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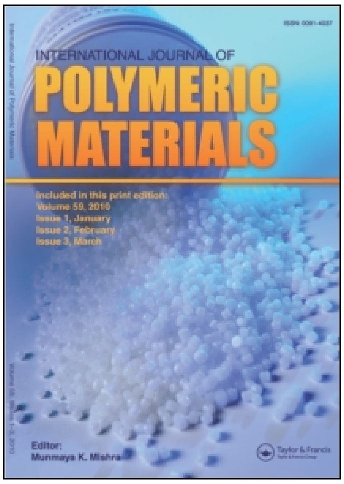

International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:
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To cite this Article Kolaik, J. , Kopeĉek, J. , Vacík, J. and Janáĉek, J.(1976) 'Relaxation Behavior of Poly(N-monosubstituted Methacrylamides)', International Journal of Polymeric Materials, 5: 1, 89 — 97
To link to this Article: DOI: 10.1080/00914037608072391
URL: http://dx.doi.org/10.1080/00914037608072391

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Intern. J. Polymeric Mater., 1976, Vol. 5, pp. 89–97

Printed in Reading, England

Relaxation Behavior of Poly(N-monosubstituted Methacrylamides)

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(*Received January 30, 1975*)

A free-oscillating torsional pendulum was used to investigate the effect of substituents R on the dynamic mechanical relaxation behavior of poly(N-monosubstituted methacrylamides) in the temperature interval from −196 to 130°C. A comparison with the corresponding polymethacrylates shows that the relaxation motion of the side groups R, which gives rise to the low temperature dispersion (below −130°C), is virtually independent of whether R is attached to COO or CONH groups. On the other hand the obtained data give evidence that a strong intermolecular interaction and high steric hindrances suppress the onset of the motion of CONH—R side chains as a whole. For the same reason the glass transition temperature of the poly(N-monosubstituted methacrylamides) is about 100°C higher than that of the corresponding polymethacrylates. The incorporation of low molecular weight substances leads to reduction of the low-temperature dispersion and to formation of a new secondary dispersion at a temperature of about −100°C (1 Hz); with increasing concentration of the diluent this new dispersion becomes more intensive and shifts toward lower temperatures. These and the earlier data indicate that the transformation of the secondary relaxation processes due to the effect of diluents is likely of more general character.

INTRODUCTION

The relaxation motion of the side chains in polymethacrylates gives rise to several dispersions below the glass transition temperature. The secondary β_1 dispersion, which appears at temperatures around 20°C (1 Hz), is usually attributed[1,2] to the hindered rotation of COOR side chains as a whole. The low temperature (γ) dispersion is considered[1] to be caused by conformational changes of the R group. For R equal to CH_3 a reorientation is assumed[1,3] to start at temperatures close to the temperature of liquid helium; for C_2H_5 a low temperature dispersion was found[3,4] at a temperature of about −230°C and the mobility of some higher alkyls sets in at temperatures around −180°C.

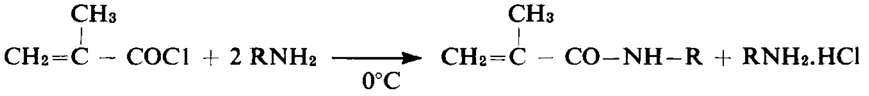
The insertion of a polar or bulky substituent into R group brings about a shift of the γ dispersion toward higher temperatures. The temperature of the onset of the β_1 relaxation motion is not significantly affected[1,2,5] by the size, shape and polarity of the R group, but in polymethacrylic acid (R = H)—apparently due to decrease in steric hindrances—the β_1 dispersion is localized[6] at about -20°C (1 Hz). The data[6] obtained on a set of copolymers of 2-hydroxyethyl methacrylate (HEMA) with methacrylic acid (MAAc) show, that molecular mechanism of the β_1 dispersion in polymethacrylic acid is analogous to that in polymethacrylic esters.

A significant shift of the secondary dispersion to higher temperatures appears when amide groups are introduced into the side chains.[7] For example the volume fraction 0.2 or 0.4 of methacrylamide (MAAm) in copolymers with HEMA accounts for a shift of the β_1 dispersion temperature from 28°C to 55°C or 70°C (1 Hz), respectively; the secondary dispersion of the copolymers containing even more MAAm and of PMAAm itself can be expected to lie at temperatures above the measured interval, viz. above 130°C. Also from the comparison of the relaxation behavior of polyacrylamide (PAAm) with that of polyacrylic esters it follows,[7] that the presence of amide groups results in a decrease of molecular mobility in glassy state. The cause of relatively high temperatures of the secondary transitions in PMAAm and PAAm can be sought in the strong intermolecular forces and, in the first place, in the high steric hindrances of the conformational changes. It is known about the low molecular weight amides[8,9] that owing to electron delocalization, the C(O)—N bond assumes the character of a partial double bond and the amide group becomes approximately planar. For these reasons the hindered rotation about the C(O)—N bond is characterized by barriers of about 20 kcal/mole and rotation of the amide group as a whole around the C—C(O) bond is sterically hindered as well.[8] An assumption was thus expressed[7] that analogous reasons lead to the low molecular mobility in PMAAm and in PAAm.

An objective of this paper has been to compare more precisely the effect of amide and ester groups on the main and secondary dispersions. To this purpose we studied several N-substituted PMAAm analogous to the esters of polymethacrylic acid studied previously in great detail. At the same time we wanted to complete the series of studies of physical properties of poly(N-mono-substituted methacrylamides) whose medical application can be expected.[10–13]

EXPERIMENTAL PART

Monomers. All the used N-substituted methacrylamides were prepared by the reaction of methacryloyl chloride with the relevant amine according to general equation



$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}} - COCl + 2\,RNH_2 \xrightarrow[0°C]{} CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}} - CO{-}NH{-}R + RNH_2.HCl$$

The solvent was chosen (Table I) so as to precipitate the resulting amine hydrochloride. The reaction proceeds at 0°C by a dropwise addition of 20 wt.% solution of the amine to 20 wt.% solution of methacryloyl chloride in the same solvent. After addition of the whole quantity of the amine the reaction mixture was stirred for an hour and allowed to reach the room temperature. The precipitated amine hydrochloride was filtered off on a Büchner funnel and washed with the solvent. Octylpyrocatechol was added as an inhibitor and the filtrate was concentrated in a vacuum evaporator. The crude monomers were purified by rectification or multiple crystallization (Table I); the reaction yields were 60–70% of the theory. Purity of the products was estimated by GLC analysis on 1 m long columns packed with 10% Apiezon on Chromosorb W.

TABLE I

Synthetized monomers and their physical properties

Monomer	Solvent	Boiling point °C/torr	Melting point °C
N-methyl methacrylamide	benzene	68–69/2.5	—
N-ethyl methacrylamide	benzene	60–61/0.5	—
N-butyl methacrylamide	benzene diethyl-ether	86/0.5	—
N-(2-hydroxypropyl)methacrylamide	acetonitrile	—	69

Polymerization. The polymerization was carried out by radical mechanism at 60°C. N-alkyl methacrylamides were polymerized without diluent whereas N-(2-hydroxypropyl) methacrylamide was polymerized in the presence of 30 vol.% of dimethylformamide. In all polymerizations 0.5 %wt. of diisopropylperoxy dicarbonate[14] was used as initiator and 1% mol. of ethylene dimethacrylate[15] was added as cross-linking agent. All components were weighed into an Erlenmeyer flask, bubbled through with pure nitrogen (20 minutes) and squeezed under inert atmosphere into a mould consisting of two plane-parallel brase plates provided with a polypropylene coating and sealed with a silicone packing. The full mould was placed for 16 hrs into a thermostating bath kept at 60°C.

After removal from the mould the polymer was cut to samples of 0.5 × 6 × 60 mm size. In order to remove the unreacted residues of monomer and initiator the samples were extracted by ethanol at room temperature. The extracted samples were dried to constant weight at 80°C in vacuo of a rotary oil pump. The swelling of the samples was carried out in ethanol or water vapors; the swelled samples were sealed into glass ampoules and stored for one month at room temperature to attain the equilibrium. The temperature dependence of the components of the complex shear modulus was determined by means of a free-oscillating torsional pendulum. In the course of the measurement the samples were kept under dry nitrogen and the temperature was increased from that of liquid nitrogen to about 130°C at a rate of about 0.5°C/minute. The main (α) transition temperature was read off as the temperature of the main loss maximum on the temperature dependence of the Young loss modulus measured by Rheovibron DDV-II. The measurements were carried out at constant frequency of 110 Hz and with the heating rate of 1°C/min in temperature interval from 100–250°C.

RESULTS AND DISCUSSION

The relaxation behavior of the studied poly(N-substituted methacrylamides) in the region of low-temperature dispersion is similar to that of the corresponding polymethacrylates (Table II). Similarly to poly(methyl methacrylate) also PMMAAm (Figure 1) does not show any dispersion between −196°C and −100°C. On the other hand it is obvious (Figure 2) that PEMAAm exhibits a loss peak below −196°C. It is thus evident that the C_2H_5 group is sufficiently large to give rise to a distinct low temperature dispersion in accordance with the behavior of poly(alkyl methacrylates). For R$=CH_3$—$(CH_2)_3$ a very clean-cut loss maximum appears (Figure 3) at a temperature around $T_\gamma = -195$°C, which is about 20°C lower than that of poly(*n*-butyl methacrylate) (Table II). A strengthening of the intermolecular forces due to the introduction of the hydroxyl group in side chains leads to a shift of the γ

TABLE II

Effect of the side groups R on the temperature of the low-temperature- and main-dispersions for esters and N-monosubstituted amides of the polymethacrylic acid

R:		CH_3—	CH_3CH_2—	$CH_3(CH_2)_3$—	$CH_3CH(OH)CH_2$—
T_γ, °C	amid	—	< -196 (1 Hz)	-195 (1 Hz)	-125 (1 Hz)
	ester	—	-232 (9 Hz)[a]	-175 (1 Hz)[b]	-130 (1 Hz)[c]
T_α, °C	amid	240 (110 Hz)[d]	215 (110 Hz)	175 (110 Hz)	170 (110 Hz)
T_g, °C	ester	103 (dil.)[e]	64 (dil.)[e]	18 (dil.)[e]	76 (dil.)[e]

[a] Ref.[3]; [b] Ref.[16]; [c] according to[17] both the poly-(2-hydroxyethyl methacrylate) and the poly(2-hydroxypropyl methacrylate) show the same $T_\gamma = -100$°C (1 kHz), which corresponds[16] approximately to $T_\gamma = -130$°C (1 Hz); [d] appreciable degradation of the polymer; [e] Ref.[18].

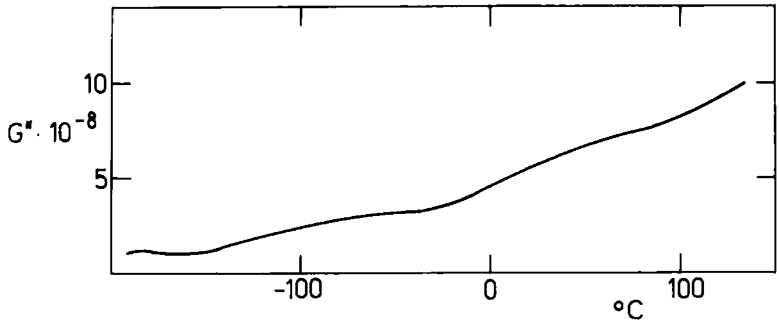


FIGURE 1 Temperature dependence of the loss modulus (dyn/cm^2) of poly(N-methyl methacrylamide).

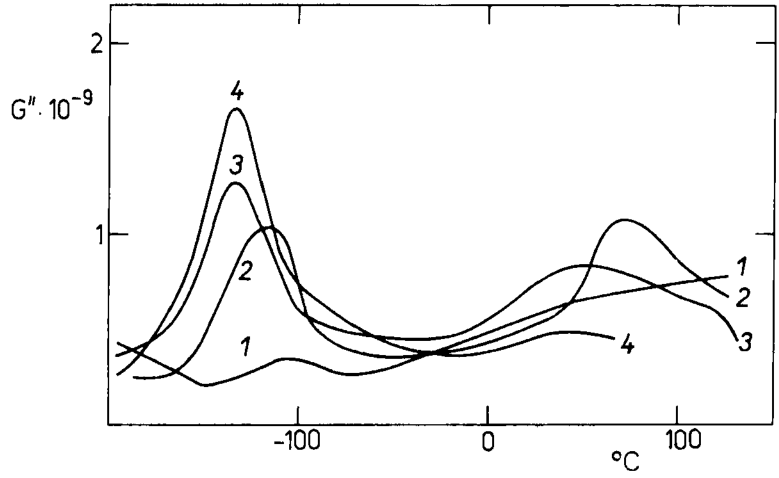


FIGURE 2 Temperature dependence of the loss modulus (dyn/cm^2) of poly(N-ethyl methacrylamide).

Weight fraction of water: 1 traces; 2 0.03; 3 0.05; 4 0.09.

dispersion toward higher temperatures (Figure 4) by approximately 70°C. The presence of hydroxyl group in polymethacrylates affects T_γ in the same way, as follows for instance from the comparison[19] of poly(*n*-propyl methacrylate) ($T_\gamma = -175$°C; 1 Hz) and PHEMA ($T_\gamma = -133$°C; 1 Hz). In summary it can be said, that the hindered rotation of the group R is practically independent of whether it is attached to COO or CONH groups. In this way the most frequent hypotheses, that the low temperature dispersion of polymethacrylates depends solely upon the relaxation motion of the groups R, is repeatedly proved.

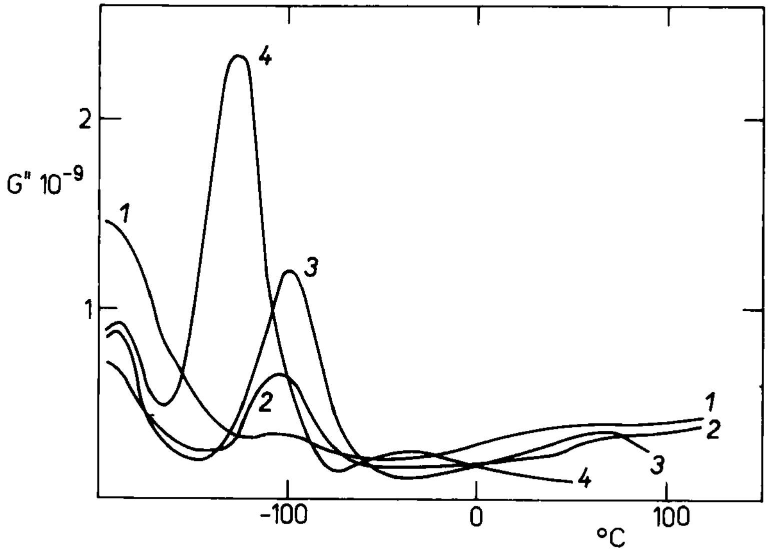


FIGURE 3 Temperature dependence of the loss modulus (dyn/cm^2) of poly(N-butyl methacrylamide).

Weight fraction of ethanol: 1 0.00; 2 0.04; 3 0.11; 4 0.37.

The intensity of the γ relaxation—judged from the magnitude of the loss maximum—in the series of poly(N-substituted methacrylamides) increases with increasing length of the side chain (Figures 2–4) similarly to the corresponding series of polymethacrylates. The intensity and temperature position of the γ dispersion are adequately reflected also in the temperature dependence of the storage modulus G' (Figure 5). The growing extent of the γ molecular motion leads to a decrease of the storage modulus level in the temperature interval from −100 to 100°C. At the same time, however, it is obvious that frozing-in of the molecular mobility at temperatures approaching −196°C manifests itself by relatively small differences between storage moduli of the samples measured.

The incorporation of some low molecular weight substances into poly(N-substituted methacrylamides) gives rise to a new (β_{sw}) loss maximum at approximately −100°C (Figures 2–4), whereas the γ maximum simultaneously decreases or eventually disappears. (The occurrence of a small β_{sw} maximum at dry sample of PEMAAm indicates, either that the drying procedure was not efficient enough to remove the last traces of water, or that a small amount of water was absorbed by the sample during the operations before the measurement.) In all cases the β_{sw} maximum rises and shifts toward lower temperatures with increasing content of the diluent. The overall changes of the temperature dependence of the loss modulus patterns due to the addition of diluents are the

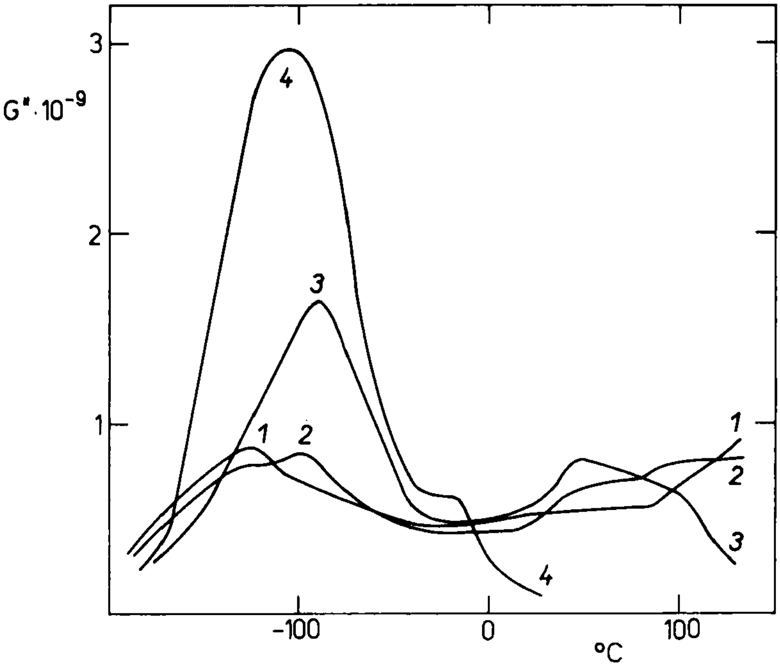


FIGURE 4 Temperature dependence of the loss modulus (dyn/cm^2) of poly N-(2-hydroxypropyl)methacrylamide.

Weight fraction of water: 1 0.00; 2 0.01; 3 0.12; 4 0.28.

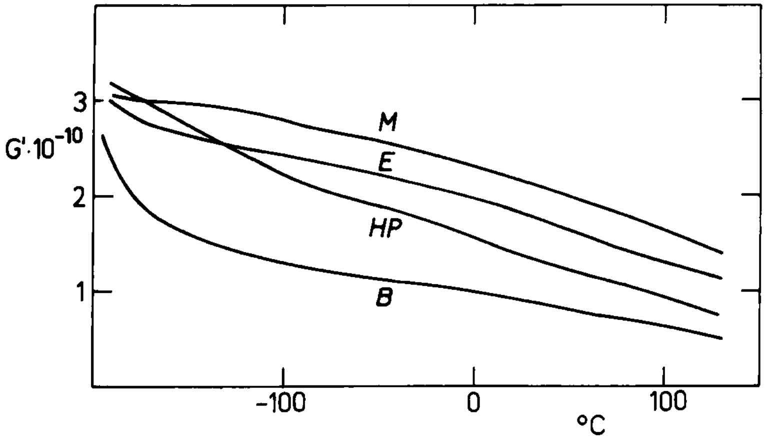


FIGURE 5 Temperature dependence of the storage modulus of poly(N-monosubstituted methacrylamides).

M poly(N-methyl methacrylamide); E poly(N-ethyl methacrylamide); B poly(N-butyl methacrylamide); HP poly N-(2-hydroxypropyl)methacrylamide.

same as with poly(alkylmethacrylates) or poly(hydroxyalkyl methacrylates).[19–21] We can infer that the interaction of the polar diluent molecules with the amide groups of the side chains suppresses the original and gives rise to a new relaxation motion; the presence of the hydroxyl groups in the side chains does not seem to bring into this process any specific feature. The higher temperature of the β_{sw} dispersion can be explained[21] by the assumption that it is caused by the motion of some larger units probably consisted of the side chains and the bound molecules of the diluent. The obtained data thus indicate, that the transformation of γ to β_{sw} dispersions by the diluents is probably more general.

None of the measured polymethacrylamides showed the secondary dispersion up to 130°C (Figures 1–4) in contrast to polymethacrylates with the same R group. (Because of the large cross-section of the samples only the main transition, accompanied by a considerable decrease in the tensile modulus, could be identified by means of Rheovibron DVV-II.) The suppression of the relaxation motion of the CONH—R side chains can be looked for in strong intermolecular interaction of amide groups (the energy of the hydrogen bonds[22] in low molecular R′—CONH—R amides amounts to 5 kcal/mole) and in the steric hindrances due to the rigid planar arrangement of the amide groups.[8] The experimental evidence gathered so far does not allow us to judge the role of either effect. Somewhat more light could be thrown into this question by a study of the relaxation motion in poly(N-disubstituted methacrylamides) or even better by a similar investigation of the polymers of N-mono- and di-substituted acrylamides. The glass transition temperatures, T_g, of the measured polymers can be roughly estimated from the main transition temperatures, T_a, determined with the aid of the dynamic mechanical measurements. A comparison of the literature data[1,15] shows that between the both temperatures holds an approximate relation $T_g = T_a$—(20–30°C). Taking that into account we can say (Table II) that T_g of poly(N-substituted methacrylamides) is on the average about 100°C higher than that of the respective polymethacrylates. A decrease in T_g by an addition of diluents leads to a shift of the main loss maximum (Figures 2–4) into the temperature region measured, viz. under 130°C. From the data obtained we can conclude that the CONH groups in methacrylate polymers significantly suppress the mobility of the main and side chains.

References

1. N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids*, Wiley, London (1967).
2. J. Heijboer in *Physics of Non-Crystalline Solids*, J. A. Prins (ed.), North-Holland Publ. Co., Amsterdam (1965).
3. K. M. Sinnott, *J. Polymer Sci.* **35**, 273 (1959).

4. K. Shimizu, O. Yano, Y. Wada, and Y. Kawamura, *J. Polym. Sci., Polym. Phys. Ed.* **11**, 1641 (1973).
5. F. Lednický and J. Janáček, *J. Macromol. Sci.-Phys.* **B5**, 335 (1971).
6. J. Kolařík and M. Štol, *Polymer J.* **5**, 158 (1973).
7. J. Kolařík and K. Dušek, *J. Macromol. Sci.-Phys.* **B10**, 157 (1974).
8. W. E. Stewart and T. H. Siddall, *Chem. Rev.* **70**, 517 (1970).
9. R. L. Jones, *Trans. Faraday Soc.* **66**, 249 (1970).
10. J. Kopeček and H. Bažilová, *Europ. Polym. J.* **9**, 7 (1973).
11. J. Kopeček and H. Bažilová, *Europ. Polym. J.* **10**, 465 (1974).
12. J. Kopeček, L. Šprincl, and D. Lím, *J. Biomed. Mater. Res.* **7**, 179 (1973).
13. L. Šprincl, J. Vacík, J. Kopeček, and D. Lím, *J. Biomed. Mater. Res.* **5**, 197 (1971).
14. F. Strain, W. E. Bissinger, W. R. Dial, H. Rudoff, B. J. deWitt, H. C. Stevens, and J. Langston, *J. Am. Chem. Soc.* **72**, 1254 (1950).
15. J. Kolařík, J. Vacík, and J. Kopeček, *Intern. J. Polymeric Mater.*, in press.
16. J. Kolařík, *J. Macromol. Sci.-Phys.* **B5**, 355 (1971).
17. M. Shen and J. D. Strong, *J. Appl. Phys.* **38**, 4197 (1967).
18. R. A. Haldon and R. Simha, *J. Appl. Phys.* **39**, 1890 (1968).
19. J. Janáček and J. Kolařík, *Intern. J. Polymeric Mater.*, in press.
20. M. Shen and E. H. Cirlin, *J. Macromol. Sci.-Phys.* **B4**, 293 (1970).
21. J. Kolařík and J. Janáček, *J. Polymer Sci.* **A-2, 10,** 11 (1972).
22. K. Gopal and S. A. Rizvi, *Z. Phys. Chem. N.F.* **81**, 330 (1972).