

EFFECT OF DILUENTS
ON THE MICROSYNTERESIS
IN POLY(2-HYDROXYETHYL METHACRYLATE) GELS
INDUCED BY TEMPERATURE CHANGES

K. DUŠEK and B. SEDLÁČEK

*Institute of Macromolecular Chemistry,
Czechoslovak Academy of Sciences, Prague 6*

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Microsyneresis in poly(2-hydroxyethyl methacrylate) gels caused by decreasing solvent power of the swelling agent and induced by temperature changes depends on the dilution of the system during polymerization. Gels were prepared in the presence of varying amounts of butanol, water, and ethylene glycol as diluents and were subsequently swollen in butanol or water. Development and changes in turbidity were studied as a function of temperature. The temperature at which the turbidity starts to develop in gels swollen in butanol is determined mainly by their degree of swelling. Structural inhomogeneities preceding phase separation during copolymerization can be detected by temperature induced development of turbidity (gels swollen in water) and especially by analyzing the size of heterogeneities using the turbidity ratio method (gels swollen in both butanol and water). Formation of inhomogeneities or heterogeneities during polymerization is usually connected with an increase in size of microseparated particles.

In the preceding paper¹, we have shown that poly(2 hydroxyethyl methacrylate) gels prepared in the absence of diluents exhibit the phenomenon of microsyneresis if they are first swollen in a solvent and if its dissolution power for the polymer is then decreased by changing the temperature. For example, gels swollen in butanol at 80°C got turbid when the temperature was lowered. The development of turbidity was explained by the formation of solvent droplets inside the gel after the compatibility limit for the given concentration of solvent inside the gel was reached. It was proved that microsyneresis could be related to the polymer-solvent interaction parameter χ and especially to its temperature dependence. Further on, we brought an evidence that such a gel with microseparated solvent was not in an equilibrium state: the turbidity slowly disappears and the microseparated solvent is transferred slowly to the surface of the sample. The question why the excess solvent is not immediately expelled (and the sample does not deswell), but prefers to separate inside in a microscopic form can be answered as follows: in gels of low crosslinking density, the retractive forces of locally deformed network are very weak and the relaxation times of loosely crosslinked networks are enormously long², soth at the driving force for the equilibrium macrosyneresis (deswelling) is very weak.

As concerns the size of microseparated solvent particles, two principal factors were considered — the retractive force of the network acting against expansion of the droplet and interfacial

tension on the gel-droplet boundary favouring the expansion. As a result of interplay of these two factors, the system can reach a minimum energy at a certain size of particles. Both larger and smaller particles would increase the energy¹. This so-called pseudoequilibrium model¹ is based on the assumption of homogeneity of the swollen network which, we believe, is more or less fulfilled in networks prepared in the absence of diluent. Despite of the existence of a very low concentration of some "primary" heterogeneities in swollen and dry gels¹, no correlation has been found between them and heterogeneities resulting from temperature induced microsynthesis.

In gels prepared by polymerization in the presence of solvents, the assumption of homogeneity is not obvious. It is known that the presence of diluents during crosslinking polymerization may lead to macro- or microsynthesis if their concentration exceeds a limiting (critical) value³. In both cases, the structure is fixed by crosslinking and becomes permanent. Therefore the turbidity is transient if phase separation is not followed by crosslinking and permanent if it is.

If the concentration of the diluent is lower than the critical concentration, the gels are transparent in both dry and swollen state. It is not clear, however, whether the transparency is a sufficient guarantee for homogeneity. If a diluent is present during polymerization, fluctuations in segment density are possible and, if so, they may become partly fixed by crosslinks. Such fixed fluctuations would influence the easiness of the subsequent temperature induced microsynthesis and the size of separated particles. Elucidation of the last two problems was the aim of the present work. The possibility of recognizing the closeness of a system to the critical dilution during copolymerization was the practical aspect of the work.

EXPERIMENTAL

The gels were prepared from redistilled monomers (2-hydroxyethyl methacrylate and ethylene dimethacrylate used as crosslinking agent) and diluents in the presence of 0.07% (by weight of monomers) of isopropyl percarbonate as initiator. The polymerization proceeded under nitrogen in Teflon or glass molds at 60°C for 5–8 h. After polymerization, the samples were repeatedly extracted at 100°C with the solvent that was subsequently used as the swelling agent.

The degree of swelling was determined dilatometrically using the Abbé comparator (Zeiss, Jena, East Germany) by measuring the dimensional changes of a piece of gel. The procedure was described in detail previously¹. The changes in the degree of swelling accompanying the changes in turbidity were measured separately under the same conditions.

The turbidity of samples of gels was measured in the spectrophotometer Optica Milano CF 4 at three wave lengths (436, 546, 700 nm). The samples were placed in a thermostated glass cell filled with the swelling agent. The heating and cooling cycles were slightly different for different samples and are not explicitly indicated. In most cases, the gel was held first at a temperature 70–80°C in the swelling agent for 2 h and gradually cooled at a rate of about 0.1 deg/min. Because of slow volume changes, especially in butanol, the equilibrium degree of swelling was not reached in most cases. However, the state of the gel was sufficiently well characterized by the corresponding degree of swelling: at the same degree of swelling, the temperature characterizing the sudden change of light absorbance depended little on the previous thermal history of the swollen gel.

The size and concentration of particles separated in the turbid gel were determined by the turbidity ratio method described previously (cf.^{1,4,5}). The relative refractive indices of the

separated phase corresponding to the given degree of swelling of the gel were calculated from the temperature dependence of the refractive index of the pure solvent and from the composition and temperature dependence of the refractive index of the swollen gel in the same way as described in the preceding communication¹. A reference is made to the same paper as far as a more detailed discussion of problems connected with the application of the turbidity ratio method is concerned.

RESULTS AND DISCUSSION

Poly(2-hydroxyethyl methacrylate) gels were prepared in the presence of varying amounts of diluents – butanol, water, or ethylene glycol and, after extraction, swollen in butanol or water. Swelling in butanol at higher temperatures gave transparent gels unless the critical concentration of diluent during polymerization was exceeded. When the swollen gel was cooled, it got turbid independently of dilution, but the temperature at which a sudden loss of transparency could be recorded depended on the type and concentration of diluent present in the course of polymerization. Gels swollen in water that were transparent at room temperature became turbid on heating only exceptionally. Among a great number of prepared gels only those exhibited temperature induced development of turbidity that were polymerized in the presence of only slightly less diluent than is the critical value. When this critical concentration was surpassed, permanent heterogeneities were fixed in the gel, and after swelling in water the gels were turbid at any temperature, but the turbidity was temperature-dependent.

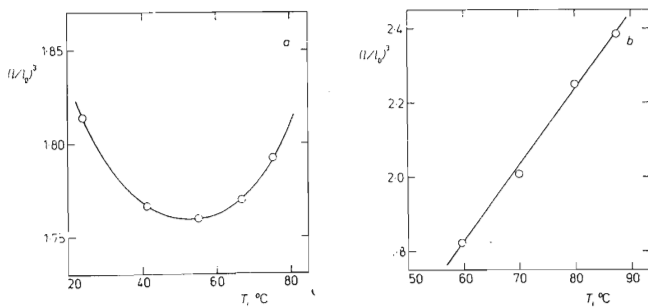


FIG. 1

Temperature Dependence of Volume Degree of Swelling of Poly(2-Hydroxyethyl Methacrylate) Gels

a Swelling in water (the gel with 0.2% ethylene dimethacrylate structure unit, preparation in the presence of 40% water); *b* swelling in butanol (the gel with 0.32% ethylene dimethacrylate unit).

The difference between the two diluents, if used as swelling agents, can readily be understood if we look at their interaction with the polymer. On Figs 1a and 1b the volume degree of swelling $(l/l_0)^3$ (l and l_0 are lengths of the swollen and dry gel, respectively) is plotted as a function of temperature. One can see that gels swollen in butanol markedly deswell with falling temperature, whereas the degree of swelling of gels in water is much less temperature-dependent and reaches a minimum value at 55°C. The development of turbidity in subcritically and supercritically diluted samples goes parallel: the maximum turbidity is always reached at 50–60°C.

In Table I, a part of experimental results is presented that may illustrate the general effect of the diluent on the onset and development of turbidity. The values of the cloud point temperature T_c were obtained by slowly cooling gels swollen in butanol; they correspond to the sudden increase in turbidity and depend on the degree of dilution, but cannot reasonably be correlated with the volume fraction of the diluent, φ_1^0 , used in copolymerization. The fact that the gels are not swollen to equilibrium may be the reason. Indeed, we got a fairly good correlation when T_c was plotted against the actual degree of swelling, as indicated in Fig. 2. Only the gel prepared in the presence of 20% of water does not fit the expected dependence; the reason is not yet clear enough. With increasing degree of swelling, T_c is shifted to higher temperatures for the same reason as the cloud points of concentrated solutions of a linear polymer are shifted to higher temperatures, when the polymer concentration increases. A rough estimate of the cloud point temperature for uncrosslinked

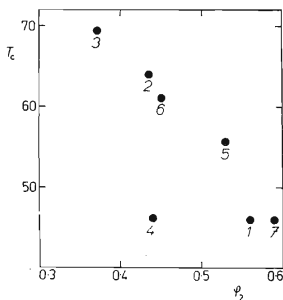


FIG. 2

Dependence of the Cloud Point Temperature, T_c , on the Volume Fraction of the Polymer in the Gel Swollen in Butanol

Type of diluent and its volume fraction before polymerization: 1 without diluent, 2 butanol 0.2, 3 butanol 0.4, 4 water 0.2, 5 water 0.41, 6 water 0.465, 7 ethylene glycol 0.485.

TABLE I

Effect of Diluent on Development of Turbidity in Poly(2-hydroxyethyl Methacrylate) Gels

T temperature of measurement in °C, τ reading of extinction on the photometer at the wave length $\lambda_a = 436$, $\lambda_b = 546$, and $\lambda_c = 700$ nm, d thickness of the swollen gel in mm, $(l_0/l)^3$ volume fraction of the polymer in the gel; m relative refractive index, $m = n_0/n_s$ (n_0 and n_s are refractive indices of the solvent and swollen gel, respectively), L_{ab} and L_{ac} diameters of separated particles (in μm) calculated from τ_a/τ_b and τ_a/τ_c , respectively, φ_1^0 volume fraction of the diluent in the mixture with monomers at 25°C, c concentration of crosslinking agent in monomers (in wt.-%).

T	τ_a	τ_b	τ_c	τ_a/τ_b	τ_a/τ_c	d	$(l_0/l)^3$	m	L_{ab}	L_{ac}
Swelling agent/diluent: butanol/butanol										
$\varphi_1^0 = 0$; $c = 0.2\%$; $T_c = 46^\circ\text{C}$										
40	0.372	0.205	0.109	1.815	3.41	2.404	0.561	0.955	0.16	0.19
35	0.748	0.400	0.212	1.87	3.53	2.396	0.566	0.955	0.15	0.18
$\varphi_1^0 = 0.20$; $c = 0.2\%$; $T_c = 64^\circ\text{C}$										
55	0.214	0.108	0.047	1.98	4.55	2.354	0.436	0.966	0.14	0.17
45	0.482	0.218	0.088	2.21	5.48	2.355	0.436	0.964	0.12	0.16
35	0.850	0.372	0.152	2.28	5.59	2.355	0.436	0.965	0.11	0.15
30	1.07	0.469	0.194	2.28	5.52	2.352	0.434	0.965	0.11	0.15
$\varphi_1^0 = 0.40$; $c = 0.2\%$; $T_c = 69.5^\circ\text{C}$										
65	0.312	0.161	0.077	1.94	4.06	2.280	0.372	0.968	0.14	0.18
60	0.767	0.383	0.165	2.00	4.64	2.281	0.372	0.968	0.14	0.17
55	1.35	0.662	0.285	2.04	4.74	2.283	0.371	0.969	0.14	0.17
$\varphi_1^0 = 0.55$; $c = 0.1\%$										
69	0.158	0.156	0.145	1.013	1.09	1.87	0.456	0.961	4.5	4.5
59.5	0.815	0.830	0.895	0.982	0.91	1.88	0.452	0.965	4.3	4.9
69 ^a	0.062	0.055	0.074	1.13	0.84	1.424	0.558	0.952	3.6	>5
59.5 ^a	0.642	0.587	0.590	1.09	1.085	1.454	0.525	0.956	3.8	4.5
$\varphi_1^0 = 0.55$; $c = 0.5\%$										
89	0.895	0.653	0.446	1.37	2.00	2.23	0.465	0.958	2.3	2.55
80.5	0.990	0.706	0.485	1.40	2.04	2.21	0.469	0.959	2.1	2.45
69.2	1.185	0.861	0.600	1.38	1.98	2.20	0.473	0.959	2.3	2.6
butanol/water										
$\varphi_1^0 = 0.20$; $c = 0.2\%$; $T_c = 46^\circ\text{C}$										
40	0.153	0.085	0.049	1.80	3.12	1.614	0.442	0.964	0.16	0.24
35	0.305	0.162	0.085	1.88	3.59	1.615	0.964	0.964	0.15	0.185

TABLE I
(Continued)

T	τ_a	τ_b	τ_c	τ_a/τ_b	τ_a/τ_c	d	$(l_0/l)^3$	m	L_{ab}	L_{ac}
$\varphi_1^0 = 0.41; c = 0.2\%; T_c = 56^\circ\text{C}$										
50	0.216	0.130	0.075	1.66	2.88	2.470	0.550	0.955	0.45	0.48
45	0.433	0.260	0.145	1.66	2.98	2.460	0.551	0.955	0.45	0.43
30	0.830	0.456	—	1.82	—	2.460	0.565	0.955	0.16	—
50	0.190	0.114	—	1.67	—	2.452	0.553	0.954	0.45	—
45	0.458	0.226	—	2.02	—	2.440	0.557	0.954	0.14	—
30	1.03	0.555	—	1.85	—	2.463	0.566	0.955	0.15	—
$\varphi_1^0 = 0.465; c = 0.2\%; T_c = 61^\circ\text{C}$										
60	0.113	0.072	0.043	1.57	2.62	2.683	0.452	0.961	0.8	0.9
50	0.757	0.398	0.185	1.90	4.10	2.665	0.458	0.962	0.15	0.175
50	0.750	0.403	0.188	1.85	4.00	2.664	0.458	0.962	0.16	0.18
butanol/ethylene glycol										
$\varphi_1^0 = 0.482; c = 0.2\%; T_c = 43^\circ\text{C}$										
40	0.318	0.145	0.064	2.19	4.97	1.96	0.590	0.952	0.12	0.17
30	0.920	0.404	0.164	2.28	5.61	1.96	0.590	0.953	0.115	0.16
40	0.800	0.342	0.147	2.34	5.34	1.96	0.590	0.952	0.10	0.16
30	1.18	0.513	0.221	2.30	5.34	1.96	0.590	0.953	0.11	0.16
40	0.531	0.238	0.111	2.24	4.80	1.96	0.590	0.952	0.12	0.17
30	1.48	0.648	0.274	2.29	5.40	1.96	0.590	0.953	0.115	0.16
water/water										
$\varphi_1^0 = 0.45; c = 0.2\%$										
30	0.093	0.046	0.024	2.02	3.90	2.350	0.515	0.935	0.14	0.18
35	0.219	0.108	0.054	2.03	4.06	2.350	0.515	0.935	0.135	0.18
40	0.485	0.237	0.109	2.04	4.45	2.351	0.515	0.935	0.135	0.17
45	0.710	0.348	0.158	2.04	4.48	2.351	0.515	0.935	0.135	0.17
50	1.01	0.500	0.219	2.02	4.60	2.352	0.514	0.935	0.14	0.17
$\varphi_1^0 = 0.46; c = 5.0\%$										
24	0.394	0.194	0.093	2.02	4.22	2.42	0.580	0.928	0.14	0.17
30	0.424	0.212	0.099	2.00	4.28	2.42	0.580	0.928	0.14	0.17
40	0.459	0.230	0.108	1.99	4.25	2.41	0.582	0.927	0.14	0.17
50	0.481	0.236	0.110	2.03	4.36	2.40	0.585	0.927	0.135	0.17
60	0.477	0.234	0.108	2.04	4.41	2.40	0.585	0.927	0.135	0.17
70	0.450	0.221	0.106	2.03	4.25	2.39	0.584	0.927	0.135	0.17
80	0.411	0.206	0.098	2.00	4.20	2.39	0.584	0.926	0.14	0.17

TABLE I
 (Continued)

T	τ_a	τ_b	τ_c	τ_a/τ_b	τ_a/τ_c	d	$(l_0/l)^3$	m	L_{ab}	L_{ac}
ethylene glycol/water										
$\varphi_1^0 = 0.70; \quad \epsilon = 0.2^\circ$										
30	0.114	0.084	0.061	1.36	1.87	1.02	0.515	0.935	1.8	2.1
40	0.383	0.300	0.212	1.28	1.81	1.01	0.517	0.935	2.2	2.25
50	0.313	0.246	0.176	1.27	1.78	1.01	0.517	0.935	2.2	2.3
60	0.132	0.097	0.070	1.36	1.89	1.02	0.516	0.935	1.8	2.05

^a Different sample.

poly(2-hydroxyethyl methacrylate) of a very high molecular weight in butanol gives 80°C for about 5% of the polymer^{6,7} which would be consistent with the expected value of T_c , if the measurements were extended to that concentration. Therefore, we may conclude that T_c of gels swollen in butanol is sensitive neither to possible inhomogeneities, nor to the presence of crosslinks. However, the degree of crosslinking in all gels is low so that the latter statement has a limited range of validity. The structural insensitivity of T_c is due to the strong temperature dependence of interaction of the polymer with butanol.

The turbidity itself, and especially the size of separated particles calculated by the turbidity ratio method give better characteristics of structural differences in gels (cf. Table I). In gels prepared in the presence of 0–40% of butanol, the separated solvent particles have approximately the same size despite of the change in turbidity amounting almost to an order of magnitude. This behaviour is in agreement with the pseudoequilibrium model of microsyneresis¹. With 55% butanol the limit necessary for phase separation during polymerization is exceeded: the gels are permanently turbid and the size of separated particles increases several times. It must be noted, however, that the values of L (diameter of the separated particle) for the gel with 55% butanol and 0.1% crosslinking unit are only estimates because the scattering function is very flat in this range of turbidity ratios. High values of L indicate that microsyneresis starts before the network formation is completed. The size of separated particles decreases with increasing degree of crosslinking because the elastic response of the locally deformed network is stronger and prevents the separated particle from growing. At the same time, the gel with higher degree of crosslinking is more turbid which points out a stronger phase separation at higher crosslinking densities. This is in line with theoretical predictions⁶. In the gel prepared in the presence of 48.2% ethylene glycol, particles of the same size are separated as in samples with

0–40% butanol and the size is independent of turbidity. According to the present results, one may conclude that gels prepared with 0–40% butanol and 48.2% ethylene glycol are at least of the same homogeneity as gels prepared without diluent.

The critical concentration of water, if it is used as a diluent, is $\sim 46\%$ under the given polymerization conditions and with 0.2–0.4% crosslinking agent. The lowest concentration of water in the polymerization, sufficient for temperature – induced development of turbidity, is $\sim 41\%$ so that gels are usually transparent at room temperature if the amount of diluent varies between 41–45%; higher concentrations of water yield gels that are permanently turbid. However, the limits indicated above vary somewhat; this is probably due to the varying amount (0.5–1.5%) of impurities (*e.g.* ethylene glycol) in the monomer. If 20% water is present during polymerization in the system, the size of separated particles is the same as in gels prepared in the absence of any diluent. Dilution with 41 and 46.5% water changes the size of the particles: at low turbidities, L is large and falls with increasing turbidity which indicates a superposition of two kinds of heterogeneities. The larger heterogeneities are evidently connected with the state of the system during copolymerization and are formed more easily than the smaller ones. The latter are of the same size as particles formed in homogeneous gels as a result of temperature changes and are very probably of the same origin. The possibility of superposition of primary and secondary heterogeneities was mentioned in connection with investigation of temperature induced microsineresis in gels prepared in the absence of solvent¹; the volume fraction of primary heterogeneities was, however, lower than appears to be in the present case.

Swelling in water cannot be used for structural comparison of homogeneous and inhomogeneous gels, because L can be calculated only for those gels that exhibit temperature induced microsineresis. The separated water particles are smaller than particles of butanol (primary heterogeneities) separated in the same gel. However, it is necessary to bear in mind that temperature affects more drastically the interaction gel–butanol than the interaction gel–water. The gel with 46% water and 5% ethylene dimethacrylate structure unit exhibits permanent turbidity which is only slightly temperature-dependent. The effect of physical structure of the network on microsineresis is very strong in the case of gel prepared in the presence of 70% ethylene glycol. This gel is transparent after polymerization, but gets turbid when ethylene glycol is exchanged for water. Although ethylene glycol is a good solvent for poly(2-hydroxyethyl methacrylate), its concentration during polymerization is so high that it can give rise to inhomogeneities or lead to microsineresis. This assumption is supported by the large size of separated particles (Table I).

In conclusion, one can see that diluents affect temperature-induced microsineresis and optical properties of gels in two ways: by changing their degree of swelling and by producing inhomogeneities or heterogeneities in the structure of the gel. These imperfections can be detected and characterized by investigating the optical properties of the system with microseparated solvent. The formation of inhomogeneities

is characteristic of a narrow concentration region of the diluent preceding phase separation and cannot be easily detected in another way. Experiments being now in process show that in the case of inhomogeneous gels (*i.e.* gels prepared in the presence of 41–45% water) the turbidity develops at a certain stage of copolymerization and disappears again.

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