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Chain Flexibility of Polymethacrylic Systems Bearing Aromatic Polar Groups with Alkylene Spacers As Studied by the T_g of Polymers and Copolymers with 2-Hydroxyethyl Methacrylate

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ABSTRACT: The chain flexibility of polymethacrylic systems prepared by the free-radical polymerization of 4-(methacryloyloxy)acetanilide (MOA), 4-(2-(methacryloyloxy)ethyloxy)acetanilide (MOEA), and 4-(6-(methacryloyloxy)hexyloxy)acetanilide (MOHA) and copolymers with 2-hydroxyethyl methacrylate (HEMA) is analyzed on the basis of the glass transition temperature of the corresponding homo- and copolymers. This is done taking into consideration the effect of the length of the side spacer group (ethyleneoxy or hexyleneoxy) introduced between the acrylic ester group and the aromatic polar side residue, which correspond to the chemical structure of a well-known drug, paracetamol. The glass transition temperature of copolymers with HEMA are analyzed according to empirical treatments which consider the influence of the distribution of monomeric units on the T_g of the copolymer samples. The T_g of the pure alternating diads is determined by the application of equations suggested by Barton and Suzuki and Mathot, based on the entropic theory, giving values of $T_{g\mathrm{MOEA-HEMA}} = 347.5$ K and $T_{g\mathrm{MOEA-HEMA}} = 273$ K, sensibly lower than the average value expected from the additive contribution of the T_g of the corresponding homopolymers. The behavior is related to the flexibility introduced by the alkylene spacer segments.

Introduction

The glass transition temperature of polymeric systems has multifunctional dependences on the microstructural characteristics of high molecular weight macromolecules[1,2] and from a phenomenological point of view has been considered a function of either fundamental thermodynamic or molecular parameters. In this sense, several theories have been proposed by using the free volume concepts[3,4] or thermodynamic approaches.[5] It has been demonstrated that the free volume concepts are useful from a qualitative point of view, but they cannot be used quantitatively to describe the glass relaxation process, even for polymeric systems with similar chemical structure but different physical arrangement.[6] It is necessary to take into account that intramolecular forces, chain flexibility, and chain geometry play an important role. The thermodynamic theory of Gibbs and DiMarzio[5,7] and more recent extensions based on it suggested by Barton[8] and Couchman[9] seem to be more realistic because the interaction and flexibility of chains in terms of hole energy and flex energy are considered. In the case of copolymer systems, several empirical treatments taking into consideration the interactions between similar and dissimilar monomeric units in terms of the distribution of sequence of monomers along the macromolecular chains have been proposed.[8–10]

On the other hand, in the past few years we have been interested in the synthesis, microstructural characterization, and biomedical application of polymeric systems bearing side residues derived from classical organic compounds with pharmacological activity.[11] Following the model proposed by Ringsdorf in 1975,[12] we designed the preparation of hydrophilic acrylic copolymers by the free-radical polymerization of 2-hydroxyethyl methacrylate (H) with methacrylic esters in which the ester side group was constituted by a residue of the well-known drug paracetamol, 4-hydroxyacetanilide. This residue was linked directly to the carboxyl ester group or through a flexible spacer group constituted by an oxyethylene or oxyhexylene segment as drawn in Chart 1. The flexibility of the side substituents of the macromolecular backbone and in addition the stiffness of the high molecular weight polymeric chains have important consequences for the biochemical activity of the active side components and also their hydrolytic behavior in biological media.

The present paper describes the effect of the length of the spacer group and of the microstructural distribution of monomeric units on the flexibility of high molecular weight copolymers of hydroxyethyl methacrylate with three methacrylic derivatives of paracetamol.

Experimental Section

Preparation of Monomers. 4-(2-(Methacryloyloxy)ethyloxy)acetanilide (MOEA) and 4-(6-(methacryloyloxy)hexyloxy)acetanilide (MOHA) were synthesized in two steps as described elsewhere.[13,14] First, we prepared an intermediate derivative by a Williamson reaction of 4-hydroxyacetanilide with 2-chloroethanol for MOEA and with 6-chloro-1-hexanol for MOHA. The monomers were prepared by the reaction of these intermediates with methacryloyl chloride according to a Schotten–Bauman reaction described elsewhere.[15] The acrylic derivative was obtained in mild conditions, avoiding the uncontrolled polymerization of the double bond. MOA, MOEA, and MOHA after purification are crystalline solids with melting points of 126, 117, and 65 °C, respectively.

2-Hydroxyethyl methacrylate (HEMA), supplied by HYDRON Europe Ltd., containing less than 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.

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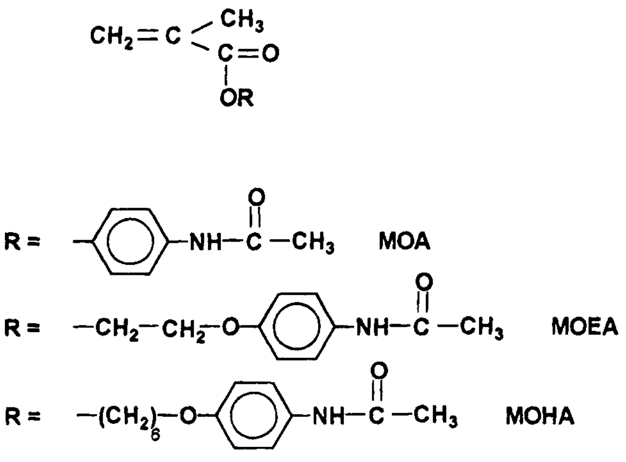
Chart 1



N,*N*-Dimethylformamide (DMF) was dried over anhydrous magnesium sulfate for 2 days and later 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.

Copolymerization. Copolymerization reactions were carried out in DMF solution at 50 °C in Pyrex glass ampules sealed off under high vacuum. Monomer and initiator concentrations were 1 and 1.5×10^{-2} mol·L^{-1}, respectively. The sealed ampules were shaken vigorously and immersed in a thermostatic 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 diethyl ether–hexane mixture cooled at 0 °C. The isolated polymeric samples were washed twice with the precipitant mixture and dried under vacuum until a constant weight was attained.

The copolymers obtained from different mixtures of MOEA and HEMA and of MOHA and HEMA were analyzed by ^{1}H-NMR spectroscopy with a Bruker AM-200 spectrometer working at 200 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 DSC-4 calorimeter. Measurements and calibration were carried out at heating rates of 4, 8, and 16 °C/min under a nitrogen atmosphere (50 mL/min). The difference in T_g values obtained at these heating rates was less than 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 (≃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 prior to the measurement run.

Results and Discussion

The free-radical copolymerization of the three monomers (MOA, MOEA, and MOHA) with HEMA in dried DMF solutions was studied in a wide composition interval with molar fractions of MOA, MOEA, and MOHA ranging from 0.1 to 0.9 in the monomer feed. The reaction time was regulated to reach conversions lower than 10 wt % in order to satisfy the differential copolymerization equation.[16] The conversion of monomers to copolymers was determined gravimetrically after exhaustive drying of the isolated copolymer samples. The average composition of the copolymer samples were determined from the corresponding ^{1}H-NMR spectra registered in DMSO-d_6 at 80 °C. The molar fractions of MOA, MOEA, and MOHA in the monomer feed and in the copolymer chains are collected in Table 1. The reactivity ratios of these monomers were determined by the application of the linearization methods of the copolymerization equation suggested by Fineman and Ross[17] and Kelen and Tüdös[18] as well as the nonlinear least-squares analysis suggested by Tidwell and Mortimer,[19] considering that the mechanism of copolymerization fits the terminal model described by Mayo and Lewis.[16] The values obtained are collected in Table 2.

Table 1. Average Molar Composition of Acrylic Copolymers Prepared by the Free-Radical Polymerization of MOA, MOEA, and MOHA with HEMA in DMF Solution at 50 °C

F_M[a] (feed)	m_{MOA}[b]	conv, wt %	m_{MOEA}[c]	conv, wt %	m_{MOHA}	conv, wt %
0.10	0.14	6.3	0.08	4.6	0.08	5.3
0.20	0.26	5.4	0.15	4.5	0.18	5.0
0.30	0.40	5.0	0.24	3.9	0.26	5.8
0.40	0.50	4.8	0.31	4.7	0.36	6.2
0.60	0.73	5.6	0.51	5.3	0.56	5.4
0.80	0.88	6.8	0.74	5.0	0.78	4.7
0.90	0.94	6.5	0.85	4.8	0.87	4.9

[a] Molar fraction of the acrylic monomer (MOA, MOEA, and MOHA) in the monomer feed. [b] Data taken from ref 28. [c] Data taken from ref 43.

Table 2. Reactivity Rations of MOA, MOEA, MOHA, and HEMA Acrylic Monomers for the Free-Radical Copolymerization in DMF Solution at 50 °C

	copolymerization system					
method	MOA	HEMA	MOEA	HEMA	MOHA	HEMA
Fineman–Ross	2.19	0.95	0.66	1.39	0.86	1.12
Kelen–Tüdos	2.11	0.86	0.69	1.44	0.88	1.15
Tidwell–Mortimer	1.94	0.78	0.67	1.39	0.87	1.19

From the average values of the reactivity ratios and taking into account well-known statistical relations, we determined the "run number", R, defined by Harwood and Ritchey in 1964[20] as the average number of monomer alternations in a copolymer per 100 monomer units. This parameter provides a useful description 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. Values of R have been determined in terms of reactivity ratios and probability statistics for different values of monomers (MOA, MOEA, and MOHA) molar fractions in the feed, covering a wide interval of compositions. Figure 1 shows the variation of R with the molar fraction of the three monomers in the monomer feed. In the case of the MOA–HEMA system, a maximum value of $R = 42$ is reached for a MOA molar fraction in the feed about 0.40. For the MOEA–HEMA and MOHA–HEMA systems, a maximum value of $R = 50$ is reached for a MOEA molar fraction in the feed about 0.60 and for a MOHA molar fraction in the feed about 0.50. This means that the MOEA–HEMA and MOHA–HEMA systems present a sequence distribution close to the ideal behavior, with a random arrangement of both monomeric units along the copolymers chains.

According to the random character of these copolymerization processes, it is possible to consider that the addition of monomer units to growing copolymer chains follows the classical terminal model, and therefore, it is possible to apply the statistical relations for the first-order Markovian transition probabilities P_{ii}, P_{ij}, and P_{jj} according to the following equations:[21]

$$P_{ij} = 1 - P_{ii} = 1/(1 + r_i x)$$

$$P_{ji} = 1 - P_{jj} = 1/(1 + r_j/x)$$

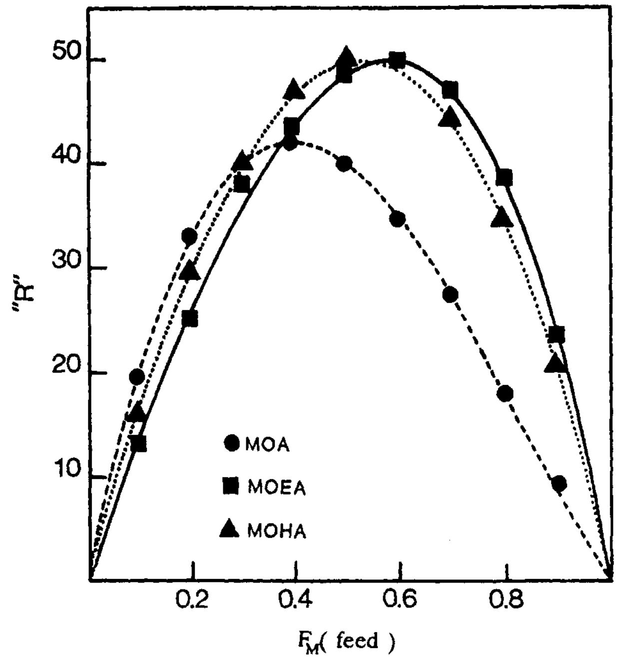


Figure 1. Variation of the "run number" of statistical copolymers of MOA, MOEA, and MOHA with HEMA as a function of the molar fraction of the corresponding methacrylic monomer in the feed, F_M.

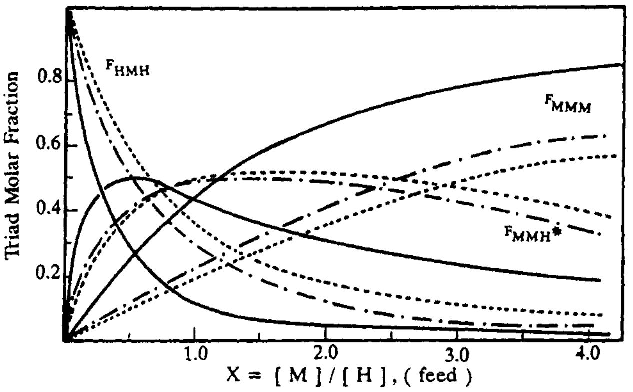


Figure 2. Statistical distribution of M-centered sequences of triads with the ratio of concentrations of M and H in the monomer feed. M represents MOA, MOEA, and MOHA and H, HEMA. (—) MOA–HEMA copolymers; (• • •) MOEA–HEMA copolymers; (– • –) MOHA–HEMA copolymers. MMH* = MMH + HMM.

where $x = [M_i]/[M_j]$ is the ratio of concentrations of monomers i and j in the monomer feed. In this sense, Figure 2 shows the statistical distribution of MOA, MOEA, or MOHA centered triads as a function of the ratio of concentration of monomers (MOA, MOEA, or MOHA) and HEMA in the feed. It is clear from this figure that the mole fraction of alternating MOA, MOEA, and MOHA centered triads decreases drastically, whereas the mole fraction of homotriads increases smoothly with increasing ratio x. However, the mole fraction of heterotriads having one HEMA unit MMH* = MMH + HMM reaches a maximum at about $F_{MOA} = 0.30$ for the MOA–HEMA system, and $F_{MOEA,MOHA} = 0.50$ for the MOEA–HEMA and MOHA–HEMA systems.

Table 3. Glass Transition Temperature of Monomers and Polymers of MOA, MOEA, and MOHA Determined by DSC

	system	T_g, K	$\bar{M}_n$
monomers	MOA	268	219
	MOEA	259	263
	MOHA	237	319
polymers	PMOA	471	1.83×10^5
	PMOEA	385	2.50×10^5
	PMOHA	318	1.62×10^5

It is well known that the behavior and the physical and chemical properties of copolymeric systems depend not only on the chemical composition of these systems but also on the distribution of the units along the macromolecular chains (microstructure) and on the relative stereochemical configuration of the side chains if the main chain has pseudoasymmetric carbons. In this sense, it would be of interest to analyze the influence of these factors on the thermal behavior of the copolymers prepared. In order to know the influence of the side substituents on the flexibility of high molecular weight polymeric chains and the relationship between the size and polarity of the side ester residue on the flexibility of the repeating MOA, MOEA, and MOHA units, we analyzed the glass transition temperatures of the corresponding monomers and high molecular weight homopolymers ($\bar{M}_n > 25\,000$) as indicated in the Experimental Section. The T_g of the monomers was determined by quenching molten samples with liquid nitrogen to avoid their crystallization. Experimental values of the T_g of the monomers and polymers are quoted in Table 3.

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. Figure 3 shows the relationship between the T_g values and the number of carbon atoms of the spacer group of the monomers together with those of the corresponding homopolymers. The glass transition of the monomers decreases with increasing length of the spacer group.

The presence of long flexible n-alkyl substituents has a profound effect on the T_g of macromolecules, including polyolefins,[22,23] poly(p-alkylstyrenes),[24] polyacrylates,[25] and polymethacrylates.[25,26] As the length of the n-alkyl side chain increases, T_g decreases within each of these families of polymers. The T_g of monomers decreases linearly with increasing number of methylene groups in the spacer group between the acetanilide residue and the acrylic ester group. This fact indicates that the introduction of the spacer group increases the flexibility of the repeating unit. However, in the case of homopolymers, the T_g decreases more significantly with increasing number of CH_2 groups in the spacer segment. This might be related to the intramolecular interactions of neighboring units along the macromolecular chains. It is clear that the introduction of the spacer group gives rise to a drastic increasing of the flexibility of the polymer segments by decreasing the steric hindrance of the rigid aromatic side groups when they are located near the polymer backbone.

In a previous work we determined the glass transition temperature of poly(hydroxyethyl methacrylate) (poly H), giving a value of 358 K.[27,28] The difference between this value and the T_g of PMOA, PMOEA, and PMOHA (see Table 3) permits the application of treatments that consider the variation of T_g of copolymer systems according to the distribution of comonomer units along the macromolecular chains.

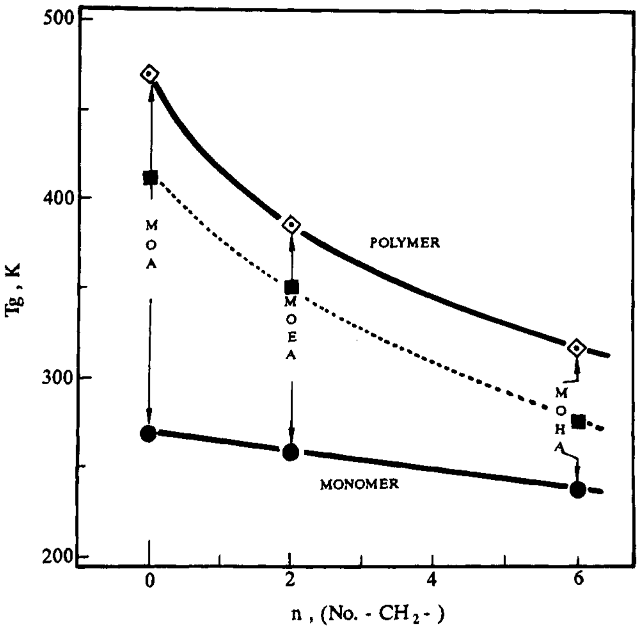


Figure 3. Variation of the glass transition temperature of MOA, MOEA, and MOHA acrylic monomers (●) and homopolyers (◇) with the length of the spacer group between the aromatic polar side residue and the acrylic ester function. Solid squares correspond to the glass transition of the pure alternating diad, T_{gMH}, calculated by the application of experimental data to eqs 1 and 3.

Figure 4 shows the variation of the glass transition temperature of copolymers with the composition of the macromolecular chains expressed as the molar fraction of monomeric units. The glass transition temperature of MOA–HEMA copolymers is between those of the corresponding homopolymers and its variation with the average molar composition fits the straight line connecting the T_g of MOA and HEMA homopolymers. However, this is not the behavior of the systems prepared with flexible spacer groups, MOEA–HEMA and MOHA–HEMA. In both cases, there is a negative deviation of the experimental T_g with respect to the linear variation expected according to the assumption that the thermal properties of random copolymers, i.e., specific volume, chain stiffness, or molar cohesive energy, could be interpreted in terms of additive combinations of the properties of the corresponding homopolymers.[8,29] None of the three copolymerization systems fits the reciprocal additive rule suggested by Fox in the fifties.[30]

It is well established that increasing the length of a flexible alkyl side chain brings a monotonic decrease in the value of T_g in a series of vinyl polymeric homologues.[31] This phenomenon, caused by the increase of the free volume with increasing length of the side chain, gives rise to a reduction in steric hindrance to segmental mobility, which is often refered to as "internal plasticization".[32] Recently, Percec et al.[33,34] have analyzed in detail the effects of monomer structure and copolymer composition on the glass transition of binary liquid crystalline copoly(vinyl ether)s. They found positive and negative deviations of the experimental glass transition temperature from calculated additivity rules. These deviations were ascribed to an increase or decrease of free volume in the copolymer, this deviation being interpreted qualitatively on the basis of the chemical structure of the corresponding monomeric units. Systems in which T_g values exhibit a negative deviation from their calculated additive values are specific for copolymers with polar or mesogenic side groups separated from the macromolecular backbone by flexible spacers of highly dissimilar length.[34] Accordingly, as shown in Figure 4, in addition to the drastic decrease of the T_g for the MOEA–HEMA and MOHA–HEMA systems with respect to similar compositions of MOA–HEMA systems, a depression of the corresponding T_g values is clearly observed. Moreover, there are compositions that give T_g even lower than those of the corresponding homopolymers. The "internal plasticization" associated with the flexibility of the spacer group is better seen in the diagrams of Figure 5, which shows the difference between the experimental T_g and the value determined according to the classical additivity rule for mixtures, considering the fractional distribution of the comonomeric systems. As expected, the MOA–HEMA system fits adequately the binary combination rule but the MOEA–HEMA system deviates negatively and the deviation for the MOHA–HEMA system is even more noticeable. It is interesting to stress here that the maximum deviation is reached for a molar composition of the copolymer systems very close to $m_M = 0.5$, i.e., equimolecular copolymer systems, which also corresponds to the maximum value of the run number R (see Figure 1), approximately. This means that the maximum decrease of the experimental T_g value with respect to that expected from the additive contribution is associated with the higher alternance of sequences of MOEA and MOHA with HEMA units, i.e., for copolymer chains in which the interactions between the side groups

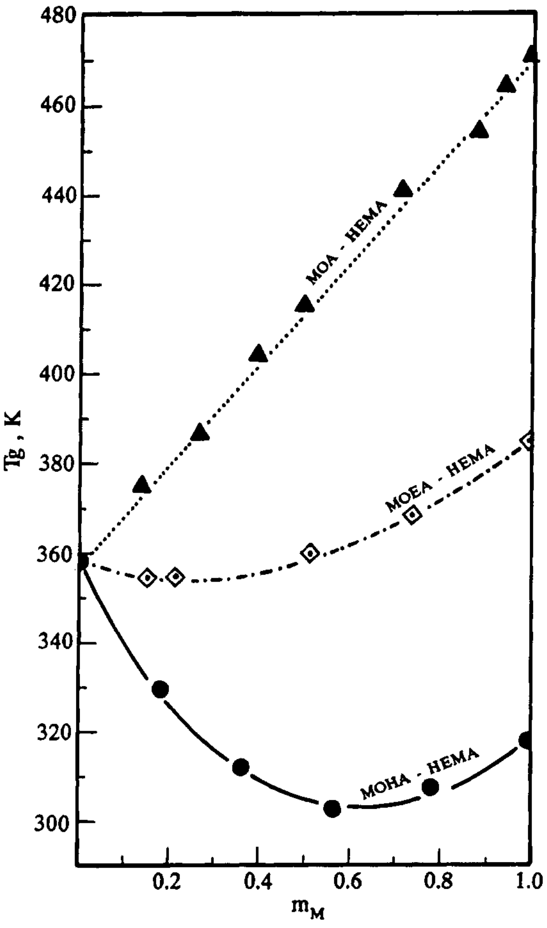


Figure 4. Variation of the T_g of copolymers prepared by the free-radical polymerization of MOA, MOEA, and MOHA with HEMA at low conversion with the average molar fraction of the corresponding acrylic monomer m_M in the copolymer chains.

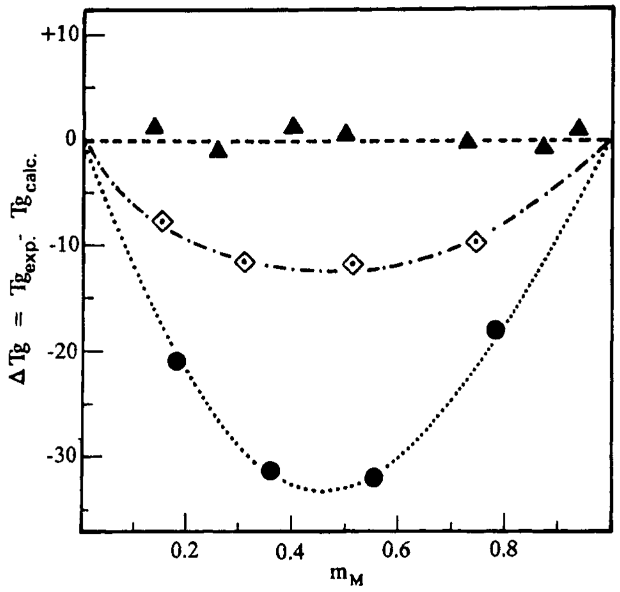


Figure 5. Deviation of the glass transition temperature of M–H copolymers with respect to the normal rule of additive contribution versus the molar composition of copolymer chains: (▲) MOA–HEMA; (◇) MOEA–HEMA; (●) MOHA–HEMA copolymer systems.

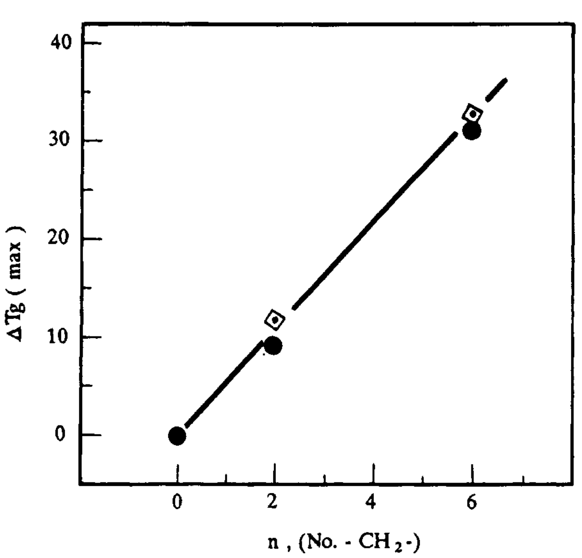


Figure 6. Dependence of the maximum deviation of T_g with respect to the additive contribution on the length of the alkylene spacer group. The MOA–HEMA system is taken as reference. (◇) Values from Figure 5; (●) difference between the T_g of the corresponding monomers, MOA, MOEA, and MOHA.

of the methacrylic monomeric units of interest are minima. Curiously, this analysis gives results rather similar to the variation of the T_g of the corresponding acrylic monomers with the length of the spacer group. In fact, as shown in Figure 6, there is an excellent linear relationship between the difference of the T_g of the monomers MOEA and MOHA with respect to that of MOA and the number of methylene groups of the spacer segment, as is the case with the maximum difference of the T_g for practically equimolecular systems. The interpretation of this result is that the flexibility of the spacer group is the only factor controlling the T_g of copolymer systems when dipolar interactions between neighboring units are absent, as happens with the free monomers.

We have observed that according to the experimental data shown in Figure 4, the T_g's of the random copolymers studied in this work do not fit a single mixture rule like that suggested in the fifties by Fox.[30] On the other hand, the thermodynamic theory proposed by Gibbs and DiMarzio[35] is based on the change of configurational entropy of the compounds as a function of the temperature. At equilibrium it postulates that the configurational entropy equals zero at glass formation. However, the theory does not consider the effect of the chemical structure and organization of the monomers on the mobility of a polymeric chain.[10,36] Several models have been suggested to take into consideration a microstructural structure and the effect of the distribution of monomeric units along the copolymer chains.[8,10,37] From a general point of view, in a copolymer formed from monomer M and H, there are four possible sequences of pairs of repeating units, which may be represented as MM, HH, MH, and HM diads, being the components of the system the two homopolymers and the alternating copolymer. Assuming the dominance of the nearest-neighbor interactions, the copolymer glass transition behavior would be determined by an additive contribution of the three types of comonomeric pairs.[7] In this sense, Hirooka and Kato[38] have pointed out that the sequential distribution in a copolymer chain affects the glass transition temperature, and Tonelli[39] has suggested that the effects in many statistical copolymers may have an intramolecular origin as specific molecular interactions between adjacent monomer units. Barton,[8] Uematsu and Honda,[40] and Hirooka and Kato[41] independently have suggested equations based on the "entropic theory" by extension of the pioneering work by DiMarzio and Gibbs,[7] taking into consideration the T_g's of both homopolymers and that of the alternating copolymer, T_{g12}, together with the average composition and sequence distribution specified by the values of the mole fractions of MM, HH, and MH or HM diads. Barton[8] by extension of the Gibbs–DiMarzio treatment has suggested the following empirical equation to describe the variation of T_g with the average composition and microstructural distribution of monomeric units of copolymer chains:

$$T_g = n_{MM}T_{gMM} + n_{HH}T_{gHH} + (n_{MH} + n_{HM})T_{gMH} \qquad (1)$$

where n_{ij} (i,j = M,H) 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:

$$n_{ij} = \frac{n_{ij}\alpha_{ij}}{\sum(n_{ij}\alpha_{ij})}$$

DiMarzio[42] has defined the bond fraction based on a lattice model which requires that each configuration of the 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 be in the main 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(methacrylic esters) would have a total of four flexible bonds per monomer unit, poly(acrylic esters) would have three flexible bonds, but 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.[42] According to the chemical structure of monomers MOA, MOEA, MOHA (Chart 1), and HEMA, the cor-

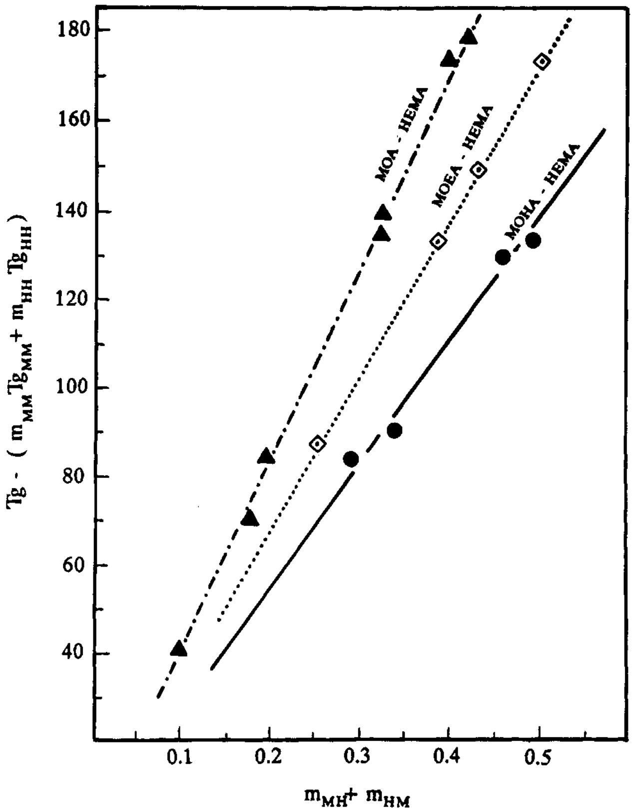


Figure 7. Application of the linearized expression of Barton's treatment (eq 2) to the copolymer systems.

responding repeating units give diads along the copolymer chains with a number of flexible bonds $\alpha_{MM} = \alpha_{MH} = \alpha_{HM} = \alpha_{HH} = 8$. The parameter n_{ij} can be calculated from the corresponding reactivity ratios by the application of well-known statistical considerations.[20,29] Equation 1 can be rearranged to give a linear equation as follows:

$$T_g - n_{MM}T_{gMM} - n_{HH}T_{gHH} = (n_{MH} + n_{HM})T_{gMH} \qquad (2)$$

The application of experimental data for the three copolymerization systems gives the diagrams drawn in Figure 7. From the slopes of the straight lines, values of $T_{gMOA-HEMA} = 410$ K, $T_{gMOEA-HEMA} = 347$ K, and $T_{gMOHA-HEMA} = 273$ K for the pure alternating diad were obtained. Recently, Suzuki and Mathot[41] have suggested a new expression of Barton's equation that allows us to determine with minimum data the glass transition temperature of copolymer systems by introducing the run number defined above according to the following equation:

$$T_g = m_M T_{gMM} + m_H T_{gHH} + (R/R^*)(T_g(R^*) - \bar{T}_g) \qquad (3)$$

where m_M and m_H are the molar fractions of monomeric units in the copolymer chains, T_{gMM} and T_{gHH} are the glass transition temperatures of the corresponding homopolymers, R is the run number, R^* is the value of R for $m_M = m_H = 0.5$, $T_g(R^*)$ is the glass transition temperature of an equimolecular random copolymer, and $\bar{T}_g$ is the average arithmetical value of the T_g of both homopolymers. If the T_g values of the copolymer samples are plotted against R, the diagrams shown in Figures 8 and 9 for the MOEA–HEMA and MOHA–HEMA systems are obtained. The solid line corresponds to the prediction via eq 3, and the dashed straight line corresponds to the middle point of the T_g values predicted for random copolymers at a given value of R. The extrapolation of this line to $R = 0$ gives the value of $\bar{T}_g$, whereas the extrapolation to $R = 100$ provides the T_{gMH} value. The values of each T_{gMH} for the two systems obtained from the diagrams of Figures 6 and 7 are $T_{gMOEA-HEMA} = 347.5$ K and $T_{gMOHA-HEMA} = 273$ K, which are similar to those obtained by the application of Barton's treatment. The $T_{gMH} = 408$ K for the MOA–HEMA system was obtained and reported elsewhere.[28]

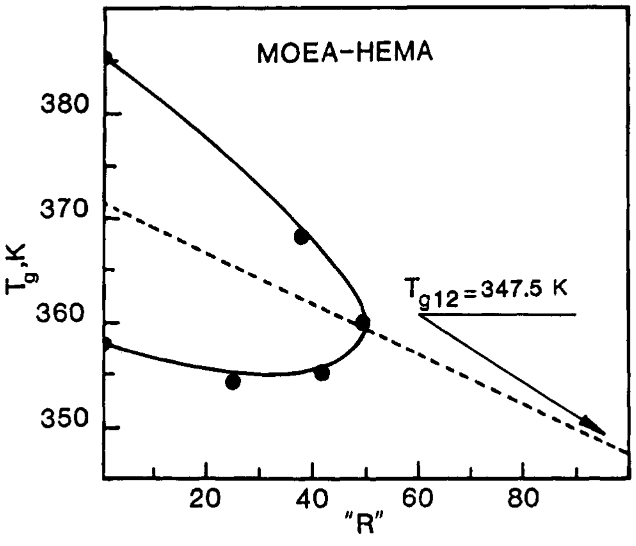


Figure 8. Variation of the T_g with the run number R for MOEA–HEMA copolymers. The elliptical line corresponds to the application of eq 3. The straight line corresponds to the mid values of T_g for each two points of the diagram with the same R, connecting T_{gMH} at $R = 0$ and $T_{gMOEA-HEMA}$ at $R = 100$.

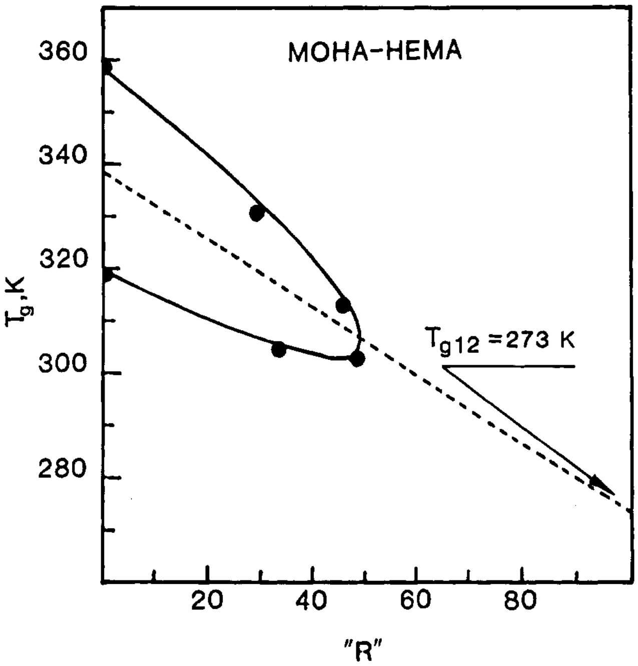


Figure 9. Variation of T_g with the run number R for MOHA–HEMA copolymers. The elliptical line and straight line have the same meaning as in Figure 8.

It is clear from the T_{gMH} values that the alternating diad, MH or HM, for the three systems presents a glass transition temperature sensibly lower than the arithmetical average of the T_g of both homopolymers in each case. The physical significance of these results is that the alternating diad shows a much higher flexibility than the one expected from the combination of both kinds of monomeric units, according to the glass transition temperature of the corresponding homopolymers. It is interesting to stress here that the T_{gMH} determined by the empirical treatments considered in this paper decreases with the length of the spacer group following the diagram drawn in Figure 3, with a similar trend to that of the T_g of the corresponding homopolymers.

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