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Behaviour of a Turbid Swollen Gel During Continuous Heating, Equilibration and Cooling

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Summary

Using the integral and differential turbidity ratio methods, processes occurring during the continuous heating, equilibration and cooling of the PHEMA gel have been characterized. Microseparated particles were shown to be responsible for the turbidity changes below 40°C, even if not exclusively. The role of large scatterers called fluctuation microregions in the individual periods has been discussed.

1. Introduction

The problem of temperature induced microsyneresis in the poly(2-hydroxyethyl methacrylate) gel has been dealt with in some previous papers (DUŠEK and SEDLÁČEK 1969, SEDLÁČEK and KOŇÁK 1982ab). The whole turbidity effect arising after sudden cooling was ascribed to the microsyneresis of the excess solvent (secondary heterogeneities). The turbidity remaining at higher temperatures was assigned to the primary heterogeneities (without closer specification); finally, they were identified with large scatterers called fluctuation microregions, the probable role of which during the swelling-deswelling processes in a transparent gel was confronted with experiment.

The aim of this paper is to characterize the turbidity behaviour of a swollen PHEMA gel during continuous heating and cooling (with an isothermal period at 80°C in between) in terms of changes in the integral and differential turbidities and sizes of scatterers. On the basis of all data obtained, a plausible mechanism of processes occurring in the system within the individual periods has been proposed.

2. Procedures and Methods

Samples of the poly(2-hydroxyethyl methacrylate) gel, crosslink density ≈0.2%, thickness ≈0.2 cm, were of the same origin as those studied in previous papers (DUŠEK and SEDLÁČEK 1969, SEDLÁČEK and KOŇÁK 1982ab). The gel strips were placed in a thermostated vessel with pure n-butanol and subject to a treatment described in section 3.

The turbidity of samples was measured at the wavelengths (in vacuo) $\Lambda_0 = 435.8$, $\Lambda_1 = 546.1$, $\Lambda_2 = 684.3$ nm using a Perkin-Elmer-Hitachi 340 spectrophotometer. Only relative turbidities $\tilde{\tau}_0$, $\tilde{\tau}_1$, $\tilde{\tau}_2$ identical with the direct spectrophoto-

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meter readings were used throughout the paper (i.e. without corrections for the unit thickness and changes in volume, and for the log-to-ln conversion factor needed for obtaining the absolute values). As the changes in turbidity were very steep, both isochronous and isothermal interpolations were used to obtain comparable data.

The scatterer size was estimated by the integral (ITR) and differential (DTR) turbidity ratio methods (cf. SEDLÁČEK and ZIMMERMANN 1982 and the literature cited therein). The ITR method consists in the measurement of the individual pairs of the relative (or absolute) integral turbidities $\tilde{\tau}^i$ (or τ^i) at the given wavelengths; their ratio $T_{ab} = \tilde{\tau}^i_a/\tilde{\tau}^i_b$ (a=0, 1; b=1, 2; $a \neq b$) can be converted into the relative scatterer size $\alpha = \pi L/\lambda$ (where L is the diameter of the spherical scatterer and λ is the wavelength in the medium). The ITR method is suitable for a qualitative characterization of changes in a complicated (e.g. dynamical) system as the data obtained are an average of all the present components at best. In order to discern individual components, the DTR method may be used under favourable conditions, i.e. if only a single component varies in the system. For this purpose, the turbidity differences $\tilde{\tau}^d = \tilde{\tau}^i_i - \tilde{\tau}^i_j$ are to be applied instead of $\tilde{\tau}^i$ to form the ratio $T_{ab} = \tilde{\tau}^d_a/\tilde{\tau}^d_b$; $\tilde{\tau}^i_i$ and $\tilde{\tau}^i_j$ are the integral relative turbidities measured at the two successive times t_i and t_j. The $\tilde{\tau}^d$'s are related to that process only which is responsible for the changes in turbidity from $\tilde{\tau}^i_i$ to $\tilde{\tau}^i_j$.

3. Results and Discussion

The integral (ITR) and differential (DTR) turbidity ratio methods have been used for characterization of the swelling-deswelling processes occurring in the PHEMA gel suspended in butanol due to the following temperature régime: (a) Starting period consisted in that the turbid gel (with initial turbidities $\tilde{\tau}_0 = 0.483$, $\tilde{\tau}_1 = 0.297$, $\tilde{\tau}_2 = 0.193$) was cooled from 25 to 20°C during 6 min; the deswelling process at 25°C (leading to the successive disappearance of the microseparated phase) was thus interrupted and the turbidity increased by additional phase separation to $\tilde{\tau}_0 = 0.638$, $\tilde{\tau}_1 = 0.389$, $\tilde{\tau}_2 = 0.246$. In the second part of this period, the continuous heating began immediately and, within 6 min, the temperature reached 25°C accompanied by a decrease in turbidity to $\tilde{\tau}_0 = 0.580$, $\tilde{\tau}_1 = 0.357$, $\tilde{\tau}_2 = 0.229$. (b) The proper heating period continued nearly linearly from 25°C reaching 80°C within 80 min. (c) The isothermal period at 80°C lasted 228 min. (d) Cooling period followed immediately and the temperature decreased almost linearly from 80 to 25°C during 52 min. (e) Finishing period 25→15°C closed the experiment within 40 min.

The time* dependence of turbidity is illustrated by Fig.1, curve 1 (to save space, only $\tilde{\tau}_1$ is given). Experimental points measured in very short intervals (1 min) cannot be plotted there; however, their scatter is so small that the points lie mostly close to, or are identical with, the given curve. Both the heating and cooling branches of the almost linear time (or temperature*) dependence of turbidities $\tilde{\tau}_0$, $\tilde{\tau}_1$, $\tilde{\tau}_2$ have a bend where a pronounced change in the loss or increase of turbidity takes place. Extrapolation of these linear regions gives an intersection (identical with the cloud point) on each branch which almost exactly corresponds to the temperature 40 ± 1.5°C attained for all the three turbidities and for both dependences of turbidity on time and temperature. This finding suggests a change in the mechanism of formation (disappearance) of turbidity. It was shown earlier (DUŠEK and SEDLÁČEK 1969) that the turbidity induced by sudden cooling is to be ascribed to the microseparation of the excess solvent. It seems that in the given régime, beyond (before) the bend, the microseparated phase is exhausted (begins to form). The steepness of the linear part of the dependence where the microseparated phase disappears (or begins to form) is a function of the rate of heating (cooling) of the given system, but we have not examined it in detail.

A. Heating period 25→80°C

In the course of heating (rate ≈0.7°C/min) turbidity varies very quickly at the beginning (Fig.1, Table 1), so that the individual processes mentioned above may be expected to proceed in parallel: superposition may of course cause both mutual support and competition. At the disappearance of the microseparated phase, there may be cooperation of both the pressure gradient (caused by contraction of the gel network during the cooling part of the starting period and remaining to some extent during heating) and the concentration gradient caused by the increased lack of solvent in the gel phase. On the other hand, the turbidity increase caused by microregions is compensated by its decrease due to equilibration of the gel (SEDLÁČEK and KOŇÁK 1982). For this reason, it was not surprising that, at the beginning of the heating, the integral size of scatterers obtained from relative turbidities had no pronounced predominating effect of small particles of the microseparated phase found previously (DUŠEK and SEDLÁČEK 1969); the data at the end of the experiment, however, give sufficiently distinct evidence of such predominance (see below).

The integral size of the scatterers present in the system increases in the course of heating, being nearly constant above 40°C (Table 2). The apparent scatterer dimensions have reached the range where the turbidity decreases with size; however, this alone cannot explain the observed decrease in turbidity at higher temperatures (Table 1, cf. also Fig.1).

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*Time and temperature are correlated almost linearly (curve 2)

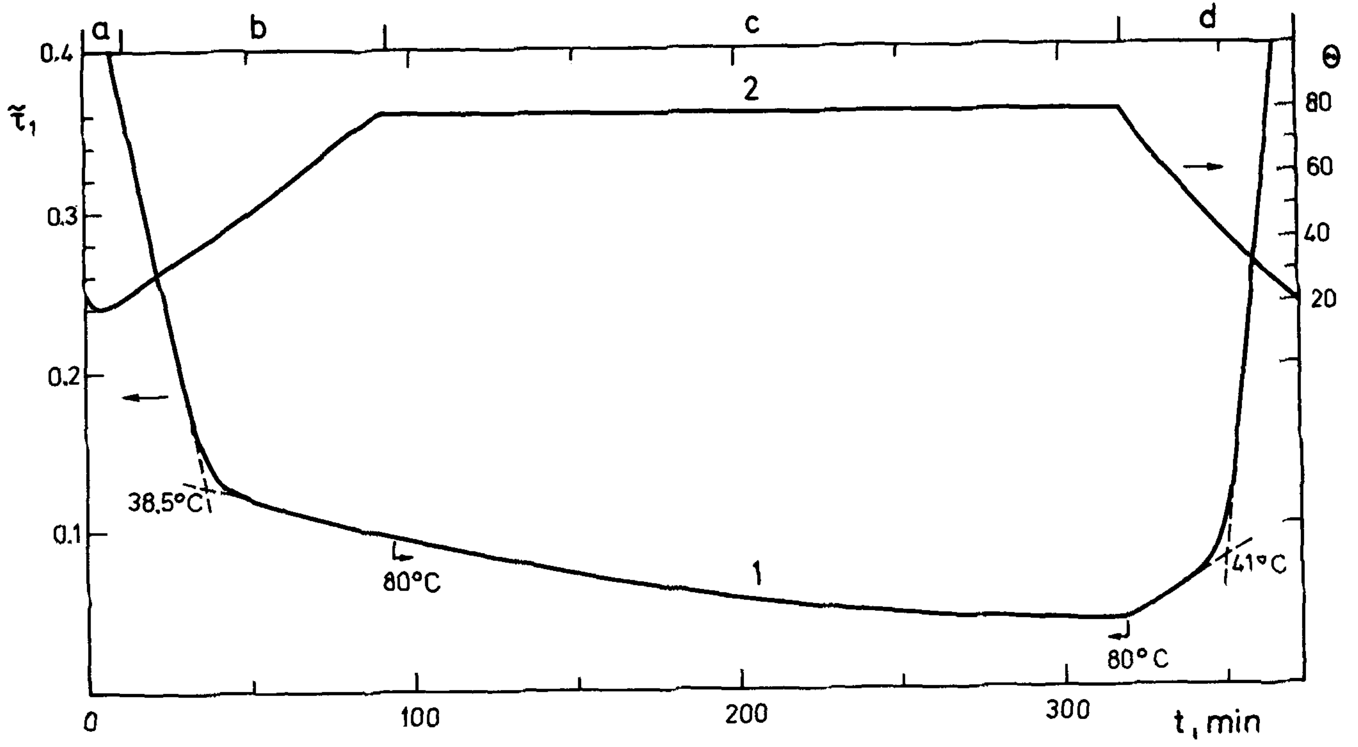

Figure 1. Changes in relative turbidity $\tilde{\tau}_1$ (546.1 nm) with time (1) and in temperature θ (°C) with time (2): (a) starting (0-12 min), (b) heating (12-92 min), (c) isothermal (92-320 min), (d) cooling (320-372 min) periods; (e) finishing period (372-412 min) not given

TABLE 1. Changes in the integral relative turbidities $\tilde{\tau}_0$, $\tilde{\tau}_1$, $\tilde{\tau}_2$ (measured at 435.8, 546.1, 684.3 nm) with temperature during heating and cooling of swollen gel (turbidities obtained by isothermal interpolation)

	Heating			Cooling		
°C	$\tilde{\tau}_0$	$\tilde{\tau}_1$	$\tilde{\tau}_2$	$\tilde{\tau}_0$	$\tilde{\tau}_1$	$\tilde{\tau}_2$
25	0.580	0.357	0.229↓	↑0.970	0.536	0.298
30	0.392	0.262	0.200↓	↑0.565	0.331	0.183
35	0.236	0.173	0.128↓	↑0.313	0.186	0.108
40	0.182	0.139	0.114↓	↑0.188	0.118	0.073
45	0.152	0.124	0.105↓	↑0.132	0.088	0.055
50	0.144	0.120	0.101↓	↑0.110	0.071	0.043
55	0.138	0.116	0.099↓	↑0.097	0.062	0.037
60	0.134	0.113	0.096↓	↑0.087	0.055	0.033
65	0.129	0.109	0.093↓	↑0.080	0.050	0.030
70	0.125	0.106	0.090↓	↑0.073	0.046	0.028
75	0.120	0.102	0.087↓	↑0.068	0.043	0.026
80	0.114	0.096	0.082↓ →	↑0.066	0.040	0.024

TABLE 2. Changes in the integral sizes, L_{01}, L_{12}, L_{02} (µm), with temperature during heating and cooling of swollen gel

	Heating			Cooling		
°C	L_{01}	L_{12}	L_{02}	L_{01}	L_{12}	L_{02}
25	0.50	1.32	0.83↓	↑0.178	0.227	0.202
30	1.69	3.84	2.73↓	↑0.221	0.223	0.223
35	2.72	3.53	3.06↓	↑0.249	0.264	0.264
40	3.07	4.50	3.69↓	↑0.72	0.74	0.73
45	3.56	4.76	4.07↓	↑1.66	0.83	1.29
50	3.70	4.76	4.14↓	↑1.15	0.54	0.77
55	3.75	4.82	4.20↓	↑1.00	0.49	0.61
60	3.78	4.79	4.19↓	↑0.82	0.51	0.51
65	3.79	4.82	4.21↓	↑0.67	0.51	0.55
70	3.81	4.78	4.21↓	↑0.78	0.55	0.64
75	3.83	4.82	4.24↓	↑0.83	0.53	0.62
80	3.76	4.83	4.20↓ →	↑0.43	0.51	0.47

Furthermore, similarly to the conclusion made in the preceding paper (SEDLÁČEK and KOŇÁK 1982), we must assume that the real size of these scatterers is in any case markedly lower than the apparent one, following subtraction of a contribution of the defects or impurities from the integral turbidity.

Therefore, the DTR method was used and data were obtained (Table 3) which document that the higher the temperature the larger the scatterers responsible for the loss of turbidity (Table 1). In the given case the size of the scatterers seems to increase with increasing temperature interval Δ_θ (difference between the reference temperature, 25°C, and the temperature of interest) which might suggest participation of major scatterers in the loss of turbidity at higher temperatures. More conclusive data may be obtained by choosing higher reference temperatures, because in this case the reference temperatures delimit the range under study from below: indeed, the highest L values were found in the range 50-80°C.

TABLE 3. Sizes of scatterers, L (μm), disappearing in the course of heating 25→80°C, determined by the DTR method (differential turbidities $\tilde{\tau}^d$ were calculated for the temperature interval Δ_θ, °C)

Δ_θ	25-30	25-40	25-50	25-60	25-80	30-60	40-60	40-80	50-80
L_{01}	0.149	0.149	0.152	0.156	0.169	0.163	0.459	1.85	3.31
L_{12}	0.137	0.161	0.181	0.192	0.215	0.261	3.32	3.80	4.39
L_{02}	0.144	0.155	0.168	0.174	0.193	0.205	1.91	2.79	3.76

B. Isothermal period 80°C

The relative turbidities $\tilde{\tau}_0$, $\tilde{\tau}_1$, $\tilde{\tau}_2$ decreased monotonically within the isothermal period (228 min) from the initial values 0.114, 0.096, 0.082 to 0.066, 0.040, 0.024 respectively, without reaching final values yet. These data are distinctly lower than the "equilibrium" turbidities obtained by heating a transparent gel to 80°C (cf. SEDLÁČEK and KOŇÁK 1982a). The state of the gel does not seem to be identical in the two cases: while in the experiment just cited the fluctuation microregions (domains with a lower polymer concentration than that of their surroundings) tend to equilibrium during the isothermal periods at lower temperatures, in this experiment the same thing occurs mainly at 80°C, as testified by the high initial turbidity values (Table 1) which greatly exceed the "equilibrium" turbidities. Hence, the decrease in turbidities during the isothermal period is easy to explain, in analogy to the transparent gel, by equilibration, i.e. by transport of solvent from the microregions into the gel phase. A question remains open as to what may have caused such a large decrease.

The integral average equivalent sizes of all scatterers in the gel, L_{01}, L_{12}, L_{02}, decreased within the isothermal period from the original respective values 3.8, 4.8, 4.2 μm to 0.43, 0.51, 0.47 μm. Data obtained by the DTR method are sufficient to demonstrate that a continuous heating of the gel to 80°C has led to the formation of a broad spectrum of major fluctuation microregions (5-7 μm) which disappeared by equilibration only within the isothermal period at 80°C. At this time, the internal order was loosened to such a degree that a more complete equilibration of the gel became possible. This is also confirmed by the ITR method which yields very low average sizes of the microregions at the end of the isothermal period.

C. Cooling period 80→25°C

No effect of an anomalous decrease in turbidities immediately after the onset of cooling could be observed, unlike the transparent gel (cf. SEDLÁČEK and KOŇÁK 1982). Turbidities $\tilde{\tau}_0$, $\tilde{\tau}_1$, $\tilde{\tau}_2$ increased continuously to the respective values 0.970, 0.536, 0.298 at 25°C (which increased further to 1.597, 1.111, 0.644 at 15°C). First, the integral sizes of all the scatterers present increased somewhat with decreasing temperature (cf. Table 1), but at 25°C reached the values 0.170, 0.206, 0.184 μm respectively, typical of the predominance of particles of the microseparated phase.

The DTR method provided data on the sizes of forming scatterers (particles), summarized in Table 4.

TABLE 4. Sizes of scatterers, L (μm), formed in the course of cooling 80→25°C determined by the DTR method (differential turbidities $\tilde{\tau}^d$ were calculated for the temperature interval Δ_θ, °C)

Δ_θ	50-80	40-80	40-50	30-50	30-40	25-80	25-60	25-50	25-40	25-30
L_{01}	0.84	0.445	0.378	0.180	0.173	0.156	0.155	0.151	0.146	0.124
L_{12}	1.23	1.16	1.10	0.186	0.166	0.204	0.201	0.198	0.187	0.213
L_{02}	1.02	0.733	0.596	0.184	0.169	0.179	0.178	0.174	0.166	0.162

It can be seen that at lower temperatures the decisive contribution to the total turbidity in the process of cooling is due to particles of the microseparated phase. At higher temperatures, both turbidity and the average particle size are mostly affected by the existence of the fluctuation microregions which are markedly smaller than those investigated during heating. This seems to be a direct consequence of a much more complete equilibration of the gel before the cooling period than that before the isothermal period. With proceeding contraction of the gel network, the deswelling pressure rises and leads first to an increase in the size of microregions (Table 2). This process becomes then masked by the setting in of microsyneresis.

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