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Secondary Relaxations of Swollen Polymethacrylates and Methacrylate Copolymer†

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Studies of relaxation behavior of a series of glassy polymethacrylates show that polar groups, comonomers and diluents affect the secondary transitions of the polymers in a similar manner as they affect the main transition regions. Polar groups in the side chain increase the transition temperatures. Increasing diluent causes a decrease in transition temperatures and some new secondary dispersions.

A systematic investigation of the mechanical relaxation behaviour in the glassy state is advantageously carried out on polymers of the polymethacrylate and polyacrylate type, since they allow the preparation of a large number of homologs with side chains of different chemical composition and substituted with different groups. Moreover, these polymers are usually amorphous, so that the relaxation behaviour is not complicated by the presence of the crystalline phase. The papers published so far in the field of polymethacrylates and polyacrylates can in principle be divided into three groups. In the first place, papers should be mentioned devoted to the relaxation behaviour of glassy polymers in the dry state. The initial studies concerning the effect of the hydrocarbon side chain length were carried out by Hoff *et al.*,¹ Illers,² and Heijboer;³ the latter author concentrated his attention on the investigation of the mobility of cycloalkyl substituents on the side chains of polymethacrylates.^{4,5} Dynamic mechanical measurements of some hydroxyalkyl methacrylates in the dry state were performed by Shen.^{6,7} The second group comprises works by Shen and co-workers^{6,8,9} who were dealing with the problem of the effect of low molecular weight compounds on secondary relaxations; a special

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attention was devoted to the problems of the effect of interactions of polar diluents with polar groups of the side chains of polymethacrylates. Finally, some attention has also been paid to the relaxation behaviour of the copolymers of methacrylates and acrylates with side chains of different composition.⁴

The above problems of the secondary relaxations of polymethacrylates were studied in our laboratory from all three viewpoints mentioned here. Our efforts were concentrated on the study of some selected methacrylate polymers and copolymers summarized in Table I. In our report we would like to recapitulate briefly the conclusions of our earlier works and to point out some problems as yet unsolved.

TABLE I
Polymethacrylates Studied

Side Chain	Polymer	
—COOCH ₃	PMMA	poly(methyl methacrylate)
—COOCH ₂ CH ₂ CH ₃	PPMA	poly(propyl methacrylate)
—COOCH ₂ CH ₂ CH ₂ CH ₃	PBuMA	poly(<i>n</i> -butyl methacrylate)
—COOCH ₂ CH ₂ CH ₂ CH ₂ CH ₂ CH ₃	PHMA	poly(<i>n</i> -hexyl methacrylate)
—COOCH ₂ CH ₂ OH	PHEMA	poly(2-hydroxyethyl methacrylate)
—COOCH ₂ CH ₂ OCH ₂ CH ₂ OH	PHEOEMA	poly(2-(hydroxyetoxy) ethyl methacrylate)
—COOCH ₂ CH ₂ OCH ₃	PMOEMA	poly(methoxyethyl methacrylate)
—COOCH ₂ CH ₂ OCH ₂ CH ₂ CH ₃	PPOEMA	poly(propoxyethyl methacrylate)
—COOH	PMAAc	polymethacrylic acid
	Copolymers	
	HEMA—MMA	2-hydroxyethyl methacrylate—methyl methacrylate
	HEMA—BuMA	2-hydroxyethyl methacrylate— <i>n</i> -butylmethacrylate
	BuMA—MMA	<i>n</i> -butyl methacrylate—methyl methacrylate
	HEMA—MAAc	2-hydroxyethyl methacrylate—methacrylic acid

POLYMETHACRYLATES IN THE DRY STATE

Besides α dispersion corresponding to the glass transition, polymethacrylates exhibit (Figure 1) the secondary (β_1) dispersion at temperatures about 10°C (1 Hz) and the low-temperature (γ) dispersion at temperatures lower than —130°C.^{10,11} The low-temperature relaxation above the liquid nitrogen temperature is missing for PMMA and PEtMA, since the alkyl group of the

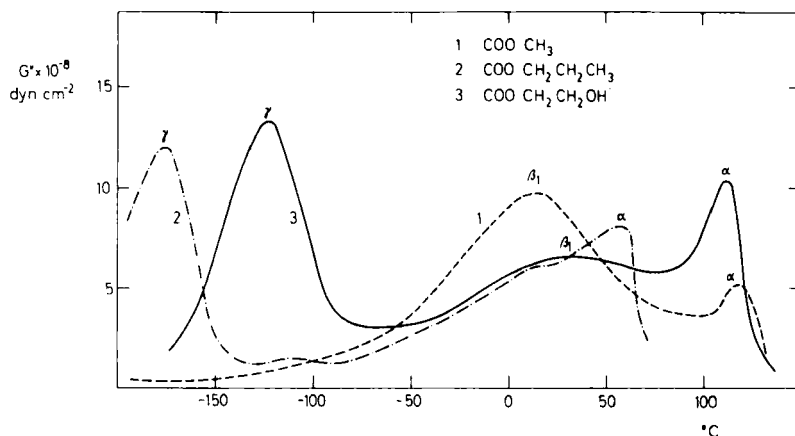


FIGURE 1 Temperature dependence of the loss modulus of poly(methyl methacrylate)(1), poly(propyl methacrylate)(2) and poly(2-hydroxyethyl methacrylate)(3) (cf. Ref.^{10,11}).

side chain possesses less than three units.¹ On the other hand, for polymers with a longer side chain the α and β_1 relaxation regions overlap⁴ owing to the temperature decrease of the glass transition T_g . It is also well known¹² that the introduction of a polar group into the side chain causes an increase in the glass transition temperature, and consequently in T_α . We found¹¹ (Figure 1) that the substitution of the end methyl group in PPMA with the hydroxyl group (PHEMA) leads to an increase in temperature not only of the main (α) but also of both secondary transitions: the β_1 dispersion assigned to the hindered rotation of the $-\text{COOR}$ side groups is shifted from 15°C to 28°C, and the γ dispersion attributed to the rotational isomerism of the $-\text{R}$ group is shifted from -175°C to -130°C . Thus, it is easy to see that the hydroxyl group at the end of the side chain affects the mobility both of the main chain and of the side chain $-\text{COOR}$ as well as of its end part $-\text{R}$.

A similar effect of the hydroxyl group was also observed when it was attached to longer side chains, as follows from a comparison between PHMA¹³ and PHEOEMA^{11,14} (Figure 2); the temperature position of the respective dispersions is approximately the same as that of PPMA or PHEMA, but their intensities are lower. Since PHEOEMA contains an ether oxygen inside the side chain, the specific effect of the oxygen had to be determined in more detail. We regarded¹⁵ poly(propoxyethyl methacrylate) and poly(methoxyethyl methacrylate) as models suitable for this purpose. Both polymers exhibit (Figure 2) dispersion near -150°C , and PPOEMA exhibits another dispersion at a temperature lower than -175°C which was missing for the polymer with shorter side chains. It may be inferred that the dispersion detected at a lower temperature corresponds to the hindered rotation of the propyl group of

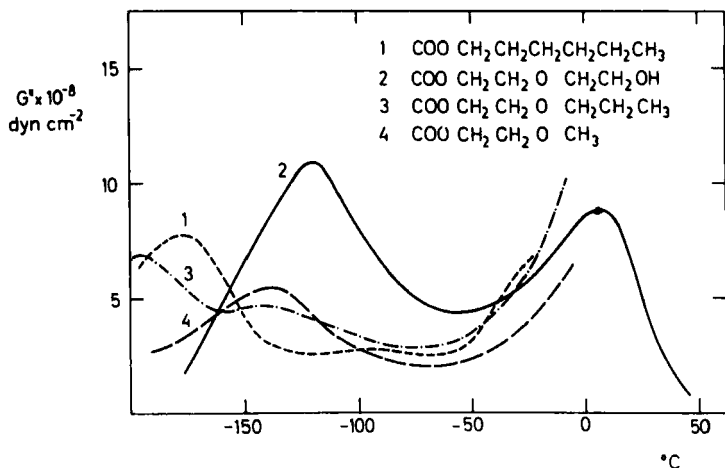


FIGURE 2 Temperature dependence of the loss modulus of poly(hexyl methacrylate)(1), poly(2-(hydroxyethoxy)ethyl methacrylate)(2), poly(propoxyethyl methacrylate)(3) and poly(methoxyethyl methacrylate)(4) (cf. Ref.^{11,13,15}).

PPOEMA bonded to the ether oxygen, and is therefore missing for PMOEMA ; the other dispersion is probably due to hindered rotations of the central parts of the side chains of both polymers. It seems therefore that the substitution of the methylene group with the oxygen inside the side chain of PHMA has as the consequence the splitting of the low-temperature relaxation of PHMA into two parts, namely, one at a temperature lower than $T_{\gamma} = -175^{\circ}$, the other at a higher temperature. For all the three polymers mentioned here having side chains with six units bonded to the COO— group, the β_1 dispersion could not be identified owing to its overlapping by the main transition region.

SYSTEM POLYMER—LOW MOLECULAR WEIGHT COMPOUND

The low-temperature relaxation behaviour of polymethacrylates containing the hydroxyl group in the side chain changes markedly in the presence of very low concentrations of diluents, particularly water. These changes appear in the regions of α and γ dispersion and also near -80°C . It was found¹⁴ that PHEMA with very low water concentrations exhibits a new secondary dispersion β_{sw} at -70°C , which is shifted to lower temperatures with increasing diluent content, and the intensity of which markedly increases (Figures 3, 4). At the same time, γ relaxation assigned to the hindered rotations of the hydroxyethyl part of the side chain is first reduced and then vanishes altogether.

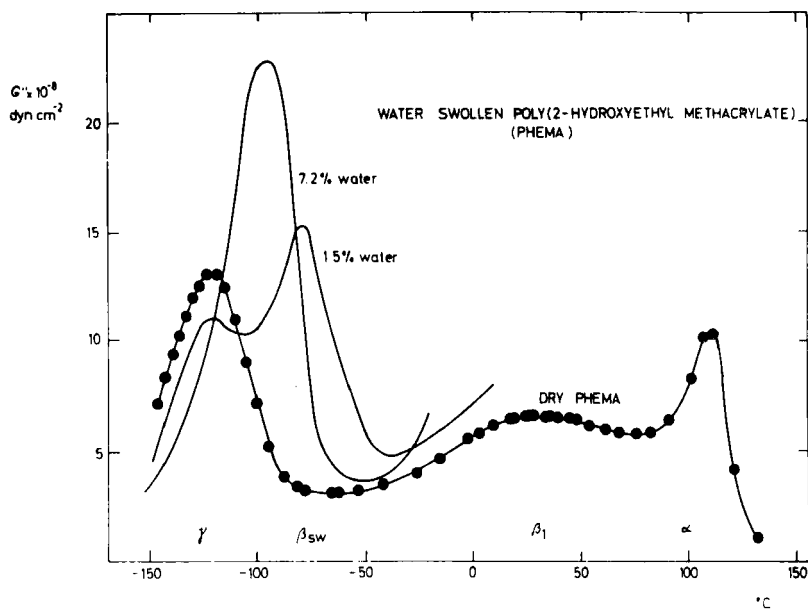


FIGURE 3 Temperature dependence of the loss modulus of poly(2-hydroxyethyl methacrylate) in the dry state and swollen with 1.5 and 7 wt. % water (cf. Ref.¹⁶).

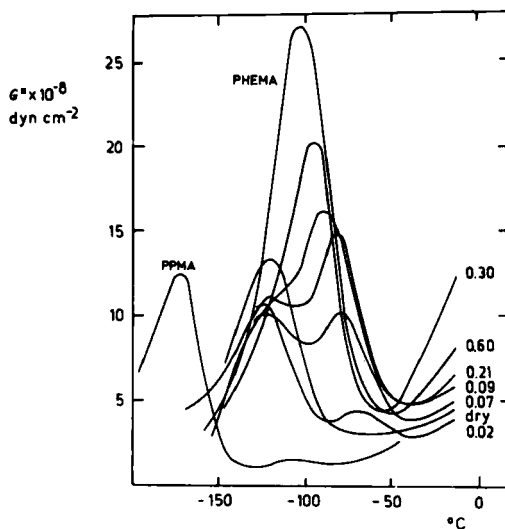


FIGURE 4 Effect of molar fraction (related to the molecular weight of the monomer repeat unit) of water on the relaxation behaviour of PHEMA in the region of the γ and β_{sw} maximum. For sake of comparison the loss modulus of dry poly (propyl methacrylate) is given (cf. Ref.¹⁴).

A conclusion was forwarded therefore¹⁴ that the interaction of the diluent molecule with the hydroxyl, or also with the ester group of the side chain, leads to a transformation of the γ process into the β_{sw} process.

Considerable attention was devoted later to the alterations in the parameters of the β_{sw} dispersion of PHEMA with the content of water and of other low molecular weight compounds.¹⁷⁻¹⁹ It was found¹⁸ that in the low concentration region the systems PHEMA-water, -ethylene glycol, -glycerin have higher β_{sw} maxima than those containing monohydric alcohols, acetone, pyridine, and chloroform. The more pronounced effect of diluents of the first group was ascribed¹⁸ to the ability of their molecules to interact (by forming hydrogen bonds) with two or more side chains of PHEMA. A similar conclusion about the bonding of one water molecule to two amide groups by means of two hydrogen bonds was formulated²⁰ earlier on the basis of measurements of the low-temperature relaxations of polycapromide containing water.

The concentration dependence of temperature and intensity of the β_{sw} and α dispersions of PHEMA was investigated in detail¹⁹ on samples swollen in ethylene glycol (Figure 5a), formamide (Figure 5b), *n*-propanol, and water. If the diluent did not separate as the second phase at the temperatures of measurements, the temperature of both dispersions decreased with increasing volume fraction of diluent v_1 and approached T_a of the diluent. Figure 6 shows the concentration dependence of T_a and $T_{\beta_{sw}}$ of the system PHEMA-ethylene glycol which remained homogeneous over the whole range of concentrations measured, and of the system PHEMA-water where phase separation at v_1 near 0.25 prevents a further decrease in the dispersion temperatures with concentration. The concentration dependence of T_a of the system PHEMA-ethylene glycol could be described by an equation derived by Bueche and Kelley:²¹

$$T_a = [T_{a2} + (k_a T_{a1} - T_{a2})v_1] / [1 + (k_a - 1)v_1], \quad (1)$$

where k_a is a constant and T_a, T_{a1}, T_{a2} are temperatures of the main transition of the swollen PHEMA, dry PHEMA and diluent read off as the peak of the loss maximum G'' (1 Hz). In the concentration range in which no signs of the separation of diluent were seen, Eq. (1) could be used also for systems containing formamide and propanol; the values of constant k_a thus obtained are given in Table II. For the system PHEMA-ethylene glycol, k_a corresponds to the ratio of the expansion coefficients of the free volumes of diluent and polymer, which indicates the additivity of free volumes of the components.

Eq. (1) also allowed a description of the concentration dependence of $T_{\beta_{sw}}$ (substituted for T_{a2}), even though the resulting constant $k_{\beta_{sw}}$ cannot be assigned the original meaning because the extent of the β_{sw} process is proportional to the content of diluent, and dry PHEMA does not exhibit this

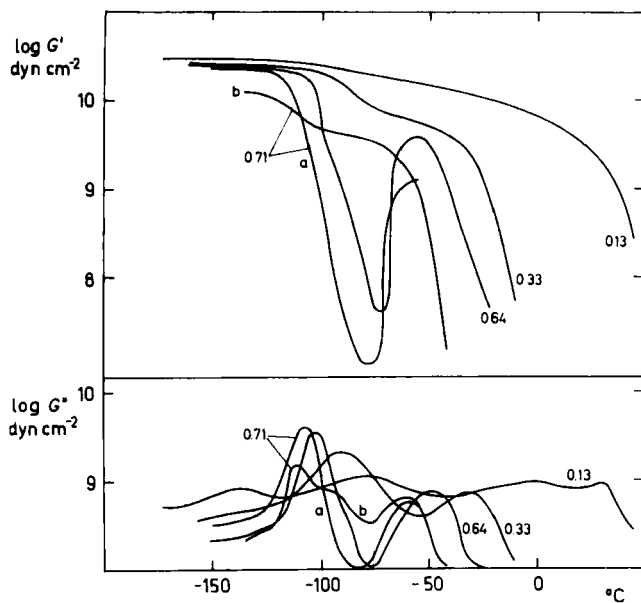
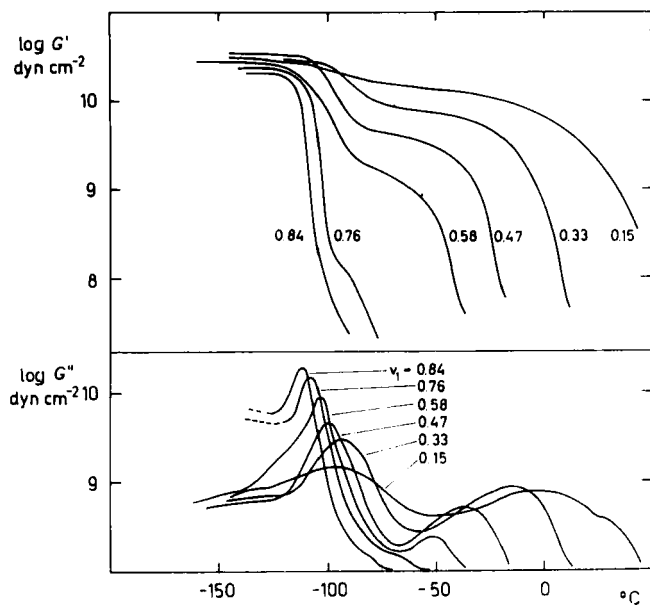


FIGURE 5 Effect of volume fraction of ethylene glycol (a) and formamide (b) on the temperature dependence of the moduli G' and G'' of PHEMA (cf. Ref.¹⁹).

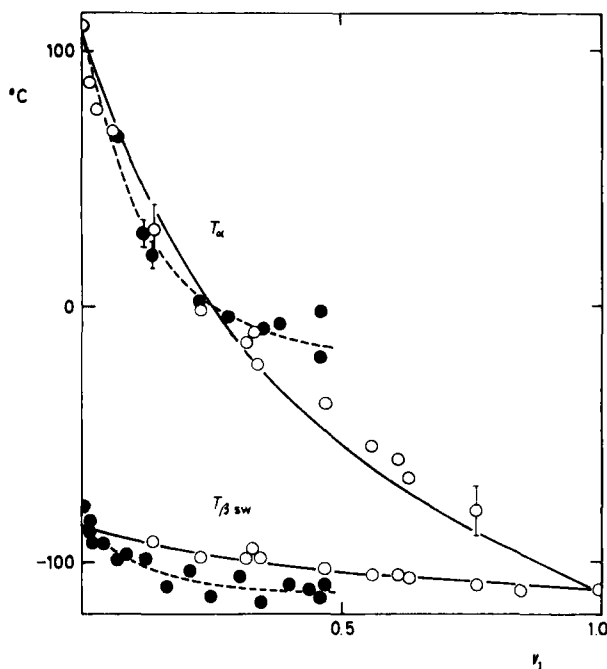


FIGURE 6 Effect of the volume fraction of water (●) and ethylene glycol (○) on T_{α} and $T_{\beta sw}$ of PHEMA. Full lines calculated according to Eq. (1) (cf. Ref.¹⁹).

TABLE II
Coefficients k_{β} and $k_{\beta sw}$ of Eq. (1) and Temperature $T^{\circ}_{\beta sw}$ for
Poly (2-hydroxyethyl Methacrylate)-Diluent Systems¹⁹

Diluent	k_{α}	$k_{\beta sw}$	$T^{\circ}_{\beta sw}$ °C
Ethylene glycol	3.0	2.6	-86
Formamide	3.6	3.6	-60
<i>n</i> -Propanol	(2.1)	(1.1)	(-80)

dispersion and a corresponding rise in the expansion coefficient. It was nevertheless possible, by means of Eq. (1), to determine the limiting values of $T_{\beta sw}$ for the volume fraction of the diluent $v_1 = 0$ and $v_1 = 1$. It can be seen from Table II that $T^{\circ}_{\beta sw}$ for $v_1 = 0$ depends on the type of diluent and is not a characteristic of the polymer itself. The experimental data also revealed that β_{sw} dispersion is always located at temperatures higher than the glass transition of the diluent.

If on cooling, partial separation of the diluent in the form of the second phase occurs in the system PHEMA-diluent, further maxima corresponding

to melting or glass transition in the diluent phase may be observed on the temperature dependence of the loss modulus.¹⁹ In this respect, the temperature dependences of the G' and G'' moduli of the system PHEMA-formamide are illustrative (Figure 5b). At $v_1 > 0.60$ the modulus G' decreases by two orders of magnitude between -120 and -80°C ; this is followed by a steep increase with temperature up to the glassy state at -55°C ; only if the temperature is increased further does the storage modulus drop and the system passes into the rubberlike state. The cause of the formation of a maximum on the G' vs. T curve is the separation and crystallization of a part of formamide in the originally supercooled homogeneous system. If the system is cooled again from -55°C , then in the second cycle of measurements the storage modulus decreases monotonically with temperature (Figure 5b; curve 0.71, b), since the separated formamide is present in the stable form.

The effect of ethylene glycol concentration on the overall change of the modulus G' from the glassy into the rubberlike state is shown in Figure 7, where G'_b represents the boundary between the β_{sw} and α dispersions, G_e is the equilibrium modulus in the rubberlike state, and G'_{eN} is higher than the equilibrium modulus by the contribution of unrelaxed entanglements. It is obvious that the decrease in the storage modulus caused by the β_{sw} process, $\Delta G'_{\beta sw} = G'_{-130^\circ\text{C}} - G'_b$, increases with the diluent concentration and for $v_1 > 0.5$ exceeds

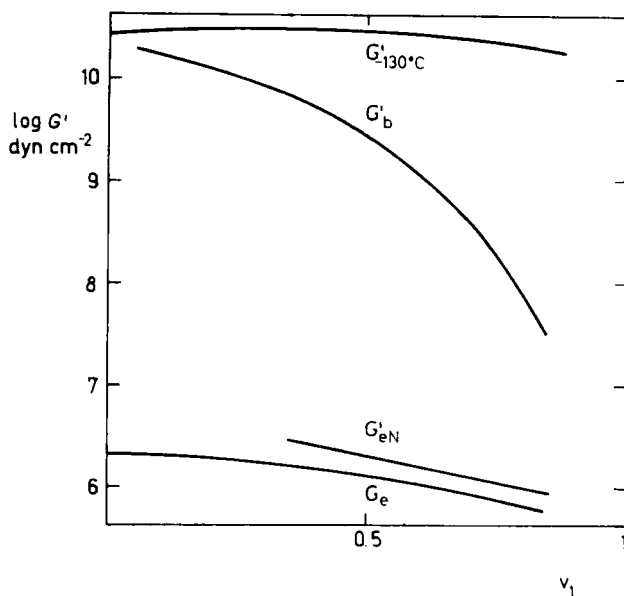


FIGURE 7 Effect of concentration of ethylene glycol on the decrease in the modulus G' from the glassy to the rubberlike state (cf. text) (cf. Ref.¹⁹).

considerably the value of one logarithmic decade. If one denotes similarly $\Delta G'_a = G'_b - G'_{eN}$, it can be seen that $\Delta G'_{\beta_{sw}}$ increases at the expense of $\Delta G'_a$ and at higher diluent concentrations represents an essential part of the overall decrease in the modulus of elasticity. From the data obtained a conclusion¹⁹ was drawn that at $T_{\beta_{sw}}$ motion of the diluent molecules sets in along with the motion of the side chains, and contributes largely to the intensity of the β_{sw} dispersion.

Changes similar to that in the low-temperature relaxation region are also probably induced by diluent in the region of the β_1 relaxation.^{11,22} However, it is very difficult to obtain reliable data, since this relaxation is overlapped by the main transition already in the presence of a very low concentration of the diluents. An example of alterations of the G'' vs. T dependence due to water which seem to be qualitatively analogous to that in the low-temperature relaxation region is given in Figure 8a. These results led to the view that owing to the interaction of a molecule of the diluent with the hydroxyl or ester group the hindered rotations of the R— and —COO— groups set in at elevated temperatures. The temperature decreases with increasing concentration of diluents also in the case of the β_1 dispersion (Figure 8b). The effect of the diluent concentration on the temperature location of PHEMA dispersions can be seen schematically in Figure 9.

A specific behaviour during the incorporation of diluents was found for PHEOEMA¹³ (Figure 10). The low-temperature dispersion is also reduced by swelling, but at temperatures higher than T_γ two secondary dispersions are

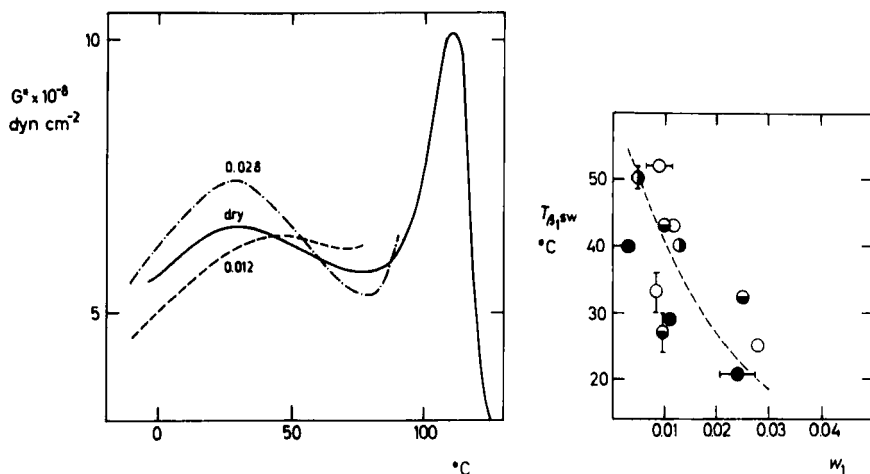


FIGURE 8 Effect of weight fraction of diluents on the temperature position of the β_1 dispersion of PHEMA (cf. Ref.¹¹). (a) water; (b) (○) water, (●) propanol, (◐) chloroform, (◑) diethylene glycol.

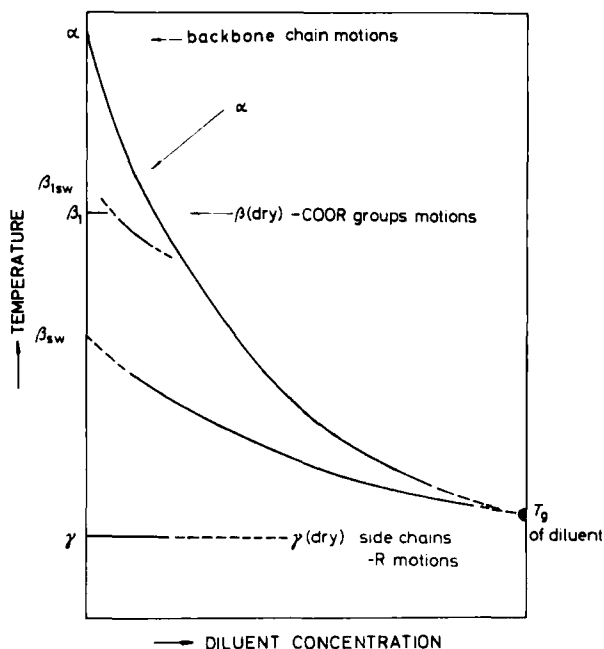


FIGURE 9 Schematic view of the effect of diluent concentration on the temperature position of the dispersions of poly(2-hydroxyethyl methacrylate).

formed, viz., one at -90°C and the other—designated β_{sw} —at temperatures lower than -40°C . The intensity of both dispersions increases with the diluent concentration; dispersion β_{sw} is shifted to lower temperatures while the dispersion at -90°C does not change its temperature position, so that both dispersions eventually coincide. The onset of mobility of the side chains in two stages is probably a consequence of the presence of ether oxygen inside the side chains. A detailed molecular mechanism of these dispersions is not yet quite clear.

COPOLYMERS

In the copolymers HEMA-BuMA the low-temperature relaxations of side chains of the components somewhat affect²³ each other (Figure 11). With increasing concentration of BuMA in HEMA the γ maximum of HEMA becomes lower and asymmetrically extended toward lower temperatures. At a molar fraction of BuMA from 0.4 to 0.6, two loss maxima arise corresponding to the BuMA and HEMA components. Copolymers having the molar fraction

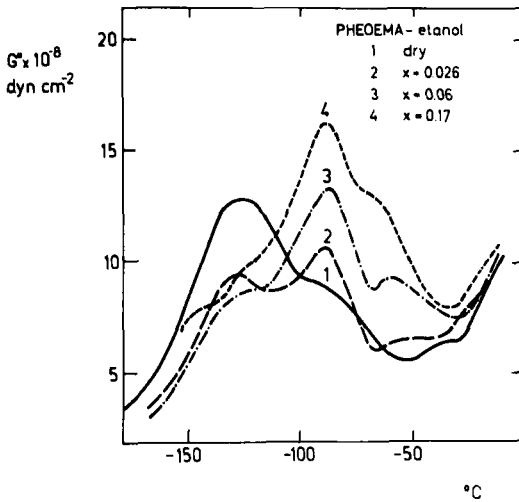
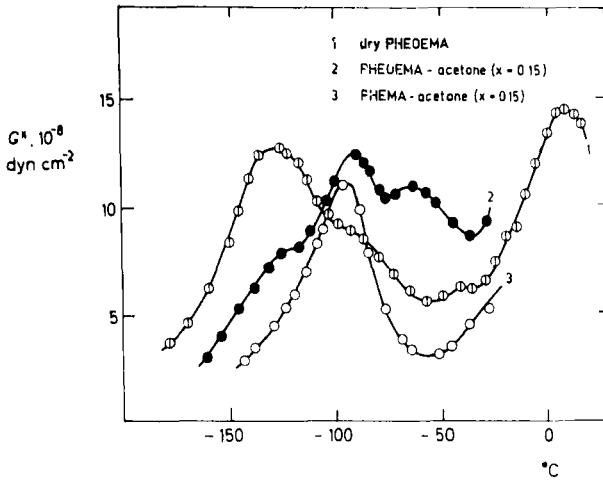


FIGURE 10 Effect of the molar fraction of acetone (a) and ethanol (b) on the temperature dependence of the loss modulus of PHEOEMA (cf. Ref.¹³).

of BuMA higher than 0.60 exhibit only the γ maximum of BuMA deformed toward higher temperatures. It is evident, therefore, that the incorporation of monomer repeat units of the second component into polyads of the predominant component does not lead to the possible limiting cases, i.e. either to the formation of the second loss maximum or to a systematic shift of the existing loss maximum on the temperature scale according to the average

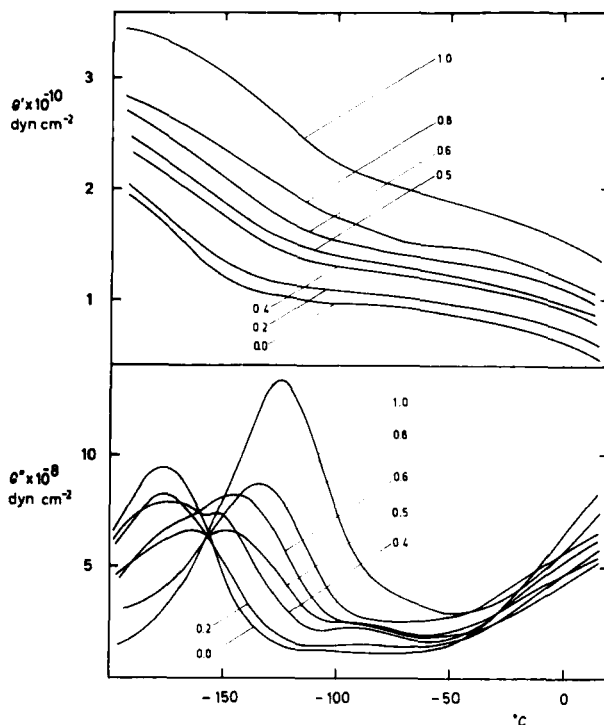


FIGURE 11 Temperature dependence of the moduli G' and G'' of the copolymers HEMA-BuMA (cf. Ref.²³). The values given in the Figure indicate molar fractions (related to the molecular weight of the monomer repeat units) of HEMA in the copolymer.

composition, as it is the case for the main transition²⁴ (Figure 12). The γ dispersion of copolymers is characterized by broadening of the spectrum of relaxation times, which indicates an extension of the scale of conditions (intermolecular forces and steric hindrances) under which the relaxation motions of the side chains take place. The existence of two loss maxima at the equimolar composition indicates that the relaxation motion of the side chains in the polyads occurs under conditions similar to those in homopolymers (changes in the temperature position with respect to the maxima of homopolymers can to a certain extent be assigned to overlapping of the peaks). The presence of water in the equimolar copolymer (Figure 13) leads to the transformation of the γ process of the HEMA components into the β_{sw} process in a similar way as in PHEMA, while the γ dispersion of the BuMA component remains preserved at -175°C similarly to the homopolymer. It can be deduced, therefore, that the mobility of the side chains is affected by the composition of copolymers; however, it is not a function of the average composition, but probably depends on the close surroundings of the respective side chains.

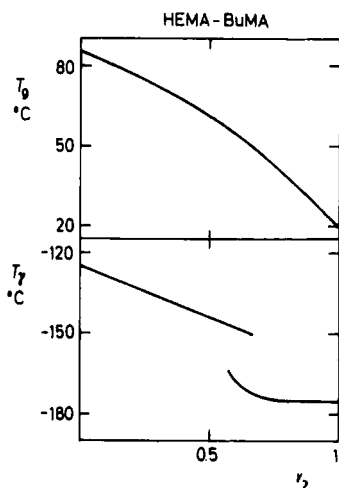


FIGURE 12 Dependence of T_g and T_γ on the volume fraction of BuMA in the copolymers HEMA-BuMA (cf. Ref.²³).

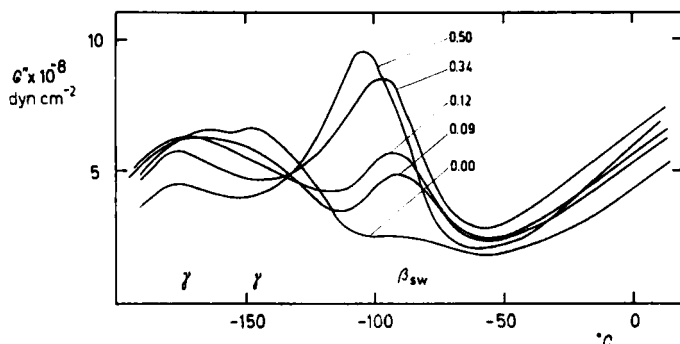


FIGURE 13 Effect of water on the temperature dependence of the loss modulus of the equimolar copolymer HEMA-BuMA. Water content is given as the molar fraction of water related to the HEMA component (cf. Ref.²³).

To elucidate the effect of the composition and concentration of a certain type of side chains on the temperature and intensity of γ dispersion, the copolymers HEMA-MMA,¹⁰ BuMA-MMA¹⁰ (Figure 14) and HEMA-MAAc²⁵ (Figure 15) were investigated. No overlapping of two low-temperature dispersions could be observed for those copolymers, because above the liquid nitrogen temperature PMMA and PMAAc do not exhibit any γ relaxation. Judging by the height of the loss maximum G'' and by the change in the modulus $\Delta G'$ the intensity of the γ dispersion of the copolymers appeared

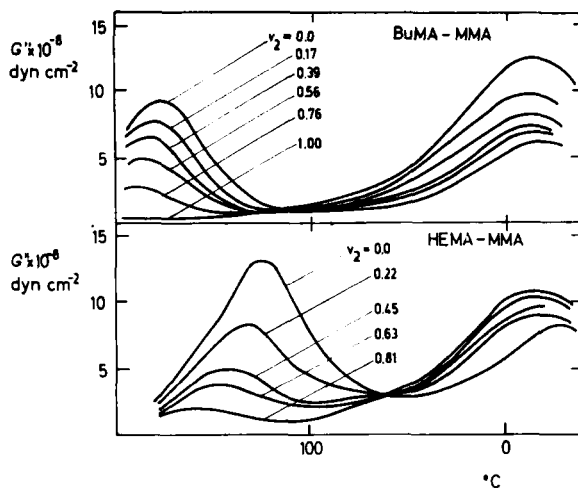


FIGURE 14 Effect of the volume fraction of MMA in the copolymers BuMA-MMA (upper Figure) and HEMA-MMA (lower Figure) on the temperature dependence of the loss modulus (cf. Ref.¹⁰).

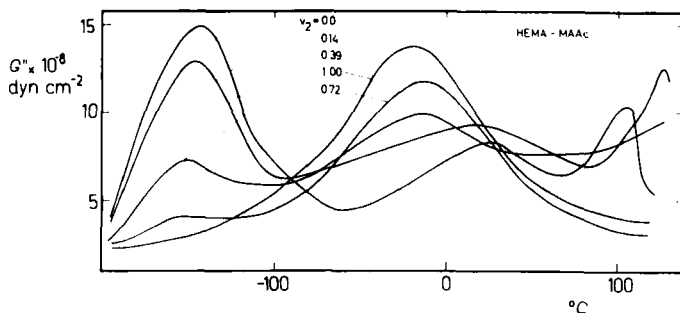


FIGURE 15 Effect of the volume fraction of MAAC in the copolymers with HEMA on the temperature dependence of the loss modulus (cf. Ref.²⁵).

proportional to the volume fraction of HEMA or BuMA (Figures 16, 17). Consequently, the relaxation strength of the side chains (energy losses per one side chain) seems to be constant for a certain type of the side chains and independent of their concentration in the polymer.

The dependence of T_γ on the volume fraction of MMA or MAAC is given in Figure 18. In our earlier paper¹⁰ we tried to interpret the decrease in T_γ in terms of an increase in free volume available to the side chains $\text{HO}-\text{CH}_2\text{CH}_2-$ or $\text{CH}_3-(\text{CH}_2)_3-$ due to the dilution with the MMA component. It seems natural that the side chains of monomer repeat units adjacent to the MMA

units are less sterically hindered. On the other hand, however, it can be seen from Figure 18 that the effect of MAAC is weaker even though the MAAC side group is smaller than that of MMA. It is obvious, therefore, that the decrease in the steric hindrances of the γ process is compensated for to a large extent by an interaction of the remaining hydroxyethyl side chains with the carboxylic groups.²⁵ The resulting temperature position of the γ dispersion is thus dependent on the relative effect of both factors, i.e. of the steric hindrances and intermolecular interaction.

While the temperatures of the β_1 dispersion of PHEMA, PMMA and PBuMA differ only little, T_{β_1} of PMMAc is approximately 48° lower than that of PHEMA (Figure 15). Figure 19 shows the continuous decrease in T_{β_1} of the copolymers HEMA-MAAc from 28°C for PHEMA to -20°C for PMMAc.

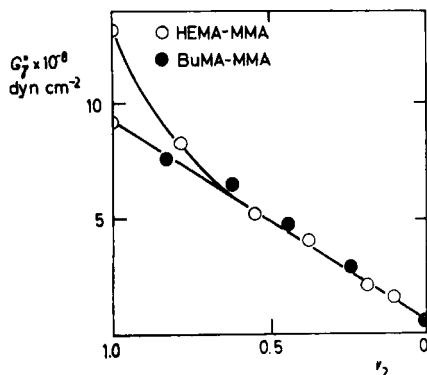


FIGURE 16 Effect of the volume fraction of MMA on the height of the γ maximum of the copolymers HEMA-MMA and BuMA-MMA (cf. Ref.¹⁰).

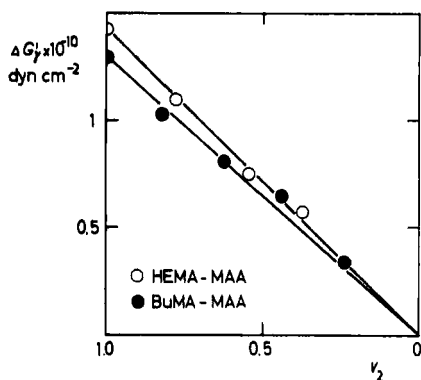


FIGURE 17 Effect of the volume fraction of MMA on the drop in the modulus G' in the region of the γ maximum of the copolymers HEMA-MMA and BuMA-MMA (cf. Ref.¹⁰).

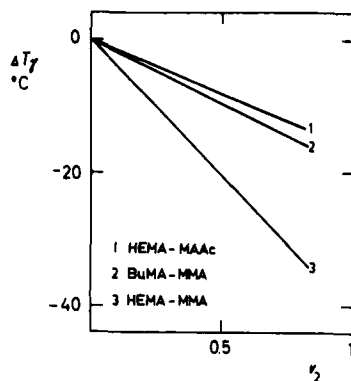


FIGURE 18 Effect of the volume fraction of MMAc or MMA on the decrease in T_γ of the copolymers with HEMA and BuMA (cf. data. Ref.^{10,25}).

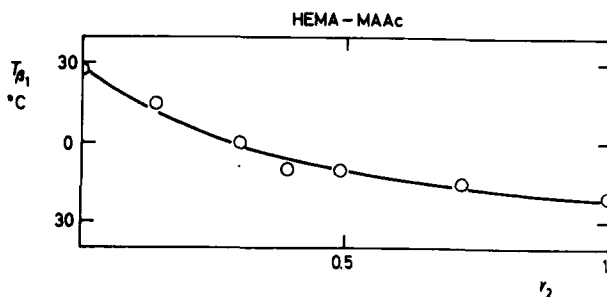


FIGURE 19 Dependence of T_{β_1} of the copolymers HEMA-MAAc on the volume fraction of MAAc (cf. Ref.²⁵).

The curve thus obtained could be described²⁵ by means of Eq. (1) using the parameter $k_{\beta_1} = 3$. Although in the region of the β_1 dispersion of polymethacrylates an increase in the expansion coefficient indicating an increase in free volume was detected,²⁶ the value for PMMAc is not known, and k_{β_1} cannot therefore be compared with the free-volume characteristics. In contrast with the γ process, it can be seen for the β_1 process that the decrease in steric hindrances prevails over the increase in the intermolecular forces due to the incorporation of MAAc. The increase in the MAAc content leads also to a continuous increase in both the height and area of the β_1 maximum (Figure 15), so that the loss maximum of PMAAc is approximately twice as high as the corresponding maximum of PHEMA. Since the changes of the intensity and temperature of the β_1 dispersion with composition are continuous, it can be inferred that the corresponding molecular motion in PMMAc is analogous to that in PHEMA, and thus also in polyalkyl metha-

crylates. Owing to the low value of $T_{\beta 1}$ and high energy losses in PMAAc it seems likely²⁵ that some local motions of the main chains participate in the β_1 process.

It follows from the data collected here that some factors, such as polar groups, comonomers, and diluents affect the secondary transitions of glassy polymethacrylates in a similar way as they do the main transition region. The introduction of polar groups into the side chains increases T_g as well as T_γ and $T_{\beta 1}$. Temperatures T_g and $T_{\beta sw}$ of PHEMA decrease with increasing diluent content converging to the glass transition temperature of the diluent. Some concentration dependences, such as e.g. $T_{\beta sw}$ vs. v_1 or $T_{\beta 1}$ vs. volume fraction of MAAC, may formally be described by Eq. (1) originally derived for similar dependences of the glass transition temperature. On the other hand, glassy polymethacrylates exhibit some specific features, of which the formation of new secondary dispersions due to diluents should be mentioned in the first place. At present it seems that besides collecting experimental data there is an urgent need for a molecular theory which would cover both the main transition region and the region of secondary transitions in the glassy state.

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