

Hysteresis Effects During the Phase Transition in Solutions of Temperature Sensitive Polymers

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Abstract

It is demonstrated, for the first time, that well-known phase transitions induced by changes in temperature in solutions of polymers containing both hydrophilic and hydrophobic functional groups could be followed by noticeable hysteresis effects. A well-known phase transition accompanied by a sharp change in fluid properties, in particular its optical density can be induced by many external influences, including temperature changes occurring in the solutions of polymers containing both hydrophilic and hydrophobic functional groups. Since intensification subsequent hydrophobic interactions, leading to loss of solubility of the polymer molecules, resulting, in particular, a significant increase in the turbidity of the medium and are accompanied by a pronounced hysteresis phenomena. Hysteresis phenomena in the processes of molecular-scale play an important theoretical and practical interest in linkage with the development of advanced nano-level technology. In particular, the issue of the development of molecular "trigger" switches, and other analog electronic systems, implemented on submolecular level was actively discussed. In fact, under the same physical conditions of the environment of macromolecules system can be in two different states, which resolves the issue of programming such molecules. State of these polymers depends on their way of formation and thermodynamic variables. Observed effect could be utilized directly for information recording into the structure on the basis of stimulus-sensitive macromolecular chains. In fact, it is a first step towards creating memory of quasi-biological elements.

1. Introduction

Phase transitions in solutions of hydrophilic macromolecules have been studied on a long term basis [1]. It is noted that transitions followed by sharp change of solution's properties, specifically – optical density, could be induced by variety of external actions (electricity, electromagnetic emission of different wave-length, change of temperature, pressure, acidity, etc.). This variety of action might be modified and adjusted for information recording in heterogeneity environment [2–4] or in any distributed media connected not only in polymer solu-

tions [5]. Generally, these transfers are connected with sharp change of macromolecules' solubility which is caused by change of hydrophobic-hydrophilic balance, stimulated by external actions [6].

Phase transitions under impact of temperature change are pertinent to the most studied [7]. In this case, with the increase of temperature strengthening hydrophobic interactions arise. This fact causes the loss of solubility by polymer molecules, which particularly expressed by significant increase of medium turbidity which could be easily seen.

In spite of that temperature sensitive polymers phase transitions in solutions have been studied

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more than 30 years, previously there wasn't any mention about hysteresis effects inherent to these transitions in literature [8]. The hysteresis effect, followed by phase transitions in water solutions, is detected for the first time in this work. Wherein mechanism of phase transitions passing under the heat impact is similar in many aspects to transitions caused by light emission, then existence of hysteresis effects in other cases could be envisioned.

Hysteresis effects in molecular scale processes have significant practical interest in connection with the development of nanotechnology. Elaboration and amplification of molecular communicators, triggers and other analogues of electronic elements implemented at molecular and submolecular levels are widely discussed nowadays [9, 10].

Macromolecule's fragment showing hysteresis properties could be considered as a submolecular analogue of trigger, which represents memory unit recording 1 bit of information. Currently these memory cells are widely utilized in different modern computer and storage devices. The simplest trigger option represents electronic scheme on two transistors, one of them is in ON state, while the other is in OFF state. Information recording is accomplished by switching off transistor from one state to another.

Noting that under the same external conditions studied physical-chemical system could be also found in two different states suitable for two different branches of hysteresis loop. One of these states could be accorded with logical zero and the other – with logical one. Any system possessed the hysteresis properties could be utilized for conception of logical zero and one. Particularly, one of the first memory cells were realized on hysteresis effects passing under the ferrites' magnetization. Including each molecule of analysed polymer (more precisely, chain of hydrophilic and hydrophobic groups) could be considered as memory cell recording 1 bit of information.

Intermolecular interactions in diluted solutions of polymers are quite weak. Particularly, interpretation suggested below is based on the consideration of single macromolecules' properties. Therefore possibility to transit controllably molecules from one state to another (at the same thermodynamic variables for solution in general) could be already considered as an example of liquid-phase system possessing the ability to fixate information. Hysteresis effects in polymer solutions are prerequisites for the development of liquid-phase systems of keeping information on quasi biological

basis. "Programmable" molecules represent evident interest for nanotechnology, particularly, for targeted delivery of drug components on sub cell level [11]. In prospect this study could be a basis for formation of quasi biological computers [12].

2. Experimental

2.1. Materials

Pyren, Sigma as a luminescence label was used without additional purification. Poly(acrylic acid) (PAA) with weight-average molecular weight of 250 kDa were purchased from Aldrich Chemical Co. (USA) and used without further purification.

2,2-azobis(isobutyronitrile) (AIBN, Aldrich Chemical Co., USA) was purified by recrystallisation from ethanol.

Poly(N-isopropylacrylamid) (PNIPAM) was synthesized by free radical polymerization in ethanol solution with AIBN as an initiator (0.005 mol/L). In a typical procedure, argon was bubbled through the solution for 10 min prior to polymerization. After polymerization at 60 °C the mixtures were cooled to room temperature, dissolved in the 10-fold excess of ethanol and reprecipitated in diethyl ether three times to remove unreacted monomers. Then the polymer was collected by filtration, dried under vacuum for 2 days. The yield of PNIPAM after purification was higher than 70%.

The partially neutralized PAA (with 25–35 percentages of ionized carboxylic groups) was prepared by adding 100 ml of sodium hydroxide solution at 0.1 M concentration to 0.01 M PAA solution. Aqueous solution of water-soluble interpolymer complex of NIPAAm and PAA was prepared by adding of 0.05 M PNIPAAm water solution to partially neutralized PAA at stoichiometric ratio.

2.2. Optical density (Turbidity) Measurements

Optical density of polymer solutions was determined under the different temperatures in the range from 30 °C to 36 °C with Shimadzu UV/VIS-2401 PC spectrophotometer (Japan) at the wavelength of 400 nm. This device has embedded by thermo-electrically temperature-controlled cell positioner CPS-240A (Shimadzu, Japan) which allows regulating temperature to 0.1 °C. While recording temperature dependences from optical density temperature change Δ was 0.1 °C.

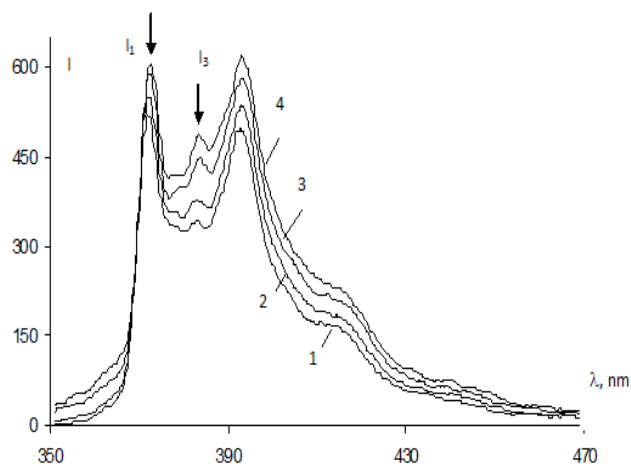


Fig. 1. Fluorescent emission spectrum of pyrene luminescence in PNIPAM solution at different temperatures: 1 – 32 °C; 2 – 33 °C; 3 – 34 °C; 4 – 35 °C.

2.3. Fluorescent Measurements

The fluorescent emission spectrum of polymers solutions were recorded on a Perkin-Elmer LS 55 Luminescence spectrophotometer (Perkin-Elmer Instruments, UK).

Wave-length of light excitation was 335 nm. I_3/I_1 values were characterized an influence of hydrophobic interactions were calculated on basis of intensities of the third vibratory peak (I_3) to the first (I_1) at wave-lengths 373 and 383.5 nm, respectively (Fig. 1).

A dilute aqueous solution of pyrene (2 μ M) was prepared by the next procedure. Pyrene was initially dissolved in ethanol (0.4 mg/mL), then 100 μ L of this solution was transferred into a volumetric flask (100 mL) and the ethanol was dried under a steam of nitrogen for several minutes. Then flask was filled in with distilled water and used after 1 night of aging. The aqueous solution of pyrene was utilized as a solvent for polymers.

2.4. Molecular Weight Determination

Molecular weight and average molecular weight of PNIPAAm were determined using a GPC equipped with an Agilent 1100 series RI detector, quaternary pump, and columns with pore sizes of 250, 500, and 1000 Å. The molecular weights were calibrated with poly(ethylene oxide) standards. It was found that synthesized PNIPAAm sample had $M_w = 270$ kDa and $M_n = 95$ kDa has been characterized.

3. Results

Data of luminescence spectroscopy for lumiphores solutions in presence of PNIPAAm and PNIPAAm-PAA mixtures (1:1) in the process of heating and cooling correspondingly are represented at (Figs. 2 and 3).

Curves 1 and 2 at (Figs. 2 and 3) were obtained under increase and decrease of temperature, respectively.

Selection of PNIPAAm and PAA couple was also specified since these polymers form complex through hydrogen bonding which is stable at quite high values of pH.

It is seen that specified curves differ considerably, i.e. phase transitions in solutions, which contain PNIPAAm, passing under the impact of temperature changes is followed by noticeable hysteresis effects. It is also seen that hysteresis loop area for case of water solution of PNIPAAm-PAA mixtures surpasses pure PNIPAAm solution almost twice.

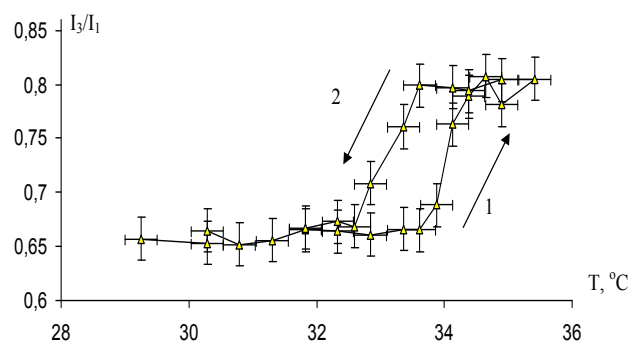


Fig. 2. Temperature dependence of I_3/I_1 ratio of pyrene in PNIPAAm water solution, obtained at increase (1) and decrease (2) of temperature.

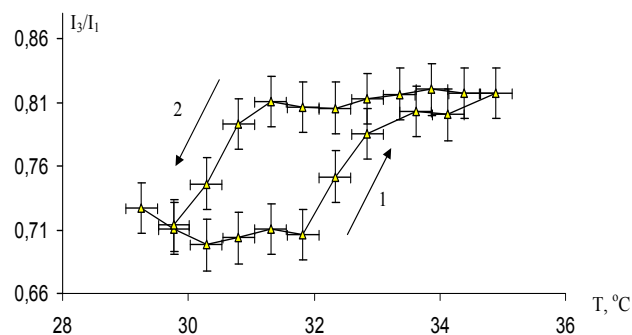


Fig. 3. Temperature dependence of I_3/I_1 ratio of pyrene in PNIPAAm-PAA mixture aqueous solution, obtained at increase (1) and decrease (2) of temperature.

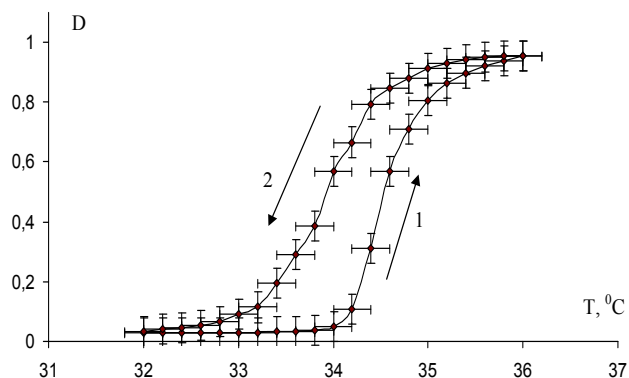


Fig. 4. Temperature dependence of optical density of PNIPAM aqueous solution from the temperature, obtained at increase (1) and decrease (2) of temperature.

Dependence of optical density of PNIPAM solution from temperature is shown on (Fig. 4.) Curves 1 and 2 are obtained at increase and decrease of temperature, respectively. It is seen that these curves don't concur as well as for results obtained by methods of luminescence spectroscopy.

4. Discussion

Commonly strengthening of hydrophobic interactions that take place with increase of temperature is liable for phase transition in solutions of temperature sensitive polymers. Moreover, PNIPAM is classical example of temperature sensitive polymer. At present time, measurement of luminescence spectrums of such labels as pyren is considered as direct method of hydrophobic-hydrophilic balance's shift delineation in polymers solutions. Utilizing pyren as luminophore increase of I_3/I_1 characteristic testifies strengthening of hydrophobic interactions. Particularly, this method was applied earlier for hydrophobic interactions' role study in interpolymer reactions.

The nature of change of I_3/I_1 ratio (Fig. 2) depicts that in solution of pure PNIPAM sharp strengthening of hydrophobic interactions at temperatures in the area of phase transition takes place and that completely acknowledges current conception of transition mechanism for temperature sensitive polymers [13]. Notice that essentially spasmodic transfer of I_3/I_1 value takes place at temperature increase as well as decrease. In a manner of speaking considered system liable for two levels of hydrophobic property (minimum and maximum). That implicates that extent of system's hydrophobic level in area before and after phase transition remains approximately constant. And it

corresponds to well known interpretation [13] considered type of phase transition when individual fragments of macrochains become involved in formation of intramolecular micelles by means of hydrophobic interactions which are intensifying with temperature increase. Constancy of I_3/I_1 value at higher temperatures than phase transition could be connected with roughly same composition of micelles', formed by links of PNIPAM amphiphilic macromolecules.

In solution containing PNIPAM and PAA, transfer from one I_3/I_1 value to another is less sharp. Apparently, influence on micelles' composition is caused by formation of complex with PAA stabilized by weak hydrogen bonds. Emphasize that PAA was utilized at quite high ionization extent (presence of 0.003 M NaOH) in experiments (Fig. 3). Apparently the same factor had an influence on area covered by hysteresis loop. In this case impediment of conformational transfers in PNIPAM molecule which is located in complex with PAA molecules were stabilized by hydrogen bonds carries its own contribution.

Data of luminescence spectroscopy are confirmed by direct measurements of PNIPAM solution's optical density. As seen from the (Fig. 4) dependence of turbidity system from increase and decrease of temperature shows us hysteresis effects.

Explanation of sharp phase transitions in systems on basis of hydrophilic polymers is based on works of Khutoryanskiy and Staikos [13]. This interpretation utilizes S-like dependences of parameter, characterizing the systems behaviour from temperature. That could be swelling degree of hydrogel either optical density or any value related to sizes of macromolecular coils. Schemed curve is shown on (Fig. 5).

As seen from (Fig. 5), the sharp shift from one part of curve to another (line AB) occurs at tranquil increase of temperature. In accordance with this scheme temperature of direct transfer is T_2 (marked with arrow). Same figure illustrates that reverse transfer occurring at another temperature (line CD, T_1). Over wise, hysteresis effects in water solutions of amphiphilic macromolecules should take place with change of temperature. That was observed in experiment.

S-shaped dependence of macromolecular coils' sizes (swelling degree for cross-linking analogue) responds to formation of intramolecular micelle, characterised by hydrophobic-hydrophilic balance. Their formation proceeds with increasing temperature which responds to thermodynamic work done

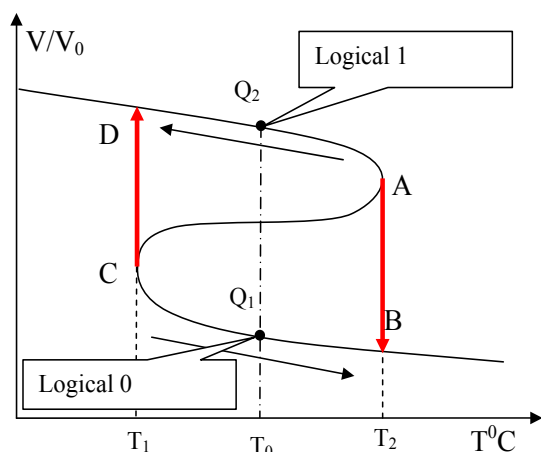


Fig. 5. To temperature gels collapse (theoretical dependence of relative volume of system from temperature).

against the hydrophilic forces (forces of stretching macromolecular clew), i.e. it is connected with overpassing of potential barrier. To put it simple, micelle formation is a cooperative effect and could take place only when hydrophilic interactions on suitable part of chain will be suppressed, what requires work to do, which was mentioned above.

Overpassing of analogical potential barrier, conjugated with work done against the hydrophobic interaction, is required at decreasing temperature.

As (Fig. 5) depicts, at the same temperature T_0 could exist two different states of system (Q_1 and Q_2) consequently such system could be memory cell as it was mentioned above. One of these state could be treated as logical zero (Q_1), another one (Q_2) – as logical one.

If we take into account that considered above interpretation of phase transition mechanism is based on hydrophobic-hydrophilic balance inside the molecule then in certain measures it is possible to predict states responding to transitional case.

At the same temperature different state of one molecule could be implemented, however in micelle formation partakes limited number of chains. Consequently, we can predict states in which one part of molecule is in Q_1 and the second is in Q_2 . These states are problematical to implement by variation of system's temperature in general, however utilizing other methods we can implement changes in states. This makes relevant further study of hysteresis effects passing at phase transition in solutions of hydrophilic polymers. Particularly, phase transitions induced by optical range emission are interesting from the view of information technology. Increase of temperature differences of direct and reverse transition are interesting, and could be

implemented by selection of complexation conditions, as it mentioned in our experiment.

5. Conclusion

On the example of PNIPAAm solution it was shown that phase transition in water solutions of amphiphilic polymers under temperature change is characterized by noticeable hysteresis effects.

Interpretation of those effects could be given on basis of consideration of hydrophobic-hydrophilic balance within the single macrochain.

This interpretation allows to make an assumption that separate fragments of chain could be considered as molecular triggers carrying out functions of binary memory cells.

This is a basis for further studying of hysteresis effects in the solutions of stimulus-sensitive polymers, with possibility to synthesise "programmable" macromolecules'.

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