Solubility Parameter of an *N*-Isopropylacrylamide Gel

Yasuhiko Yagi, Hiroshi Inomata, and Shozaburo Saito*

Department of Molecular Chemistry and Engineering, Faculty of Engineering, Tohoku University, Sendai, 980, Japan

Received December 10, 1991
Revised Manuscript Received February 17, 1992

Introduction

The solubility parameter is a fundamental thermodynamic property of polymers and is used extensively for the discussion of the miscibility of polymers in solvents. In this paper, the solubility parameter of an *N*-isopropylacrylamide (NIPA) gel has been determined via swelling experiments. The theory of Gee[1] predicts that a polymer is swollen to a maximum in a solvent whose solubility parameter is the same as that of the polymer. The determination of the solubility parameter of an NIPA gel can lead to the understanding of the thermoresponsive volume phase transition of an NIPA gel in water.[2-4]

Experiments

Materials. NIPA monomer, provided by Eastman Kodak Co., was purified by recrystallization from a benzene/*n*-hexane mixture. The solvents used in this experiment are listed in Table I. All these solvents were supplied by Wako Pure Chemicals Co. and used without further purification.

Sample Preparation. Gel samples were prepared by a previously reported procedure.[4] The gel samples were immersed in an excess amount of the organic solvents at 25 °C until equilibrium was attained. As a reference volume, V_0, we adopted the volume when the gel was synthesized in a capillary glass tube of 1.6-mm diameter in water, d_0.

After equilibration, the diameter of the gel, d, was measured for each solvent by calibrated scale photography. The swelling ratio of the gel, Q ($=V/V_0$), was calculated from the equilibrium gel diameter, d, and the reference diameter, d_0, as follows:

$$Q = V/V_0 = (d/d_0)^3 \quad (1)$$

The previously reported value of the swelling ratio of the NIPA gel in water at 25 °C[4] was used for comparison.

Theory

Gee[1] extended the theory of Hildebrand and proposed that a requirement of mutual solubility is that the solubility parameter of the polymer, $\delta_{polymer}$, and that of the solvent, $\delta_{solvent}$, should not differ by much. That is, when $\delta_{polymer}$ equals $\delta_{solvent}$, the polymer shows a maximum swelling in the solvent. The theory of Gee was represented by eq 2 where Q = swelling ratio, Q_{max} = maximum swelling ratio,

$$Q/Q_{max} = \exp[-a\,Q(\delta_{solvent} - \delta_{polymer})^2] \quad (2)$$

$\delta_{solvent}$ = solubility parameter of the solvent, $\delta_{polymer}$ = solubility parameter of the polymer, and a = constant.

Equation 2 can be rewritten as follows:

$$[Q^{-1} \ln (Q_{max}/Q)]^{1/2} = |a^{1/2}(\delta_{solvent} - \delta_{polymer})| \quad (3)$$

By plotting $[Q^{-1} \ln (Q_{max}/Q)]^{1/2}$ against $\delta_{solvent}$, $a^{1/2}$ and $\delta_{polymer}$ can be determined from the slope and the intersection of the horizontal axis, respectively.

Table I
Solvents Used in This Study and Their Solubility Parameters[5]

solvent	solubility param at 25 °C, $(cal/cm^3)^{1/2}$
acetaldehyde	10.6
acetone	9.9
aniline	10.3
1-butanol (1-BuOH)	11.4
diethylamine (DEA)	10.6
dimethylformamide (DMF)	12.1
dioxane	10.0
ethanol (EtOH)	12.7
methanol (MeOH)	14.5
1-propanol (1-PrOH)	11.9
tetrahydrofuran (THF)	9.1

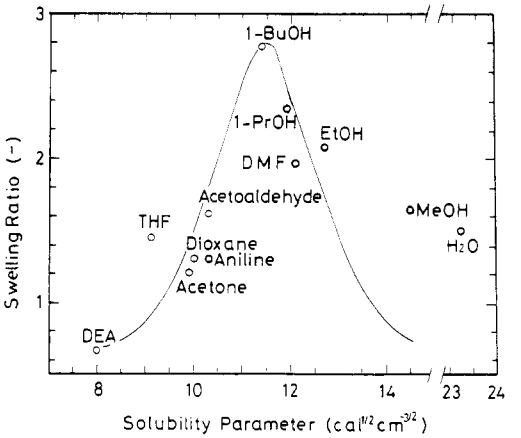

Figure 1. Relationship between the swelling ratio of the *N*-isopropylacrylamide gel and the solubility parameter of the various solvents.

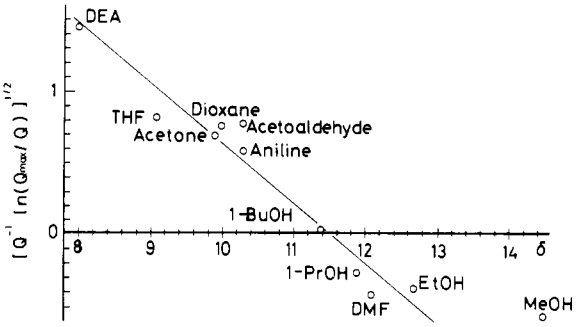

Figure 2. Plots of $[Q^{-1} \ln (Q_{max}/Q)]^{1/2}$ versus the solubility parameter of the solvents.

Results

Figure 1 shows the relationship between the swelling ratio of the NIPA gel and the solubility parameter of the various solvents. The swelling ratio in water was also plotted for comparison with that in the organic solvents. The NIPA gel exhibited the largest swelling ratio in 1-butanol (δ = 11.4) among the solvents used. The solvent 1-butanol was able to swell the NIPA gel, and we found that water was not good for the NIPA swollen gel. Figure 2 shows the relationship between $[Q^{-1} \ln (Q_{max}/Q)]^{1/2}$ and $\delta_{solvent}$. All the swelling data for the solvents except methanol can be correlated with a linear relation, confirming the applicability of Gee's theory. From the plot, δ_{gel} = 11.5 and a = 0.176 were acquired by a least-squares regression. The experimentally determined solubility

0024-9297/92/2225-2997$03.00/0 © 1992 American Chemical Society

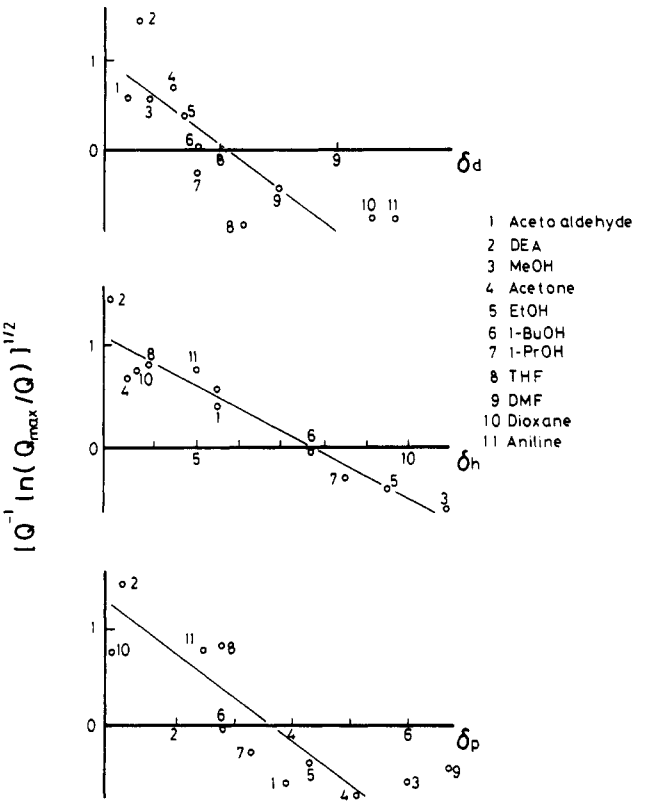

Figure 3. Plots of $[Q^{-1} \ln (Q_{max}/Q)]^{1/2}$ versus δ_d, δ_p, and δ_h of the solvents.

parameter of the NIPA gel, $\delta_{gel} = 11.5$, is very close to that of the polymer of NIPA, $\delta = 11.18$, which was evaluated by a group contribution technique.[6] With the values of a and δ_{gel}, eq 2 can correlate the experimental data well (solid line in Figure 1). However, the swelling ratio in methanol or water shows a large deviation from the correlation with eq 2 as shown in Figure 1. This deviation may be considered to result from a polarity of methanol and water. The solubility parameter may be divided into a three parts

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (4)$$

where δ_d = contribution of the dispersion force, δ_p = contribution of the polar force, and δ_h = contribution of hydrogen bonding. With the values of δ_d, δ_p, and δ_h, we tried to correlate the experimental data with eq 3. The results are plotted in Figure 3. It may be noted that the correlation with δ_h could represent the experimental data including those for methanol. This may suggest that hydrogen bonding plays an important role in the swelling of an NIPA gel.

Acknowledgment. We thank Mr. S. Yamamoto for supporting the swelling experiments.

References and Notes

(1) Gee, G. *Trans., Inst. Rubber Ind.* **1943**, *18*, 266.
(2) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984**, *81*, 6379.
(3) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987**, *87*, 1392.
(4) Inomata, H.; Goto, S.; Saito, S. *Macromolecules* **1990**, *23*, 4887.
(5) Barton, A. F. M. *Chem. Rev.* **1975**, *75*, 731.
(6) Ahmad, H. *J. Macromol. Sci., Chem.* **1982**, *A17*, 585.

Registry No. NIPA, 25189-55-3; DEA, 109-89-7; DMF, 68-12-2; THF, 109-99-9; 1-BuOH, 71-36-3; EtOH, 64-17-5; MeOH, 67-56-1; 1-PrOH, 71-23-8; CH_3CHO, 75-07-0; CH_3COCH_3, 67-64-1; NH_3Ph, 62-53-3; dioxane, 123-91-1.