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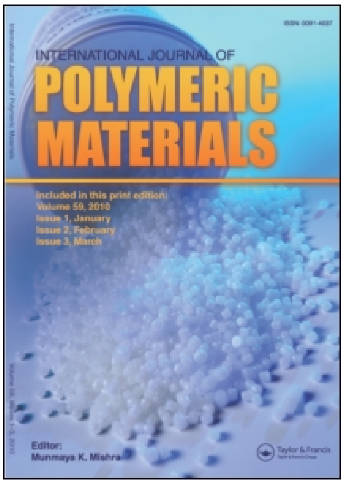

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# Effect of the Composition of the Copolymers of 2-Hydroxyethyl Methacrylate and n-Butyl Methacrylate on the Parameters of the Low-Temperature Relaxation Motions of the Side Chains

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The random copolymers of 2-hydroxyethyl methacrylate and n-butyl methacrylate were used to investigate the effect of the concentration of the side chains on the parameters of their low-temperature relaxation motions. The dynamic mechanical measurements were performed on a torsion pendulum at a frequency about 1 Hz in the temperature region from −196 to 20°C. The presence of the second component (up to a content of about 40% by weight) causes a decrease in the height and a deformation of the low-temperature loss maximum of the prevailing component, while the shift of the loss maximum on the temperature axis is not pronounced. Two loss maxima, analogous to the loss maxima of the homopolymers, appear only at compositions close to the equimolar composition; the sorbed water prevailingly affects the mobility of the 2-hydroxyethyl methacrylate side chains. The results indicate that the low-temperature relaxation motion of the side chains in polymethacrylates depends on the interaction of the individual side chains with their close surroundings, and not on the average composition of the copolymers.

## INTRODUCTION

Our earlier work,[1] also devoted to a systematic study of the relaxation motions of the side chains in polymethacrylates, referred to the effect of the concentration of the identical side chains on the parameters of the resulting low-temperature (γ) dispersion. In the present work we have attempted to establish in which way the side chains of different composition affect each other as to their low-temperature relaxation motions. For this purpose, the copolymers of 2-hydroxyethyl methacrylate (HEMA) and n-butyl methacrylate (BMA) were selected, since the low-temperature dispersions of homopolymers occur at different temperatures, i.e. −125°C (1 Hz) and −175°C (1 Hz), and within the temperature region from −196 to 20°C the dry polymers do not show any further dispersions[1] which would complicate an interpretation of the data acquired in the measurements.

## EXPERIMENTAL PART

Polymerization and preparation of samples of polymethacrylates were performed under conditions similar to those described[2] earlier. Isothermal polymerization was carried out at 50°C (about 6 hours); the concentration of isopropyl percarbonate used as initiator was approximately $3 \times 10^{-6}$ mol $cm^{-3}$ of the polymerization mixture. To facilitate the preparation of samples for measurements, 30% by vol. (related to the final polymer) of the mixture water-diethyl oxalate was used as diluent. The composition of the mixture was so chosen as to preclude phase separation during polymerization. The concentration of ethylene dimethacrylate as the crosslinking agent was $2 \times 10^{-5}$ mol $cm^{-3}$ and was constant in all samples. The samples, approximately 70 × 6 × 1.5 mm in size, were extracted at room temperature in an excess of ethanol and dried to constant weight *in vacuo* at 50°C. The temperature dependence of the components of the complex shear modulus of elasticity was determined on a torsion pendulum using the method of free vibrations at a frequency about 1 Hz.

## RESULTS AND DISCUSSION

Within the temperature range from −196 to 20°C, all polymers under investigation exhibited only low-temperature (γ) loss maxima, caused (cf. Ref. 1, 3) by hindered rotatory motions of side chains bound to the groups COO, i.e. $CH_3—(CH_2)_3—$ or $HO—(CH_2)_2—$ (Figure 1). Moreover, with some copolymers a slight indication of the secondary (β) loss maximum at a temperature about −80°C was observed, which demonstrated the presence of a very small amount of low-molecular weight components in the samples.[3,4] The first BMA fractions in the copolymers with HEMA lead to a decrease in the height of the low-temperature loss maximum, $G''\gamma$, and the corresponding

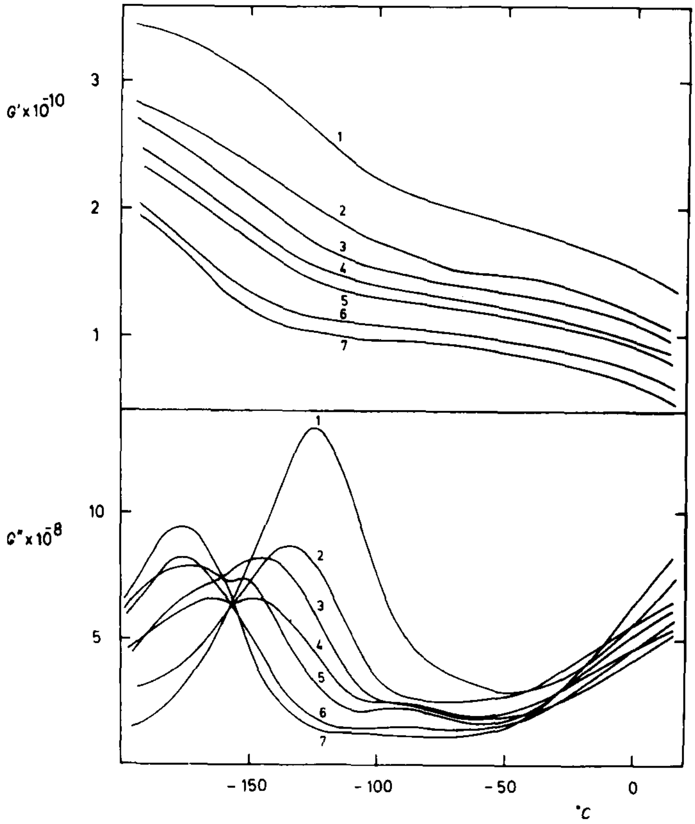

FIGURE 1 Temperature dependence of the storage modulus $G'$ (dyn cm$^{-2}$) and loss modulus $G''$ (dyn cm$^{-2}$) of the copolymers of 2-hydroxyethyl methacrylate and n-butyl methacrylate.

Molar fraction of 2-hydroxyethyl methacrylate $x_H$ (related to the molecular weight of the monomeric units):

1 1.00; 2 0.80; 3 0.60; 4 0.50; 5 0.40; 6 0.20; 7 0.00.

temperature, $T\gamma$, an asymmetric extension of the loss maximum in the direction of lower temperatures, and a drop of the storage modulus $G'$ over the whole temperature interval under study. At a molar fraction of HEMA $x_H = 0.8$, only one low-temperature loss maximum could still be seen on the temperature course of the loss modulus [$x_H = n_H/(n_H + n_B)$, where $n_H$ and $n_B$, respectively, denote the number of moles of the monometric units of HEMA and BMA in a volume unit of the copolymer]. A pronounced decrease in the height of the $\gamma$ loss maximum of HEMA, observed if small amounts of the copolymerization component are added, is similar to that found for the copolymers HEMA-methyl methacrylate.[1] Whereas at $x_H = 0.6$ only a slight indication of the low-temperature loss maximum BMA can be seen, at $x_H = 0.5$ and 0.4 there are two quite distinct loss maxima, which of course overlap to a great extent. This overlapping has as a consequence that the loss peak of the HEMA or BMA component is apparently shifted to a lower or higher temperature, respectively. However, the results obtained so far indicate unambiguously that within the range $0.6 \geq x_H \geq 0.4$ there exist in the copolymers two discernible kinds of low-temperature relaxation processes. The low content of HEMA ($x_H = 0.2$) in BMA leads to a depression of the low-temperature loss maximum of BMA and to its extension in the direction of higher temperatures; $T\gamma$, however, remains approximately identical with the temperature found for poly (n-butyl methacrylate), i.e. −175°C (1 Hz).

By analogy with the dielectric behaviour, a quantity $\Delta G$, which equals to the drop of the modulus $G'$ due to the onset of a certain relaxation motion, can be regarded as the most suitable measure of the extent of the relaxation processes. We have established in a previous work[1] that the intensity $\Delta G\gamma$ of the low-temperature relaxation process is approximately the same for PHEMA and PBMA, i.e. 1.4 and $1.3 \times 10^{10}$ dyn cm$^{-2}$. For the copolymers under study, $\Delta G\gamma$ cannot be reliably calculated from isochronal measurements (cf. Ref. 5), since the side chains partaking in the relaxation motions are not of the same kind. Therefore, the difference between the $G'$ values read off at temperatures $T\gamma - 60$ deg and $T\gamma + 60$ deg has been taken as an estimate for $\Delta G\gamma$ (in the case of two low-temperature loss maxima an average value was considered to be $T\gamma$; if $T\gamma$ was lower than −140°C, double the value of the difference of the $G'$ values read at $T\gamma$ and $T\gamma + 60$ deg was used). Nevertheless, even by means of these approximate values it can be demonstrated (Table I) that the total intensity of the low-temperature relaxation processes of the copolymers under investigation remains constant. A conclusion can be made, therefore (cf. Ref. 1), that the energy losses related to one side chain are concentration-independent and virtually the same in copolymers as in homopolymers.

TABLE I

Effect of the composition of the copolymers of 2-hydroxyethyl methacrylate and n-butyl methacrylate on the density, $d$ (20°C), and intensity of the low-temperature relaxation process, $\Delta G\gamma$

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $x_H{}^a$ | 1.00 | 0.80 | 0.60 | 0.50 | 0.40 | 0.20 | 0.00 |
| $w_H{}^b$ | 1.00 | 0.79 | 0.58 | 0.48 | 0.38 | 0.19 | 0.00 |
| $d^c$(20°C), g cm$^{-3}$ | 1.279 | 1.221 | 1.176 | 1.154 | 1.135 | 1.095 | 1.059 |
| $\Delta G\gamma$ $10^{-10}$, dyn cm$^{-2}$ | 1.4 | 1.3 | 1.3 | 1.2 | 1.3 | 1.2 | 1.3 |

[a] $x_H = n_H/(n_H + n_B)$, where $n_H$ and $n_B$ designate the number of moles of the monomeric units of HEMA and BMA, respectively, in a volume unit of a copolymer; [b] weight fraction of HEMA in the copolymer; [c] copolymer density was determined in the preceding paper.[6]

If, therefore, $\Delta G\gamma$ is approximately constant for the whole series of copolymers, then a decrease in the level of the storage modulus (within the region from $T\gamma + 60$ deg to 0°C) with the BMA content cannot be regarded as a consequence of an increasing extent of the low-temperature molecular motion, but must be assigned to a decrease in density, polarity, etc; we therefore attempted to correlate the $G'$ modulus with the copolymer density (Figure 2). The densities were measured[6] at 20°C, so that with the exception of PBMA all copolymers lay below the glass transition temperature. The $G'_{-65}$ values, read at −65°C and not yet affected by the glass transition, were used in the correlation. It can be seen from Figure 2, that the modulus $G'_{-65}$ can be considered approximately linearly proportional to the copolymer density.

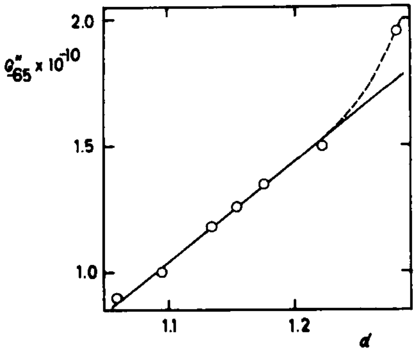

FIGURE 2 Dependence of the modulus $G'_{-65}$ (dyn cm$^{-2}$) read at −65°C on the copolymer density, $d$ (g cm$^{-3}$).

An estimation of the effect of the HEMA and BMA side chains concentration upon their low-temperature relaxation motion is impeded by an overlapping of the $\gamma$ loss maxima (Figure 1). To achieve a separation of the relaxation processes we made use of former results,[3,4] namely, that the incorporated low-molecular weight compounds bring about the transformation of the $\gamma$ relaxation process into the $\beta$ process, which occurs at higher temperatures. To attain a transformation, in the first place, of the component having higher $T\gamma$, i.e. HEMA, the samples were swollen with water; in these measurements, samples with the equimolar composition ($x_H = 0.5$) were used. It can be seen from Figure 3 that with increasing concentration of water (its molar fraction, $x_W$, is related to the content and molecular weight of a monomeric unit of the HEMA component), the right-hand $\gamma$ loss peak of the copolymer occurring at about −145°C disappears, while the $\beta$ maximum gradually grows larger and is shifted toward lower temperatures (around −100°C). The transformation of the $\gamma$ relaxation process into the $\beta$ process of the HEMA component is thus analogous to that in the homopolymer.[3,4] On the other hand, the low-tempera-

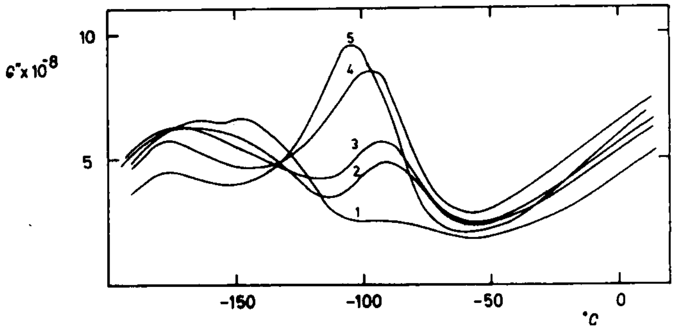

FIGURE 3 Effect of the concentration of water on the temperature dependence of the loss modulus $G''$ (dyn cm$^{-2}$) of an equimolar copolymer of 2-hydroxyethyl methacrylate and n-butyl methacrylate.

Molar fraction of water $x_W$ (related to the content and molecular weight of the monomeric unit of 2-hydroxyethyl methacrylate): 1 0.00; 2 0.09; 3 0.12; 4 0.34; 5 0.50.

ture dispersion of the BMA component is located at the same temperature as the $\gamma$ dispersion of PBMA, i.e. at $-175$°C, and is clearly visible even at the molar fraction of water $x_W = 0.50$, which is sufficient for a total transformation of the above-mentioned relaxation processes of the HEMA component.[3] It is evident, therefore, that neither the presence of 50 mol. % of HEMA in the copolymer nor a considerable concentration of a low-molecular weight compound (water) has virtually any effect upon the mobility of a certain fraction of the BMA side chains.

It follows from the above that in the low-temperature dispersion region the copolymers under study behave quite differently than in the transition region from the glassy to rubberlike state.[6] This transition is characterized[6] by the fact that the shape of the spectrum of the retardation times is independent of the copolymer composition, and the position of the spectrum on the time axis varies linearly with the composition of the copolymers (free or specific volumes of the copolymerization components compounded additively). On the other hand, in the region of the low-temperature dispersion an addition (up to about 40% by weight) of the second component leads to a deformation of the loss maximum of the prevailing component, the temperature shift of the loss maximum being insignificant. The presence of more polar (HEMA in BMA) or less polar (BMA in HEMA) side chains manifests itself in an asymmetric broadening of the loss maximum on the side of higher or lower temperatures, respectively; the corresponding distribution function of the relaxation times would therefore exhibit a relative increase in the region of longer or shorter times, respectively. Thus, an incorporation of the monomeric units of the second component into the polyads of the prevailing component ($x_H < 0.4$; $x_H > 0.6$) does not lead to any of the possible limit cases, i.e. either the formation of the second loss maximum or a unified change of the interaction of all the side chains with the surroundings, but has as its consequence a broadening of the spectrum of the conditions (intermolecular forces and steric effects), under which the low-temperature relaxation of the side chains occurs.

It is evident that in copolymers having the equimolar composition the conditions of formation of polyads are virtually the same for both components. Since the copolymers of this and a similar composition ($0.4 \leq x_H \leq 0.6$) exhibit two loss maxima, it is obvious that in the polyads thus formed there occur relaxations of the side chains analogous to those occurring in the homopolymers. The intermolecular forces and steric hindrances inside these polyads remain unaffected even when a low-molecular weight compound is incorporated, if its molecules are preferentially bound to the side chains of the other copolymerization component. A conclusion can be drawn, therefore, that the low-temperature ($\gamma$) relaxation of the side chains of polymethacrylates is considerably affected by the composition of copolymers; the mobility of the side chains, however, is not a function of the average composition, but depends on their interaction with the immediate surroundings.

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