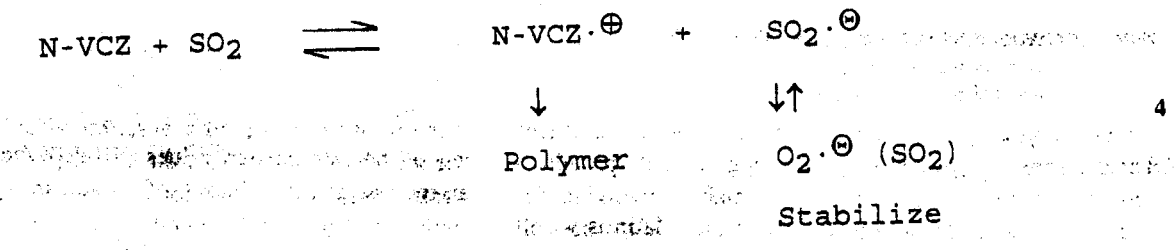

viscosities, the average value being 0.101 dL g^{-1} in 1,2-dichloroethane at 30 °C. SO_2 is also a charge transfer electron acceptor like NO_2, and initiates the polymerization through a charge transfer mechanism (**Structure 4**):

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Gel Fibers

See: Polyacrylonitrile Gel Fibers

Gel-like Spherulite Press Method

See: Polyethylene, High Performance (Gel-Like Spherulite Press Method and Ultradrawing)

Gel Spinning

See: Poly(vinyl alcohol) (High Strength and High Modulus)
Poly(vinyl alcohol) Fiber (High Strength and High Modulus)
Ultra-Strong Polyethylene Fibers

Gelan Gum

See: Welan Microbial Polysaccharide

Gelatin

See: Gelatin (Molecular Weight Distributions)

GELATIN (Molecular Weight Distributions)

Chi Wu
Department of Chemistry
The Chinese University of Hong Kong

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Gelatin constitutes a class of proteinaceous substances derived from a naturally occurring parent protein—collagen—through certain processes mainly involving destruction of collagen's secondary structure. Gelatin is well known for its property of forming elastic gels at room temperature at relatively low concentrations: a few percent of gelatin in water. During the gelation process, gelatin molecules re-naturalize into a collagen-like structure, i.e., a triple-stranded helix. Gelatin is widely and extensively used in the food, photographic, and pharmaceutical industries as an important stabilizer ingredient (e.g., for pulverulent formulations of carotenoids and vitamin A).[1,2]

Much experimental research has been done both on the practical uses of gelatin and on fundamental aspects of the gelation process.[3–5] Researchers have investigated the conformational changes of gelatin molecules in solution, the sol-gel transition, and the rheologic properties of gelatin gels across decades.[6–11] Much less attention, on the other hand, has been given to gelatin's molecular characterization. This is due mainly to its polyelectrolyte and polydisperse nature. For example, in size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC), besides the calibration problem, it is difficult to find a commercially available column which is ready to be used to analyze a widely distributed gelatin with sufficient resolution, especially when the weight-average molecular weight exceeds 300,000 g/mol.

At room temperature, there are two kinds of intermolecular actions in aqueous gelatin solution. One such interaction is the electrostatic activity in the presence of electric charges on the polypeptide chain. Another is the formation of hydrogen bond between the amino acid units. These interactions have to be eliminated in order to identify the true molecular characteristics of gelatin. Adding salts (as in solutions of synthetic polyelectrolytes) is one way to screen the electrostatic interaction and suppress the polyelectrolyte effect. However, most types of salts added in aqueous gelatin solution at room temperature will not prevent the hydrogen bonding, which is reflected in either gelation or aggregation, depending on the gelatin concentration. Only certain salts, such as KSCN and LiBr, are capable of screening out electrostatic interactions while preventing the formation of the hydrogen bond.

When salts are present in aqueous gelatin solution, it is known that there is a problem of preferential sorption of the salt in the domain of gelatin molecules, just as synthetic polyelectrolytes in aqueous salt solutions. In principle, only the apparent molecular parameters can be measured via strong sorption. Thus, in order to determine the true molecular parameters, the apparent molecular parameters are extrapolated to infinitely dilute salt concentration. Even this time-consuming procedure, however, does not guarantee that the extrapolated values will give the true molecular parameters, as the behavior of gelatin in aqueous solution with and without salts could be completely different.

Considering this preferential sorption, some researchers have used non-aqueous solvents, such as formamide, glycerol, and trifluoroethanol, to dissolve gelatin[12] with an assumption that those non-aqueous solvents can suppress the above two types of intermolecular interactions. Veis and Anesey[13] investigated the gelatin solutions in formic acid and its mixtures with dimethylformamide at room temperature. Later, Stejskal et al.[14] used formamide as single solvent in static LLS experiments, demonstrating that formamide can be used for dissolving gelatin at room temperature. It has been suggested that formamide interacts with gelatin by a rather specific, chelated solution owing to the similarity between formamide and gelatin peptide linkages and the known cyclic dimerization of carboxylic acids and amides.

As an absolute method, laser light scattering (LLS) has been used extensively to characterize polymers. Current-model LLS spectrometers can perform both static and dynamic measurements. In static LLS, the angular and concentration dependence of absolute scattered intensity are measured; the weight-average molecular weight (M_w), the z-average radius of gyration ($<R_g^2>_z^{1/2}$), and the second virial coefficient (A_2) can be determined from the measured absolute scattered intensities. In dynamic LLS, the intensity-intensity time correlation function is measured. By making a Laplace inversion, we can convert the measured correlation function into a characteristic line-width distribution ($G(\Gamma)$) which could be further reduced to a translational diffusion coefficient distribution ($G(D)$) or even to a molecular weight distribution (MWD) if we can establish a calibration between D and M.

PREPARATION

When gelatin is extracted from collagen, the entire structure of the collagen fiber is lost. This extraction process requires both chemical and thermal treatments, such as in acidic or basic environment and heating. The commercial manufacturing process results in a material that is complex and heterogeneous at the molecular level. In order to establish a general methodology to characterize the molecular weight distribution of gelatin, two special, laboratory-prepared gelatins (courtesy of Dr. B. Klaus and Dr. B. Wilfried, DGF, Deutsche Gelatine-Fabriken Stoess AG, Eberbach, Germany) were used. One is an A-type (Bloom value 310, Batch #: 50100), the other a B-type (Bloom value 200, Batch #: 21020)—termed hereinafter gelatin-A and

gelatin-B, respectively. In addition, a commercial gelatin from DGF (Bloom value 200, 176497) was studied. Analytical grade formamide (BASF AG, Germany) was used as solvent. Both gelatins and formamide were used without further purifications. The gelatin solutions of 1 to 5 mg/mL were prepared by dissolving certain amount of gelatin in formamide first at 50 °C for one hour and then at room temperature for at least one day. An estimate of 12% water in gelatin was assumed when we calculated the final gelatin concentration. Such prepared solutions were finally clarified with a 0.22 μm Millipore filter in order to remove dust. All laser-light-scattering measurements were taken at 25.0 ± 0.1 °C.

PROPERTIES

The angular dependence of the excess absolute time-averaged scattered intensity, $R_{vv}(\Theta)$ known as the excess Rayleigh ratio, of gelatin formamide solution was measured. For a dilute gelatin solution at concentration C (g/ml) and light-scattering angle Θ, $R_{vv}(\Theta)$ can be approximately expressed as (**Equation 1**),[15]

$$\frac{KC}{R_{VV}(\theta)} \cong \frac{1}{M_W} \cdot \left(1 + \frac{1}{3}\langle R_g^2\rangle_z q^2\right) + 2A_2C \qquad 1$$

where $K = 4\pi^2 n^2 (\frac{\partial n}{\partial c})^2 / N_A \lambda_0^4$) with N_A, n, and λ_0 being Avogadro's number, the solvent refractive index, and the wavelength of light in vacuo, respectively, and $q = (4\pi n/\lambda_0)\sin(\Theta/2)$. By measuring $R_{vv}(\Theta)$ at different C and Θ, we can determine M_w, $\langle R_g^2\rangle_z^{1/2}$, and A_2 from the Zimm plot which incorporates Θ and C extrapolations on a single grid.

Figure 1 shows a typical Zimm plot of gelatin-B in formamide at 25 °C. Based on Equation 1, we can determine: $\langle R_g^2\rangle_z^{1/2}$ from the slope of $[KC/R_{vv}(\Theta)]_{C=0}$ vs. q^2; A_2 from $[KC/R_{vv}(\Theta)]_{\Theta=0}$ vs. C; and M_w from the intercept

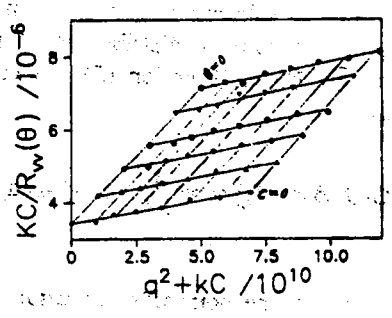

FIGURE 1. Typical Zimm plot of gelatin-B in formamide at 25 °C, where C ranges from 1 to 5 mg/ml and Θ, f from 30° to 90°. *Source*: Redrawn from C. Wu, *J. Polym. Sci. Polym. Phys. Ed. 32*, 803 (1994). With permission.

of $[KC/R_{vv}(\Theta)]_{C=0,\ \Theta=0}$. They are listed in **Table 1**. The positive values of A_2 show that formamide is a good solvent for dissolving gelatin at room temperature.

The measured intensity time correlation function $G^{(2)}(t,\Theta)$ of gelatin solution in the self-beating mode has the following form (**Equation 2**),[16]

$$G^{(2)}(t) = \langle I(t)I(0)\rangle = A[1 + \beta |g]^{(1)}(t)|^2 \qquad 2$$

where A is the measured baseline; β, a parameter depending on the coherence of the detection; t, the delay time; and $g^{(1)}(t)$, the first order electric field (E) correlation function. In a proper measurement, the difference between the measured baseline A and the calculated baseline $G^{(2)}(t\to\infty)$ should be no more than 0.1%. For a polydisperse sample, $|g^{(1)}(t)|$ can be related to the normalized characteristic line-width distribution $G(\Gamma)$ by (**Equation 3**)

$$|g^{(1)}(t)| = \langle E(t)E^*(0)\rangle = \int_0^\infty G(\Gamma)e^{-\Gamma t}d\Gamma \qquad 3$$

$G(\Gamma)$ can be retrieved from a Laplace inversion of $|g^{(1)}(t)|$ by using a computer program CONTIN.[17] In general, Γ is a function of both C and Θ. As C increases, the interactions between polymer molecules will affect the diffusion process, which is normally a linear function of C when solution is dilute. On the other hand, as Θ increases, the intramolecular motions will influence Γ. These two effects can be expressed in the following form (**Equation 4**),[18]

$$\Gamma/q^2 = D(1 + k_dC)(1 + f\langle R_g^2\rangle_z q^2) \qquad 4$$

where k_d is the diffusion second virial coefficient and f is a dimensionless number depending on polydispersity, polymer chain structure, and solvent quality. The theoretical values of f for a number of Gaussian models (linear and branched chains) have been predicted.[19] D can be related to the hydrodynamic radius R_h by using the Stokes-Einstein Equation: $R_h = k_BT/(6\pi\eta D)$ with k_B, T, and η being the Boltzmann constant, the experimental temperature, and the viscosity of formamide, respectively. The calculated values of $\bar{D}$, R_h, k_d, and f are also listed in Table 1, where $\bar{D}$ is calculated from Γ (= $\int G(\Gamma)\Gamma d\Gamma$). The positive values of k_d further confirm that formamide is indeed a good solvent for gelatin at room temperature. It is interesting to find that the values of f are very close to the ones predicted for a random-coil in good solvent. The ratio of $\langle R_g^2\rangle_z^{1/2}/R_h$ for gelatin in formamide is about 1.84 which shows that gelatin is a broadly distributed linear polymer.[20] Our results show

TABLE 1. Static and Dynamic LLS Results of Gelatins in Formamide at 25 °C

Gelatin	$10^{-5}M_w$ / $mol^{-1}g$	$\langle R_g^2\rangle_z^{1/2}$ / nm	10^4A_2 / $g^{-2}mol.ml$	$10^8\bar{D}$ / cm^2s	R_h / nm	K_d / $g^{-1}ml$	f
A	2.92	33	3.7	3.58	18.0	35	0.15
B	3.71	38	6.2	3.11	20.5	63	0.17
176497	3.46	37	4.5	3.24	19.8	50	0.16

The following M_z, M_w, and M_n were obtained from dynamic LLS where the calibration of $D = 5.98 \times 10^{-5} M^{-0.58}$ was used.

Gelatin	10^{-6} M_z / $mol^{-1}g$	10^{-5} M_w / $mol^{-1}g$	10^{-5} M_n / $mol^{-1}g$	M_w:M_n
A	8.30	3.61	1.57	2.3
B	1.56	3.00	1.65	1.8
176497	3.86	3.48	1.32	2.7

Source: C. Wu, *J. Polym. Sci. Polym. Phys. Ed. 32*, 803 (1994). With permission.

that gelatin in formamide at room temperature behaves, more or less, like a random coil.

With the calculated k_d, $\langle R_g^2\rangle$, and f, we can easily transform $G(\Gamma)$ at finite C and θ into G(D) at C = 0 and θ = 0 on the basis of **Equation 5**. **Figure 2** shows a typical plot of G(D) for gelatin-A in formamide at 25 °C. In order to transform G(D) to a molecular weight distribution (MWD), we have to establish a calibration between D and M, i.e.,

$$D = k_D M^{-\alpha D} \qquad 5$$

where k_D and α_D are two calibration constants. In principle, k_D and α_D can be determined by measuring the values of $\bar{D}$ and M_w for a set of narrowly distributed standards[21] or by estimating them from polymer conformation, solvent quality, and viscosity data.[22]

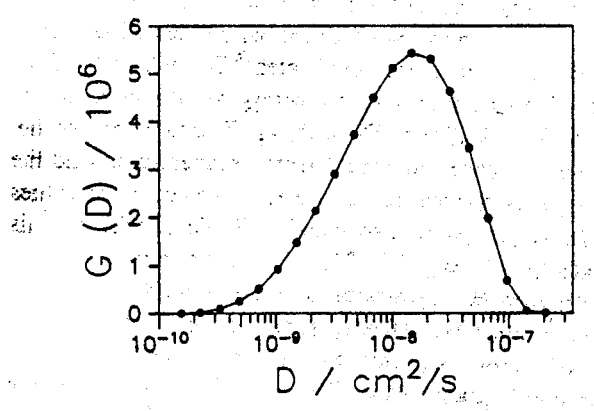

FIGURE 2. Typical diffusion coefficient distribution G(D) of gelatin-A in formamide at 25 °C. *Source*: Redrawn from C. Wu, *J. Polym. Sci. Polym. Phys. Ed. 32*, 803 (1994). With permission.

For gelatin, it is rather difficult in practice to obtain a set of narrowly distributed standards with different molecular weights. In order to overcome this difficulty, two methods have been used to obtain k_D and α_D. Method I is a combination of static and dynamic laser light scattering results of two or more broadly distributed samples. Method II is a combination of laser light scattering and size exclusion chromatographic results of one broadly distributed sample. The detail of these two methods can be found elsewhere.[23] Both methods showed that $k_D = (5.98 \pm 0.30) \times 10^{-5}$ and $\alpha_D = 0.580 \pm 0.005$ where D and M are in the units of cm^2/sec and g/mol, respectively.

After having k_D and α_D, MWD can be calculated according to the following principle: on the basis of Equations 1 and 3, as $C \to 0$ and $\theta \to 0$, we have (**Equation 6**)

$$\int_0^\infty G(D)\, dD = \gamma \cdot \int_0^\infty F_Z(M)\, dM \qquad 6$$

where γ is a normalization constant and $F_z(M) = M\,F_w(M) = M^2F_n(M)$ with the subscripts z, w, and n meaning intensity, weight, and number distribution of molecular weight, respectively. Using Equation (5), we can rewrite Equation (6) as

$$\int_0^\infty \alpha_D \cdot D \cdot G(D)\, d[\ln(M)] = \gamma \cdot \int_0^\infty M \cdot F_Z(M)\, d[\ln(M)] \qquad 7$$

After a comparison of the both sides of **Equation 7**, we have

$$F_Z(M) = \frac{\alpha_D \cdot D \cdot G(D)}{\gamma^M} \qquad 8$$

In **Equation 8**, we have taken the integrand as one way to represent the same polymer distribution. On the basis of Equations (5) and (8), we are ready to calculate $F_z(M)$ from G(D) and further F_w (M) and $F_n(M)$, where γ as a constant is irrelevant to the distributions.

Figure 3 shows typical normalized weight distributions of molecular weight, $f_w(M)$, of gelatin-A (circles) and gelatin-B (triangles). Based on these two distributions, we were able to calculate, M_z, M_w, and M_n, which are summarized in Table 1.

In practice, the size exclusion chromatograph (SEC) is a more established method for the characterization of molecular weight distribution. For comparison, the SEC elution curves of gelatin-A and gelatin-B are also presented in Figure 3 as an inset. It shows that the molecular weight distributions obtained from our LLS measurements are similar to the distributions obtained from SEC measurements: gelatin-A is broader and gelatin-B is bimodal. Unfortunately, we cannot directly compare the molecular weight distributions obtained from LLS with those from SEC at the present time because it is very difficult to obtain an absolute calibration of our SEC columns for gelatin characterization.

APPLICATIONS

Since we have confirmed that formamide is a good solvent for dissolving gelatin at room temperature, our experimental results suggest that the gelatin chain in formamide at room temperature is flexible and has a random-coil

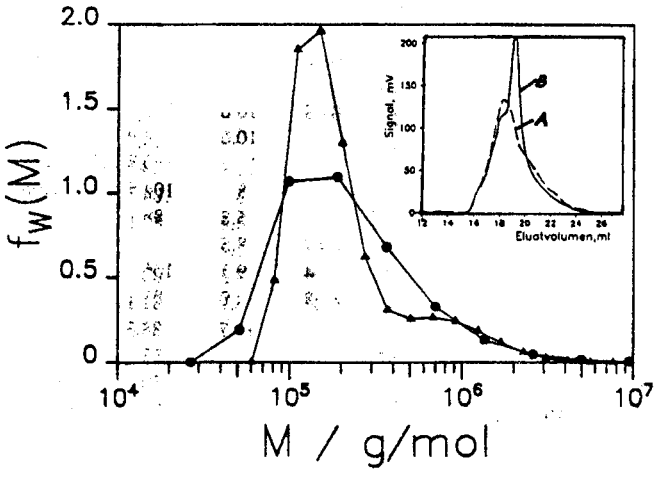

FIGURE 3. Normalized weight distributions, $f_w(M)$, of gelatin-A (circles) and gelatin-B (triangles). The inset shows the SEC elution curves of these two gelatins. *Source*: Redrawn from C. Wu, *J. Polym. Sci. Polym. Phys. Ed. 32*, 803 (1994). With permission.

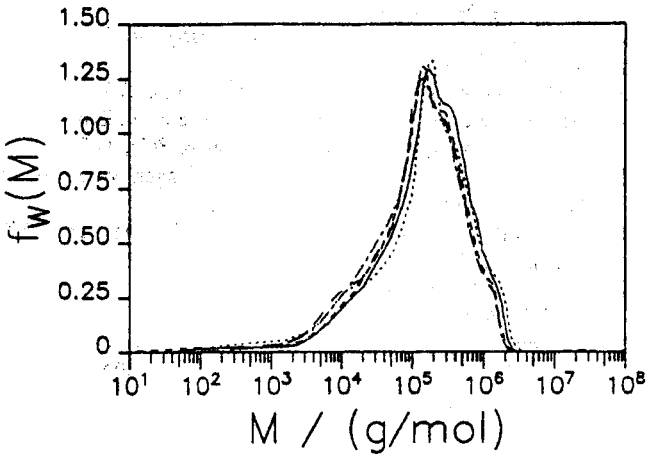

FIGURE 4. Weight distributions of five different B-200 gelatin samples (162378, 166401, 176497, 164623, and 172640). The weight-average molecular weights range from 2.41×10^5 to 3.67×10^5 g/mol and M_w/M_n from 3.7 to 5.3.12. *Source*: Redrawn from C. Wu, *Macromolecules 26*, 5423 (1994). With permission.

conformation. Both the effects of polyelectrolytes and hydrogen bonding in gelatin molecules are eliminated in formamide so that it can be used as a solvent in other solution methods to characterize gelatin.

It should be noted that the above-listed calibration between D and M, i.e., k_D and α_D, are independent on a particular laser light scattering instrument as long as formamide as solvent and room temperature (25 °C) are used, which means that with this calibration, dynamic light scattering becomes a good, absolute, and fast experimental method for characterizing the molecular weight distribution of gelatin even if it does not have the same resolution as SEC.

In addition, in the future, with the known values of k_d and f in Table 1, we should be able to determine the molecular weight distribution of a given gelatin sample by measuring *only* one dilute gelatin solution at *only* one scattering angle. **Figure 4** shows such an application of using a combination of dynamic laser light scattering and size exclusion chromatography to characterize five different commercial B-200 gelatin samples (162378, 166401, 176497, 164623, and 172640). The weight-average molecular weights ranges from 2.41×10^5 to 3.67×10^5 g/mol and M_w/M_n from 3.7 to 5.3. Due to some experimental uncertainties in the baseline, we should not be too concerned about both the lower and higher molecular weight tails.

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GELATION, PHYSICAL (Atactic Polystyrene)

Jeanne François and Dominique Sarazin
Institut Charles Sadron/ULP

For a long time, physical gelation in polymer solutions was believed to be limited to crystallizable polymers. Discovery by Tan et al.[1] of the ability of atactic polystyrene (aPS) to exhibit this phenomenon in several solvents was first considered astounding and suspicious but was confirmed. Among the various solvents used, carbon disulphide (CS_2) has attracted attention because it exhibits the highest temperature gelation. We present the current state of the science.

PHASE DIAGRAMS: SOL-GEL TRANSITION

Tan et al[1] showed that atactic polystyrene with molecular weights ranging from $4*10^3$ to $2*10^6$ are capable of gelation in many solvents. **Table 1** compares thermodynamic properties of the solvents and their gelation capability. The solvent properties considered are the Hildebrand solubility parameter δ, the Flory-Huggins parameter χ, and the molar volume V_M. There are no correlations between δ or χ and the gel stability expressed by the sol-gel transition temperature, T_{gel}, and the gelation enthalpy, ΔH_{gel}. For several solvents capable of promoting gelation (Lines 3–9 of Table 1), the stability of the gel seems to increase with increasing V_M, while ΔH_{gel} remains almost constant, as shown in **Figure 1**. But the CS_2 behavior is completely different since, despite its much smaller molar volume, T_{gel} and ΔH_{gel} are much higher than those measured for the other solvents. CS_2 is definitely a very particular gelling solvent; this is why the aPS-CS_2 system has been the object of numerous investigations.

For a sample of a given molecular weight, T_{gel} varies with the polymer concentration c_p as shown in **Figure 2**.

TABLE 1. Relation Between Properties of Solvents and the Gelation of aPS. δ is the Solubility Parameter $(cal/cm^3)^{1/2}$, χ is the Solvent-Polymer Interaction Parameter, V_M is the Molar Volume of the Solvent (cm^3/mole), ΔH_{gel} is the Gelation Enthalty (kJ/mole), and T_{gel} is the Gelation Temperature for a aPS Sample With Mw = $6.7*10^5$ at 166g/L

Solvent	δ	χ	ΔH_{gel}	V_M	T_{gel} (°C)
Carbon disulfide	10	0.40	26.3	60	8
n-amyl acetate	7.8	0.45	11.7	148.6	−52
Isoamyl acetate	8.5		11.4	148.6	−56
n-butyl acetate	8.5	0.48	10.6	131.7	−65
n-propyl acetate	8.8		10.6	114.9	−68
1 Chloropentane	8.3		12.2	120.7	−76
1-Chlorobutane	8.1		8	104.5	−79
1-Chloropropane	8.1		5.8	88.1	−86
Methyl ethyl ketone	9.3	0.47	8.5		
Toluene	8.9	0.44	9.5	106	−88
Furane tetrahydro	9.1	0.38	6.9	81.1	−100
Nitropropane	10.3		11.7	88.3	
Methylene chloride	9.7			63	no gel
Chloroform	9.3	0.42		80	no gel
Carbon tetrachloride	8.6	0.48		96	no gel
1-2-Dichloroethane		0.47			no gel
Trichloroethane	9.2				no gel
p-dioxane	10	0.46			no gel
Benzene	9.2	0.45		89	no gel
Aniline	10.3				no gel
Benzaldehyde	9.4				no gel
Nitrobenzene	10			108.3	no gel
Decalin	8.8			154	no gel

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