

## Dynamic mechanical study of the transition from swollen particles to hydrogel caused by neutralization

Z. Sedláková<sup>1</sup>, K. Bouchal<sup>1</sup>, M. Ilavský<sup>1,2,\*</sup>

<sup>1</sup> Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic

<sup>2</sup> Faculty of Mathematics and Physics, Charles University, 180 00 Prague 8, Czech Republic

Received: 5 January 2000/Accepted: 23 May 2000

### Summary

The copolymer of 2-(2-carboxybenzoyloxy)ethyl methacrylate (CEM) with butyl methacrylate (BMA) (BMA/CEM = 40/60 wt.) and terpolymers CEM/BMA/2-hydroxyethyl methacrylate (HEMA) ((BMA + HEMA)/CEM = 40/60 wt.; HEMA/BMA = 35/5, 30/10, 20/20 and 10/30) were prepared by emulsion radical copolymerization in water in the presence of sodium dodecyl sulfate and their dynamic mechanical behaviour was investigated as a function of the degree of neutralization  $\alpha$ . Main attention was devoted to the transition from swollen particles to physical gel with increasing degree of neutralization and to the structure of formed hydrogels. From the results it followed: (a) the transition from swollen particles to the gel state occurs in a narrow neutralization interval at  $\alpha \sim 0.45$  for BMA/CEM copolymer; increasing the HEMA content shifts the transition to lower  $\alpha$  values; (b) with increasing shear strain  $\gamma$ , the hydrogels passed from the gel to liquid state and this transition at the critical strain  $\gamma_c$  was reversible; (c) junctions in the gel state are probably formed by the hydrophobic interactions of the ends of CEM units which form clusters and the junction concentration is independent of the HEMA content and degree of neutralization  $\alpha$ ; (d) increasing degree of neutralization  $\alpha$  and the HEMA content (increasing polarity of the system) stabilizes the junctions and the critical  $\gamma_c$  values increase; (e) the values of the low-strain storage  $G'_0$  and loss  $G''_0$  moduli together with critical strains  $\gamma_c$  did not depend on angular frequency  $\omega$  in the interval  $10^{-1}$  - 10 rad/s.

### Introduction

Functionalized polymer systems with a carboxylic groups in the side chains were prepared mainly by radical polymerization of aliphatic, aliphatic-aromatic and aromatic acids (1-4). In such a way, both strong (4) and weak (1) polyacids could be prepared. A considerable change in acidity and physical properties was achieved in functionalized polymers and copolymers of vinyl derivatives of aromatic acids (3-6). These polyacids are weak acids, but their anions enter into strong interactions with  $\text{Ca}^{++}$  and  $\text{Cu}^{++}$  cations (7). Functionalized polymers and copolymers containing units substituted with aliphatic-aromatic acids are mainly based on acrylate and methacrylate derivatives of these acids (8-10). The monomers such as 2-(4-carboxyphenoxy)ethyl methacrylate (10) and 2-(2-carboxybenzoyloxy)ethyl methacrylate (8, 9) were reported in literature.

In our previous paper (11), we have described the synthesis of 2-(2-carboxybenzoyloxy)ethyl methacrylate (CEM) and characterized the reactivity of CEM in the emulsion radical polymerization and copolymerization with butyl methacrylate (BMA) in aqueous solution in the presence of a redox initiation system and sodium dodecyl sulfate as emulsifier. In such a way, poly[2-(2-carboxybenzoyloxy)ethyl methacrylate-co-

\* Corresponding author

e-mail: ilavsky@kfpy.troja.mff.cuni.cz

butyl methacrylate] latexes, containing submicron cation exchanger particles with the content of COOH groups ranging from 1.1 to 3.1 mmol COOH/g of dry copolymer, were prepared. The size of particles in water strongly increased during titration with a 0.1 M solution of NaOH as strongly hydrophilic carboxylate groups are formed on the chain. At pH  $\sim$  6.5, the particles dissolved and transformed into hydrogel, i.e., a continuous swollen physical network was formed. One can expect that at these pH, the carboxylic groups are ionized and that the repulsion interaction of negative charges on the chain together with the mixing tendency of these anions with outer water causes the transformation (12, 13) of individual particles to solution and finally to a physical gel. Determination of pH at which the transition takes place has great practical importance, especially in ophthalmology (14). It is desirable that latex particles containing a drug be introduced on the eye and that small increase in pH transform them to hydrogel covering the eye and subsequently release the drug.

It was shown (15,16) that the transition from liquid state (individual swollen particles) to the gel state can be detected by dynamic mechanical spectroscopy. This transition resembles the sol-gel transition in gelation of thermoreversible gels (16), such as in poly(vinyl chloride) or poly(vinyl alcohol). In the first approximation (17,18), the transition (physical gel point, where the first infinite structure in the system is formed (19,20)) can be determined as the crossover of the dynamic storage ( $G'$ ) and loss ( $G''$ ) shear moduli; usually  $G'' > G'$  is found in the liquid state and  $G' > G''$  in the solid state. Dynamic mechanical functions can be also used for characterization of the gel structure, e. g., from the value of the storage modulus  $G'$  in the gel state, the concentration of physical junctions can be determined (13).

The objective of this paper is experimental investigation of the transition from swollen particles to the gel state of the CEM/BMA copolymer and CEM-BMA-2-hydroxyethyl methacrylate terpolymers by dynamic mechanical measurements. Measurements at various frequencies and shear strains were carried out in dependence on the degree of neutralization and composition of the systems.

## Experimental

*Sample preparation.* The synthesis of 2-(2-carboxybenzoyloxy)ethyl methacrylate (CEM) was described in detail in our preceding paper (11). Emulsion radical copolymerizations of CEM with butyl methacrylate (BMA) and its terpolymerizations with BMA and 2-hydroxyethyl methacrylate (HEMA) were carried out in water in a glass autoclave in the presence of sodium dodecyl sulfate at  $25 \pm 0.1$  °C with a stirrer speed of 500 rpm. Polymerization: [monomers] =  $1 \text{ mol dm}^{-3}_{\text{H}_2\text{O}}$ ,  $[\text{K}_2\text{S}_2\text{O}_8] = [\text{K}_2\text{S}_2\text{O}_5] = 7.3 \text{ mmol dm}^{-3}_{\text{H}_2\text{O}}$ , [sodium dodecyl sulfate] =  $10 \text{ g dm}^{-3}_{\text{H}_2\text{O}}$ , the weight ratio monomers/aqueous phase was 0.2. Five samples with mole fractions: BMA/HEMA/CEM = 40/0/60, 30/10/60, 20/20/60, 10/30/60 and 5/35/60 were prepared (for details, see (11)).

Latexes were neutralized to various degrees with an 0.5 M NaOH aqueous solution at temperature  $T_p$ . During neutralization, water was added in such amounts that the weight ratio of monomers to the aqueous phase was 0.15 regardless of the degree of neutralization. The samples were stored for 15 min and then transferred to a Rheometrics apparatus. In most cases the samples were in the form of a viscous liquid or paste.

*Dynamic mechanical measurements.* Dynamic mechanical behaviour was measured with a Rheometrics SYS-4 apparatus. Oscillatory shear measurements were performed with

parallel-plate geometry at 25 °C. The angular frequency  $\omega$  varied from 0.1 to 10 rad/s and shear strains  $\gamma$  between 0.01 and 1.0 were employed. The real,  $G'$ , and imaginary,  $G''$ , components of the complex shear modulus,  $G^*$ , and loss tangent,  $\text{tg } \delta = G''/G'$ , were determined.

## Results and discussion

*Effect of deformation, ionization and thermal history on stability of hydrogels.* An example of the strain dependence of the storage,  $G'$ , and loss,  $G''$ , moduli measured at frequency  $\omega = 10$  rad/s is shown in Figure 1 for BMA/CEM = 40/60 hydrogel with neutralization degree  $\alpha = 0.7$ ; the hydrogel was neutralized at temperature  $T_p = 25$  °C and measured at  $T_m = 25$  °C. As expected, in the region of low shear strains,  $0.01 \leq \gamma \leq 0.1$ , the linear viscoelastic behaviour with values of both moduli independent of strains is observed. For higher deformations with increasing strain  $\gamma$ , the modulus  $G'$  decreases and loss modulus  $G''$  slightly increases; at the critical gel point value,  $\gamma_c = 0.52$ , the crossover of both the moduli is observed. While for  $\gamma < \gamma_c$ , the solid-like behaviour with  $G' > G''$  is observed, for  $\gamma > \gamma_c$  the liquid-like behaviour with  $G'' > G'$  is found. Subsequent run with decreasing strain  $\gamma$  roughly reproduces the strain dependences of both moduli obtained with increasing  $\gamma$ ; the gel formation takes place at a slightly higher  $\gamma_c$  value (0.56) and the  $G'$  modulus in the linear viscoelastic region obtained in decreasing  $\gamma$  run is  $\sim 25\%$  lower than the initial value. From Figure 1 thus it follows that in the first approximation, the same hydrogel structure was reformed in the decreasing  $\gamma$  run (breaking and formation of physical junctions is reversible). Similar results were obtained for all hydrogels. From these measurements it is not possible to decide whether the liquid state is formed by highly water-swollen particles or by concentrated solution of polymer molecules.

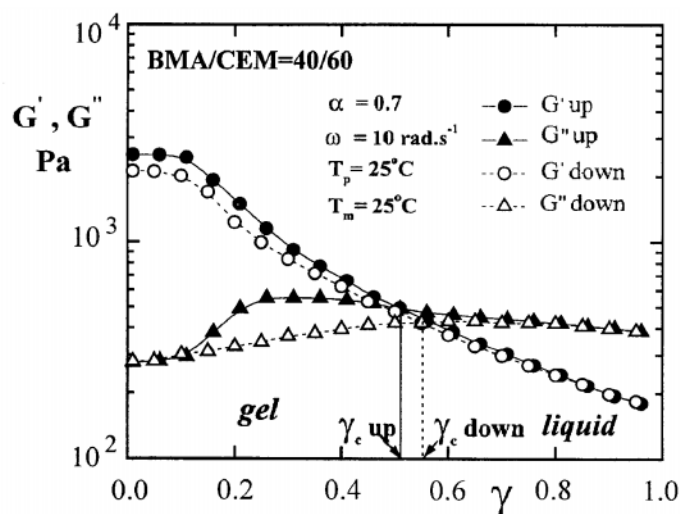


Figure 1. Dependence of the storage and loss moduli,  $G'$  and  $G''$ , on shear strain  $\gamma$  for CEM/BMA hydrogel with degree of neutralization  $\alpha = 0.7$ . Critical strain,  $\gamma_c$ , is determined as the crossover of  $G'$  and  $G''$  moduli

The dependences of the critical shear strain,  $\gamma_c$ , on the degree of neutralization  $\alpha$  are shown in Figure 2 for BMA/CEM = 40/60 neutralized at  $T_p = 25$  °C and measured at  $T_m = 25$  °C with increasing  $\gamma$  at three different strain rates. Within experimental scatter,

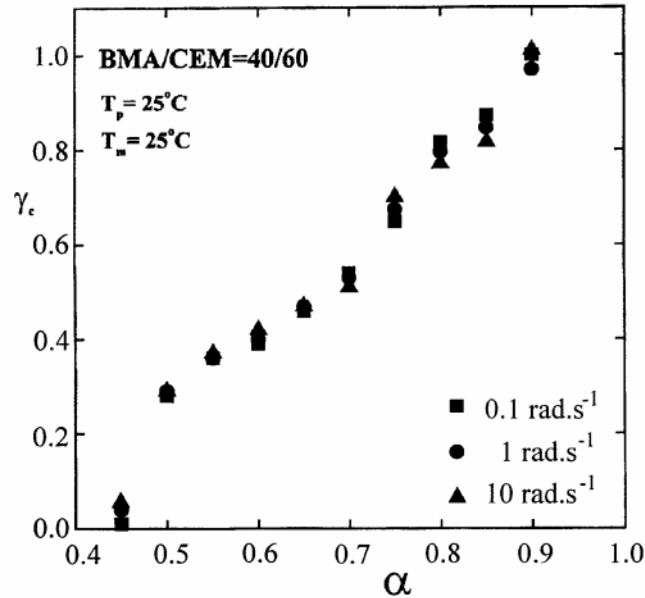


Figure 2. Dependence of the critical strain,  $\gamma_c$  on the degree of neutralization  $\alpha$  for CEM/BMA copolymer neutralized at  $T_p = 25 \text{ }^\circ\text{C}$  and measured at  $T_m = 25 \text{ }^\circ\text{C}$

the  $\gamma_c$  values are independent of  $\omega$ , which means that the junction strength is frequency-independent. On the other hand, the  $\gamma_c$  values show a pronounced increase with increasing  $\alpha$ , which means that increasing neutralization stabilizes physical gel junctions and shifts the solid-liquid transition to higher strains.

The effect of thermal history on the structure of hydrogels is shown in Figure 3 in which the strain dependences of  $G'$  and  $G''$  moduli are shown for BMA/CEM = 40/60 with  $\alpha = 0.5$  measured at  $\omega = 10 \text{ rad/s}$  and  $T_m = 25 \text{ }^\circ\text{C}$ . From Figures 3a and 3b it follows that increasing the additional aging (curing) time from 60 to 120 min after the initial aging time  $t_p$  ( $t_p = 60 \text{ min}$  after neutralization in all cases so that the total aging time  $t_a = t_p + 60 \text{ min}$  or  $t_a = t_p + 120 \text{ min}$ ) has virtually no effect on the  $G'$  and  $G''$  dependences on  $\gamma$  and  $\gamma_c$  values. Neutralization in the liquid state at  $T_p = 85 \text{ }^\circ\text{C}$  and subsequent cooling down to  $25 \text{ }^\circ\text{C}$  leads to a decrease in both low-strain moduli (Figs 3c and 3d), but  $\gamma_c$  values remain virtually unaffected. The temperature cycle - neutralization at  $T_p = 85 \text{ }^\circ\text{C}$  with cooling down to  $25 \text{ }^\circ\text{C}$  and subsequent heating to  $85 \text{ }^\circ\text{C}$  and cooling to  $25 \text{ }^\circ\text{C}$  again - gives twice larger moduli  $G'_0$  and  $G''_0$  than in the previous case (Figs 3e and 3f); also in this case, the  $\gamma_c$  values are roughly constant. This means that increasing aging time has in all cases no effect on strain dependences of moduli but neutralization at a higher temperature,  $T_p = 85 \text{ }^\circ\text{C}$ , decreases the junction concentration. It can be concluded that the strain stability of junctions, given by the  $\gamma_c$  value, is in the first approximation independent of the neutralization temperature, thermal history and of the aging time.

*Effect of ionization and HEMA concentration on formation and structure of hydrogel.* The dependence of low-strain storage,  $G'_0$ , and loss,  $G''_0$ , moduli on the neutralization degree,  $\alpha$ , is shown in Figure 4 for copolymer BMA/CEM = 40/60. Gradual formation of hydrogel can be seen for degrees of neutralization  $\alpha \geq 0.47$ ; for  $\alpha \geq 0.6$ , the gel structure is fully developed and moduli  $G'_0$  and  $G''_0$  are virtually independent  $\alpha$ . As expected for gel state, the  $G'_0$  values are always higher than  $G''_0$  ( $\sim$  an order of magnitude) and only a very small increase in  $G'_0$  with increasing  $\omega$  is observed.

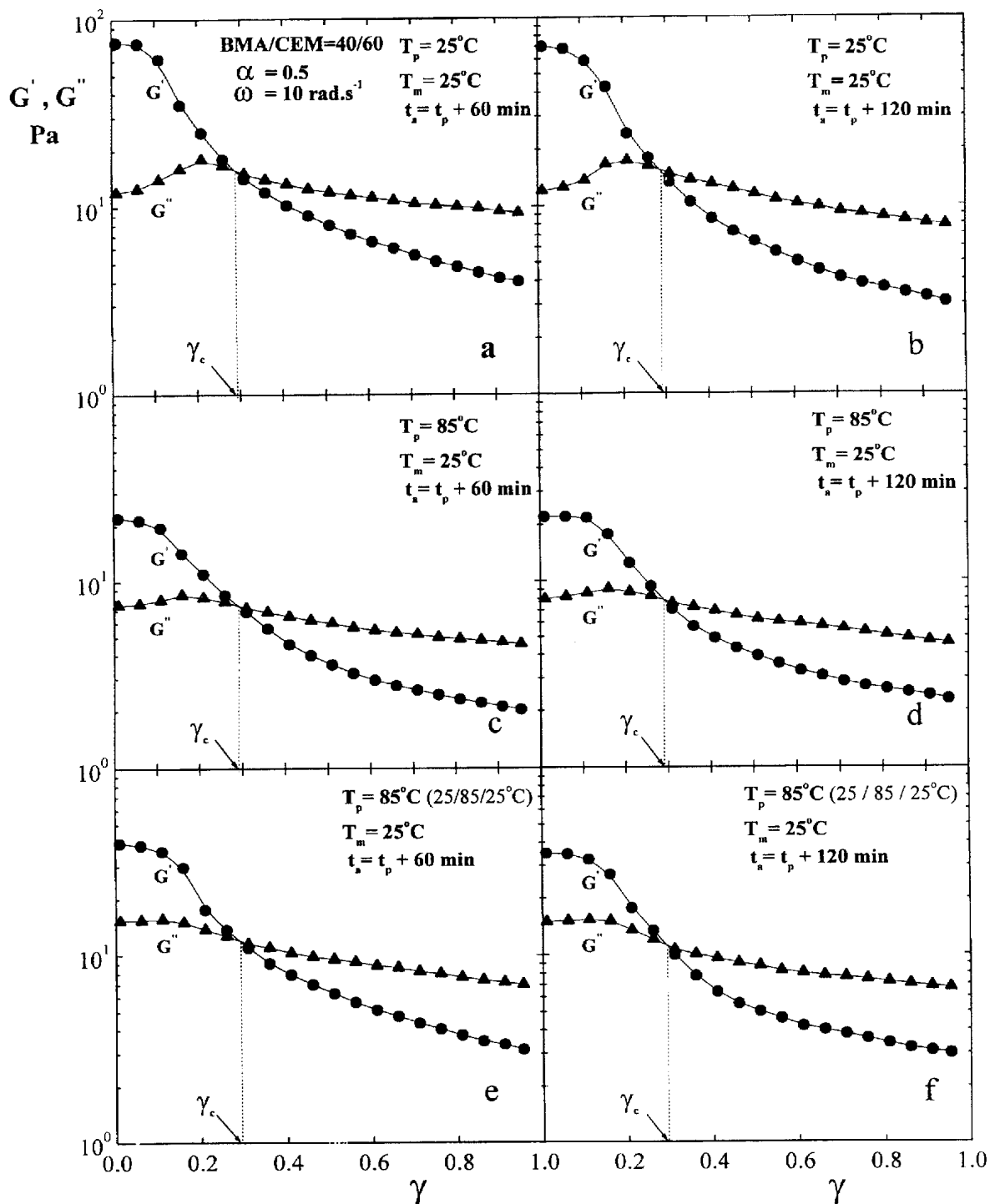


Figure 3. Dependence of the storage and loss moduli,  $G'$  and  $G''$ , on the shear strain  $\gamma$  for CEM/BMA copolymer with  $\alpha = 0.5$ . Temperature of measurements  $T_m = 25^\circ\text{C}$ ,  $t_p$  is the initial aging time before measurement ( $t_p = 60$  min in all cases) and  $T_p$  is neutralization temperature. (25/85/25  $^\circ\text{C}$ ) denotes temperature cycle: after neutralization at  $85^\circ\text{C}$ , the sample was cooled down to  $25^\circ\text{C}$  and after curing for 60 min (or 120 min), it was heated again to  $85^\circ\text{C}$  and cooled down to  $25^\circ\text{C}$  and measured

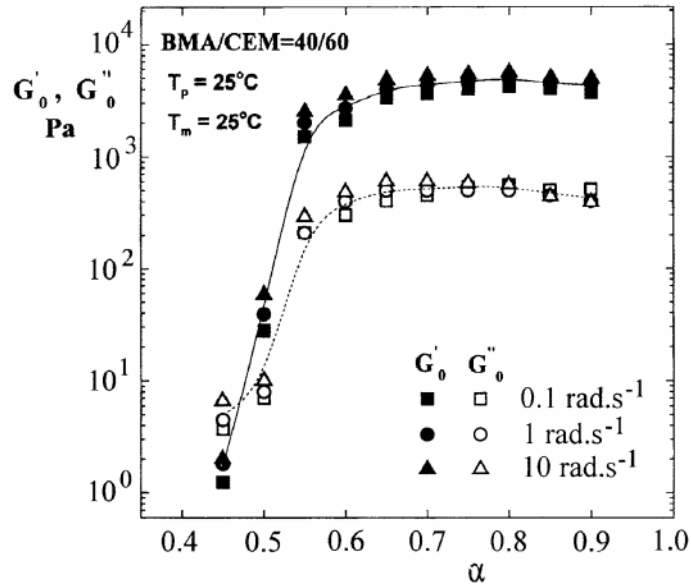


Figure 4. Dependence of the low-strain storage  $G'_0$  and loss  $G''_0$  moduli on the degree of neutralization  $\alpha$  for CEM/BMA sample neutralized at  $T_p = 25^\circ\text{C}$  and measured at  $T_m = 25^\circ\text{C}$

The independence of storage modulus  $G'_0$  on  $\alpha$  means that increasing neutralization of the carboxylic groups of CEM does not change the concentration of physical junctions in the system. Using the rubber-elasticity theory, the concentration of elastically active physical junctions  $\nu_d$  relative to the dry state (or molecular weight of the chain between junctions  $M_c$ ) can be determined from the storage modulus  $G'_0$  by the equation (12,13)

$$G'_0 = \nu_d \nu^0 R T_m' \quad (1)$$

where  $R$  is the gas constant,  $T_m' = 298\text{ K}$  is temperature of measurements and  $\nu^0$  is the volume fraction of the dry polymer in the swollen state. From the conditions of latex formation and neutralization  $\nu^0 = 0.15$  for all  $\alpha$  values. If we take an average value of  $G'_0 = 4 \times 10^3\text{ Pa}$  (calculated from the region of  $\alpha > 0.6$  regardless of  $\omega$ ), then from Eq. (1), the  $\nu_d = 1.05 \times 10^{-5}\text{ mol cm}^{-3}$  was calculated; this value gives  $M_c = \rho/\nu_d = 1.2 \times 10^5$  ( $\rho = 1.3\text{ g/cm}^3$  is the density of dry polymer). This  $M_c$  value is about an order of magnitude ( $M_c = 1.4 \times 10^4$ ) higher than that found for poly(2-hydroxyethyl methacrylate) (21).

The effect of increasing concentration of the HEMA comonomer in terpolymers neutralized at  $T_p = 25^\circ\text{C}$  and measured at  $T_m = 25^\circ\text{C}$  and  $\omega = 10\text{ rad/s}$  on the dependence of moduli  $G'_0$  and  $G''_0$  on  $\alpha$  is shown in Figure 5. As expected, replacement of hydrophobic comonomer BMA by hydrophilic comonomer HEMA destabilizes swollen particles and shifts the gel formation to lower degree of neutralization  $\alpha$ . On the other hand, the  $G'_0$  values at high ionizations are roughly independent of HEMA concentration. The independence of the concentration of physical junctions on HEMA and  $\alpha$  values (Figs 4 and 5) suggests that these junctions are predominantly formed by hydrophobic interactions of CEM side chain ends, which are stabilized by polar interactions of ionized and nonionized carboxylic groups with water (micelle-like structure of benzene rings).

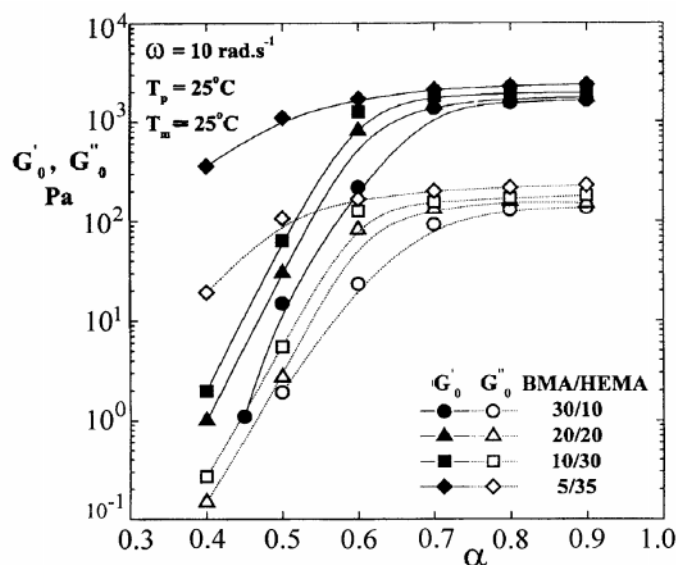


Figure 5. Dependence of the low-strain storage  $G'_0$  and loss  $G''_0$  moduli on the degree of neutralization  $\alpha$  for terpolymers CEM/(BMA+HEMA) = 60/40 for indicated BMA/HEMA ratios

A pronounced effect of the BMA/HEMA ratio on the dependence of  $\gamma_c$  on  $\alpha$  for terpolymers neutralized at  $T_p = 25^\circ\text{C}$  and measured at  $T_m = 25^\circ\text{C}$  ( $\gamma_c$  determined from the increasing  $\gamma$  run) can be seen in Figure 6. As expected, for all four samples, the  $\gamma_c$  values increase with  $\alpha$  and at a constant  $\alpha$ , a large increase in  $\gamma_c$  values with increasing content of HEMA in terpolymers is found. As it was found that the HEMA/BMA ratio does not affect the junction concentration, the results shown in Figure 6 suggest that the hydrophilic HEMA component stabilizes strain strength of physical CEM junctions, similarly to the degree of neutralization  $\alpha$ .

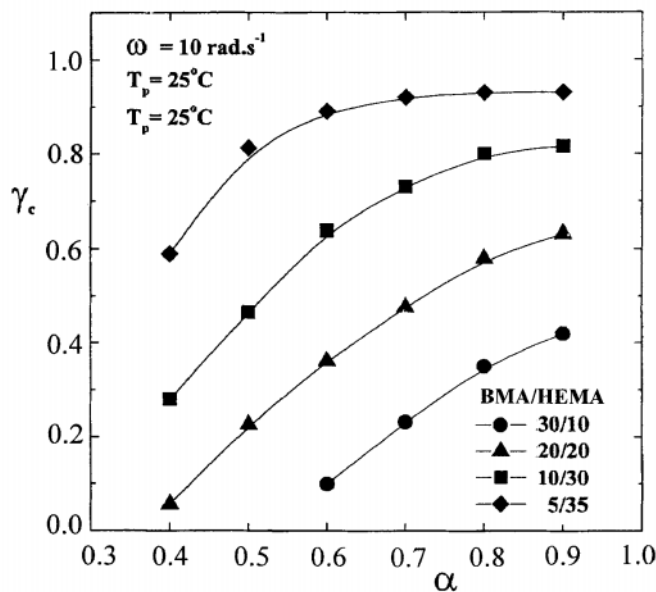


Figure 6. Dependence of the critical strain  $\gamma_c$  on the degree of neutralization  $\alpha$  for terpolymers CEM/(BMA+HEMA) = 60/40 for indicated BMA/HEMA ratios

## Conclusions

From the above discussed results, we can conclude: (a) in transition from swollen particles to hydrogel, physical junctions in the gel are formed by CEM units of the chain (probably by hydrophobic interactions of ends of side chains of CEM units); (b) the concentration of junctions (given by CEM fraction) in the system does not depend on the BMA/HEMA ratio in terpolymers; on the other hand, increasing HEMA content shifts the hydrogel formation to lower degrees of neutralizations; (c) the strain strength of junctions is stabilized by increasing polarity of the system caused by increasing degree of neutralization  $\alpha$  and by increasing the content of HEMA comonomer in terpolymer hydrogels; (d) thermal and aging history does not affect the stability of hydrogel at 25 °C. From the above discussion it also follows that measurements of dynamic mechanical properties is a strong tool for determination of the presence of certain structures (or molecular physical interactions) or physical crosslinks, but cannot determine which groups take part in the junction formation. These measurements can be used for quantitative determination of the transition from swollen particles to the gel state as dynamic function values change by several orders of magnitude.

**Acknowledgements.** Financial support the Academy of Sciences of the Czech Republic (grant No. K2050602/12), Grant Agency of the Charles University (grant No. GAUK 46/1998/B) and of Ministry of Education of the Czech Republic (project No. VZ 1132000) is gratefully acknowledged.

## References

1. Katchalsky A (1954) *J Polym Sci* 12: 159
2. Osawa E, Wang K, Kurikawa O (1965) *Makromol Chem* 83: 100
3. Sakaguchi Y, Nishino J, Tamaki K (1971) *Kobunshi Kagaku* 28: 789, *Chem Abstr* (1972) 76: 100283
4. Žůrková E, Bouchal K, Kálal J, Paleta O, Dědek V (1986) *Angew Makromol Chem* 141: 131
5. Winslow EP, Gershman NE (1963) *J Polym Sci A* 1: 2383
6. Tirrell D, Vogl O (1980) *Makromol. Chem.* 181: 2097
7. Tamaki K, Imai K, Nishimo J, Sakaguchi Y (1973) *Kobunshi Kagaku* 30: 608; *Chem Abstr* (1974) 80: 71324
8. Matshuda H, Migoshi N (1973) *J Appl Polym Sci* 17: 1941
9. Nakabayashi N, Masahura E (1973) *Polym Prepr (Am Chem Soc, Div Polym Chem)* 20: 300
10. Portugall M, Ringsdorf H, Zentel R (1982) *Makromol Chem* 183: 2311
11. Sedláková Z, Bouchal K, Ilavský M (1992) *Angew Makromol Chem* 201: 33
12. Hasa J, Ilavský M, Dušek K (1975) *J Polym Sci, Polym Phys Ed* 13: 253
13. Ilavský M (1981) *Polymer* 22: 1687
14. Sedláková Z., Bouchal K., Michalcová J., Bleha M. *New Hydrophilic Materials for Ophthalmology; 36th Microsymposium "High-Swelling Gels", Prague 1995*
15. Ferry JD (1980) *Viscoelastic Properties of Polymers*, 3rd ed, Wiley, NY
16. te Nijenhuis K (1997) *Adv Polym Sci* 130: 1
17. Tung CH-YM, Dynes PJ (1982) *J Appl Polym Sci* 27: 569
18. Chambon F, Winter HH (1985) *Polym Bull* 13: 499
19. Ilavský M, Bubeníková Z, Bouchal K, Fährnich J (1996) *Polymer* 37: 3851
20. Ilavský M, Dušek K (1986) *Macromolecules* 19: 2139
21. Ilavský M, Hasa J (1968) *Collect Czech Chem Commun* 33: 2142