 2, there are four possible sequences of pairs of repeating units, which may be represented as 11, 22, 12, and 21 diads, being the components of the system, the two homopolymers and the alternating copolymer. Assuming the dominance of nearest neighbor interactions, the copolymer glass transition behavior would be determined by an additive contribution of the three types of comonomeric pairs.[2] In this sense, Hirooka and Kato[21] have pointed out that the sequence distribution in a copolymer chain affects the glass transition temperature, and Tonelli[22] has suggested that the effects in many statistical copolymers may have as an intramolecular origin specific molecular interactions between adjacent monomer units.

Johnston[23] has proposed an expansion of the treatment suggested by Fox based on the free-volume theory, assigning to 11, 22, and 12 or 21 diads their own T_g values. Using the probabilities of having various linkages (P_{11}, P_{22}, P_{12}, P_{21}) which can be calculated from statistical considerations,[19] Johnston derived an equation that can be written

$$\frac{1}{T_g} - \frac{W_1P_{11}}{T_{g11}} - \frac{W_2P_{22}}{T_{g22}} = \frac{1}{T_{g12}}(W_1P_{12} + W_2P_{21}) \qquad (2)$$

where T_g is the copolymer glass transition, W_1 and W_2 are the weight fractions of monomer units 1 and 2, T_{g11} and T_{g22} are the glass transition temperatures of both homopolymers, and T_{g12} is the glass transition of the alternating copolymer. Figure 3 shows the linear diagram obtained after application of the experimental data to Johnston's treatment according to eq 2. From the slopes of the straight lines we obtain the values of T_{gAH} and T_{gOH} quoted in Table III.

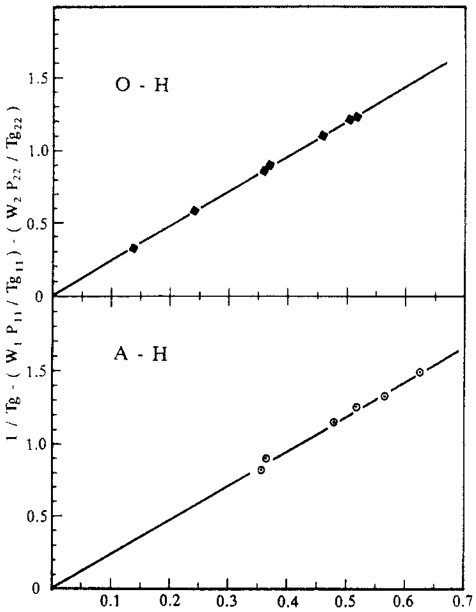

Figure 3. Application of the linearized expression of Johnston's treatment to the copolymer systems O–H and A–H prepared by free radical polymerization in DMF solution at 50 °C.

Table III. Glass Transition Temperature of Alternating Sequences, T_{gMH} (M = O or A), for Copolymers O-H and A-H Determined According to the Methods Indicated in the Table

	T_{gMH} (K)		
system	Johnston	Barton	Suzuki
O–H	426	431	431
A–H	422	425	424

Barton,[24] by extension of the Di Marzio and Gibbs equation[2] based on the "entropic theory", proposed the following equation:

$$T_g = n'_{11}T_{g11} + n'_{22}T_{g22} + (n'_{12} + n'_{21})T_{g12} \qquad (3)$$

where n'_{ij} is the molar fraction, n_{ij}, of ij sequences in a copolymer weighted according to the number of rotatable bonds α_{ij} in an ij sequence ($i,j = 1,2$)

$$n'_{ij} = \frac{n_{ij}\alpha_{ij}}{\sum_{ij}(n_{ij}\alpha_{ij})} \qquad (4)$$

Recently, Di Marzio[25] considered a new definition of the bond fraction based on a lattice model theory which requires that each configuration of polymer segments fits onto the lattice. The bonds taken into consideration for the contribution to the flexibility or stiffness of nearest neighbor units need not only be in the backbone but can also be in the side groups, with the only requirement that on rotation about a particular bond, a new shape is obtained. Thus, poly(methyl methacrylate) would have a total of four flexible bonds per monomer unit; however, polystyrene would have only two, since the rotation of the benzene ring about the bond connecting it to the polymer backbone does not give a configurationally distinguishable position.[25] In view of the chemical structure of O, A, and H repeating units and taking into consideration these arguments, the different kinds of diads along the copolymer chains would present a number of flexible bonds, $\alpha_{11} = \alpha_{12} = \alpha_{21} = \alpha_{22} = 8$; n_{ij} can be calculated from the comonomer reactivity ratios by application of well-known statistical

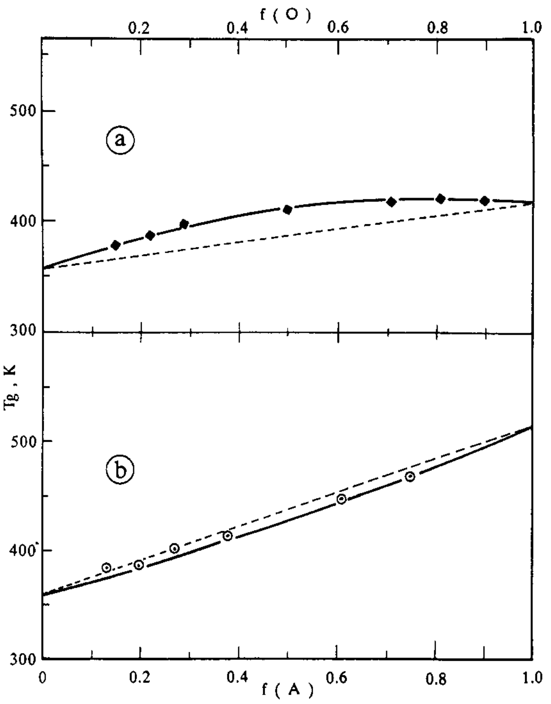

Figure 4. Variation of the glass transition temperature of O-H (a) and A-H (b) copolymers with the molar fraction of O and A units in the copolymer chains. The solid lines correspond to the application of Barton's treatment with the T_{gOH} and T_{gAH} collected in Table III.

considerations.[19] As in the Johnston treatment, eq 3 can be expressed

$$T_g - n'_{11}T_{g11} - n'_{22}T_{g22} = (n'_{12} + n'_{21})T_{g12} \qquad (5)$$

Application of Barton's treatment to the data gives the diagrams shown in Figure 4. The straight line connecting the T_gs of the homopolymers corresponds to the application of the Gibbs-Di Marzio model, whereas the solid line corresponds to application of eq 5 according to the treatment suggested by Barton, with the values of T_{g12} collected in Table III.

On the other hand, Suzuki and Mathot[26] suggested a new expression of Barton's equation that allows us to estimate with minimum data the glass transition of copolymer systems by introducing the "run number", R (defined before), according to the following equation:

$$T_g = n_1T_{g11} + n_2T_{g22} + (R/R^*)[T_g(R^*) - \bar{T}_g] \qquad (6)$$

where R is the run number, n_1 and n_2 are the molar fractions of monomer units in the copolymer chains, T_{g11} and T_{g22} are the glass transitions of the corresponding homopolymers, R^* is the value of R for $n_1 = n_2 = 0.5$, $T_g(R^*)$ is the glass transition of an equimolecular random copolymer, and $\bar{T}_g$ is the average arithmetical value of the T_gs of the homopolymers, $\bar{T}_g = {}^1/_2(T_{g11} + T_{g22})$. If the T_gs of the copolymer samples are plotted against R, we obtain the diagrams drawn in Figures 5 and 6, where the solid lines correspond to the prediction of eq 6 and the straight lines correspond to the middle point of the T_g values predicted for random copolymers at a given value of R. A significant algebraic characteristic of this line is that the extrapolation at $R = 0$ gives the value of $\bar{T}_g$, whereas the extrapolation at $R = 100$ provides T_{gMH} (M = O or A). The values obtained from the diagrams are similar to those obtained by the application of the linear expression of the treatment by Barton and are collected in the third column of Table III.

The excellent agreement between the theoretical predictions according to the three treatments and the experimental values obtained for both systems demonstrates that the glass transition temperature of these copolymers is affected by the distribution of comonomeric units along the copolymer chains. Moreover, it is a very interesting fact that the glass transition of the alternating diads O-H and A-H are rather similar and the predicted T_g of the alternating diad O-H is approximately only 7 K higher than that of the alternating diad A-H, which is in good agreement with the difference between the T_gs of the monomers O and A. It is necessary to take into consideration that in the pure alternating sequences O-H and A-H, the intramolecular interactions of AA and OO neighboring units are replaced by interactions of O and A with the very flexible hydroxyethyl side group of the H units. If we consider that H is a methacrylic ester with a polar hydroxyl group separated from the macromolecular backbone by five flexible bonds, it is reasonable that the interactions between the side groups of O-H diads are rather similar to those of OO sequences, giving rise to a rather similar T_g.

However, in the case of A-H diads, the stiffness of this sequence is sensibly lower than that of the AA sequences because the methacrylamide groups are changed by alternating methacrylamide and methacrylic ester elements and the intramolecular interactions of AA units are replaced by those of the sensibly more flexible sequence A-H. Logically, it can be expected that the difference of the T_gs of O-H and A-H alternating sequences arises from

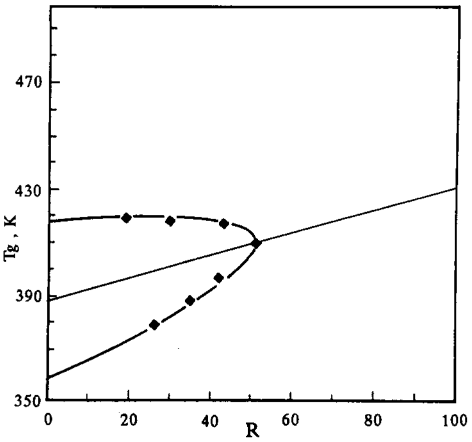

Figure 5. Variation of T_g with the "run number" (R) for O-H copolymers. The elliptical line corresponds to the prediction of eq 6. The straight line corresponds to the midvalues of T_g for each two points of the diagram with the same R (Figure 2) connecting $T_{g1/2}$ at $R = 0$ and T_{gOH} at $R = 100$.

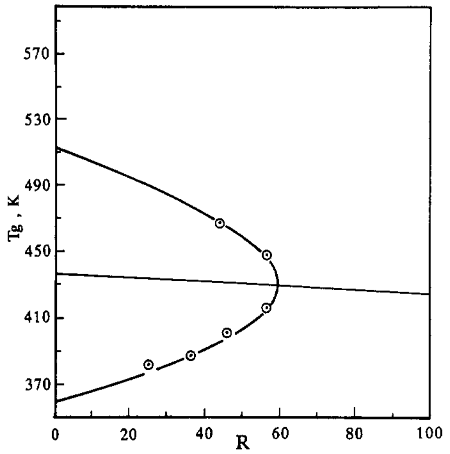

Figure 6. Variation of T_g with the "run number" (R) for A-H copolymers.

the intermolecular interactions, just as happens with the low molecular weight monomers O and A.

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