STRUCTURAL CHANGES IN SWOLLEN POLYMER GELS INDUCED BY SOLVENT EXCHANGE*

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Heterogeneous gels are formed as a result of phase separation when they are prepared in the presence of a diluent of low solvent power. It is shown that the heterogeneous structure is not stable and reversible in uncrosslinked or lightly crosslinked gels if phase separation took place at the end of network formation. When the heterogeneous structure is fixed by crosslinking it becomes stable to a certain degree. The optical investigation of changes occurring in poly(2-hydroxyethyl methacrylate) gels, when a poor solvent is exchanged for a good solvent or *vice versa*, characterizes the stability of the heterogeneities and mechanism of the solvent exchange. The turbidity ratio method shows that in the primary stage the heterogeneities decrease in size or disappear but are recovered to a certain degree in the later stages when a poor solvent is replaced by a better one. The observed behaviour is explained by slow mechanical relaxation of the network.

When the quality of a solvent in a swollen polymer gel gets worse, excess solvent may separate in the microform to yield a gel–solvent dispersion. If this phenomenon called microsyneresis occurs during network formation, the heterogeneous structure of the gel becomes fixed.

The copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate in the presence of supercritical amounts of water is an example of such a fixation[1]. 2-Hydroxyethyl methacrylate–water mixtures are good solvents for the polymer unless the concentration of monomethacrylate is low; as the monomers disappear during the copolymerization, the solvent gets poorer and eventually microsyneresis takes place. If this occurs before the completion of polymerization, the heterogeneities become fixed, which gives rise to a permanent turbidity of the gel. However, there is some evidence that not all heterogeneities are necessarily permanent. Moreover, the optical investigation of the gels has shown that not all inhomogeneities in the gels are of the same nature; those formed as a result of microsyneresis are accompanied by larger ones which are also present in a "homogeneous" gel formed in the presence of subcritical amounts of water[2,3]. Regions of higher crosslinking density or associates due to hydrophobic bonding can be assumed[4–6].

An exchange of the poor solvent (water) for a better solvent can shed light upon the nature of heterogeneities. For this purpose we have exchanged water in the gel for solutions of magnesium perchlorate which are good solvents for poly(2-hydroxyethyl methacrylate)[7] and followed the changes in turbidity, degree of swelling, and size and number of heterogeneities determined by the turbidity ratio method[2,3] assuming their spherical shape and composition equal to that of the ambient solution.

EXPERIMENTAL

Gels were prepared by crosslinking copolymerization of 2-hydroxyethyl methacrylate with ethylene dimethacrylate (0·1—0·6%) in the presence of water (47—50%) at 60°C (Table I). The polymerization was initiated with isopropyl percarbonate (0·1%) and proceeded six hours. The gels were extracted with water and kept in water for several months. All of them were more or less turbid.

The solvent exchange was performed in the measuring cell of a double-beam spectrophotometer (Optica Milano, type CF4) equipped with a circulating system allowing a rapid exchange of the liquid surrounding the gel. In the course of measurements, the liquid in the cell was periodically replaced by a fresh solution to keep constant the composition of the solution being in contact with the gel. After water was replaced by 0·887M magnesium perchlorate, the turbidity of the sample was recorded at three wavelengths (436, 546, and 700 nm) as a function of time. In some cases the backward exchange $Mg(ClO_4)_2 \rightarrow H_2O$ was also performed. The changes of the degree of swelling were determined dilatometrically using an Abbé comparator (Zeiss, Jena) as described earlier[3].

The size and number of heterogeneities in the gel were calculated by the turbidity ratio method[2,3] using the equations

$$(\tau_a/\tau_b)_0 = (\lambda_a^2/\lambda_b^2)(S_1/S_2) = f(L), \qquad (1)$$

$$N_p = (2\pi/\lambda^2)(\tau/S), \qquad (2)$$

TABLE I

Characterization of 2-Hydroxyethyl Methacrylate Gels and Equilibrium (∞) Turbidity (τ), Diameter (L_{ab}) and Number (N_p) of Particles after the $H_2O \rightarrow Mg(ClO_4)_2$ Exchange

$a = 436$ nm, $b = 546$ nm, 25°C.

Gel No	Co-monomer[a] %	Water %	τ_b^∞	L_{ab}^∞ μm	$\log N_p^\infty$
1	0·1	47	0·95	0·17	11·64
2	0·1	48·5	—	—	—
3	0·1	50	—	—	—
4	0·32	40	6·78	0·17	13·55
5	0·6	50	3·37	0·14	13·43

[a] Ethylene dimethacrylate.

where τ is the turbidity of the sample, λ is the wavelength of light in a medium with the refractive index n_s, S is the scattering function for the relative refractive index m at a given λ, N_p is the number (cm^{-3}) and L is the size of particles. The subscript 0 denotes values obtained by extrapolation to $c = 0$, the subscripts a and b refer to the selected pair of wavelengths. For this reason, isochronal turbidities at three wavelengths were obtained by interpolation of the respective turbidity-time dependences. The refractive index of the swollen gel phase (n_s') was calculated from concentration dependence of the refractive index of magnesium perchlorate solutions and composition of the gel phase solution. The time dependent composition of the gel phase solution was calculated from the degree of swelling of the gel allowing for a slight positive selective sorption of perchlorate in the gel[7]. The refractive index of the swollen gel was calculated assuming additivity of contributions of the polymer component and gel phase solution. The composition of heterogeneities was assumed equal to that of the outer solution.

RESULTS AND DISCUSSION

Features of the Solvent Exchange

Typical features of the $H_2O \rightarrow 0.887$M-Mg(ClO$_4$)$_2$ exchange can be extracted from examples given in Figs 1a $-$ d (cf. Table I). Fig. 1a represents typical curves obtained for the gel prepared in the presence of 47% water and 0.1% crosslinking agent. (The amount of water is supercritical, the critical amount being $42-43\%$.) If the amount of water during polymerization is increased to 50%, curves of the same character are obtained as in the preceding case, but they are more pronounced in their extrema and the changes occur faster (Fig. 1b). If the amount of the crosslinking agent is increased while keeping the dilution during polymerization constant (50%), the character of the dependences approaches the case of lower dilution and lower crosslinking density: the changes occur at much slower rate (Fig. 1c,d). We can summarize the results as follows: in all cases, the turbidity τ initially decreases, passes through a more or less sharp minimum, increases again and reaches a steady value after several days (Table I). The volume of the gel increases. The size of heterogeneities, L, steeply increases and reaches a maximum in the vicinity of τ_{min}; the maximum is followed by a steep decrease in L. The number of heterogeneities, N_p, passes through a deep minimum. There is always a difference in L's calculated from τ_{436}/τ_{546} and τ_{436}/τ_{700} which is an evidence for polydispersity; however, no clear cut correlation could be found between the polydispersity and history of the gel.

A completely different picture is obtained for the backward exchange Mg(ClO$_4$)$_2 \rightarrow$ $\rightarrow H_2O$; in the range available for measurements the turbidity continuously increases and L changes little (Fig. 1e). A significant dependence on the history is seen in Fig. 1f; when the gel first equilibrated in Mg(ClO$_4$)$_2$ is brought into contact with water for some time and then water exchanged again for Mg(ClO$_4$)$_2$, the decrease in τ is monotonous, the particles remain small and their size constant.

FIG. 1

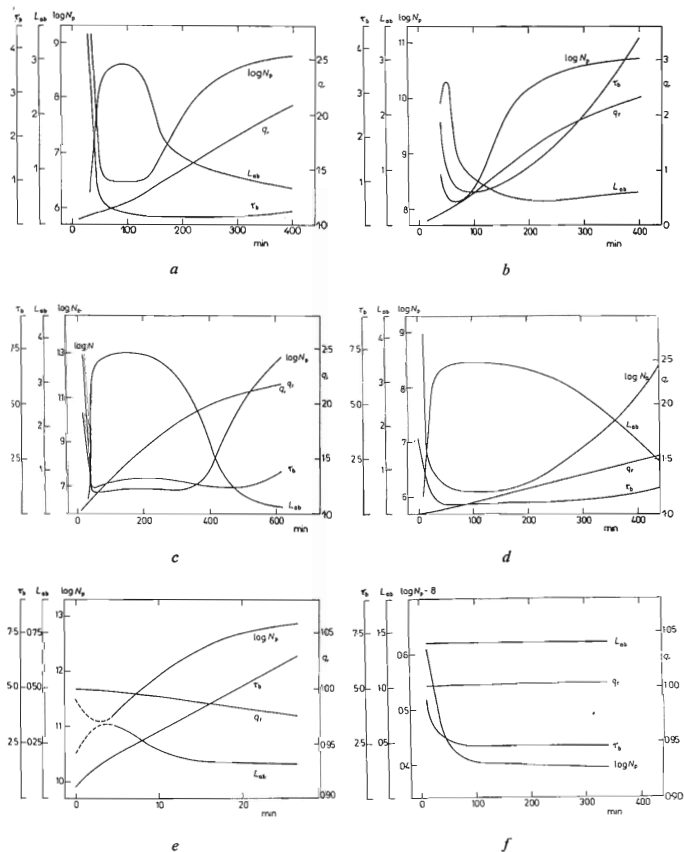Change of the Turbidity (τ_b), Diameter of the Particles (L_{ab}, μm), Number of Particles (N_p, cm^{-3}) and Relative Degree of Swelling (q_r) During the Solvent Exchange

a) Gel 1, $H_2O \rightarrow Mg(ClO_4)_2$; *b*) Gel 3, $H_2O \rightarrow Mg(ClO_4)_2$; *c*) Gel 4, $H_2O \rightarrow Mg(ClO_4)_2$; *d*) Gel 5, $H_2O \rightarrow Mg(ClO_4)_2$; *e*) Gel 1, $Mg(ClO_4)_2 \rightarrow H_2O$; *f*) Gel 2 after a partial $Mg(ClO_4)_2 \rightarrow H_2O$ exchange subjected again to $H_2O \rightarrow Mg(ClO_4)_2$ exchange; $a = 436$ nm, $b = 546$ nm, 25°C.

Explanation of the Results

The changes observed during the solvent exchange can be explained as follows:

a) At least a part of inhomogeneities is fixed, because the turbidity redevelops whereas gels with temperature induced turbidity[8] clear up very rapidly and irreversibly.

b) The data point to the existence of small ($\sim 0.1 - 0.3$ μm) and large ($2 - 4$ μm) heterogeneities which behave differently during the solvent exchange. The difference of one order of magnitude in L would not disappear if a higher refractive index were ascribed to the large inhomogeneities than is the refractive index of the bulk gel. The optical behaviour results from superposition of small and large inhomogeneities.

c) The small inhomogeneities are due to microsyneresis presumably in the form of small droplets. Such a conclusion follows also from a large number of experiments performed earlier[2,3]. During the solvent exchange, the diffusion of $Mg(ClO_4)_2$ is evidently fast, compared with the volume increase, due to long relaxation times of the loosely crosslinked network. That is why the solvent exchange causes first a swelling-in of the gel into the voids (droplets). Small droplets are unstable due to an unfavourable interfacial energy component[3] so that swelling-in causes a disappearance of droplets rather than their continuous contraction. The minimum of τ (Fig. 1*a* − *d*) corresponds to the point when almost all droplets have disappeared; however, because of the fixation of structure by crosslinking the gel remembers sites of former residence of the droplets and tends to relax again the local stresses which have arisen from coalescence of the droplets. This results in reformation of the droplets, again by increasing their number rather than their size (Fig. 1*a* − *d*). Because of the high initial turbidity of the gels preventing the performance of turbidity measurements, an approximate equality of sizes of heterogeneities in water and $Mg(ClO_4)_2$ swollen gels could not be confirmed, but reference is made to the data[2] pointing again to droplets of a diameter $0.1 - 0.3$ μm in turbid gels equilibrated with water.

d) The large inhomogeneities much fewer in number[2,3] can only "be seen" when the droplets are not numerous. If at all, they undergo a slower transformation than the droplets. What happens to the large inhomogeneities is obscured by an increasing number of small droplets, but equilibrium data for the gel 1 (Fig. 1*a*) show that L is again ~ 0.2 μm while τ is low. This is in contrast with water swollen gels, where one gets much larger L's at such low values[2] of τ and suggests a destruction of large formations by perchlorate.

e) The reverse exchange $Mg(ClO_4)_2 \rightarrow$ water (Fig. 1*f*) is characterized by an almost linear increase in turbidity and constant size of separated particles (Fig. 1*f*). New droplets are formed during this process similarly to a homogeneous and even uncrosslinked gel when a good solvent is exchanged for a poor one. The size of the just existing and new droplets does not differ much.

f) Increasing the degree of crosslinking (Figs 1*b*, 1*c* and 1*d*) slows down the disappearance of large inhomogeneities and/or reformation of droplets, but eventually the value of *L* for the gel in equilibrium is again the same as for other gels. Evidently, crosslinking hinders the motion of chains necessary for cooperative rearrangements.

g) Points (*d*)−(*f*) suggest that some sort of association in the water swollen poly-(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) gel, presumably due to hydrophobic bonding, is responsible for the existence of large inhomogeneities. In perchlorate solutions, such associates cannot exist due to water structure-breaking effect of perchlorate and its selective sorption on the copolymer. Previous results[3,8] indicate, however, that there must be in the gels also regions of inhomogeneous crosslinking, because these exist also in organic media and are not sensitive to temperature changes.

REFERENCES

1. Dušek K., Sedláček B.: European Polymer J. *7*, 1275 (1971).
2. Sedláček B.: This Journal *32*, 1398 (1967).
3. Dušek K., Sedláček B.: This Journal *34*, 136 (1969).
4. Gouda J. H., Provodator K., Warren T. C., Prins W.: Polymer Letters *8*, 22 (1970).
5. Ilavský M., Prins W.: Macromolecules *3*, 415, 425 (1970).
6. Warren T. C.: *Thesis.* Syracuse University 1969.
7. Dušek K., Bohdanecký M., Vošický V., Sedláček B.: IUPAC International Symposium on Macromolecules, Leiden 1970.
8. Dušek K., Sedláček B.: This Journal *36*, 1569 (1971).

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