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International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

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To cite this Article Kolařík, J.(1980) 'Effect of Urea on Dynamic Relaxation Behaviour of Poly(2-hydroxyethyl methacrylate)', *International Journal of Polymeric Materials*, 8: 4, 275 – 283

To link to this Article: DOI: 10.1080/00914038008077955

URL: <http://dx.doi.org/10.1080/00914038008077955>

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Effect of Urea on Dynamic Relaxation Behaviour of Poly(2-hydroxyethyl methacrylate)

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(Received July 11, 1978)

Effect of urea on the dynamic relaxation behaviour of poly(2-hydroxyethyl methacrylate) (PHEMA) was studied by means of a torsion pendulum in a temperature range from -196°C to $+130^{\circ}\text{C}$. The incorporation of urea decreases the glass transition temperature of PHEMA, whereas the temperature of the secondary (β_1) relaxation of the oxycarbonyl groups does not change appreciably; the extent of the low-temperature (γ) relaxation assigned to the hindered rotation of the hydroxyethyl side groups is reduced. In contradistinction to other low-molecular weight compounds urea does not give rise to a characteristic diluent dispersion in PHEMA. A decrease in the molecular mobility with increasing urea content manifests itself in an increase in the storage modulus below the temperature of the β_1 dispersion ($T_{\beta_1} = 28^{\circ}\text{C}$) (antiplasticizing effect). The atypical effect of urea on the relaxation behaviour of PHEMA was tentatively assigned to a strong interaction of the components which is evidenced by densification of the system. The effect of water on the relaxation behaviour of the system PHEMA-urea is analogous to that assessed for PHEMA.

1. INTRODUCTION

Molecular mobility of polymers in the glassy state is specifically affected by incorporation of low molecular weight compounds.^{1–3} Diluents change the intensity and temperature of dispersions (relaxations, transitions) characteristic of the dry polymers and at the same time give rise to a new (diluent) dispersion in the temperature range from -60°C to -140°C . It was shown that parameters of this dispersion depend both on the type and concentration of the diluent and on the polymer composition.^{3–8} The diluent dispersion is usually assigned to the hindered rotation of the diluent molecules⁹ or of the kinetic units composed of a diluent molecule and either the side chain or a short segment or the main chain.^{3,10,11}

The effect of polar diluents on the molecular mobility was extensively studied with poly(2-hydroxyethyl methacrylate) and its copolymers.^{3-7,12-14} Dry PHEMA shows three dispersions in temperature range from -196°C to $+130^{\circ}\text{C}$: the α -dispersion at temperature $T_{\alpha} = 104^{\circ}\text{C}$ (1 Hz), which corresponds to the glass transition, and the β_1 and γ dispersions at temperatures $T_{\beta_1} = 28^{\circ}\text{C}$ (1 Hz) and $T_{\gamma} = -133^{\circ}\text{C}$ (1 Hz) assigned to the hindered rotation of the $-\text{COOR}$ or $-\text{R}$ groups, respectively. The incorporation of diluents gives rise to a diluent (β_d) dispersion at temperatures around -70°C . With increasing diluent concentration this dispersion shifts towards lower temperatures and its intensity increases; at the same time, γ relaxation is reduced and eventually vanishes altogether. A conclusion was therefore forwarded¹⁵ that the interaction of the diluent molecule with the hydroxyl or with the ester group, leads to a transformation of the γ process into β_d process. The motion of the diluent molecules is presumed to set in along with that of hydroxyethyl side groups and to significantly contribute to the intensity of the β_d dispersion.^{3,4}

It has been found for PHEMA-ethyleneglycol and PHEMA-formamide systems^{3,4} that with increasing diluent content the temperature T_{β_d} decreases towards the glass transition temperature of the diluent. The secondary β_d transition thus gradually acquires character of the "glass transition" of the system side chains-diluent. In this connection a question has arisen which effect on the molecular mobility would have a diluent with T_g above the temperature of ordinary β_d dispersions. A diluent dispersion at higher temperatures, e.g. -50 to -20°C , has up to now been observed for polycaprolactam-acetamide or -formamide systems.⁸ Bearing in mind the foregoing results¹⁶ we have used urea as a diluent. Since the melting point of urea¹⁷ is 132.7°C , then in accordance with the rule¹⁸ $0.5 T_m \leq T_g \leq 0.67 T_m$ (in K) the T_g of urea can be expected in the temperature range from -70 to 0°C .

2. EXPERIMENTAL

The samples of PHEMA containing urea were prepared by cross-linking copolymerization using ethylene-dimethacrylate as the crosslinker. The monomer of (2-hydroxyethyl methacrylate) contained 0.32 wt. % of ethylene-dimethacrylate, 0.5 wt. % of methacrylic acid and ca 5 wt. % of 2-(hydroxyethoxy)ethyl methacrylate. The monomer was diluted with a half volume of water, to attain the solubility of urea in the polymerizing mixture. The polymerization reaction was initiated with ammonium persulfate-potassium pyrosulfite redox system (ca 0.01 wt. %) and carried out between two parallel glass plates at $22 \pm 2^{\circ}\text{C}$ for 40 hours. The cut-out samples, ca $70 \times 10 \times 1.5 \text{ mm}^3$

in size, were gradually dried at room temperature, at 50°C and finally at 70°C over phosphor pentoxide. The samples containing water were sealed in glass ampoules and kept at room temperature for a month at least. After the dynamic mechanical measurements had been made the samples were dried and the approximate water content was determined from the weight loss (one cannot warrant that at drying some urea was not lost). The urea content in all samples was determined after a subsequent extraction with water (at room temperature for 2 weeks) and drying at 70°C over P₂O₅ to a constant weight (the weight of the initiator was subtracted).

The temperature dependence of the components G' and G'' of the complex shear modulus $G^* = G' + iG''$ was determined with a freely oscillating (near 1 Hz) torsional pendulum with digital recording of damped oscillations.²¹ The measurements were carried out with increasing temperature ($\sim 1^\circ\text{C}/\text{min}$) starting from the liquid nitrogen temperature up to the glass transition temperature of the samples. Diffraction patterns were taken with flat film camera using CuK α radiation. The samples with urea weight fraction $w_u \leq 0.115$ were amorphous and presumably homogeneous, whereas for samples with $w_u \geq 0.23$ the phase separation accompanied by crystallization of the urea was detected (Figure 1). The critical solubility of urea in PHEMA which is apparently situated between $w_u = 0.115$ and 0.23 was not determined.

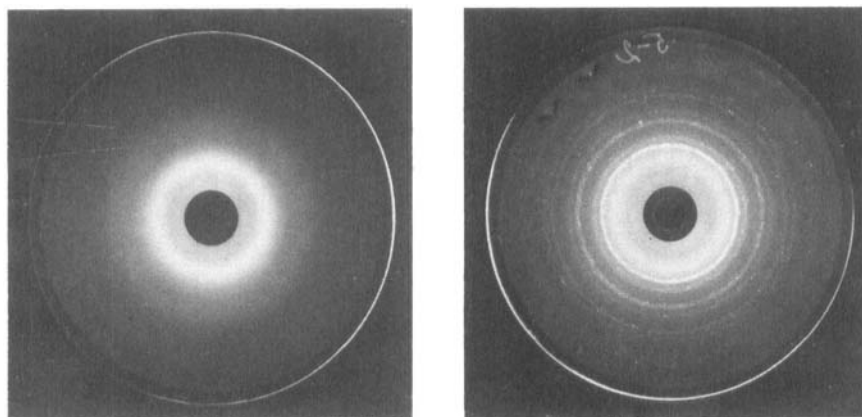


FIGURE 1 Diffraction patterns of PHEMA containing urea. Volume fraction of urea: (a) 0.115; (b) 0.23.

3. RESULTS AND DISCUSSION

Nonextracted sample of PHEMA polymerized without urea exhibits (Figure 2) a glass transition at temperature $T_g = 95^\circ\text{C}$ (1 Hz), a secondary transition

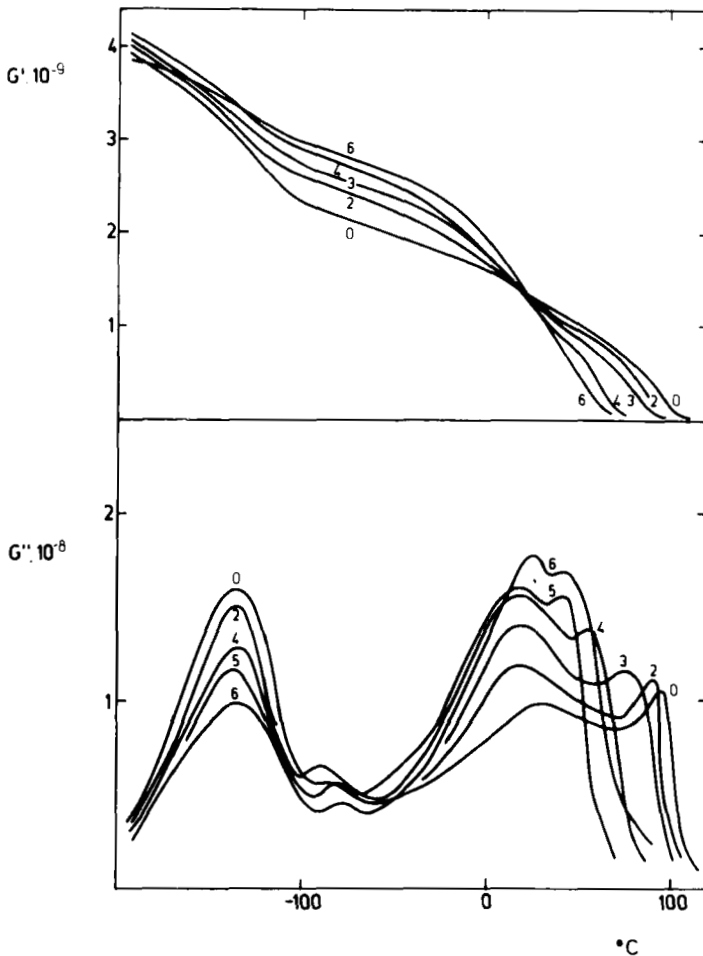


FIGURE 2 Effect of urea on temperature dependence of the storage and loss moduli (in Pa) of PHEMA. Sample compositions shown in Table I.

β_1 at $T_{\beta_1} \cong 29^\circ\text{C}$ (1 Hz), a foreshadowing of the diluent loss maximum at about -80°C , and a low-temperature γ transition at $T_\gamma = -135^\circ\text{C}$ (1 Hz). The temperature position and height of the γ and β_1 loss maxima are in accordance with former data for dry PHEMA; the decrease of T_α (by about 9°C) and the shadow of the diluent dispersion indicate the presence of traces of low molecular weight substances (cf.⁸), which were not removed under mild drying conditions. The diluent maximum completely vanished and T_α increased to 104°C (Figure 3) when the sample was extracted with water, dried at 70°C and annealed at 120°C . An identical temperature dependence

of G' and G'' after extraction and drying exhibited also the samples 5, originally used to assess the effect of urea (Figure 2). The results indicate that urea in the polymerizing mixture does not perceptibly affect the molecular mobility of PHEMA (deprived of all low molecular weight admixtures). Only the equilibrium swelling of the extracted samples in water did slightly decrease proportionally to the initial urea concentration (Table I).

TABLE I

Effect of urea on parameters of the dispersions of poly(2-hydroxyethyl methacrylate)

Sample	w_u^a	v_u^b	d^c Mg/m ³	$w_{H_2O}^d$	$\frac{G_y^e}{G_y^{e0}}$	$\frac{A_y^f}{A_y^0}$	$\frac{\Delta G_y^g}{\Delta G_y^{g0}}$	$\frac{2G_y^{hg}}{\Delta G_y}$	$T_{\beta_1}^i$ °C	T_α^i °C
0	0	0	1.284	0.410	1	1	1	0.180	29	96
1	0.011	0.011	1.289	0.407	0.96	0.93	0.93	0.186	23	93
2	0.021	0.020	1.292	0.395	0.93	0.90	0.90	0.186	18	87
3	0.039	0.038	1.296	0.390	0.88	0.90	0.87	0.182	19	75
4	0.068	0.066	1.302	0.367	0.79	0.80	0.80	0.178	19	58
5	0.115	0.111	1.310	0.353	0.71	0.71	0.71	0.180	19	43
6	0.230	0.223	1.311	0.367	0.61	0.64	0.60	0.183	25	44

^a weight fraction of urea; ^b volume fraction of urea; ^c density; ^d equilibrium weight fraction of water after extraction of urea; ^e ratio of the γ loss maximum height of the sample with urea to that of the sample without urea; ^f area ratio of the γ loss maxima plotted as G'' versus $1/T$ (cf.¹); ^g ratio of the storage modulus decrements (cf.¹) in the range of the γ dispersion, $\Delta G_y^g = G'(T_y - 60^\circ\text{C}) - G'(T_y + 60^\circ\text{C})$; ^h approximate parameters of the Fuoss-Kirkwood distribution of relaxation times (cf.^{1,19,20}); ⁱ temperature location of the loss maximum (at 1 Hz).

With increasing urea content in samples the temperature of the main transition T_α decreases and also the T_{β_1} drops by about 10°C (Table I; Figure 2), whereas temperature T_γ remains constant; α and β_1 maxima rise, partly due to their overlapping, γ maximum, on the contrary, is reduced. As this reduction is more pronounced than would correspond to the mere decrease in the volume fraction of the polymer (Table I), one can infer that the urea molecules interact with the side chains. This strong interaction is also evidenced by the fact that the density of the PHEMA-urea systems is higher (Figure 4) than that calculated from the volume additivity of the components (even though the density of the crystalline urea was used). All the samples containing urea show a residual β_d hump of approximately the same magnitude as the nonextracted sample polymerized without urea. Thus, urea affects the relaxations of PHEMA very much like other low molecular weight substances do, but it does not give rise to a diluent dispersion between -50°C and -120°C . In this respect urea differs from all diluents studied until now (water, ethylene glycol, formamide, propanol etc.^{3,4,15}), all of them producing at volume fraction 0.1 a loss maximum of the height around 1×10^8 Pa. The

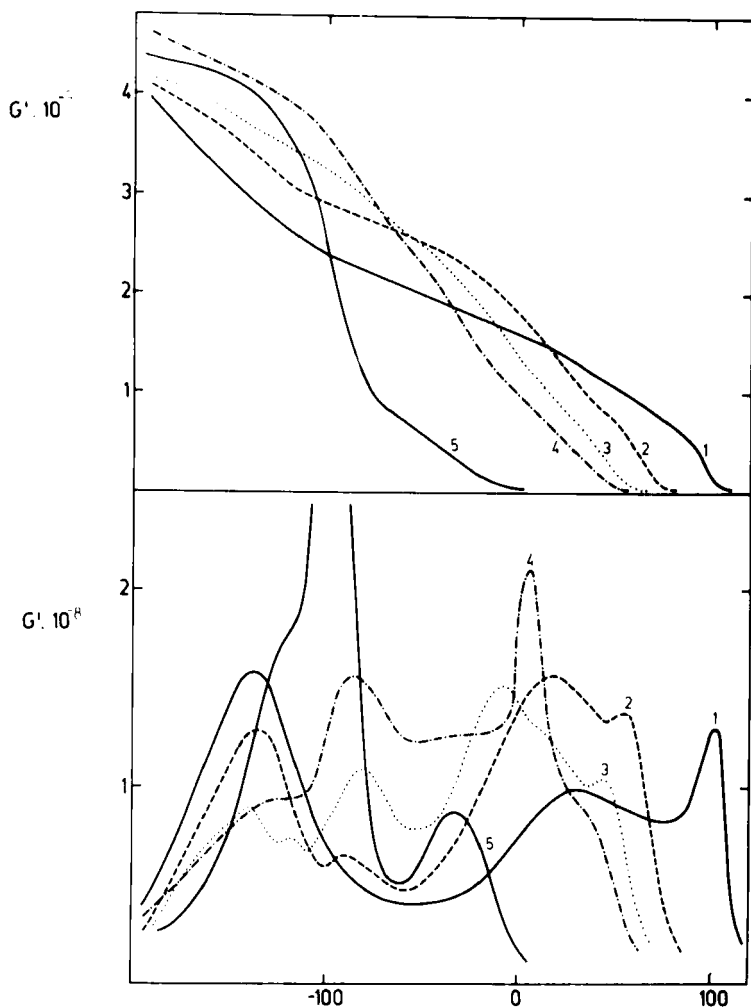


FIGURE 3 Effect of water on temperature dependence of storage and loss moduli (in Pa) of PHEMA containing 0.115 volume fraction of urea.

- (1) extracted (without urea), dried and annealed sample;
- (2) dried sample;
- (3) weight fraction of water: 0.03;
- (4) 0.1;
- (5) 0.25.

consequences of the water addition to the PHEMA containing urea (Figure 3) are analogous to that found for pure PHEMA: the α maximum is shifted towards lower temperatures and at the volume fraction of water equal to 0.1 it fully overlaps the β_1 maximum; the β_d maximum intensifies and its

temperature decreases, whereas the γ maximum is further reduced and finally vanishes.

The changes of the molecular mobility caused by urea are reflected adequately also on the temperature dependence of the storage modulus G' (Figure 2). The decrease in the storage modulus within the region of the $(\alpha + \beta_1)$ transition is the larger and steeper, the higher is the content of urea; all the determined curves intersect at temperatures around T_{β_1} . The differences in the moduli of the samples with different urea content also diminish at liquid nitrogen temperature which is an obvious consequence of the freezing-in of the most molecular motion (perhaps with the exception of the rotation of methyl groups, which is not significant for storage and dissipation of mechanical energy¹). Since urea reduces the γ process—both height and area of the loss maximum decrease, whereas the shape remains almost unchanged (Table I)—without giving rise to another secondary relaxation, the concomitant drop of the storage modulus in the range $T_\gamma - T_{\beta_1}$ is reduced and the level of the modulus is elevated.

In earlier papers^{3, 4} we have concluded that the mobility of the hydroxyethyl side chains with bound (or interacting) molecules of the incorporated diluent sets in at temperature T_{β_d} of the originating diluent dispersion. The reduction of the extent of the γ relaxation caused by diluents accounts for an increase of the storage modulus at temperatures below T_{β_d} . Similarly, water suppresses molecular mobility of the hydroxyethyl side groups of poly(2-hydroxyethyl acrylate) and thus increases the modulus G' below -95°C , at which the relaxation of the whole side chains is released.⁶ The increase of the modulus of PHEMA below T_{β_d} owing to the presence of water (except for the weight fraction 0.25) is apparent also with samples containing urea (Figure 3). It is obvious that the suppression of molecular mobility—evidenced by the decrease of the loss and increase of the storage moduli—is caused by urea at $T < T_{\beta_1}$ and by water at $T < T_{\beta_d}$. The mobility of diluent molecules can set in either at the temperature of some of the relaxations already existing in the dry polymer or at the temperature of an originating diluent dispersion. From what has been found as yet one can infer that likewise the molecules of water and other diluents participate in the β_d process, a certain motion of the urea molecules is initiated at T_{β_1} along with the motion the oxycarbonyl groups. The reason for the qualitatively different effect of urea can be sought in its strong interaction with PHEMA accounting for a decrease of the free volume in the glassy state (Figure 4), in relatively high (hypothetical) glass transition temperature etc. A possible (but not proven) formation of physical network (cf.²²) due to the incorporation of urea as a "bifunctional" low molecular weight substance cannot be of primary importance, for ethylene glycol, formamide, glycerin^{4, 23} etc. give rise to an extensive relaxation process at temperatures around -100°C . Neither molecular weight of the diluent

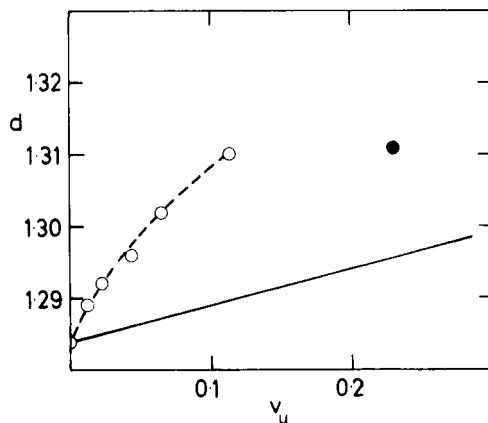


FIGURE 4 Density (in Mg/m^3) of PHEMA-urea system in dependence on volume fraction of urea.

Full curve — calculated dependence (see text); ● heterogeneous sample 6 (Table I).

does seem to be significant for the effect of the diluent on the molecular mobility of polymers. One can conclude that the chemical composition and physical constants of the diluent do not suffice for anticipating its influence on molecular mobility of a particular polymer, i.e. on the intensity and the temperature of the existing dispersions and on the origin of new dispersions and the temperature dependence of their parameters.

The increase in the modulus of glassy polymers (below the temperature T_r of a relaxation) on addition of low molecular weight compounds is apparently a general phenomenon ensuing from the reduction of the secondary relaxation processes. If the temperature T_r is sufficiently high so that the modulus increases with the increasing diluent concentration at room temperature, the diluent is conventionally regarded as an antiplasticizer. This term is not accurate because the antiplasticizers decrease T_g similarly to plasticizers.^{2, 22, 24, 25} With polycarbonates²⁵ it was observed that the increase in the modulus (at room temperature) at a concentration of the antiplasticizer was the more pronounced the steeper was the decrease of T_g with concentration of the antiplasticizer. According to the criterion mentioned above urea can be regarded as an "intermediate" type for it works as a plasticizer at temperatures above 22°C , whereas below this temperature it effects as an antiplasticizer (Figure 2). From this it follows that to qualify the effect of a particular (anti)-plasticizer it is more convenient to determine the storage and loss moduli over a broad temperature span below the T_g than to measure the modulus, yield stress etc. at room temperature. The antiplasticizing effect can be expected with that low molecular weight compounds which suppress the existing relaxations in glassy state without giving rise to new relaxations.

The final result will also be codetermined by the type of polymer, because it was shown³⁻⁷ that the formation and parameters of a diluent relaxation process depend both on polymer and diluent. The elucidation of the mechanism of antiplasticization is in a great extent identical with the explanation of the more general problem of how the diluents affect the molecular mobility of glassy polymers.

Acknowledgement

The author wishes to thank Dr. J. Baldrián of this Institute for taking the diffraction patterns.

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