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Turbidity of Transparent Swollen Gels

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Summary

Using the integral and differential turbidity ratio methods it was recognized that a special type of optical heterogeneities called fluctuation microregions is probably responsible for the small changes observed in the turbidity of the transparent gel of poly(2-hydroxyethyl methacrylate) caused by rising temperature and swelling (in butanol). Their dynamics and possible mechanisms are discussed.

1. Introduction

Usually, the term "transparent" applies to such condensed compounds and systems which do not absorb light in the given region of wavelengths and which are optically homogeneous (the physical homogeneity not being conditio sine qua non). However, in real transparent systems always a small turbidity appears due to light scattering on optical heterogeneities (VAN DE HULST 1957, HELLER 1957, KERKER 1969). They may be of various origin, from those on the molecular level to rough dispersions, impurities and disturbances (cf. SEDLÁČEK and KOŇÁK 1982). Two of these optical heterogeneities were recognized previously in poly(2-hydroxyethyl methacrylate) gels (DUŠEK and SEDLÁČEK 1969): strong turbidity arising in the gel (swollen at 80°C) by sudden cooling was explained by microsyneresis of the excess solvent in the form of droplets; small turbidity found in the transparent gel was ascribed to the primary heterogeneities some μm in size without closer specification.

The aim of this work is to show that the transparent gel swollen in butanol may achieve different turbidities if temperature and the degree of swelling are changed, and also explain plausibly the mechanism of processes occurring as their consequence.

2. Procedures and Methods

Samples of the poly(2-hydroxyethyl methacrylate) gel, network density c. 0.2%, 0.2 cm thick, were prepared by using a procedure described earlier (DUŠEK and SEDLÁČEK 1969).

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Also data on the degree of swelling* were taken from this paper.

The turbidity of gels placed with butanol in a cell 1.00 cm was measured at the wavelengths (in vacuo) $\Lambda_0 = 435.8$, $\Lambda_1 = 546.1$ and $\Lambda_2 = 684.3$ nm using a Perkin-Elmer-Hitachi 340 spectrophotometer. The direct spectrophotometer readings used throughout the paper as "relative turbidities" $\tilde{\tau}$ were not corrected for the unit thickness, log-to-ln conversion factor and for the dilution of gels due to the volume changes of the gel strips during the swelling-deswelling process: this is not necessary (and partly not attainable*) as the number of scatterers was not estimated.

The integral (ITR) and differential (DTR) turbidity ratio methods were used for the scatterer size estimation (for details see SEDLÁČEK 1965, 1967; SEDLÁČEK et al. 1978, 1979; SEDLÁČEK and ZIMMERMANN 1982). The ITR method yields information on the average (apparent or equivalent) size of all the scatterers just present in the system. For this purpose, a ratio $T_{ab} = \tilde{\tau}^i_a/\tilde{\tau}^i_b$ $(= \tau^i_a/\tau^i_b)$ of the individual pairs (ab) of the relative ($\tilde{\tau}^i$) or absolute (τ^i) integral turbidities (measured at the respective wavelengths Λ_a and Λ_b; $a=0,1$; $b=1,2$; $a \neq b$) is successively created; use can be made of tables** (SEDLÁČEK et al. 1978, 1979) for converting T_{ab} to the relative scatterer size $\alpha = \pi L/\lambda$, where L is the diameter of the scatterer and λ is the wavelength in the medium. Using the ITR method, also a process occurring in the system may be qualitatively characterized; however, the resulting data may differ significantly from those of the individual components. Adequate results are obtained, if only a single component is changing, by the DTR method where the differential turbidities $\tilde{\tau}^d = \tilde{\tau}^i_i - \tilde{\tau}^i_j$ are applied instead. While the integral turbidities $\tilde{\tau}^i_i$ and $\tilde{\tau}^i_j$ characterize the response of the whole system at times t_i and t_j, their differences, $\tilde{\tau}^d$, are related only to that process which is responsible for the change in turbidity from $\tilde{\tau}^i_i$ to $\tilde{\tau}^i_j$. Thus, the data obtained by the DTR method may contribute significantly to the elucidation of the mechanism of the process studied.

3. Results and Discussion

A. Heating of gel (with isothermal periods)

Turbidity of apparently quite transparent gels obtained by longterm swelling at constant temperature in a liquid can be regarded as equilibrium. To achieve this, the following

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*For the determination of the scatterer concentration, a new estimation of the degree of swelling simultaneously with the turbidity measurements would be needed; unfortunately, appropriate techniques are not available.

**By inadvertence, the basic wavelength (in water) given in tables is $\lambda_1 = 409.3$ nm instead of the correct value, $\lambda_0 = 326.7$ nm.

procedure was chosen: A gel thermostated in butanol at room temperature for one year was maintained at 25°C in the final stage. In an experiment lasting 9 hours, the temperature was gradually raised from 25°C to 30(10)80°C, always with an isothermal period in between ranging from 120 to 30 min (Table 1).

Table 1. Swelling of transparent gel: changes in relative integral turbidity $\tilde{\tau}^i$ and apparent average equivalent size of scatterers, L (μm), during heating from 25 to 80°C

°C	Period			$\tilde{\tau}^i_0$	$\tilde{\tau}^i_1$	$\tilde{\tau}^i_2$	L_{01}	L_{12}	L_{02}
25	I	30	E	0.069*	0.060*	0.056*	3.95	5.47	4.60
30	H	10	B	0.068	0.060	0.057	4.06	5.58	4.71
	I	120	E	0.060	0.050	0.046	3.69	5.37	4.42
40	H	20	B	0.068	0.058	0.055	3.85	5.58	4.60
	I	50	E	0.065	0.055	0.051	3.80	5.43	4.50
50	H	20	B	0.071	0.062	0.058	3.99	5.49	4.62
	I	50	E	0.070	0.061	0.057	3.97	5.49	4.62
60	H	20	B	0.073	0.064	0.062	4.01	5.72	4.75
	I		M	0.074	0.065	0.062	4.02	5.62	4.71
	I	30	E	0.073	0.064	0.062	4.01	5.72	4.75
70	H	15	B	0.074	0.065	0.062	4.02	5.62	4.71
	I		M	0.075	0.066	0.062	4.04	5.51	4.66
	I	30	E	0.074	0.065	0.062	4.02	5.62	4.71
80	H	15	B	0.075	0.065	0.063	3.94	5.72	4.72
	I		M	0.076	0.066	0.063	3.95	5.62	4.68
	I	30	E	0.075	0.065	0.063	3.94	5.72	4.72

Period (min): H heating, I isothermal. Data measured at the B beginning, E end of the isothermal period; M small maximum; m = 0.950. *Probably influenced by an insignificant amount of microseparated phase. - Note that the absolute turbidities τ^i are more than 10 times higher than the relative ones given in the Table.

During the first three cycles a surprising rise in turbidity took place, each time after a rise in temperature; the turbidity decreased distinctly again during the isothermal period. Starting from 60°C, turbidity changed only insignificantly reaching a very slight maximum during the first part of the isothermal period followed by a small decrease in turbidity, and remaining nearly constant at its end.

In order to explain such small but distinct changes in turbidity, one must consider the extent of the individual turbidity contributions. Immediately, we may rule out the molecular scattering (too low turbidity) and the contribution from defects and impurities (nearly constant with the temperature and volume changes). Although the sample was transferred very quickly into the thermostated cell (all at 25°C), some cooling may have occurred, thus giving rise to an insignificant amount of the microseparated phase. Should this be present, its disappearance due to equilibration might explain the decrease in turbidity during the heating period 25-30°C. In any case, the observed rise in turbidity on passing to higher temperatures cannot be connected with the presence of the microseparated phase.

On the way to find a plausible explanation of the "turbidity behaviour" of transparent gels we review some opinions on their swelling behaviour: After elevation of temperature, a swelling process is initiated by an increase in the affinity of the polymer chains to the solvent lacking inside the respective domains of the gel. Still on a microscopic scale, this gives rise to local concentration gradients which mediate the transport of the solvent to the gel phase, probably from the near surroundings with the excess solvent; the existence of such microregions seems to be confirmed by the effect of the gel equilibration within isothermal periods (see below and Table 1) and by an anomalous decrease in turbidity with cooling (cf. section B). When solvent is exhausted from the microregion, a pressure gradient is created by capillary or interface tension effects. By a combination of local concentration and pressure gradients, a total gradient is formed, through which the solvent is "pumped" by flow and diffusion from the outside into the gel. Similarly to the filtration of a liquid through the membrane, such ways for transport ("pores") are preferred which offer the lowest hydrodynamic resistance against flow. As the gel strip is rather thick (~0.2 cm), some time is needed for concentration disturbances to reach the inside; additional time is required for equilibration of the gel.

Let us denote the "pore" as a system of "fluctuation microregions" for reasons given below. Thus, a continuous rise in temperature during the heating period leads to an increase in swelling which lowers, by transport of the solvent, the polymer chain concentration in the microregions (either present in the gel or just formed) - probably in domains with the lowest cross-link density. The concentration disturbances are expected to proceed through the gel in a more or less rought or diffuse front; this statement is substantiated by an analogy with the direct observation of a process in an opposite direction leading to the disappearance of the microseparated phase - the gel being still turbid inside becomes transparent at the interface with butanol (cf. section B). At the same time, another process occurs - the diffusion of solvent from the microregions into the gel phase with a higher polymer concentration and a higher need of solvent. The same process may be observed to continue within the isothermal period (cf. Table 1). Thus, the microregions may be seen as large fluctuations with a long life-time which result from a competition of several processes. The turbidity response of the gel ascribed to the fluctuation microregions is controlled by three factors, i.e. by changes in the relative refractive index and in the size and number of scatterers. By evaluating the extent of their influence on turbidity, we shall now check the concept of the fluctuation microregions for adequacy.

The effect of the relative refractive index, $m = n^*/n$, depends on the difference between the refractive indices of the scatterer (n^*) and its medium (n), i.e. between the microregion and the gel phase. Below $m = 1.0$, the turbidity decreases with increasing m, and vice versa. In the extreme, the microregions may be formed of pure butanol only - this is illustrated by Table 2 which also documents a decrease in m with rising temperature. Its effect is nearly compensated for by swelling, so that the mean value of $m = 0.950$ may be seen as adequate for the whole temperature range, at least for the size estimation (SEDLÁČEK and DUŠEK 1969); the real system changes from $m = 0.951$ (25°C, 37%), to 0.949 (80°C, 41.7%) while the recommended $m = 0.950$ requires the swelling to be 35.7% (25°C) and 42.9% (80°C), to keep the value constant. Thus, a small increase in turbidity (2-3%) appears as a result, but it cannot explain the whole effect observed (about 20% at 30→40°C). The same holds for another possible small rise in turbidity due to a relatively slow diffusion of solvent from the microregions to the gel phase, which leads to lower values of m than expected for equilibrated gels (Table 2).

Table 2
Calculated values of the relative refractive index m of microregions formed by pure butanol (or by *90% butanol + 10% dry gel, **50% butanol + 50% dry gel) suspended in a homogeneous gel containing in total 0 (dry gel), 30, 40 and 50 vol.% butanol at temperatures 25, 30, 40, 60 and 80°C

°C	Total butanol content in gel, vol.%							
	0	30	40	50	30*	40*	30**	40**
25	0.9243	0.9458	0.9532	0.9607	0.9535	0.9610	0.9845	0.9922
30	0.9235	0.9452	0.9526	0.9602	0.9530	0.9606	0.9843	0.9921
40	0.9219	0.9440	0.9516	0.9594	0.9520	0.9597	0.9840	0.9919
60	0.9189	0.9418	0.9497	0.9577	0.9501	0.9581	0.9834	0.9916
80	0.9155	0.9394	0.9476	0.9560	0.9481	0.9564	0.9827	0.9913

Swelling at $m = 0.950$ leads to the butanol content (vol.%): 35.7 (25°C), 36.5 (30°C), 37.9 (40°C), 40.4 (60°C), 42.9 (80°C).

The direct integral turbidity measurements indicate that the scatterers are somewhat polydisperse indeed, but that their apparent (average equivalent) sizes lie in a narrow range, $L_{01} = 3.7-4.0$, $L_{12} = 5.4-5.7$, $L_{02} = 4.4-4.7$ µm (Table 1), even if measured at temperatures from 25 to 80°C. The real size of microregions should be markedly lower in any case, as they are much smaller than the defects (impurities) in the gel. (For defects, $T_{ab} \rightarrow 1.0$, i.e. almost the same values are to be subtracted from $\tilde{\tau}_a^i$ and $\tilde{\tau}_b^i$: $T_{ab} = \tilde{\tau}_a^i/\tilde{\tau}_b^i$ increases, and thus the real size of microregions decreases always, irrespective of the real size of defects. Unfortunately, the extent of the defect contribution to the total turbidity is not yet attainable for estimation.) The decisive factor is that the constancy of the scatterer sizes should be preserved also if the data are corrected for the defect contribution. This is why we estimate the increase in the total number of microregions co-responsible for the turbidity effects observed if the system is heated.

The behaviour of the gel within the individual isothermal periods depends significantly on temperature. At lower temperatures, the swelling seems to stop quickly. The solvent is transported by diffusion from the microregions into the gel phase, so that the gel tends to be equilibrated; the turbidity decreases to the residual value. A small decrease in the size of scatterers can be recognized as a consequence of the preferential disappearance of larger microregions during equilibration (Table 1). This effect may be real (the loss of solvent in microregions) or caused by an increase in the relative refractive index of microregions (see also Table 2, last columns) leading to their gradual optical disappearance. - At elevated temperatures, the swelling ceases gradually, which may also lead to a small turbidity maximum (cf. Table 1). Equilibration seems to be nearly complete already at the beginning of the isothermal period; the process continues very slowly, if at all, during the first 30 min of measurement. Some microregions seem to survive and contribute to the small increase of turbidity with temperature.

B. Cooling of gel (continuous régime)

The second part of the experiment consisted in a continuous cooling of the same sample from 80 to 25°C during 40 min (Table 3). The most striking feature is a decrease in turbidity in contrast with the "equilibrium" values (Table 1). In the minimum at 46°C, the turbidities $\tilde{\tau}_0^i$, $\tilde{\tau}_1^i$, $\tilde{\tau}_2^i$ (obtained at 435.8, 546.1, 684.3 nm) assume markedly lower values (0.068, 0.051, 0.045), at least for the wavelengths 546.1 and 684.3 nm. Further decrease in temperature is accompanied by a rise in turbidity, obviously as a result of the microseparation of solvent in excess (DUŠEK and SEDLÁČEK 1969). At the end of the experiment, however, the turbidities $\tilde{\tau}_0^i$, $\tilde{\tau}_1^i$, $\tilde{\tau}_2^i$ reach respectively 0.301, 0.182 and 0.117, i.e. much lower values than those attained in similar experiments involving the originally turbid gels (SEDLÁČEK and KOŇÁK 1982, SEDLÁČEK et al. 1982).

Similar considerations as in section A are needed for explaining the experimental data, especially the minimum observed on the turbidity-temperature curve. The first response of the gel network to the relatively fast decrease in temperature (from 80 to 46°C in 13 min only) is contraction. The network density of the gel sample is rather low (0.2%) so that the network contraction is not sufficient to avert formation of the microseparated phase (below 40°C), but probably strong enough to expel the solvent present in excess in the largest microregions during the first stage of cooling. To check the assertion about the deswelling mechanism for adequacy, the differential turbidity ratio method was used; for this purpose, turbidities measured at 46°C were subtracted from those found at 60, 70 and 80°C. This demonstrated that

Table 3

Deswelling of transparent gel: changes in the relative integral turbidity $\tilde{\tau}^i$ and the apparent average equivalent size of scatterers, L (μm), during cooling from 80 to 25°C

°C	min*	$\tilde{\tau}^i_0$	$\tilde{\tau}^i_1$	$\tilde{\tau}^i_2$	L_{01}	L_{12}	L_{02}
80	0	0.075	0.065	0.063	3.94	5.72	4.72
70	2	0.070	0.056	0.052	3.95	5.73	4.71
60	7	0.066	0.052	0.049	3.31	5.54	4.32
46	13	0.068	0.051	0.045	2.93	5.08	3.92
40	17	0.079	0.055	0.046	2.21	4.66	3.39
30	27	0.145	0.090	0.065	0.614	3.23	1.90
28	29	0.159	0.096	0.069	0.421	2.35	1.11
25	40	0.301	0.182	0.117	0.424	1.38	0.738
25	45	0.291	0.174	0.111	0.398	1.20	0.612
25	65	0.293	0.176	0.113	0.408	1.34	0.681
25	16 h	0.141	0.090	0.064	0.967	3.06	1.99

*Turbidities interpolated to the time given. m = 0.950.

the scatterers disappearing after the onset of cooling are quite large (≈6 μm). The apparent average equivalent sizes of scatterers (microregions) measured by the ITR method (Table 3) confirm this observation as the sizes L_{01}, L_{12}, L_{02} decrease from 3.94, 5.72, 4.72 μm (80°C) to 2.93, 5.08, 3.92 μm respectively (46°C).

Further cooling to 40°C and lower temperatures lead to a steep decrease in the average size of the respective scatterers due to the successive formation of the microseparated phase, i.e. of the butanol droplets (L = 0.1-0.2 μm). On reaching 25°C the scatterer size decreases to the values 0.424, 1.38, 0.738 μm (in the same order of L´s); within the isothermal period, they change respectively to 0.398, 1.20, 0.612 μm (25 min), 0.408, 1.34, 0.681 μm (65 min), 0.967, 3.06, 1.99 μm (16 h). In order to distinguish the real size of the scatterers arising and disappearing in the system, the DTR method was used in the same way as above (the respective turbidity differences were obtained by subtraction of τ^i at 46°C from that at the temperature of interest). Thus, we found that the scatterers responsible for the increase in turbidity in the range from 46 to 25°C have the sizes L_{01} = 0.132, L_{12} = 0.155, L_{02} = 0.143 μm, which change respectively at 25°C to 0.158, 0.211, 0.184 μm (25 min) and 0.135, 0.188, 0.195 μm (16 h), as estimated from the decrease in turbidity during the isothermal period. We can see that the small scatterers only disappear during the isothermal period, but after 16 hours still some remain in the system. This is confirmed by the integral data given above (see also Table 3): with decreasing turbidity the size of scatterers continuously increases, without however reaching the range of apparent sizes of the large scatterers.

4. Concluding Remarks

The individual changes in turbidity characterizing the swelling-deswelling process are very small in their absolute values except those related to microsyneresis. Thus, our argumentation is based rather on their trends proved by the detailed turbidity data measured in the close time intervals. The same holds also for changes in the integral size of scatterers giving better qualitative information about the respective processes than offered by the "apparent" status of this quantity.

All trends observed seem to support the proposed concept of fluctuation microregions responsible for changes in turbidity reflecting processes like swelling (deswelling) and equilibration. We are aware that this proposal would require further work before it could be seen proved: if adequate, this model implies several questions like that of the difference between the associated thermodynamic and hydrodynamic processes in gel and in solution of the same composition. But this remains to be demonstrated.

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