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Thermotropic Polymer Gels: Smart Gel Glass

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Summary: Several attempts have been made recently in order to develop "smart" windows, which can moderate light and heat intensities. Thermotropic gels have met with growing interest because of their advanced properties. Based upon phase transitions of polymer gels, a novel thermally adjustable window, which includes a gel layer, has been developed in our laboratory. The so-called gel-glass becomes opaque when the temperature exceeds a certain value and goes back to its original transparent state when it is cooled below the critical value again. Intelligent "gel-glasses" made of these materials can moderate the amount of sunlight and radiated heat. The optical properties of the gel layer are also modified by the Joule heat of audio frequency AC current. Two types of gel-glasses have been developed and investigated. Phase transition temperature of a poly(N-isopropylacrylamide) based gel was adjusted by copolymerization and by changing of the solvent composition. The cloud point of a poly(methyl vinyl ether) – water system in a PVA gel was varied by modifying the composition of the swelling agent. In the case of electrically adjustable thermotropic windows, optical properties, energy consumption and temperature changes during the switching process were studied.

Keywords: AC voltage; electric control; gel; gel-glass; phase separation; smart window

Introduction

Over the past few decades, there has been an increasing interest in producing transparent walls, glasses and interfaces. Previously, most of them have been based on mechanical operation and need extra space. The means for varying the amount of light admitted into buildings includes curtains, blinds, sky-lids. Elimination of such mechanical systems can be solved by an interface with changeable transparency. "Smart" windows promise us a qualitatively new solution.

The idea of glasses with adjustable transparency is not new. Several attempts have been made in order to develop windows which can moderate light and heat intensities[1-3]. Electrochromic devices[4], suspended particle devices[5], phase dispersed liquid crystals and cholesteric liquid

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crystals[6] are the common methods. These materials change their transparency upon exposure to the electric stimuli of direct voltage.

The transparency can also be moderated by temperature or light intensity. Windows operating in this way are called thermotropic windows, while the materials are called thermotropic materials[7]. In some cases, they are also called “smart” or “intelligent” windows, because an increase of heat or light automatically causes a decrease in the heat or light permittivity.

Polymers which demonstrate good solubility in aqueous solutions at low temperatures but separate from solution when the temperature is raised above the lower critical solution temperature (LCST); and hydrogels which undergoes temperature-induced volume phase transition have received increased attention in recent years[8-10].

Recently, the development of thermotropic hydrogels, which may be used for constructing intelligent windows, has met with growing interest. Several attempts have been made to study the optical properties of smart gels[11-14]. Watanabe has constructed an autonomously responsive, light adjustment window, so-called “Affinity Intelligent Window”[11]. The thermotropic glazing is based on a water-soluble polymer with hydrophobic groups, an amphipathic molecule and sodium chloride. A 1 m^2 window of this type was constructed and, according to the author, this prototype was successfully operated through outdoor testing over a period of two years. Seeboth and co-workers have developed a thermotropic gel system composed of an aqueous solution of a propylene oxide and ethyl oxide[12]. They have studied the switching process and optical transmission of their systems. In our previous work we have developed a gel-glass, which offers good protection from strong sunlight and heat radiation[13].

The optical properties of polymer gels can also be modulated electrically[12]. However, it must be emphasized that the application of direct current is not suitable. Electrolysis and gas generation could be avoided by the application of audio frequency AC voltage. High frequency AC current was applied to change the optical properties of the gel layer[15]. The temperature of the gel as well as the transparency is influenced by Joule heat[16]. The influence of AC current on the optical properties of the gel as well as temperature was studied. Two different hydrogels, an active[13] poly(N-isopropylacrylamide) (PNIPAAm) and a passive[13] poly(vinyl alcohol) (PVA) swollen by poly(methyl vinyl ether)-water mixture, were used for the experiments.

Experimental

Preparation of active gel layers: The term "active gel" is used to indicate that a phase transition with an LCST occurs between the network polymer and the swelling agent.

Synthesis of chemically cross-linked poly(N-isopropylacrylamide-co-acrylamide) [P(NIPAAm-co-AAm)] hydrogels were prepared from N-isopropylacrylamide (NIPAAm; Acros Organics), acrylamide (AAm; Aldrich), N,N-methylene-bisacrylamide (BAAm; Aldrich), ammonium-persulphate (APS; Aldrich) and N,N,N',N'-tetramethylenediamine (TEMED; Aldrich) by following the usual procedure[13]. These chemicals were of analytical grade and used without further purification.

The molar ratio of monomers to cross-linker (BAAm) in hydrogels was 150:1. The NIPAAm:AAm molar ratio was varied from 100:0 to 70:30 and monomer concentration in the preparation vessel was 0.75 M. Depending on the method of measurement, the solution was poured into a glass test tube or between two glass sheets.

Preparation of passive gel layers: In passive gels, the swelling agent exhibits a liquid-liquid phase transition with an LCST. The role of the gel is to hold the liquid mixture and prevent the spatial separation after the "de-mixing" occurs.

Chemically cross-linked poly(vinyl alcohol) (PVA) hydrogels were prepared. The PVA (Aldrich, M_w=13000-23000) chains were cross-linked by glutaraldehyde (GDA; Merck) at a pH of 1.5 in a mixture of water and poly(methyl vinyl ether) (PMVE; $M_w \approx 46000$[17]; Aldrich). The procedure is published in our previous work[15].

Methods: The cloud point of gels was determined in a home made apparatus. Glass tubes containing the gel were immersed in a well stirred heating bath. The temperature was gradually raised (0.2 $\mathrm{Kmin^{-1}}$) and the transmitted light was recorded. UV-Vis spectra were produced on a GBC Cintra 10e UV-Vis spectrophotometer. Polymer gels were synthesized in a 2 mm glass cuvette. The cell holder in the spectrophotometer was maintained at the required temperature by circulating water from a thermostat. The experimental setup and method of the measurement of the electrically adjustable thermotropic windows based on polymer gels were described in our previous publication[15].

Results and Discussion

Optical properties

In order to construct an adaptive gel-glass, we have placed such a gel layer between two glass sheets. If the gel has an LCST, then the gel glass becomes opaque when the temperature exceeds a critical value. It becomes transparent again if it is cooled down. These adaptive properties make the gel-glass a promising material to moderate the amount of light and radiated heat.

Two types of polymer hydrogels, i.e. PNIPAAm and PVA gels swollen to equilibrium by a PMVE–water mixture, were used. Both systems exhibit a reversible and abrupt transparent-opaque transition as a function of temperature due to the phase separation at the lower critical solution temperature[9,18].

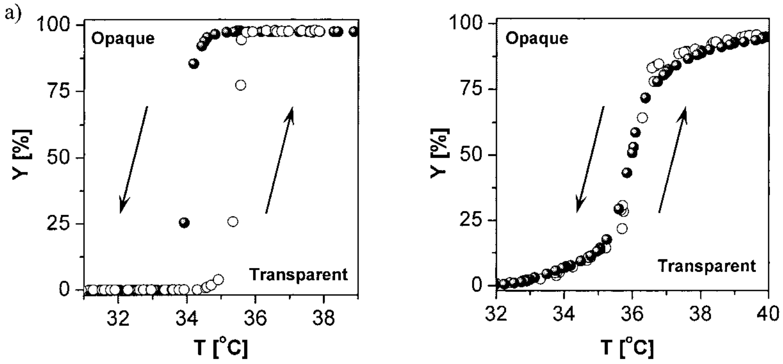

Figure 1. Temperature-dependence of the light transparency (Y) of gel layers. (a) Pure PNIPAAm active gel layer swollen by water; (b) PVA passive gel layer swollen in a mixture of PMVE (1.5 w/w%) and water.

The PNIPAAm gel has its LCST at 35.2 °C, while PMVE-water mixture in the PVA gel has its LCST at 35.1 °C. The temperature-dependence of the light intensity as it passes through the gel layers is shown in Fig. 1. We have plotted the relative change of light intensity, Y[%], as a function of temperature, T[°C][13]. As can be seen from both figures, an abrupt transparent-opaque transition occurs when the temperature exceeds the LCST. This transition was found to be reversible, but slight hysteresis occurs for the active gel (PNIPAAm). In case of the passive gels (PVA) the extent of hysteresis is small and negligible compared to the active gel. Passive gels provide longer kinetic stability after the phase separation. This is due to entanglement effects, which restrict the motion of non-cross-linked PMVE chains in the network.

For any technical application it is important to adjust the transparent–opaque transition temperature. This can be done in two ways: 1) by modify the chemical structure of the polymer network by copolymerization or 2) by using a mixture or solution, instead of water as a swelling agent.

In general, the incorporation of hydrophobic comonomers leads to a lower LCST and hydrophilic comonomers to a higher LCST. It has been found that copolymerization of N-isopropylacrylamide with acrylamide increase the phase transition temperature[19]. Fig.2a shows the effect of copolymer composition on the transparent–opaque transition temperature denoted as T_C. This figure indicates that with increasing the mole ratio of acrylamide in the polymer network results in a definite increase in transition temperature.

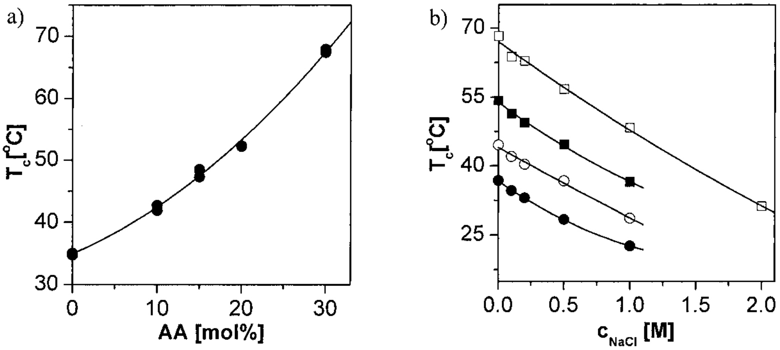

Figure 2. (a) Dependence of cloud point temperature (T_C) on copolymer composition in case of active gel. (b) Dependence of cloud point temperature on molar concentration of NaCl. Molar ratio in [P(NIPAAm-co-AAm)] is: 100:0 (●); 90:10 (○); 80:20 (■); 70:30 (□).

Phase transition temperatures of polymers and hydrogels can be strongly influenced by various salt solutions. It has been demonstrated that aqueous NaCl reduce the LCST of PNIPAAm[20]. In Figure 2.b T_C of several P(NIPAAm-co-AAm) is shown as a function of NaCl content in the swelling agent. NaCl caused a decrease in T_C in every case.

Increase of phase transition temperature of PMVE is a significant challenge. Instead of copolymerization, composition of swelling agent was modified[18]. The effect of tetrabutylammonium bromide [TBAB] was investigated. Application of TBAB results in a definite increase in transition temperature, as shown in Fig. 3.a. NaCl also affects the phase transition temperature of PMVE[18]. T_C of PMVE was measured in passive gels as a function of NaCl content in the swelling agent. NaCl, like every water-structure maker, reduce the cloud point significantly (Fig. 3.b).

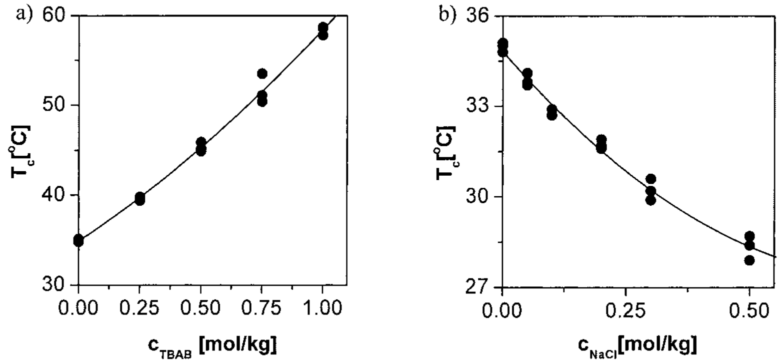

Figure 3. (a) Influence of tetrabutylammonium bromide on the transparent-opaque transition temperature of PMVE in passive gels. (b) The effect of NaCl on the transparent-opaque transition temperature of PMVE in passive gels.

Further investigations on the thermotropic optical behavior of active and passive gels were performed by UV-Vis spectrophotometer. Change in transmission was followed at various temperatures in the case of the active gel. Similar results were obtained (Fig. 4) in case of the passive gel, too. Below the phase transition temperature both gel systems show a transmittance of about 90%. Remarkable absorptions of water were observed around 1000 and 1200 nm. Below λ=400 nm the transmission decreases significantly due to absorption by the glass cuvette. Above the phase transition temperature, due to the phase separation between the polymer chains and the swelling agent, transmittance decreases to about 0%.

Electrically adjustable thermotropic gels

A special type of gel-glass is the electrically adjustable thermotropic (EAT) window where the transparency of the glass is controlled by an electric current[15]. Hence the change between transparent and opaque states can be effected simply by a button used for on-off switching of the electric power. Optical properties of EAT-windows are the same as mentioned previously.

However the change is not solved by heating the glass with external sunlight or heat radiation but by the Joule heat coming from the electric current flowing through the gel.

To avoid chemical reactions inside or on the surface of the gel, which could cause gas generation and other complications we used an audio frequency AC current. However extremely high frequency could have caused damage of the controlling system. Balancing these two effects, we decided to use around 10 kHz which is high enough to avoid electrolysis and gas generation but not so high that it would cause impedance problems. Both sinus- and square-wave were used for the measurement. The sinus wave is more useful for understanding the theoretical implications of the operation of the EAT-windows while the square wave is more efficient in the study of the actual use of the EAT-windows.

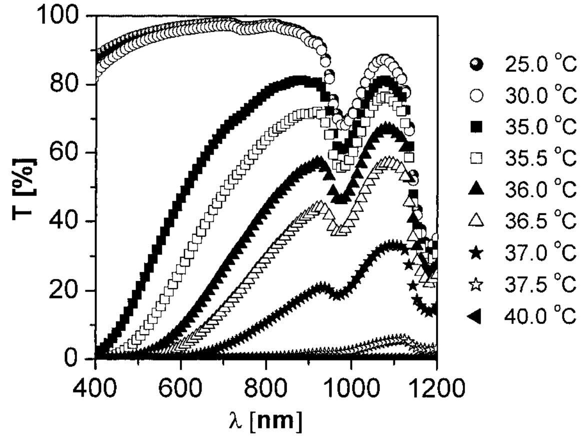

Figure 4. Spectral transmittance of an active gel sample (NIPAAm:AAm ratio was 100:0) at various temperature.

A home made system consisting of a light source, a photodiode, digital multimeters, oscilloscope and a computer were used for measuring the transparency of the windows and the parameters of the applied current simultaneously. These parameters are the light intensity, voltage, frequency and phase of the alternating current. From these data electric power could be calculated. The change of the temperature of the gel was measured with a small size thermometer.

Figure 5. shows the switching process of EAT-windows. Results can be seen for the passive gel (left column) and the active gel (right column). The applied AC voltage (U), the

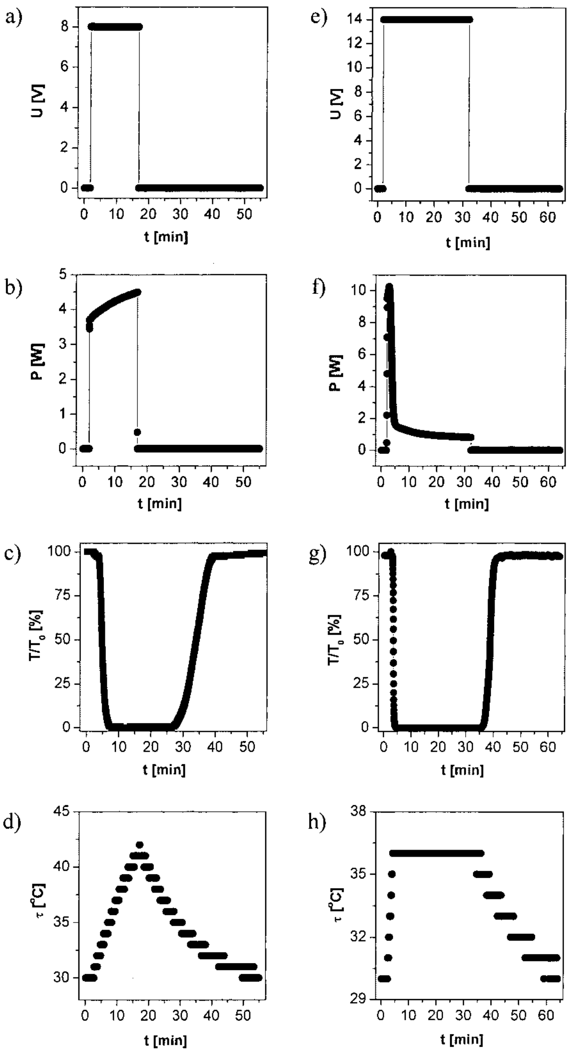

Figure 5. (column 1.) Passive gel layer heated by the Joule heat of AC power (8.0 V, square wave, 10.0 kHz). (column 2.) Active gel layer heated by the Joule heat of AC power (14.0 V, sine wave, 10.0 kHz). (a,e) Applied AC voltage (U) during the switching process; (b,f) electric power (P) supplied as a function of the switching process; (c,g) change of transmission (T/T$_0$) as a function of time; (d,h) time-dependence of the temperature (τ) inside the measuring cell.

delivered electric power (P), change of transmission (T/T_0) and the temperature (τ) of the gel can be seen as a function of time (t).

The working of passive EAT-windows can be easily understood. First the electric voltage was turned on as shown on Fig. 5.a. The behavior of the passive gel is similar to that of an electrolyte solution. The current flowed through the gel, which had a certain resistance. Joule heat was evolved and most of it was absorbed by the gel. The temperature of the gel increased as shown on Fig. 5.d. When it reached the transition temperature, the windows became opaque as shown in Fig. 5.c. After turning off the electric voltage the temperature decreased and as soon as it fell below the transition temperature the gel reversed to the transparent state again.

The working of active gel was a little different due to the special property of PNIPAAm gel. After switching on the electric voltage both active and passive gel started to warm. This increased the electric conductivity leading to increased heat absorption by the gel. This process can be seen on the Fig. 5.b and 5.f. Since the passive gel had a constant matrix, the phase transition did not change the gel itself. However, this was not the case for the active gel. At the transition temperature, the conductivity of PNIPAAm gel significantly decreases. This is caused by a structure change on the surface of the gel called skin formation effect[21-22]. The electric resistance of the gel increases, the absorbed heat decreases but it is high enough to keep the opaque state. This effect keeps the power at the optimal level, which must be ensured some other way in the case of passive gel to avoid overheating and higher operational cost.

On the basis of the responsive properties of the afore-mentioned gels, we have fabricated a window from the gel-glass as shown in Fig.6. By this window we are able control the sun light or heat radiation.

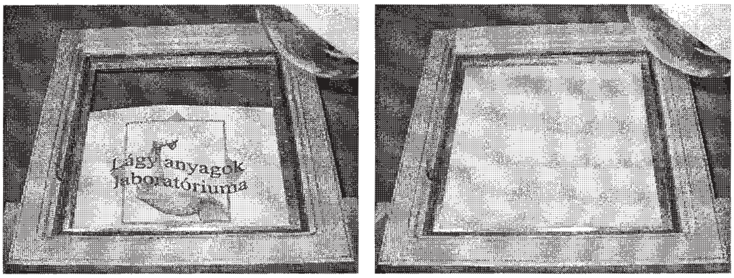

Figure 6. The transparent-opaque transition of a gel-glass as a result of radiated heat.

Conclusion

We were able to fabricate a gel-glass on the basis of "smart" polymer hydrogels with optical sensitivity to temperature change. These gels exhibit a reversible abrupt transparent-opaque transition. The transition temperature can be varied over a wide range. It has been shown that the transparency of these gels can be modulated not only by direct heat treatment but also by audio frequency electrical stimuli. In this case the abrupt change in optical properties is due to Joule heat. These materials can be used to substantially reduce the glare and so to increase the thermal and visual comfort. Another promising area is the application in greenhouses and water boiling systems for the optical and thermal control. These materials are also good candidates for large displays. Electrically adjustable gel glasses can be used as optically switched room partition in indoor applications, and also as novel display materials with low operational and prime costs.

Acknowledgements

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