tems are blocky terpolymers and even more complicated copolymers, which are extensively used in industry. These polymers or polymer mixtures can, if the blocks are sufficiently long, exhibit mesophase structures. Classical thermodynamics can predict only the behavior of these systems at $q = 0$. $\mathbf{D} = 0$ or $\mathbf{D}^0 = 0$ gives a generalized spinodal (function of q and volume fractions), which can be useful for the prediction of the appearance of such mesophases.

References and Notes

(1) Benoît, H.; Hadziioannou, G. *Macromolecules* **1988**, *21*, 1449.
(2) Benoît, H.; Wu, W.; Benmouna, M.; Moser, B.; Bauer, B.; Lapp, A. *Macromolecules* **1985**, *18*, 986.
(3) de Gennes, P.-G. *J. Phys. (Paris)* **1970**, *31*, 235.
(4) Leibler, L.; Benoît, H. *Polymer* **1981**, *22*, 195.
(5) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(6) (a) Warner, M.; Higgins, J. S.; Carter, A. J. *Macromolecules* **1983**, *16*, 1931. (b) Fischer, E. W. In *Scattering, Deformation and Fracture in Polymers*; Wignall, G. D., Crist, B., Russel, T. P.; Thomas, E. L., Eds.; Material Research Society: Pittsburgh, 1986; Vol. 79.
(7) Ould Kaddour, L.; Strazielle, C. *Polymer* **1987**, *28*, 459.
(8) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(9) Olvera de la Cruz, M.; Sanchez, I. *Macromolecules* **1986**, *19*, 2051.
(10) Einstein, A. *Ann. Phys.* **1910**, *33*, 1275.
(11) Ullman, R. Small Angle Neutron Scattering of Polymers. *Annu. Rev. Mater. Sci.* **1980**, *10*, 261.
(12) Stockmayer, W. H. *J. Chem. Phys.* **1950**, *18*, 58.
(13) des Cloizeaux, J.; Jannink, G. *Physica* **1980**, *102A*, 120.
(14) Hill, T. L. *Statistical Mechanics*; McGraw-Hill: New York, 1956.
(15) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1967.
(16) Sanchez, I. *Polymer* **1989**, *30*, 471.
(17) Debye, P. *J. Appl. Phys.* **1944**, *15*, 338.
(18) Ornstein, L. S.; Zernike, F. *Proc. Acad. Sci. Amsterdam* **1914**, *17*, 793.
(19) Zimm, B. *J. Chem. Phys.* **1948**, *16*, 1093.
(20) Benoît, H.; Benmouna, M. *Polymer* **1984**, *25*, 1059.
(21) (a) Benoît, H.; Benmouna, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1227. (b) Benoît, H.; Benmouna, M.; Strazielle, C.; Cesteros, C. Light scattering from mixtures of homopolymers and copolymers: Theoretical results and experimental examples. In *Physical Chemistry of Colloids and Macromolecules*; Ranby, B., Ed.; I.U.PA.C. Symposia, Blackwell Scientific Publications, 1987.
(22) Ijichi, L. Y.; Hashimoto, T. *Polymer Comm.* **1988**, *29*, 135.
(23) Bates, F. S.; Wignall, G. D. *Macromolecules* **1986**, *19*, 932.

Photoinduced Phase Transition of Gels

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ABSTRACT: Equilibrium swelling curves of copolymer gels of *N*-isopropylacrylamide and a photosensitive molecule, bis(4-(dimethylamino)phenyl)(4-vinylphenyl)methyl leucocyanide, were determined as a function of temperature under ultraviolet irradiation. Without ultraviolet irradiation the gels underwent a sharp, yet continuous, volume change, whereas upon ultraviolet irradiation they showed a discontinuous volume phase transition. For fixed appropriate temperatures, the gels discontinuously swelled in response to irradiation of ultraviolet light and shrank when the light was removed. The phenomena were caused by osmotic pressure of cyanide ions created by ultraviolet irradiation.

Introduction

Recently phase transitions and critical phenomena in polymer gels have attracted much attention because of their scientific interest and technological importance. Phase transitions accompanied by a reversible, discontinuous volume change as large as several hundred times, in response to infinitesimal changes in the environment condition, have been observed universally in various gels made of synthetic and natural polymers.[1–7] Variables that are known to induce a phase transition are temperature, solvent composition, pH, ionic composition, and small electric field.[8] Those findings have opened up a wide variety of possible applications of gels as sensors, chemomechanical transducers, switches, display units, memories, controllable drug delivery systems, and selective pumps.[1] For some of the applications, it will be clearly desirable if such a phase transition can be controlled by using light. The imposition of light can be done instantly, which is in contrast to other variables. For example, the temperature jump is limited by the thermal diffusion, and the pH change by ion diffusion. The electric field induced phase transition is also limited by the accompanying ion diffusion.

Recently, Irie and Kungwatchakun[11] reported a synthesis of photosensitive gels by incorporating photosensitive molecules, such as leucocyanide and leucohydroxide, into the gel network. These gels underwent volume changes upon irradiation and removal of ultraviolet light. However, a phase transition has not been observed in these synthetic gels because the condition at which the irradiation took place was far from the phase transition

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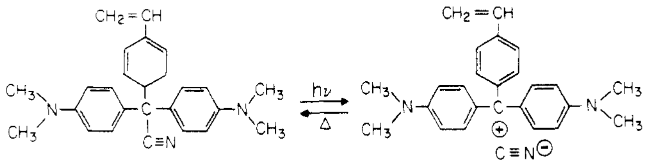

(1)

Figure 1. Chemical structure of leuco derivative molecule bis(4-(dimethylamino)phenyl)(4-vinylphenyl)methyl leucocyanide, which is sensitive to ultraviolet irradiation.

threshold. In this paper, we report the first observation of the photoinduced phase transitions of gels by introducing a leuco derivative molecule, bis(4-(dimethylamino)phenyl)(4-vinylphenyl)methyl leucocyanide, into the polymer network.

Experiments

Copolymer gels consisting of *N*-isopropylacrylamide and bis(4-(dimethylamino)phenyl)(4-vinylphenyl)methyl leucocyanide were prepared by a free radical copolymerization in dimethyl sulfoxide (DMSO) at 60 °C, under nitrogen atmosphere. *N*-Isopropylacrylamide (NIPA, Kodak Co., 0.97 g), purified by recrystallization from the mixture of petroleum ether and toluene; neutral, main polymer constituent, *N*,*N*′-methylenebis(acrylamide) (BIS, Bio-Rad Lab, 0.0003 g), cross-linker; bis(4-(dimethylamino)phenyl)(4-vinylphenyl)methyl leucocyanide (leuco, 0.02 g), photosensitive molecule; and azobis(isobutylonitrile) initiator (AIBN, 0.05 g) were dissolved in DMSO (1.0 g), which was purified by vacuum distillation under nitrogen atmosphere. The leuco molecule was synthesized in the way reported previously.[11] Its structure is shown in Figure 1. The solution was then transferred into a polyethylene tube, which had a 1.73-mm inner diameter. The reaction was carried out at 60 °C for 4 h. After gelation was completed, the gels were taken out of the polyethylene tubes, cut into 0.5–1-mm-thick disks, and then immersed in a large amount of deionized, distilled water to wash away residual chemicals and unreacted monomers from the polymer networks. Water was repeatedly changed until the diameter of the gels reached an equilibrium value, which took approximately a week.

The diameter of the gel, d, was measured by a microscope with a calibrated scale. The swelling ratio of the gel, V/V_0, was calculated from the ratio of the equilibrium gel diameter to the original diameter (d/d_0), where d_0 was 1.73 mm. The temperature was controlled within 0.04 °C by circulating water from Brinkmann Lauda RC-3 during the measurements without ultraviolet irradiation. An ultraviolet lamp, GATES MR-4 (wavelength < 254 nm), was used for ultraviolet light source. During the irradiation experiments the temperature was controlled within 0.5 °C by using a thermoelectric device.

Results

Equilibrium volumes of the gel measured as a function of temperature, with and without ultraviolet irradiation, are shown in Figure 2. When the gel was not irradiated with ultraviolet light, the gel underwent a sharp, but continuous, volume change at around 30.0 °C. Upon irradiation the gel showed a discontinuous volume transition. The temperature was raised from 25 °C gradually. At 32.6 °C, the volume of gels suddenly decreased by approximately ten times. Above the transition temperature the gel volume did not change markedly. When the temperature was lowered starting from 35.0 °C, the gel swelled discontinuously to ten times its volume at approximately 31.5 °C. The transition temperatures upon raising and lowering the temperature are different by 1.1 °C. The presence of hysteresis indicates the first-order phase transition in the ultraviolet irradiated gel.

When the temperature was fixed at 32.0 °C, the gel underwent a discontinuous swelling–shrinking switching upon irradiating and removing ultraviolet light.

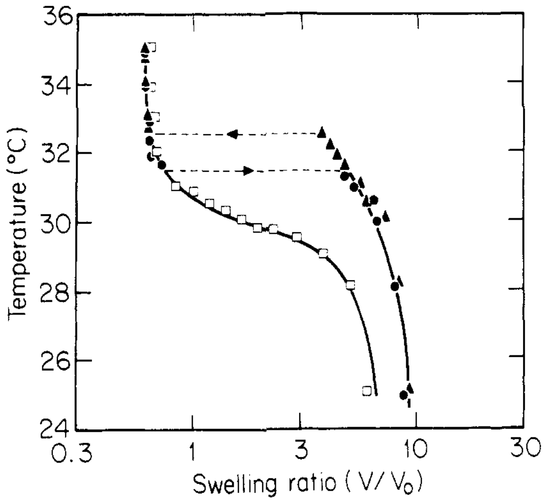

Figure 2. Degree of the swelling (the ratio of the final, equilibrium volume to the initial volume) of copolymer gels of *N*-isopropylacrylamide and the leuco derivative in water is plotted as a function of temperature. Open squares show the swelling of the gel without ultraviolet irradiation, on both raising and lowering the temperature. Filled triangles denote the swelling curve upon ultraviolet irradiation on raising the temperature. Filled circles are for the curve upon ultraviolet irradiation on lowering the temperature.

Discussions

The response of the gel to ultraviolet irradiation is well understood by considering the effect of ultraviolet irradiation on the leuco derivative molecule. Triphenylmethane leuco derivatives are normally neutral but dissociate into ion pairs under ultraviolet irradiation producing intensely colored triphenylmethyl cations.[11] In the present experiments, the color of the gel changed from pale green to dark green. Therefore, when the gel was not irradiated, it was a nonionic gel, but it became an ionic gel upon ultraviolet irradiation. It is known that an inner osmotic pressure induced by ionization of a gel brings the gel state below the coexistence curve and induces a discontinuous volume phase transition.[12] With an increase in ionization degree the volume change becomes larger and the transition temperature rises as in the case of NIPA gels.[12]

We observed that the transition temperature of the NIPA–leuco copolymer gels were lower than that of the gel consisting only of NIPA. This may be due to the difference in the solubility of NIPA and leuco derivatives in water.

Two mercury lamps with different wattages, one at 450 W with medium pressure and the other of 80 W with low pressure, were used to briefly check the effects of radiation power on the phenomena. There were no observable differences in the effects. This indicates that the photochemical reaction was already saturated by the irradiation by the 80-W lamp.

In this experiment, it is clear the polymer chain in the gel network has the exact same molecular arrangement and structure in UV lighted and unlighted gels (the distinction is the lighted or the unlighted). This experimental conclusion gives important evidence that the osmotic pressure of counterions in the gel plays an essential and principal role for discontinuous phase transitions of polymer gels.

In the photoinduced phase transition of leuco derivative gels, it is not possible to control the speed in the shrinking process, which is governed by the ion diffusion and recombination with the leuco molecules. This

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could be a drawback of the present system when it is used for technological applications. Photoinduced phase transition, however, may be triggered not only by the ionization process as presented in this paper but by molecular conformational changes such as cis–trans isomerization. In that case it will be possible to control both the swelling and shrinking by using two lights with different wavelengths. We are currently studying various systems on the basis of this idea.

We believe that the work presented here is of technological importance in developing various optical devices, such as optical switches, display units, and three-dimensional holograms. The phase transition induced by light will also provide a means to carry out high-speed kinetic experiments of volume changes in gels, where the perturbation time is extremely fast. According to the principle of kinetics of gels, the time needed for swelling and shrinking of a gel is proportional to the square of the characteristic linear dimension of a gel. It is expected that a spherical gel with a diameter on the order of micrometers will respond to environmental changes within milliseconds. In order to carry out such a fast kinetic experiment it is important that the environment be altered extremely rapidly. For this reason the light-induced phase transition will be important since the perturbation time is extremely fast.

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References and Notes

(1) Tanaka, T. *Phys. Rev. Lett.* **1978,** *40,* 820.
(2) Tanaka, T.; Fillmore, D. J.; Sun, S.-T.; Nishio, I.; Swislow, G.; Shah, S. *Phys. Rev. Lett.* **1980,** *45,* 1636.
(3) Ilavsky, M. *Macromolecules* **1982,** *15,* 782.
(4) Hrouz, J.; Ilavsky, M.; Ulbrich, K.; Kopecek, J. *Eur. Polym. J.* **1981,** *17,* 361.
(5) Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1984,** *81,* 6379.
(6) Ohmine, I.; Tanaka, T. *J. Chem. Phys.* **1982,** *11,* 5725.
(7) Amiya, T.; Tanaka, T. *Macromolecules* **1987,** *20,* 1162.
(8) Tanaka, T.; Nishio, I.; Sun, S.-T.; Ueno-Nishio, S. *Science* **1982,** *218,* 467.
(9) Ilavsky, M.; Hrouz, J.; Ulbrich, K. *Polym. Bull.* **1982,** *7,* 107.
(10) Flory, P. J. *Principle of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(11) Irie, M.; Kungwatchakun, D. *Macromolecules* **1986,** *19,* 2476. *Makromol. Chem., Rapid Commun.* **1984,** *5,* 829.
(12) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys.* **1987,** *87,* 1392.

Influence of Blend Compressibility on Extrapolated Zero-Angle Coherent Scattering and Spinodal: Limitations of RPA Analysis

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ABSTRACT: Three different statistical thermodynamic models of compressible binary polymer blends are used to compute the extrapolated zero-angle coherent scattering $S_{11}(0)$ by one of its components. The models are taken from Flory–Huggins theory, equation of state theories, and Dickman–Hall continuum modifications of lattice theories. The computed zero-angle scattering is analyzed using the conventional incompressible RPA model to produce the effective Flory interaction parameter, χ_{eff}. When input polymer–polymer interactions that are composition and molecular weight independent are used, the computed χ_{eff} values exhibit strong composition and molecular weight dependences, solely as a result of the inappropriateness of the incompressible blend model used to define χ_{eff}. The vanishing of the reciprocal of $S_{11}(0)$ is shown to describe the spinodal line for a compressible binary blend at constant volume, but this is found to differ from the constant-pressure spinodal line. While our computed χ_{eff} values display some composition-dependent trends observed experimentally, several others cannot be generated. Hence, future studies will investigate the influence of composition and molecular dependences of the polymer–polymer interactions on χ_{eff}. Nevertheless, the simplest models employed here focus on the need for analyzing experimental data with thermodynamically more faithful models than the incompressible RPA if the desire is to obtain fundamental molecular information concerning basic polymer–polymer interactions in a blend.

I. Introduction

Theories of the structure and thermodynamics of polymer blends have been of considerable interest in ascertaining those characteristics promoting mixing or producing particular morphologies of phase-separated systems. These theories have been used in conjunction with neutron-scattering data and Monte Carlo simulations to provide an important tool in studies of the effective interaction parameter that governs the phase behavior of polymer blends. Extrapolated zero-angle neutron-scattering data provides a direct approach to the blend polymer–polymer interaction parameter, but the extraction of this effective interaction parameter is based on the use of random-phase approximation (RPA)[1] that assumes blend incompressibility. While the zero scattering angle limit of the RPA agrees with incompressible Flory–Huggins theory,[2] there are several reasons why the incompressible RPA model obscures essential physics of blends, such that the extracted effective interaction parameter does

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