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

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ABSTRACT: A free-vibrating torsional pendulum was used to determine the temperature dependence of the storage and loss shear moduli of poly(methacrylic acid) (PMAAc), poly(2-hydroxyethyl methacrylate) (PHEMA) and their copolymers within the temperature range from -196 to 120°C . A decrease in the number of hydroxyethyl side chains per unit volume of polymer leads to a reduction of the low-temperature (γ) dispersion, which is simultaneously shifted toward lower temperatures. The intensity of the secondary (β_1) dispersion increases with concentration of the carboxyl groups, while its temperature falls from 28°C for PHEMA to -20°C for PMAAc. Water causes a continuous decrease in temperature and an increase in the intensity of the secondary dispersion of PMAAc. The observed changes in molecular mobility in the glassy state are interpreted qualitatively as a consequence of changes in both steric hindrance and intermolecular interaction.

KEY WORDS 2-Hydroxyethyl Methacrylate / Poly(methacrylic acid) / Copolymers / Glassy State / Relaxation Behaviour / Low-Temperature Dispersion / Secondary Dispersions / Molecular Mobility / Diluent Effect / Torsion Pendulum /

Our preceding papers^{1,2} have been devoted to the effect of concentration of the side chains on the low-temperature (γ) relaxation process in the methacrylate copolymers between -125 and -190°C . A decrease in the volume fraction of 2-hydroxyethyl methacrylate or *n*-butyl methacrylate (BMA) in their copolymers with methyl methacrylate (MMA) led to a linear reduction in the intensity of the γ process and to its shifting toward lower temperatures, without any pronounced changes in the shape of the loss maximum.¹ The drop of the temperature of the γ dispersion was tentatively interpreted in terms of an increase in the free volume accessible to the remaining side chains $\text{HO}-\text{CH}_2-\text{CH}_2-$ or $\text{CH}_3-(\text{CH}_2)_3-$. It was established, by using HEMA—BMA copolymers,² that the low-temperature relaxation motion of side chains depends on their interaction with the close surroundings and not on the average composition of the copolymers which determines³ the glass transition temperature, T_g . The effect of polar low-molecular weight compounds leads to a transformation of the γ dispersion of PHEMA into a secondary

(β_{sw}) dispersion characterized by a higher temperature and an intensity proportional to the amount of diluents.^{4,5} If nonpolar side chains are present at the same time, *e.g.*, in the HEMA—BMA copolymers, their relaxation remains almost unaffected by the polar diluent.²

A number of papers^{6–14} have been devoted to the effects of polymethacrylate composition on the secondary (β_1) dispersion parameters. This dispersion at around 20°C ; 1Hz is ascribed to the hindered rotation of the side chains around the C—C bond connecting the main and side chains. The results obtained so far have shown that the temperature at which the alkoxy carbonyl groups become mobile is virtually independent of the size of the alkyl group,^{6–9,15} but is raised^{6–10,15} by the presence of the α methyl group in the main chain. On the other hand, the relaxation time of the β_1 process determined at the T_g of the respective polymethacrylates increases rapidly with the length of the side chain.¹¹ An isotactic arrangement of poly (alkyl methacrylates) lowers the T_g and the β_1 transition temperature,^{7,12,13} while the intensity and temperature of the γ

dispersion are practically independent of the stereoregularity.¹³ If the side chains contain hydroxyl groups, the temperature of both the γ dispersion^{1,2,4} and the β_1 dispersion¹⁶ increases because of the formation of hydrogen bonds. Lately, it has been suggested that the motion of the backbone^{8,9} also participates in the β_1 relaxation process, similarly to the low-temperature relaxation of polymers without bulky side groups.¹⁴

We have tried in this work to determine the effects of incorporating MAAC monomer units (polar components without bulky side groups) on the low-temperature and secondary dispersion parameters of PHEMA. We also regarded it as useful to obtain information on the molecular mobility in PMAAC which is often a component of ionic polymers and considerably modifies their relaxation behaviour.¹⁷

EXPERIMENTAL

The samples of PHEMA, PMAAC and their copolymers were prepared by crosslinking copolymerization (Table I), using 0.3 wt% of ethylene dimethacrylate as the crosslinker. The monomer mixture was diluted by 33 vol% of water and the polymerization was initiated with a redox system of ammonium persulphate—potassium

pyrosulphite (0.05 wt%). The polymerization proceeded at 25°C for 20 hr. During the preparation of samples 5, 6, 7 (Table I), temporary turbidity was observed in the initial stages of polymerization. This turbidity was due to the limited solubility of the forming polymer in the remaining mixture of monomers and water. Samples 70×10×1 mm in size were extracted with an excess of water at room temperature for 5 days, then dried to constant weight over P₂O₅ at 80–90°C. The samples were swollen with water in 100-% RH and on attaining the required weight increment, the samples were sealed in ampoules and stored at room temperature for at least one month.

The temperature dependence of the components of the complex shear modulus $G^* = G' + iG''$ was measured with a torsional pendulum (1 Hz) with digital registration of damped oscillations.¹⁸ The measurements were made from liquid-nitrogen temperature to about 120°C, so that for copolymers with a higher content of MAAC it was not possible to determine the dispersion corresponding to the glass transition (*cf.* ref 19). Loss and storage moduli of swollen samples were determined only up to room temperature, since at higher temperatures water desorption took place.

Table I. Parameters of γ and β_1 dispersions for the copolymers of methacrylic acid and 2-hydroxyethyl methacrylate

Sample	x_M^a	v_M	$d_{20^\circ C}^c$ g/cm ³	$w_{H_2O}^b$	T_γ^c °C	$G_\gamma'' \times 10^{-8}$ dyn/cm ²	$\Delta G_\gamma' \times 10^{-10d}$ dyn/cm ²	$T_{\beta_1}^c$ °C	$G_{\beta_1}' \times 10^{-8}$ dyn/cm ²	A/A_H^{0e}	N/N_H^{0f}	N_M/N_H^{0g}
1	0.00	0.00	1.283	0.407	-133	15	1.3	28	7.8	1.0	1.00	0.00
2	0.20	0.14	1.287	0.357	-135	13	1.0	18	9.3	1.2	1.08	0.21
3	0.40	0.30	1.296	0.348	-137	8.8	0.7	0	10.3	1.5	1.17	0.47
4	0.50	0.39	1.298	0.358	-141	7.6	0.6	-10	10.3	1.7	1.22	0.61
5	0.60	0.49	1.300	0.388	-141	7.6	0.45	-10	12	1.9	1.28	0.76
6	0.80	0.72	1.310	0.51	(-146)	4.1	0.2	-15	12	2.0	1.40	1.12
7	1.00	1.00	1.320	0.88	—	(2) ^h	0.0	-20	14	2.5	1.56	1.56

^a Mole fraction of MAAC in copolymer.

^b Weight fraction of water in swollen polymer.

^c Temperature of dispersion read off for the highest loss modulus G_γ'' or G_{β_1}'' (1Hz).

^d Decrement of modulus: $[G'(T_\gamma - 60^\circ C) - G'(T_\gamma + 60^\circ C)] - [G'(T_\gamma - 60^\circ C) - G'(T_\gamma + 60^\circ C)]_{PMAAC}$.

^e Ratio of the β_1 maximum areas of copolymer and PHEMA.

^f Ratio of the number of side groups per unit volume of copolymer and PHEMA.

^g *cf.* eq 3.

^h Level of loss modulus.

RESULTS AND DISCUSSION

A decrease in the HEMA content of copolymers leads to a reduction of the low-temperature dispersion, *i.e.*, a reduction in the loss maximum, G'' , and the modulus decrement, $\Delta G'$. Furthermore, decreasing HEMA content shifts the low-temperature dispersion toward lower temperatures (Figure 1; Table I). In contrast to the HEMA—MMA copolymers,¹ we find the $\Delta G'$ and G'' values are less than values which would correspond to a linear decrease with the volume fraction of the HEMA component, v_H meaning that the energy losses per side chain unit decreases with decreasing concentration of the side chains. The T_γ depression (Table I) with increasing MAAC content is also considerably smaller than a similar decrease due to the same addition of MMA.¹ It can be inferred, therefore, that the decrease in the steric hindrances of the γ relaxation process is, to a great extent, compensated for by an interaction of the remaining hydroxyethyl side chains with the carboxyl groups. The interaction between the hydroxyl and carboxyl groups is also indicated by the fact that the swelling of copolymers in water passes through a minimum at a x_M about 0.4 (Table I).

As to the secondary β_1 dispersion, increasing the MAAC content of the copolymers leads to both a continuous drop of temperature from $T_{\beta_1}^H = 28^\circ\text{C}$ (1 Hz) for PHEMA to $T_{\beta_1}^M = -20^\circ\text{C}$ (1 Hz) for PMAAc, and a gradual increase in the height and area of the loss maximum (Figure 1; Table I). It follows from these relationships that the molecular motion which gives rise to the β_1 dispersion in PMAAc is analogous to that in PHEMA or poly(alkyl methacrylates). Compared to its ordinary esters, PMAAc exhibits the lowest T_{β_1} and the highest glass transition temperature (extrapolated¹⁹ $T_g = 230^\circ\text{C}$). This indicates that different molecular mechanisms underlie the β_1 and glass transitions.

According to the results of the IR spectroscopic measurements²⁰ on polyethylene—MAAc copolymers, at temperatures lower than 20°C practically all carboxyl groups are interconnected to form dimers with two intermolecular hydrogen bonds. Since a similar situation can be assumed for PMAAc, the causes of the low T_{β_1} should

Figure 1. Temperature dependence of moduli G' and G'' (dyn/cm²) of copolymers of MAAC and HEMA (composition of polymers is given in Table I).

be sought in low steric hindrances of the relaxation motion. Comparison of PMAAc with poly(methyl acrylate) on the one hand and with PMMA ($T_{\beta_1} = 20^\circ\text{C}$ ^{1,7,16} for 1 Hz) on the other, shows that T_{β_1} is decreased not only by the substitution of hydrogen for the methyl groups on the backbone [poly(methyl acrylate) exhibits dispersion at -120°C ⁷], but also by the same operation in the side chain although the final effect is suppressed by the formation of hydrogen bonds. Unlike the γ process, the β_1 processes is more affected by the decrease in steric hindrances due to incorporation of MAAC than by the increase in the intermolecular interaction.

The temperature dependence of T_{β_1} on the volume fraction of MAAC, v_M , can be described (Figure 2) by the equation⁵

$$T_{\beta_1} = [T_{\beta_1}^H + (k_{\beta_1} T_{\beta_1}^M - T_{\beta_1}^H) v_M] / [1 + (k_{\beta_1} - 1) v_M], \quad (1)$$

where the constant $k_{\beta_1} = 3$ is close to the values determined for the main (glass) and secondary (β_{sw}) transitions of the PHEMA—diluent system.⁵ In the case of the β_{sw} process the original meaning, *i.e.*, the ratio of the expansion coefficients

Figure 2. Dependence of temperature T_{β_1} of copolymers on the volume fraction of MAAC.

of the free volumes of the components,²¹ cannot be assigned to the constant $k_{\beta_{sw}}$, since the extent of the β_{sw} process is proportional to the diluent content, and is absent in dry PHEMA. On the other hand, an increase in the expansion coefficient indicating a more intensive increase in the free volume is observed in the β_1 transition of polymethacrylates,^{22,23} but the value for PMAAc has not been determined.

The height and area of the β_1 maximum increase with the MAAC content faster than the number of the side groups per unit volume of polymer (Figure 1; Table I). (The area of the loss maximum, A , obtained by plotting G'' against reciprocal absolute temperature is, as an integrated value,¹⁵ more suitable for an estimate of the total losses than the height of the loss maximum. The corresponding decrement of the G' modulus was not determined, since for $v_M < 0.4$ a simultaneous decrease in storage modulus due to the glass transition cannot be separated.) PMAAc contains about 56% more COO groups per unit volume compared to PHEMA, while the ratio of the heights of the loss maxima is approximately 2 and the ratio of the areas is 2.5 (Table I). If we designate the contributions of the $-\text{COOH}$ and $-\text{COO}-\text{CH}_2-\text{CH}_2-\text{OH}$ to the β_1 loss maximum area by L_M and L_H respectively, we obtain, assuming the additivity of volumes and energy losses,

$$A = L_M N_M + L_H N_H, \quad (2)$$

where N_M and N_H are the number of monomer units of the components in a unit volume of the copolymer. Since for $N_M = 0$ we have $A_H^0 = L_H N_H^0$, it holds

$$A/A_H^0 - v_H = (L_M/L_H)(N_M/N_H^0). \quad (3)$$

Figure 3. Plot according to eq 3.

It can be seen from Figure 3 that the experimental data approximately satisfy the assumption of additivity of the energy losses, while the ratio $L_M/L_H = 5/3$. It seems possible, with respect to the low temperature T_{β_1} and high energy losses, that local motions of the main chains also participate in the β_1 relaxation process of PMAAc.

The level of the storage G' modulus increases with increasing content of the MAAC component over the whole temperature range of the glassy state (Figure 1). Similarly to other methacrylate copolymers,^{1,2} the modulus rises with the density, even if for the HEMA—MAAC copolymers the densities of the components differ but little (Table I). However, the simultaneous reduction of the low-temperature molecular motion may contribute even more to the observed increase in the storage modulus level.

Our investigation of the effect of diluents on the relaxation behaviour in the glassy state was carried out only on PMAAc and equimolar copolymer (4) both swollen in water. An increase in the water concentration in PMAAc leads to a continuous shift of the β_1 maximum toward lower temperatures (Figure 4). This shift can be explained by decreasing interaction between the carboxyl groups. The depression of T_{β_1} by water is much more pronounced than that of $T_{\beta_{sw}}$ for the system PHEMA—diluent,⁵ so that even traces of water displace the β_1 maximum toward lower temperatures. The height of the loss maximum first decreases with the water concentration; later, however, the loss maximum becomes larger and narrower, while the area of

Figure 4. Temperature dependence of loss modulus (dyn/cm^2) of PMAAc swollen with water. Volume fraction of water v_d and ratio between the β_1 maximum areas of swollen and dry samples: (1) 0.00, 1.0; (2) 0.03, 1.2; (3) 0.07, 1.3; (4) 0.12, 1.5; (5) 0.35, 2.6.

Figure 5. Temperature dependence of loss modulus (dyn/cm^2) of copolymer 4 swollen in water. Volume fraction of water v_d : (1) 0.00; (2) 0.02; (3) 0.05; (4) 0.18; (5) 0.29.

the maximum increases monotonically (Figure 4). The increase in the extent of the energy losses and the modification of the spectrum of relaxation times indicate (*cf.* ref 5) that molecules of water also participate in the β_1 process in swollen samples. For none of the samples investigated could any signs be observed of water separation in the form of a second phase whose melting gives rise⁵ to a dispersion at a temperature around 0°C .

Water affects the G'' versus temperature curve of the equimolar copolymer in a way similar to that of PMAAc (Figure 5), except that at water volume fractions of $v_d=0.013$ and 0.045 there can also be seen a γ maximum at temperatures around -140°C . For higher water concentrations ($v_d \geq 0.3$) the temperature $T_{\beta_1} = -110^\circ\text{C}$ and the loss maximum height $G''_{\beta_1} \approx 3 \times 10^9 \text{ dyn/cm}^2$ of PMMAc and of copolymer 4 approximately correspond to the values determined for the system PHEMA—water.⁵ This result supports our earlier conclusion⁵ that molecules of the diluent contribute significantly to the intensity of the secondary dispersion and simultaneously affect its temperature.

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