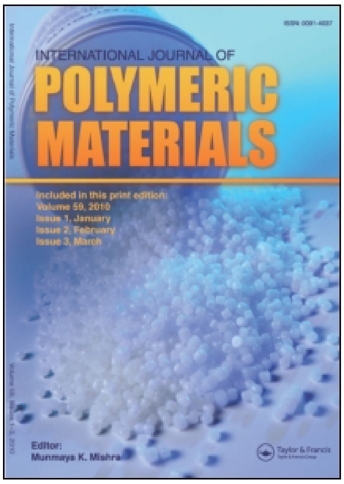

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Relaxation Behaviour of Poly(2-Hydroxyethyl Acrylate) and of Its Copolymers with 2-Hydroxyethyl Methacrylate

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The molecular mobility of poly(2-hydroxyethyl acrylate) (PHEA) and of its copolymers with 2-hydroxyethyl methacrylate (HEMA) was determined by means of dynamic mechanical measurements with a torsional pendulum. The low-temperature dispersion assigned to the motion of the hydroxyethyl groups of the side chains was observed at −133°C (1 Hz) for all polymers; its intensity increased with the content of HEMA. Another secondary dispersion of PHEA detected at −95°C (1 Hz) was ascribed to the motion of the side chains including oxycarbonyl groups. With the incorporation of HEMA the temperature of the latter dispersion remained virtually unchanged, but its intensity rapidly decreased. The main transition temperature of PHEA, $T_a = 9$°C (1 Hz) is lower than T_a of PHEMA by approximately 94°C; the effect of the copolymer composition on T_a could be described by means of a one-parameter equation. The sorption of water led to a significant decrease in the T_a of PHEA and to an intensification of the secondary relaxation process.

INTRODUCTION

Below the glass transition temperature, polymethacrylates exhibit[1] several dispersions (relaxations, transitions) connected with the motion of the —COOR side chains: the secondary (β_1) dispersion (around 20°C; 1 Hz) is ascribed to the hindered rotation about the C—C bond between the main and the side chain; the low-temperature (γ) dispersion at temperatures below −120°C (1 Hz) is regarded as a consequence of the conformation transitions of the —R groups. The interaction of low-molecular weight compounds with the —COO— groups of poly(alkyl methacrylates)[2] or —OH groups of poly(hydroxyalkyl methacrylates)[3,4] gives rise to the "diluent" (β_{sw}) relaxation process in the temperature interval between T_γ and $T_{\beta 1}$. With increasing content of the diluent in the polymers the β_{sw} maximum increases and moves toward lower temperatures.[4] PHEMA exhibits[3-5] the above transitions at temperatures $T_{\beta 1} = 28°C$ (1 Hz), $T_\gamma = -133°C$ (1 Hz), and $T_{\beta sw} = 70$ to $120°C$ (depending on the type and concentration of the diluent).

In our earlier papers[6-9] we also investigated the problem how the mobility of the side chains of PHEMA was affected by the presence of methacrylate and acrylate comonomers, i.e., of methyl methacrylate (MMA), n-butyl methacrylate (BMA), methacrylic acid (MAAc), methacrylamide (MAAm), and acrylamide (AAm). If the comonomer did not exhibit any γ relaxation above the liquid nitrogen temperature, the intensity of the γ dispersion of the copolymers was linearly proportional to the volume fraction of HEMA, v_H. The simultaneous decrease in T_γ was a function of the type of the comonomer and was qualitatively interpreted as a consequence of the diminishing steric hindrances or intermolecular interactions.

The temperature location of the β_1 process of the methacrylate copolymers, such as e.g. HEMA—MMA,[6] BMA—MMA,[6,10,11] isobutyl MA—MMA[10,11] is virtually independent of their composition. This result is in agreement with a number of earlier data indicating[1,12] that $T_{\beta 1}$ of poly(alkyl methacrylates) remains almost unaffected by the size of the substituent R. However, the increasing content of MAAc ($R \equiv H$) in the copolymers with HEMA leads[8] to a decrease in $T_{\beta 1}$ down to $-20°C$ (1 Hz) for PMAAc. On the other hand, the copolymerization of HEMA with MAAm brings about a shift of the β_1 dispersion toward higher temperatures.[9] Both these results were interpreted qualitatively[8,9] in terms of steric hindrances and intermolecular interactions. At the same time a hypothesis was forwarded[8] that in the β_1 relaxation motion of PMAAc the local motion of the main chains becomes operative to a greater extent.

The absence of the methyl group in polyacrylates has as a consequence lower temperatures of the glass (α) and secondary (β_1) transition,[1,13] while the γ maximum is localized at the same temperature as for polymethacrylates.[1] The copolymerization of MMA with methyl acrylate (MA) leads to a decrease in T_α and $T_{\beta 1}$; however, at a 50% content of MA the β_1 dispersion of the MMA component disappears, and a considerably weaker dispersion of the MA component appears.[12] It was also established for the HEMA—AAm copolymers[9] that the temperature and intensity of the secondary dispersion do not exhibit continuous changes with composition. The secondary dispersions of polyacrylates and polymethacrylates seem to reflect different molecular motions.

It has been an objective of our work to determine the relaxation behaviour of PHEA and to find out how the mobility of the side and main chains is affected by the concentration of the α methyl groups. Similarly to earlier papers,[3,4,8,9] we also investigated the effect of water as diluent, because in this way it is possible to gather further information about the mechanism of the secondary dispersions.

EXPERIMENTAL PART

Monomers. 2-Hydroxyethyl methacrylate (HEMA). The monomer was prepared by the alkaline reesterification of methyl methacrylate with glycol.[14] The reaction mixture was diluted with water and ethylene dimethacrylate was removed by several extractions with hexane. HEMA was repeatedly extracted from the aqueous solution with diethyl ether (to remove the unreacted glycol). Ether was removed by distillation and the crude HEMA was redistilled twice *in vacuo*. The purity was >99.9%; b.p. 79°C/4 mm Hg, $n_D^{20} = 1.4525$.

2-Hydroxyethyl acrylate (HEA). The Dow Chemical product was diluted with water 1 : 1; the mixture was extracted five times with petroleum ether, and then NaCl was dissolved in it up to saturation. HEA was extracted from the aqueous mixture with diethyl ether. The ether solution was dried with anhydrous Na_2SO_4, ether was removed by distillation, and crude HEA was additionally purified by twofold distillation *in vacuo*. The purity was >99%; b.p. 52°C/0.3 mm Hg, $n_D^{20} = 1.4503$.

Ethylene dimethacrylate. Supplied by Chemapol. The crude product was first extracted five times with a 5% aqueous solution of NaOH and then extracted again 20 times with a twofold volume of water. The crude product was twice redistilled *in vacuo*, and was found to be chromatographically pure.[14] B.p. 84°C/1 mm Hg; $n_D^{20} = 1.4549$.

Initiator. Diisopropylperoxy dicarbonate[15] was obtained by a reaction of isopropyl chloroformate with an aqueous solution of sodium peroxide at 5–10°C. The oily product thus obtained was washed five times with distilled water, dried with annealed Na_2SO_4 and recrystallized twice from petroleum ether; b.p. 9°C.

Polymerization. The polymerization was carried out via radical mechanism[16] in the absence of solvent at 60°C. Diisopropylperoxy dicarbonate, 0.05% by wt, was used as initiator. All samples, the composition of which is given in Table I, were crosslinked with 1% ethylene dimethacrylate.

A mixture of monomers, crosslinking agent, and initiator was weighed into an Erlenmeyer flask, flushed for 20 min with purified nitrogen to remove the dissolved oxygen, squeezed under an inert atmosphere into a mould consisting of two plane-parallel brass plates provided with a polypropylene coating and sealed with a silicone packing. After filling the mould was placed in a thermostat heated to 60°C for 16 h. On completion of the polymerization the samples were extracted with ethanol at room temperature for several

TABLE I

Parameters of dispersions of the copolymers of 2-hydroxyethyl acrylate and 2-hydroxyethyl methacrylate

Sample	ν_A [a]	$d_{20°C}$ g/cm^3	T_α [b] °C	$T_{\beta 2}$ [b] °C	$\Delta G'_r\ 10^{-10}$ [c] dyn/cm^2	$A_{\beta 2}$ [d]
1	0.00	1.283	103	—	1.80	0.00
2	0.24	1.291	66	(−90)	2.00	(0.08)
3	0.34	1.297	45	(−88)	2.20	0.17
4	0.57	1.308	28	−92	2.30	0.60
5	0.79	1.316	21	−91	2.35	0.70
6	1.00	1.324	9	−95	2.35	1.00

[a] Volume fraction of HEA in the copolymer.

[b] Temperature of dispersion read off for the peak of the loss modulus G''.

[c] Drop of the storage modulus: $\Delta G' = G'(-196°C) - G'(-50°C)$.

[d] Area of the β_2 loss maximum (in arbitrary units) obtained by plotting G'' against the reciprocal absolute temperature (cf.[1]).

days in order to remove the unreacted monomer and initiator residues. The samples 1 × 7 × 50 mm in size were dried *in vacuo* of a rotary oil pump at 80–90° to constant weight. The water containing PHEA samples were sealed in ampoules and left at room temperature for one month to attain equilibrium. Dynamic mechanical measurements were carried out at increasing temperature (approximately 1°C/2 min) by means of a torsional pendulum with a digital recording of oscillations.[17]

RESULTS AND DISCUSSION

The main transition temperature T_α decreases continuously with the volume fraction of HEA, ν_A, from $T_{\alpha H} = 103°C$ for PHEMA to $T_{\alpha A} = 9°C$ for PHEA (Figure 1; Table I). (T_α was read off for the highest value of the loss modulus G'' in the main transition region; for PHEMA it is higher by about 15°C than T_g determined dilatometrically).[18,19] Thus, the removal of the methyl group leads to a decrease in the glass transition temperature by 94°C, which equals a difference of T_g between the series of poly(alkyl methacrylates) and poly(alkyl acrylates).[1,20] The dependence of T_α on ν_A (Figure 2) may be described by the equation[21]

$$T_\alpha = [T_{\alpha H} + (k\, T_{\alpha A} - T_{\alpha H})\nu_A] \,/\, [1 + (k - 1)\nu_A] \qquad (1)$$

with $k = 2.5$. Compared to the parameters k for a series of similar vinyl copolymers[13] the obtained value is rather high. Since we did not know the temperature dependence of the expansion coefficient of PHEA, we could not estimate if the parameter k determined here corresponded to the ratio of the

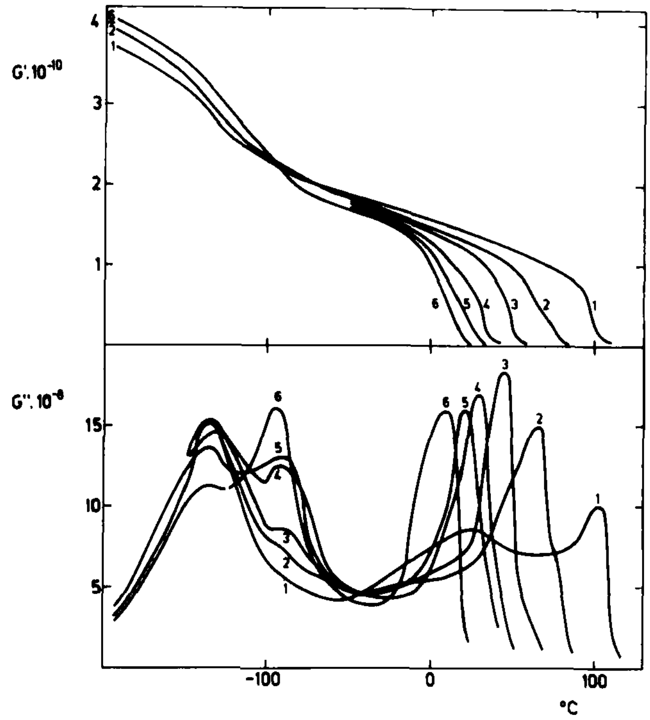

FIGURE 1 Temperature dependence of the moduli G' and G''(dyn/cm^2) of the copolymers HEA—HEMA. (Composition of the copolymers is given in Table I. For clearness' sake the modulus G'' of polymers 2, 3 and 4 within the interval from −196 to −150°C and the modulus G' of polymers 3, 4 and 5 within the interval from −196 to −50°C are not given.)

expansion coefficients of the free volumes of the components (as it is the case if the free volume of the copolymer is the sum of the free volumes of the components).[21] The results of earlier dynamic mechanical and dielectric measurements[22] of PHEA were affected by the presence of comonomers and of the crosslinking agent formed during the preparation of the HEA monomer.

An increase in the HEA content in the copolymers is also reflected in systematic changes of the energy dissipation patterns in the glassy state (Figure 1). The β_1 maximum which is observed for PHEMA at 28°C cannot be seen at $\nu_A \geq 0.24$, because it is overlapped by the α maximum. The rising fraction of the acrylate component is in the first place reflected in a growth of the loss maximum at a temperature around −90°C, further referred to as β_2. The height of the γ maximum, G_γ'', remains practically unchanged until $\nu_A = 0.57$; for PHEA, $G_\gamma'' = 11.3$ is lower by approximately 25% than for

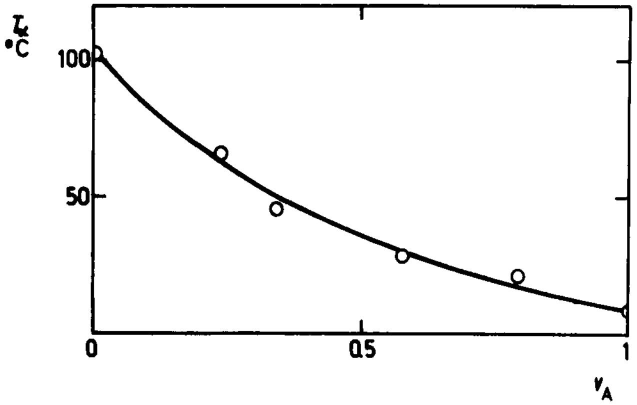

FIGURE 2 Dependence of $T\alpha$ of the copolymers on the volume fraction of HEA.

PHEMA. In all these changes of intensity with the copolymer composition the temperature location of the γ and β_2 dispersions remains fixed.

The finding that the γ relaxation motion is not sterically hindered by the α methyl groups is in agreement with the earlier results obtained for poly(alkyl methacrylates).[1] It seems therefore natural to assign the γ dispersion of HEMA and HEA to the same molecular mechanism, i.e. to a hindered rotation of the hydroxyethyl groups of the side chains, which has been discussed in detail in earlier papers.[3-8] It follows from the above, of course, that the β_2 process is necessarily connected with the onset of mobility of larger units i.e. of the side chains (including the COO groups), (Figure 3) or even of short sections

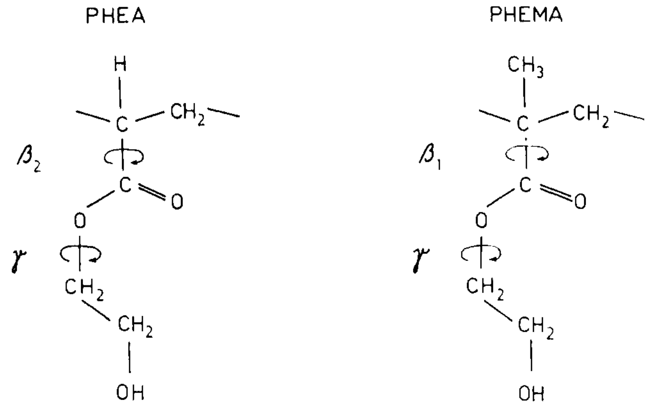

FIGURE 3 Schematic outline of the structural units whose hindered rotation is considered to give rise to the observed dispersions.

of the main chains. It should be borne in mind at the same time that the removal of the α methyl groups does not lead to regular changes in the intensity and temperature position of the β_1 dispersion, as it is the case e.g. for the copolymers[13] MMA—methyl acrylate, MMA—acrylonitrile, MMA—styrene, but that it leads to the formation of the β_2 dispersion at a temperature lower by 120°C. While the intensity of the γ dispersion of several series of methacrylate copolymers[6,8,9] was linearly proportional to the concentration of the hydroxyethyl groups, the increase in the intensity of the β_2 dispersion (expressed in Table I by the area of the loss maximum[1]) becomes faster with growing ν_A. It may be deduced that isolated acrylate monomeric units incorporated in methacrylate sections are not sufficient for the formation of the β_2 dispersion, but that the formation of acrylate sequences is necessary. The stable temperature position of the β_2 dispersion indicates that the corresponding relaxation motion is controlled by intramolecular interactions and is independent of the average composition of the copolymers. The cause of the β_2 process can therefore be sought in the onset of the molecular mobility inside the acrylate polyads. The results obtained so far do not make possible a more precise interpretation of the molecular mechanism of the β_2 dispersion and of its different character compared to the molecular mechanism of the γ or β_1 dispersion of poly(methacrylates).

With increasing content of HEMA in the copolymers the drop in the modulus G' corresponding to the main transition is shifted toward lower temperatures similarly to the α loss maximum (Figure 1). The level of the modulus G' at -50°C (which is practically unaffected by the main transition) decreases with the concentration of HEMA, while the modulus G' at -196°C somewhat increases (for $\nu_A > 0.34$ the differences are difficultly perceptible). In this way the increasing drop of the modulus $\Delta G'_r = G'(-196°\mathrm{C})—G'(-50°\mathrm{C})$ indicates (Table I) the increase in the overall molecular mobility in the glassy state due to the onset of the γ and β_2 relaxation processes.

The incorporation of water in PHEA leads to a pronounced shift of the main transition toward lower temperatures (Figure 4) similarly to PHEMA.[4] However, a characteristic feature of PHEMA was that at volume fractions of water $\nu \geq 0.23$ a part of water became separated in the form of a second phase[4] on cooling below 0°C, i.e. the increasing water content did not cause a decrease in T_α any more, but led only to an increase in the loss maximum at 0°C, which indicates melting of the water thus separated. On the other hand, all systems PHEA—H_2O investigated here remained homogeneous even at low temperatures, since none of the signs of phase separation described above could be observed. One can see therefore that PHEA can absorb a considerably larger quantity of water than PHEMA without any phase separation and resulting embrittlement below 0°C.

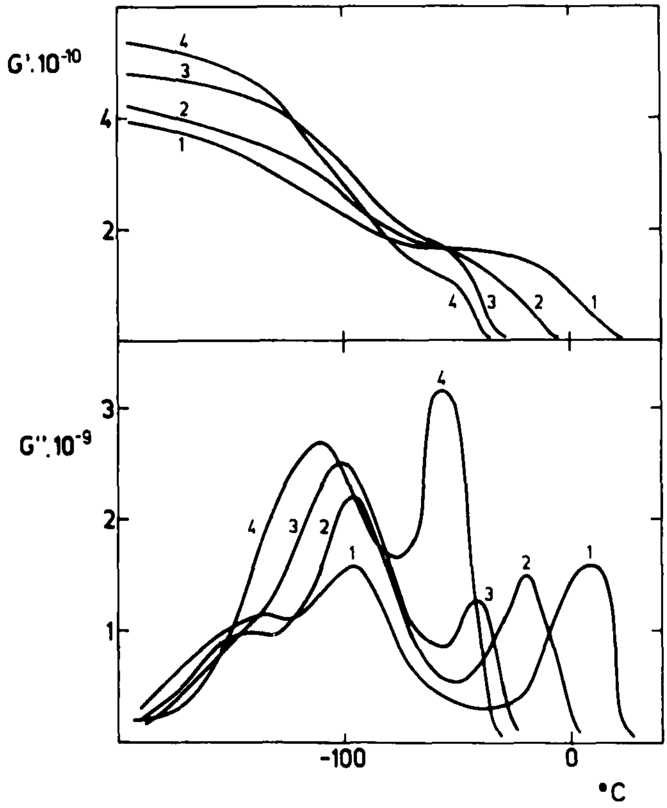

FIGURE 4 Effect of water on the temperature dependence of the moduli G' and G''(dyn/cm^2) of PHEA. Volume fraction of water: (1) 0.00; (2) 0.07; (3) 0.16; (4) 0.46.

In the glassy state the sorbed water accounts for a reduction of the γ maximum and an increase in the β_2 maximum which at the same time is shifted toward lower temperatures (Figure 4). It was found for PHEMA[3,4] that water causes a transformation of the γ process into the β_{sw} relaxation process characterized by a temperature of -70°C, which however decreases with the water content (down to -110°C). It may be deduced from the reduction of the γ maximum of the systems PHEA—H_2O (Figure 4) that a similar transformation takes place, but the newly formed dispersion is overlapped with the existing β_2 dispersion. The temperature shift of the β_2 dispersion is therefore obviously due to a decrease in the temperature of the "water" dispersion. At the same time the modulus G' in the glassy state is elevated by water content so that the total drop of the modulus $\triangle G'_r = G'(-196°C)—G'(-50°C)$ increases too. In this respect the effect of water is similar to that of nonseparating diluents (e.g. glycol) in PHEMA.[4] On the basis of the increase in the loss maximum and in the corresponding drop of the storage modulus it may be inferred that water molecules also participate in the resulting relaxation process, along with the side chains.

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