Microsyneresis Region in Poly(2-hydroxyethyl methacrylate) Hydrogels

Malcolm B. Huglin* and Daniel C. F. Yip†

Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

Received May 20, 1991; Revised Manuscript Received October 29, 1991

ABSTRACT: Hydrogels of poly(2-hydroxyethyl methacrylate) have been prepared in the presence of water, with and without added ethylene glycol dimethacrylate (EDMA) as the cross-linker. In the absence of added EDMA, microsyneresis occurred when the water content in the polymerization mixture was 36–38% w/w. Reversible turbidity appeared when these gels were immersed in water over a temperature range of 20–80 °C. Such turbidity resulted from the scattering of light by minute water droplets, formed as a consequence of poor water–polymer interactions upon temperature changes. The turbidity values were measured at three wavelengths: 436, 546, and 700 nm. Suitable treatment of the data according to the turbidity ratio method enabled the mean diameter and concentration of the scattering water droplets to be estimated as 0.1 ± 0.05 μm and 0.25–2.2% w/w of the swollen gels, respectively.

Introduction

The chemistry of 2-hydroxyethyl methacrylate (HEMA) has been studied extensively since the early 1960s.[1–6] HEMA is polymerizable in bulk to give a transparent, glassy material, which can only be swollen in water but not dissolved in it. A water-swollen poly(HEMA) is a hydrogel, in which water molecules are associated with the hydrophilic sites of the polymer via hydrogen bonding.[4] Poly(HEMA) hydrogels can also be prepared in the presence of water.[6] By this route, HEMA can be polymerized to form a homogeneous (optically clear) or a heterogeneous (turbid or opaque) preswollen gel.

We have been involved in the study of heterogeneous hydrogels, with particular attention focused on the microheterogeneity in preswollen poly(HEMA). Although microsyneresis in poly(HEMA) has been studied in some detail by Dušek, Sedláček and their co-workers,[7–15] the microsyneresis region in the gels has not been clearly defined. Here, we attempt to locate this region and to compute the size and concentration of water droplets in the hydrogels using the turbidity ratio method, TRM.[15] A series of temperature-induced microsyneresis experiments has been conducted to investigate the dynamic nature of the scatterers. The corresponding results enabled us to define the microsyneresis region in poly(HEMA) hydrogels.

Microsyneresis

Syneresis is a term used to describe the phase-separation process in gels. As illustrated in Figure 1, it may take the form of deswelling (i.e., macrosyneresis) or of a dispersion (i.e., microsyneresis). Dušek[17–19] suggested that microsyneresis will take preference over deswelling, when there are local differences in cross-linking and segment distribution in the polymer and/or the network relaxation is slower than the separation of water in the microdomains of the gel.

There are significant inter- and intramolecular packings imposed by the alternating hydrophilic and hydrophobic layers of the polymer chains within poly(HEMA) hydrogels.[16] In the presence of water, the polymer chains become aggregated and stabilized by means of hydrophobic bonding at the α-methyl position of the repeating methylene units of poly(HEMA). Reversible turbidity can be developed when a poly(HEMA) hydrogel is immersed in a thermodynamically more favorable solvent such as *n*-butanol[8] or aqueous $Mg(ClO_4)_2$ solution.[10] A similar effect can be observed when changes are made to the temperature of the swelling medium.[14] The turbidity originates from the scattering of light by discrete water droplets expelled from the polymer network which is, in turn, affected by the reorganization of polymer segments.

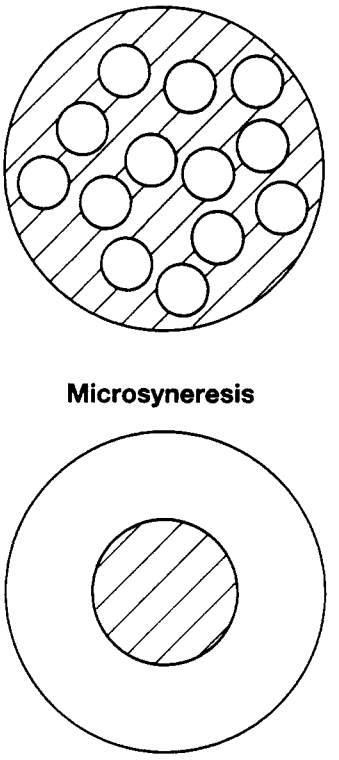

Figure 1. Schematic representation of micro- and macrosyneresis (shaded area, gel phase; unshaded area, liquid phase).

Turbidity Ratio Method (TRM)

TRM is derived from the Mie theory of light scattering. It is free from any restriction as to the particle size parameter, α, and the ratio *m* of the refractive index of

† Present address: BP Research, Chertsey Road, Sunbury-on-Thames, Middlesex, TW16 7LN, U.K.

0024-9297/92/2225-1333$03.00/0

water to that of the gel. The application of TRM in the studies of gels was first introduced by Sedláček in 1966. Since then, a number a papers have been published in connection with the application of TRM.[7-10] In the late 1970s, TRM has been used to cover particle size determination for $m > 1.0$.[11] Furthermore, it has been extended to cover the near-infrared region[12] and used in the integral and differential forms[13] for measuring the size and concentration of spherical particles. In many macromolecular light scattering systems $m > 1.0$. However, the systems considered in the present work are somewhat exceptional in the respect that $m < 1.0$. This is a consequence of the fact that the scattering centers are droplets of water, which is of extremely low refractive index. The main aspects of TRM can be found in the cited literature as well as in the excellent paper by Sedláček and Koňák.[15]

Experimental Section

Poly(HEMA) Hydrogels. HEMA (Sigma, U.K.) was purified by repeated solvent extraction and vacuum distillation.[20] The purity was checked by gas chromatography using a 1.5 m × 3.2 mm × 2.0 mm stainless steel column packed with 7.5% w/w sucrose acetate isobutyrate on Chromosorb G 100-120 mesh and was shown to be 99.9%. Ethylene glycol dimethacrylate (EDMA) (Ancomer, ATM3) was used as supplied. The hydrogels, prepared by the method described previously,[6] contained poly(HEMA) already swollen in the water present in the reaction medium. Prior to measurements on them, the hydrogels were immersed in deionized water over a period of several weeks, during which time the water was changed periodically.

Refractive Index and Turbidity Measurements. The refractive indices of gel strips were measured using an Abbé refractometer at 589 nm over a range of temperature (θ) of 20–60 °C. The turbidity values of the gel strips were measured at wavelengths 436, 546, and 700 nm, using a Pye Unicam SP-1800 double-beam spectrophotometer. The gel strip was placed vertically and rested against one side of a quartz cell filled with water. When using the double-beam spectrophotometer, the reference cell should ideally be fitted with a xerogel with exactly the same polymer composition as the hydrogel. In practice, this was impossible to achieve. The use of air as the reference is incorrect, and therefore deionized water was used as the reference. The direct spectrophotometer readings were taken to obtain turbidity ratios.[7] At elevated temperature, the gel strip was equilibrated in water for 1 h prior to the actual refractive index and turbidity measurements. The thicknesses of gel strips were measured by means of a traveling microscope or micrometer.

Freeze Fracture Scanning Electron Microscopy. The sample (a loosely cross-linked poly(HEMA) hydrogel with w_i = 38% w/w and no added EDMA) was prepared using a Hexland CT1000A Cryotrans system. It was cooled in nitrogen slush, transferred under vacuum to the cold stage of the preparation chamber, freeze-fractured, lightly etched, coated with carbon at low temperature, and moved to the microscope stage held at −180 °C with nitrogen gas. The gel was then examined using the cold-stage SEM techniques.

Results and Discussion

Hydrogel Formation. As revealed by the repeated swelling and drying experiments, the polymerization results were extremely reproducible and yielded very high conversion (ca. 98–99%). Three series of poly(HEMA) hydrogels were prepared, in which the added cross-linker concentrations were 0.0, 0.2, and 2.0% w/w. Each series of gels comprised about 18 different values of w_i, mostly within the range 35–40% w/w.

Ethanol was used to show that some cross-linking was present in gels prepared in the absence of any added cross-linker, since ethanol is a good solvent for linear poly(HEMA) which has been slightly dampened with water.[21] The use of this solvent did not afford any dissolution, but some originally turbid gels turned translucent or clear, manifesting solvent exchanged in gels. The possible cross-linking or branching might be due to the presence of a minute fraction of EDMA impurity in HEMA. Depending on w_i, these hydrogels (subsequently to be referred to as loosely cross-linked gels) after polymerization were clear (when $w_i < 36$% w/w), turbid, or opaque (when $w_i > 40$% w/w). When EDMA was added to the polymerization mixture, microsyneresis became less favorable. Permanent turbidity occurred in these systems at $w_i > 38$% w/w, and below this water concentration the gels were optically clear.

Table I
Reproducibility of Turbidity Measurements at 20 °C

gel[a]	thickness, d, cm	$\tilde{\tau}_1$	$\tilde{\tau}_2$	$\tilde{\tau}_3$
1	0.145	0.275	0.175	0.050
		(1.897)	(1.207)	(0.345)
2	0.150	0.290	0.155	0.050
		(1.933)	(1.033)	(0.333)
3	0.308	0.588	0.310	0.110
		(1.909)	(1.006)	(0.357)
4	0.310	0.600	0.285	0.110
		(1.935)	(0.919)	(0.355)
5	0.463	0.850	0.450	0.178
		(1.836)	(0.972)	(0.384)
6	0.488	0.880	0.475	0.190
		(1.803)	(0.973)	(0.389)

[a] Gels 1–6 were prepared in the absence of added EDMA, with 36.0% w/w of water. The values in parentheses represent $\tilde{\tau}_n/d$ (n = 1, 2, or 3).

Refractive Index and Turbidity Measurements. The refractive index, n_D, of poly(HEMA) hydrogels measured over the range θ = 20–60 °C decreased with increasing temperature. The relative refractive index, m, was determined as n_D(water)/n_D(gel). The value of m was unaffected by temperature changes and remained constant at 0.93. This value of m was therefore used, in conjunction with the turbidity data measured over a wider range of temperature, in the subsequent evaluation of the TRM parameters.

The turbidity ($\tilde{\tau}$) values of a large number of poly(HEMA) hydrogels, with w_i ranging from 35 to 40% w/w, were measured over the interval θ = 20–80 °C. $\tilde{\tau}$ values measured as direct spectrophotometer readings of absorbance were assigned to $\tilde{\tau}_a$, $\tilde{\tau}_b$, and $\tilde{\tau}_c$, where a = 1 = 436 nm, b = 2 = 546 nm, and c = 3 = 700 nm. The reproducibility of the turbidity measurements was excellent. In order to further assess the thickness dependence of turbidity, a number of loosely cross-linked gels with identical values of w_i and different thicknesses were analyzed. Inspection of Table I shows that the increases in turbidity ($\tilde{\tau}_1$, $\tilde{\tau}_2$, and $\tilde{\tau}_3$) were directly proportional to the increasing gel thickness (d). The directly measured turbidity $\tilde{\tau}$ is equal to the product of the true turbidity τ and d. Hence, as required later, $\tau = \tilde{\tau}/d$. Also if measurements of turbidity (i.e., absorbance) are made on the same gel at two wavelengths, it is unnecessary to know the value of d in evaluating the turbidity ratio $T_{1,2}$, because $T_{1,2} = \tau_1/\tau_2 = (\tilde{\tau}_1/d)/(\tilde{\tau}_2/d) = \tilde{\tau}_1/\tilde{\tau}_2$. This is one of the advantages of the TRM.

Determinations of Water Droplet Size (L) and Concentration (C). The diameter and the concentration of the separated water droplets were determined using the apparent relative size parameter, α^*, and the specific turbidity, sp. tur., as illustrated in Figure 2. A numerical example on how to evaluate $L_{a,b}$ and $C_{a,b}$ can be found in the Appendix of this paper. The symbols a and b are arbitrary constants 1, 2, and 3, specifying the pair of wavelengths used for evaluating L and C.

Effect of w_i on the TRM Parameters Obtained for the Loosely Cross-Linked Poly(HEMA) Gels. As can be seen from Figure 3, the absolute turbidities $\tilde{\tau}_n/d$ (n =

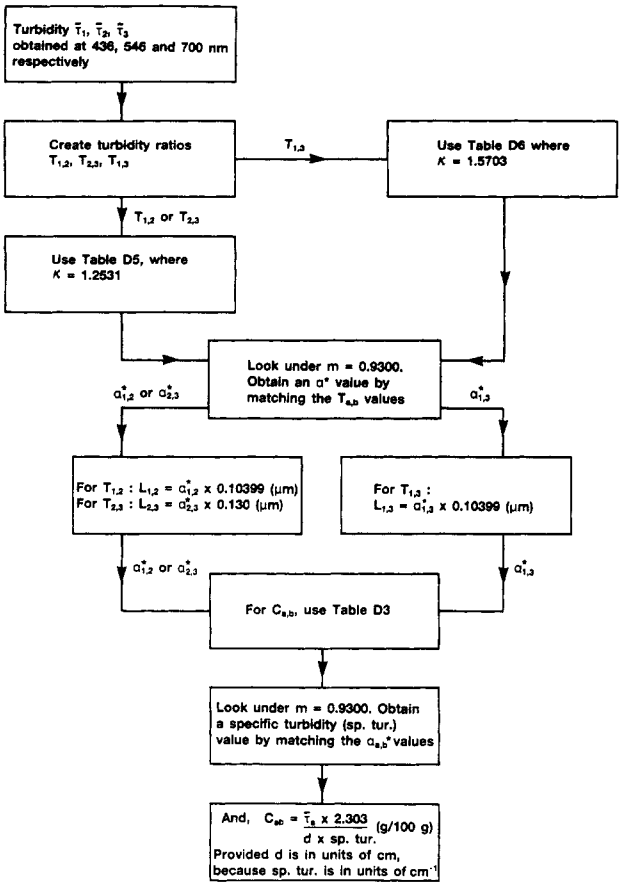

Figure 2. Flow diagram of the uses of Macro tables for the determination of TRM parameters.

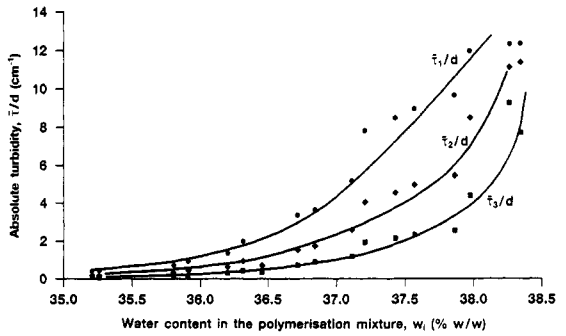

Figure 3. Effect of w_i on the absolute turbidity ($\tilde{\tau}/d$) for the loosely cross-linked poly(HEMA) hydrogels at 20 °C.

1, 2, or 3), measured at 20 °C, increased with increasing w_i. At a particular w_i, $\tilde{\tau}_1/d > \tilde{\tau}_2/d > \tilde{\tau}_3/d$ and consequently the turbidity ratios follow the sequence $T_{1,2} < T_{2,3} < T_{1,3}$. However, when the measured turbidities were extremely small (e.g., 0.001–0.01) and possibly inaccurate, the sequence of $T_{a,b}$ indicated above showed discrepancies. The variations in $T_{1,2}$, $L_{1,2}$, and $C_{1,2}$ with w_i are shown in Figure 4. Generally $T_{1,2}$ decreased with increasing w_i. The values of $L_{1,2}$ remained constant at $w_i < 38\%$ w/w. However, for $w_i > 38\%$ w/w, a significant increase in $L_{1,2}$ was observed. The increase in $L_{1,2}$ was accompanied by a reduction in $C_{1,2}$, suggesting that droplet coalescence preceded the gel point of polymerization. When w_i was 36–37.5% w/w, the diameters of the water droplet were 0.09–0.14 μm. The corresponding droplet concentrations ranged from 0.25 to 2.20% w/w of the total swollen gel. The L and C values determined from $T_{2,3}$ and $T_{1,3}$ bore a similar relationship with w_i as for $T_{1,2}$.

Effect of Temperature on the TRM Parameters Obtained for the Loosely Cross-Linked Poly(HEMA) Gels. Reversible turbidity formation was manifested in

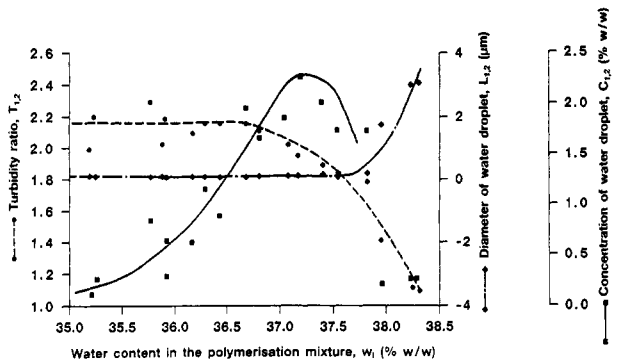

Figure 4. Variations of TRM parameters with w_i for the loosely cross-linked poly(HEMA) hydrogels at 20 °C, based on $T_{1,2}$ data.

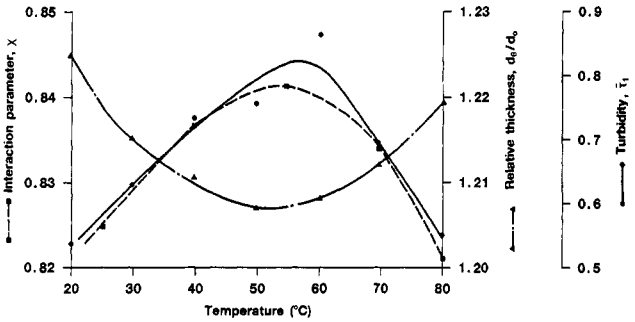

Figure 5. Temperature dependence of χ, d_θ/d_0, and $\tilde{\tau}_1$.

the gels within the range θ = 20–80 °C. Such an effect was more pronounced with the gels prepared with $w_i > 37\%$. A characteristic $\tilde{\tau}$ maximum was located at θ = 55–60 °C. Earlier studies carried out individually by Warren and Prins[16] and by Dušek and co-workers[22] have shown similar findings. In particular, Warren and Prins suggested that, for $\theta < 55$ °C, the enthalpy of dilution ΔH_{dil} is negative. At the same time, $\Delta S_{dil} < 0$, which accords with the structuring of water upon solvating the hydrophobic backbone of poly(HEMA). Moreover the increase in water structure leads to a lower enthalpy (enhanced hydrogen-bonding effect), in line with a negative ΔH_{dil}. When the temperature was greater than 55 °C, the gel increased its size. This corresponds to the disappearance of hydrophobic bondings and at such $\Delta H_{dil} > 0$. Under these conditions, water–water dispersion forces are stronger than the water–polymer interaction forces and eventually water separated out from the polymer network into discrete droplets. In order to illustrate the phase-separation process further, the temperature dependences of the relative change in gel thickness, d_θ/d_0 (where d_θ is the hydrogel thickness at a temperature θ and d_0 is the thickness of the xerogel), and the turbidity, $\tilde{\tau}_1$, of a loosely cross-linked gel with w_i = 36.7% w/w gel were measured. These values of d_θ/d_0 and $\tilde{\tau}_1$ are analyzed together with the temperature dependence of the poly(HEMA)–water interaction parameter χ taken from the literature.[22] χ is a qualitative measurement of the goodness of water–polymer interaction, dissolution of polymer occurring when a χ value is close to 0.5. In Figure 5 one can see that the maximum value of χ was 0.841 at 55 °C, indicating a relatively poor water–polymer interaction. This was accompanied by water droplet formation and a maximum $\tilde{\tau}_1$. The values of d_θ/d_0, on the other hand, showed a minimum at θ = 55 °C. Swelling is often expressed in terms of the volume fraction of the polymer ϕ_2, and the behavior of d_θ/d_0 with changing θ is thus equivalent to that of $\phi_2^{-1/3}$ for isotropic swelling.

Effect of Cross-Linker Concentrations on the TRM Parameters. Table II shows the variations in turbidity ratio, water droplet size, and concentration with EDMA

Table II
Effect of EDMA Content on TRM Parameters: Turbidity Ratio (T), Droplet Diameter (L), and Concentration (C)[a]

	added EDMA (% w/w):		
	0.0	0.2	2.0
	θ = 20 °C		
$T_{1,2}$	1.783	2.085	2.182
$T_{2,3}$	2.134	2.185	2.588
$T_{1,3}$	3.805	4.556	5.647
$L_{1,2}$	0.187	0.114	0.094
$L_{2,3}$	0.130	0.117	<0.005
$L_{1,3}$	0.161	0.114	0.057
$C_{1,2}$	1.731	3.310	1.441
$C_{2,3}$	2.818	2.482	*b*
$C_{1,3}$	2.167	3.310	5.088
	θ = 40 °C		
$T_{1,2}$	1.758	2.040	2.290
$T_{2,3}$	2.106	2.136	2.583
$T_{1,3}$	3.702	4.357	5.917
$L_{1,2}$	0.192	0.125	0.073
$L_{2,3}$	0.137	0.130	<0.005
$L_{1,3}$	0.166	0.125	0.036
$C_{1,2}$	1.881	2.785	4.014
$C_{2,3}$	2.902	2.003	*b*
$C_{1,3}$	2.328	2.758	27.247
	θ = 60 °C		
$T_{1,2}$	1.596	1.971	2.644
$T_{2,3}$	2.036	2.172	2.565
$T_{1,3}$	3.250	4.281	6.783
$L_{1,2}$	0.588	0.135	<0.005
$L_{2,3}$	0.156	0.124	<0.005
$L_{1,3}$	0.203	0.130	<0.005
$C_{1,2}$	0.501	2.685	*b*
$C_{2,3}$	2.537	2.615	*b*
$C_{1,3}$	1.834	2.891	*b*

[a] w_i = 37.9%. [b] Out of the range of determination.

concentrations. Changes in TRM parameters with EDMA contents were also examined at different temperatures. At a defined w_i, a higher EDMA level favored deswelling and the resulting gel appeared permanently turbid. The $L_{a,b}$ values tend to decrease with an increasing EDMA level, and hence the associated $C_{a,b}$ values increased, suggesting a reasonably high cross-linking density in the polymer network.

Distribution of $L_{a,b}$ in the Loosely Cross-Linked Poly(HEMA) Hydrogels. Turbidities of the gels were measured at only three wavelengths in this work, and the resulting $L_{a,b}$ values could not afford any meaningful and conclusive distribution data. For the loosely cross-linked poly(HEMA) hydrogels, values of $L_{a,b}$ lie between the range of 0.1 ± 0.05 μm. Nevertheless, from the SEM micrograph taken for a loosely cross-linked gel with w_i = 38.0% w/w (Figure 6), one can see the polydisperse nature of the microvoids (dark areas) which indicates that $L_{a,b}$ was not monodisperse.

Conclusions

From a series of temperature-induced turbidity experiments, the microsyneresis region in the loosely cross-linked hydrogels was defined as a function of the water content used in the polymerization mixture, w_i. When w_i = 36–38% w/w, microsyneresis occurred. At 55–60 °C the turbidities in the gels were at a maximum, corresponding to the breakage of hydrophobic bondings in the poly(HEMA) network. By means of the turbidity ratio method, the diameters and concentrations of water droplets were found to be 0.1 ± 0.05 μm and 0.25–2.20% w/w of the swollen gel, respectively.

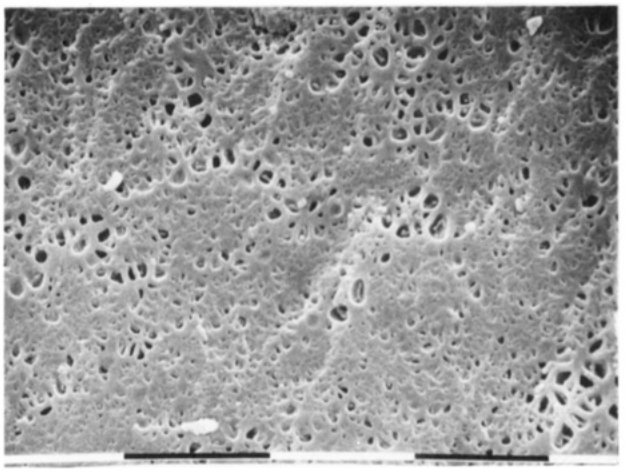

Figure 6. Electron micrograph of a freeze-fractured poly(HEMA) hydrogel prepared with no added cross-linker and 38.0% of water. Black and white bars at the foot of the micrograph correspond to lengths of 10 μm.

Acknowledgment. The provision of a maintenance grant to D.C.F.Y. by Unilever plc is gratefully acknowledged. We particularly thank Dr. B. Sedláček of the Institute of Macromolecular Chemistry at Prague for his helpful advice and for kindly making available to us the relevant tabulated Mie scattering data referred to as Macro tables D3, D5, and D6 in Figure 2 and in the Appendix of this paper. We also thank J. A. Sargent for the SEM work.

Appendix

The TRM employed here is based on Mie scattering of water droplets within a hydrogel medium. The spherical nature of the particles is implicit. Complete scattering functions involve the relative size and relative refractive index parameters. Use is made here of computer-generated functions, the data being tabulated for specific conditions in tables compiled in the Institute of Macromolecule Chemistry, Prague. Examples of the numerical procedures involved are indicated below.

Determination of the Mean Diameter (L) and Concentration (C) of the Water Droplets. The following numerical examples relate to the TRM parameters measured for a loosely cross-linked poly(HEMA) hydrogel with w_i = 36.7% w/w and no added EDMA.

(i) Measured turbidities at 30 °C: At 436 nm, $\tilde{\tau}_1$ = 0.632; at 546 nm, $\tilde{\tau}_2$ = 0.300; at 700 nm, $\tilde{\tau}_3$ = 0.135.

(ii) Turbidity ratios: $T_{1,2}$ = 2.107, $T_{2,3}$ = 2.222, and $T_{1,3}$ = 4.681.

(iii) Relative refractive index at 30 °C: $m = n(H_2O)/n(\text{gel})$, where $n(H_2O)$ is the refractive index of water = 1.3339 and n(gel) is the refractive index of the gel = 1.4343. Therefore, m = 1.3339/1.4343 = 0.93.

(iv) Gel thickness at 30 °C = 0.159 cm.

The procedures adopted in calculating L and C are as follows: First, one has to select an appropriate Macro table (see below) of turbidity ratios ($T_{a,b}$) from which the apparent size parameter α^* can be matched. Both $T_{a,b}$ and α^* are theoretically calculated quantities which are primarily related to a basic wavelength λ_0 at 326.7 nm. In the collection of the Macro tables, those coded with numbers D5 and D6 are tabulated with the theoretically calculated data of $T_{a,b}$ and α^*.

table	function	κ	m
D3	specific turbidity		0.300–0.999
D5	turbidity ratios	1.2531	0.300–0.999
D6	turbidity ratios	1.5703	0.300–0.999

The relationship between the basic wavelength λ_0 and the wavelength used in practice (i.e., selected wavelength in vacuo), Λ_1, is described as follows:

$$\Lambda_1 = \lambda_0 n(H_2O) = 326.7 \times 1.3339 = 435.8 \text{ nm} \quad \text{(A1)}$$

Furthermore, a constant wavelength quotient (κ) is defined as

$$\kappa = \Lambda_2/\Lambda_1 = 546.1/435.8 = 1.2531 \quad \text{(A2)}$$

κ is also expressed as a function of the wavelengths other than Λ_2 and Λ_1 as

$$\kappa^{b-a} = \Lambda_b/\Lambda_a \quad \text{(A3)}$$

where a and b are arbitrary constants 1–3, etc. In order to decide which table (D5 or D6) to use, one has to calculate $\kappa_b{}^{-a}$, according to the following assignments:

(1) The wavelength of 435.8 nm (practically 436 nm) is assigned as Λ_1.

(2) The wavelength of 546.1 nm (practically 546 nm) is assigned as Λ_2.

(3) The wavelength of 684.3 nm (practically 700 nm) is assigned as Λ_3.

Their corresponding κ^{b-a} values are calculated:

wavelengths in vacuo (nm)	turbidity	turbidity ratio	κ^{b-a}	macro table
$\Lambda_{a=1}$, $\Lambda_{b=2}$ (436, 546)	τ_1, τ_2	$T_{1,2}$	$(1.2531)^{2-1}$ = 1.2531	D5
$\Lambda_{a=2}$, $\Lambda_{b=3}$ (546, 700)	τ_2, τ_3	$T_{2,3}$	$(1.2531)^{3-2}$ = 1.2531	D5
$\Lambda_{a=1}$, $\Lambda_{b=3}$ (436, 700)	τ_1, τ_3	$T_{1,3}$	$(1.2531)^{3-1}$ = 1.5703	D6

Diameter of Water Droplet (L). After one has decided which particular Macro table to use, α^* is located by matching the corresponding $T_{a,b}$ value. However the calculation of L involves an adjustment of α^* to α:

$$\alpha = \alpha^* \kappa^i \quad \text{(A4)}$$

where i represents the term $b - a$, which is the power of the wavelength quotient κ.

Subsequently, L can be calculated using the expression

$$L_{a,b} = [\lambda_0 \alpha]/\pi \quad \text{(A5)}$$

in which $\lambda_0 = 326.7$ nm and α is determined via eq A4. The subscript a,b specifies the pairs of wavelengths used. For example, when $\tilde{\tau}_1 = 0.632$ and $\tilde{\tau}_2 = 0.3$, $T_{1,2} = 2.107$, and one matches $\alpha^*_{1,2}$ using table D5 under the column of $m = 0.93$.

As $\alpha^*_{1,2} = 1.05$, hence

$$L_{1,2} = [\lambda_0 \alpha^*_{1,2} \kappa^i]/\pi = [326.7(\alpha^*_{1,2})(1.2531)^0]/\pi = 103.99\alpha^*_{1,2}$$

$$= 109.19 \text{ nm } (0.109\ \mu\text{m})$$

When $\tilde{\tau}_2 = 0.3$ and $\tilde{\tau}_3 = 0.135$, $T_{2,3} = 2.222$. One matches $\alpha^*_{2,3}$ using table D6 under the column of $m = 0.93$.

As $\alpha^*_{2,3} = 0.8$, hence

$$L_{2,3} = [326.7(\alpha^*_{2,3})(1.2531)^1]/\pi = 130.28\alpha^*_{2,3}$$

$$= 104.23 \text{ nm } (0.104\ \mu\text{m})$$

Similarly when $\tilde{\tau}_1 = 0.632$ and $\tilde{\tau}_3 = 0.135$, $T_{1,3} = 4.681$. One matches $\alpha^*_{1,3}$ using table D5 under the column of $m = 0.93$.

As $\alpha^*_{1,3} = 0.8$, hence

$$L_{1,3} = [326.7(\alpha^*_{1,3})(1.2531)^0]/\pi = 103.99\alpha^*_{1,3}$$

$$= 109.19 \text{ nm } (0.109\ \mu\text{m})$$

Concentration of Water Droplet (C). The concentration, C, can be calculated using the equation

$$C_{a,b} = \tau/[\tau/C]_0 \quad \text{(A6)}$$

where $[\tau/C]_0$ is the specific turbidity (abbreviated as "sp. tur." in Figure 2 of the text). At infinite dilution, one assumes no concentration dependence of τ/C and therefore $[\tau/C]_0 = \tau/C$. The subscript a,b specifies the pair of wavelengths used. Some theoretically calculated values of $[\tau/C]_0$ are tabulated in Macro table D3 with different values of α^* and m.

In order to evaluate $C_{a,b}$, one has to convert the turbidity $\tilde{\tau}_a$ to τ using eq A7, where d_θ has been defined previously in the main text:

$$\tau = (2.303\tilde{\tau}_a)/d_\theta \quad \text{(A7)}$$

One locates $[\tau/C]_0$ values by matching with α^* under the column of $m = 0.93$ with Macro table D3. Hence, C can now be calculated using eqs A6 and A7. The following table lists the results of $C_{a,b}$:

$L_{a,b}$	$\alpha^*_{a,b}$	$[\tau/C]_0$, cm^{-1}	$\tilde{\tau}_a$	d_θ, cm	τ, cm^{-1}	$C_{a,b}$, g/100 g
$L_{1,2}$	1.050	4.938	0.632	0.159	9.143	1.852
$L_{2,3}$	0.800	2.627	0.300	0.159	4.340	1.652
$L_{1,3}$	1.050	4.938	0.632	0.159	9.143	1.852

References and Notes

(1) Wichterle, O.; Lim, D. *Nature* **1960**, *185*, 117.
(2) Nyquist, E. B. In *Functional Monomers, Vol. 2, Hydroxy Monomers. Their Preparation, Polymerisation and Applications*; Vocum, R. H., Nyquist, E. B., Eds.; Marcel Dekker Inc.: New York, 1974; Chapter 3, p 299.
(3) Peppas, N. A., Ed. *Hydrogels in Medicine and Pharmacy, Vol. II, Polymers*; CRC Press, Inc.: Boca Raton, FL, 1986.
(4) Haruvy, Y. *Polym. Bull.* **1987**, *17*, 149.
(5) Stevenson, W. T. K.; Evangelista, R. A.; Broughton, R. A.; Sefton, M. V. *J. Appl. Polym. Sci.* **1978**, *34*, 65.
(6) Huglin, M. B.; Yip, D. C. F. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 237.
(7) Sedláček, B. *Collect. Czech. Chem. Commun.* **1967**, *32*, 1374, 1398, 1595, and 1599.
(8) Dušek, K.; Sedláček, B. *Collect. Czech. Chem. Commun.* **1969**, *34*, 136.
(9) Dušek, K.; Sedláček, B. *Collect. Czech. Chem. Commun.* **1973**, *38*, 3434.
(10) Dušek, K.; Sedláček, B. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1569.
(11) Sedláček, B. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2064.
(12) Sedláček, B.; Verner, B.; Mircslav, B.; Zimmermann, K. *Collect. Czech. Chem. Commun.* **1979**, *44*, 2079.
(13) Sedláček, B.; Zimmermann, K. *Polym. Bull.* **1982**, *7*, 531.
(14) Sedláček, B.; Koňák, Č.; Zimmermann, K. *Polym. Bull.* **1982**, *8*, 125.
(15) Sedláček, B.; Koňák, Č. *J. Colloid Interface Sci.* **1982**, *90* (1), 60.
(16) Warren, T. C.; Prins, W. *Macromolecules* **1972**, *5*, 506.
(17) Dušek, K. *J. Polym. Sci., Polym. Lett.* **1965**, *3*, 209.
(18) Dušek, K. *J. Polym. Sci.* **1967**, *C16*, 1289.
(19) Dušek, K. In *Polymer Network—Structure and Mechanical Properties*; Chompff, A. J., Newman, S., Eds.; Plenum Press: New York, 1971; p 245.
(20) Al-Issa, M. A.; Davis, T. P.; Huglin, M. B.; Yahya, I. B.; Yip, D. C. F. *Eur. Polym. J.* **1984**, *20*, 947.
(21) Huglin, M. B.; Sloan, D. J. *Br. Polym. J.* **1983**, *15*, 165.
(22) Dušek, K.; Bohdanecký, M.; Prokopova, E. *Eur. Polym. J.* **1974**, *10*, 239.

Registry No. EDMA (copolymer), 25053-81-0; HEMA (homopolymer), 25249-16-5; water, 7732-18-5.