

Revisiting the Thermosensitivity of Poly(acrylamide-*co*-diacetone acrylamide)^{*}

Xin-ming Xing^a, Guang-ming Liu^a, Yan-wei Ding^a and Guang-zhao Zhang^{a, b**}

^a Hefei National Laboratory for Physical Sciences at the Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

^b Faculty of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

Abstract The lower critical solution temperature (LCST) behavior of poly(acrylamide-*co*-diacetone acrylamide) (poly(AM-*co*-DAM)) copolymer in aqueous solutions was studied. The results demonstrate the LCST linearly decreases as the molar fraction of DAM (f_{DAM}) increases. In the range of $f_{\text{DAM}} < 0.36$, the transmittance increases as f_{DAM} decreases because the more hydrophilic copolymer chains can form looser aggregates with a lower refractive index. The transmittance exhibits a minimum when f_{DAM} is less than 0.28 as the chains form micelle-like structure with a size smaller than the wavelength. The LCST decreases with the initial polymer concentration, but it levels off when the polymer concentration is high enough. Moreover, no hysteresis can be observed in the change of transmittance during the heating-cooling process because no additional hydrogen bonds are formed in the collapsed state due to the steric hindrance of the large side groups in DAM units.

Keywords: Thermosensitive; Aggregation; Hydrogen bonds; Steric hindrance; Hysteresis.

INTRODUCTION

Thermoresponsive polymers exhibiting a lower critical solution temperature (LCST) have received much attention because of their potential applications in many fields such as chromatography separation^[1, 2], monolithic valves^[3], smart windows^[4] and stimuli-responsive films^[5]. The most studied thermosensitive polymers are poly(*N*-isopropylacrylamide) (PNIPAM)^[6, 7], poly(2-carboxyisopropylacrylamide)^[8], poly(*N,N*-diethylacrylamide) (PDEAM)^[9, 10], poly(*N*-cyclopropylacrylamide)^[11], poly(*N*-ethylacrylamide)^[12] and poly(*N*-acryloyl-*N'*-propylpiperazine)^[13]. The polymer chains exist as coils in aqueous solutions at temperatures below the LCST. When temperature is above the LCST, the chains will collapse and aggregate, and even precipitate out of the solution if the polymer concentration is high enough^[14, 15]. The LCST behavior is thought to be associated with the hydrogen bonding and hydrophobic effects of the polymer chains^[16–18]. The hydrogen bonds between polymer and solvents would lower the free energy of the system since the formation of hydrogen bonds is an exothermic process^[16]. On the other hand, the specific orientation of the hydrogen bonded solvent molecules causes the entropy to decrease, leading to a positive contribution to the free energy^[16].

Generally, it is believed that the hydrophilicity-hydrophobicity balance in the system determines the thermosensitivity^[17, 18]. The LCST of a thermosensitive polymer would increase when some other hydrophilic monomers are copolymerized into the chains, whereas the LCST decreases when some hydrophobic comonomers are introduced^[19]. For monomers whose homopolymers are not thermosensitive, their copolymers

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^{**} Corresponding author: Guang-zhao Zhang (张广照), E-mail: gzzhang@ustc.edu.cn

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^a Molar fraction of DAM in the copolymer determined by elemental analysis

Size Exclusion Chromatography (SEC)

The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were measured at 40 °C by SEC using a Shimadzu LC-10AVP liquid chromatography system equipped with a Shimadzu RID-10A differential refractive index detector. A series of monodisperse polystyrenes were used as standards. *N,N*-dimethylformamide was used as the eluent at a flow rate of 1.0 mL/min (Table 1).

Turbidity Measurements

Cloud points were determined by monitoring the turbidity of solutions heated at a rate of 0.1 K/min using a UNICO 2802PCS UV-Visible spectrophotometer with the wavelength set to 500 nm. The temperature of the cell was controlled using a circulating temperature-controlled water bath with an accuracy of ± 0.1 °C and monitored by an electronic thermometer. The concentration of poly(AM-co-DAM) solutions was fixed at 1.0 mg/mL unless otherwise specified. The LCST was taken as the temperature at which the transmittance is equal to the average of the transmittance values of the high transmittance (low turbidity) and low transmittance (high turbidity) plateaus.

Dynamic Laser Light Scattering (DLS)

The average hydrodynamic radius $\langle R_h \rangle$ of the polymer aggregates was measured on a commercial laser light scattering spectrometer (ALV/DLS/SLS-5022F) equipped with an ALV-5000 multitaup digital time correlator and a CW He-Ne laser (Uniphase, 22 mW at $\lambda = 632.8$ nm) at a scattering angle of 20°.

Microcalorimetry (MicroDSC)

MicroDSC measurements were performed at a model 5100 Nano-DSC (Calorimetry Science) with a scan rate of 1.0 K/min using water as the reference. The temperature corresponding to the endothermic peak was taken as the transition temperature.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectra were measured on a commercial Nicolet Magna 750 FTIR spectrometer with a 4 cm^{-1} resolution. In a typical experiment, 10 μL of poly(AM-co-DAM)/D₂O solution (20.0 mg/mL) was added to a cell between two KRS-5 crystals (diameter 32 mm, thickness 3.5 mm) with a space of 20 μm . The IR cell was thermally controlled. An electronic thermometer with a precision of ± 0.1 °C was used to monitor the cell temperature.

RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of transmittance of poly(AM-co-DAM) solutions as a function of molar fraction of DAM (f_{DAM}) in the heating process. Globally, LCST increases as f_{DAM} decreases, similar to those reported before^[22]. Yet, the transmittance after the transition increases as f_{DAM} decreases when f_{DAM} is below 0.36. This is because the more hydrophilic copolymer chains can form looser aggregates as f_{DAM} decreases, leading to a lower refractive index.

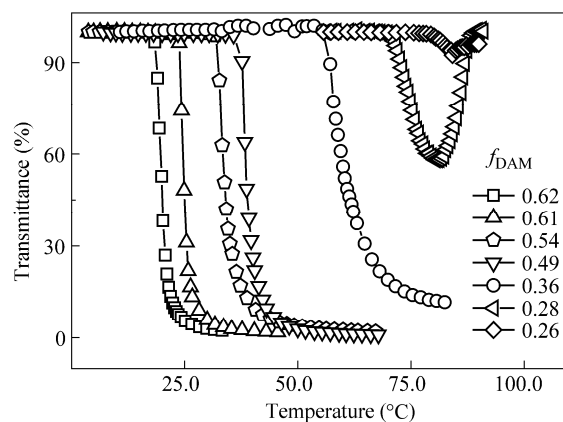


Fig. 1 Temperature dependence of transmittance of poly(AM-co-DAM) solutions as a function of molar fraction of DAM (f_{DAM})

Interestingly, the transmittance exhibits a minimum when f_{DAM} is less than 0.28. This is probably because the chains first form loose aggregates due to the association of the hydrophobic segments as temperature approaches to the LCST. Further increasing the temperature would lead the chains to pack into a micelle-like structure with the hydrophilic PAM segments on the shell, whose size is smaller than the wavelength. Thus, the transmittance increases again and exhibits a minimum. Accordingly, the composition of the copolymer has a profound effect on its LCST behavior.

Figure 2 clearly shows the LCST linearly decreases with f_{DAM} . The reason is that DAM units are more hydrophobic than AM units, and the hydrophobicity of the copolymer increases with increasing f_{DAM} , which shifts the LCST to a lower temperature. By fitting the data presented in Fig. 2, the relation between LCST and f_{DAM} can be obtained:

$$\text{LCST} = 121.0 - 1.62 f_{\text{DAM}} \quad (1)$$

Thus, the LCST of the copolymer for a given composition can be predicted based on the above equation. By extrapolation of LCST to $f_{\text{DAM}} = 0$, we can obtain the LCST of PAM homopolymer at ~ 121 °C. It is somewhat higher than the boiling point of water. Likewise, extrapolating LCST to $f_{\text{DAM}} = 1.0$ leads to the LCST of PDAM homopolymer at ~ -41 °C, which is below the freezing point of water. Obviously, we can not observe the LCST of either PAM or PDAM under usual conditions even though they may exist. Our results indicate that the moderate hydrophobicity of DAM segments can be balanced by the hydrophilicity of AM segments when they are in the same chain. Thus, the delicate balance induced by copolymerization in the system makes the LCST observed in the range between 0 °C and 100 °C possible.

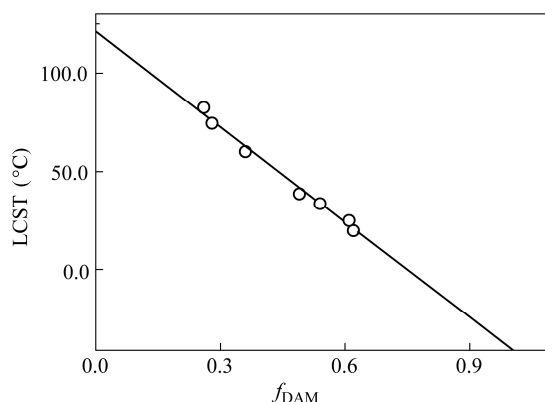


Fig. 2 Polymer composition dependence of LCST of poly(AM-co-DAM)

Figure 3 shows the concentration dependence of poly(AM-co-DAM) LCST. The LCST of poly(AM-co-DAM) solutions was reported to be independent of the concentration in the range from 10.0 mg/mL to 100.0 mg/mL, which was attributed to the molecular weight distributions and heterogeneity of the polymer-solvent system^[19]. However, a significant dependence of LCST on the concentration was observed in the range between 0.1 mg/mL to 10.0 mg/mL in the present study (Fig. 3). When the concentration is below 1.0 mg/mL, the LCST sharply decreases as the concentration increases. Then, the LCST gradually levels off at a concentration above 1.0 mg/mL. Generally, polymer concentration should have a profound effect on the cloud point of the thermosensitive polymers and can be explained as follows^[29–31]. As we know, it is difficult for polymer chains to collide and associate at a low concentration owing to the large interchain distance. However, a higher temperature allows the chains to gain more thermal energy and to aggregate at a low concentration. As the polymer concentration increases, the collision probability among polymer chains increases, and the chains are able to aggregate or even precipitate out of the solution at a lower temperature. Thus, LCST sharply decreases with the polymer concentration. When the polymer concentration is above a critical value, the interchain distance

is small enough to allow the chains to contact readily at any temperatures in the range we investigated. This is why the LCST gradually levels off when concentration is above 1.0 mg/mL.

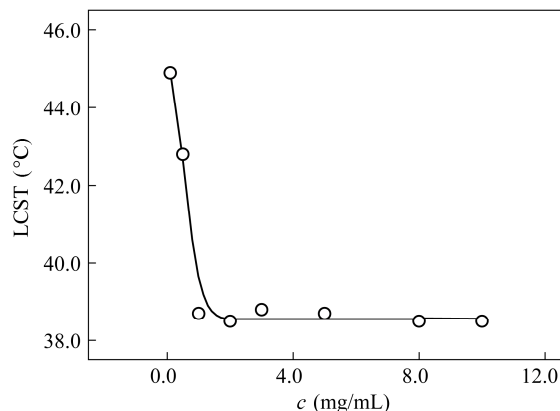


Fig. 3 Polymer concentration (c) dependence of LCST of poly(AM-co-DAM) with f_{DAM} of 0.49

Figure 4 shows the temperature dependence of average hydrodynamic radius ($\langle R_h \rangle$) of poly(AM-co-DAM) chains in water as a function of polymer concentration. $\langle R_h \rangle$ decreases with temperature at temperatures below the LCST, indicating the shrinking of the copolymer chains^[32–35]. When the temperature is above the LCST, $\langle R_h \rangle$ sharply increases first, and then gradually levels off, indicating that the chains form stable aggregates because the hydrophilic AM units on the aggregate surface are still enough to stabilize the aggregates. When the concentration is above 0.015 mg/mL, the chains form larger aggregates and precipitate out of the solution so that we cannot get the $\langle R_h \rangle$. This is because poly(AM-co-DAM) is a random copolymer and more AM units are buried in the aggregate at a higher concentration. As a result, the AM units anchoring on the aggregate surface may not be enough to stabilize the aggregates. Note that the LCST measured by DLS is lower than that determined by the turbidimeter as DLS is more sensitive to the aggregates.

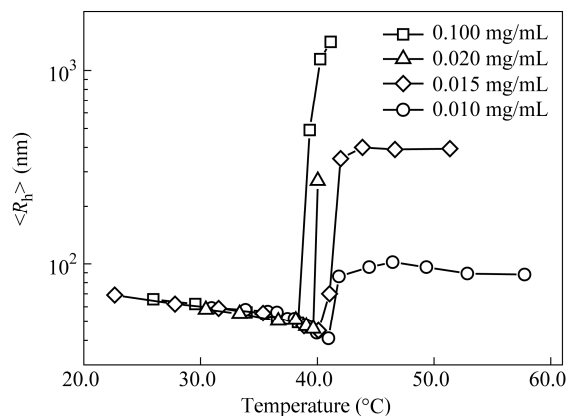


Fig. 4 Temperature dependence of the average hydrodynamic radius ($\langle R_h \rangle$) of poly(AM-co-DAM) chains in water as a function of copolymer concentration (The molar fraction of DAM (f_{DAM}) is 0.49.)

We have also studied the reversibility of the dissolution of the aggregates. Figure 5 shows the temperature dependence of transmittance of poly(AM-co-DAM) solution, where f_{DAM} is 0.49 and the heating or cooling rate is fixed at 0.1 K/min. A sharp change in transmittance can be observed in either heating or cooling process in the range between 36.0 °C and 40.6 °C with a LCST of 38.4 °C. Clearly, we do not observe an obvious hysteresis during the heating-cooling process, which usually happens for other thermosensitive polymers, *e.g.*, PNIPAM^[32].

Actually, we found poly(AM-*co*-DAM) copolymers do not exhibit such a hysteresis at any polymer compositions, and the aggregates can be reversibly dissolved. The facts indicate that poly(AM-*co*-DAM) copolymer chains do not form additional hydrogen bonds in the collapsed state^[32, 33, 36, 37].

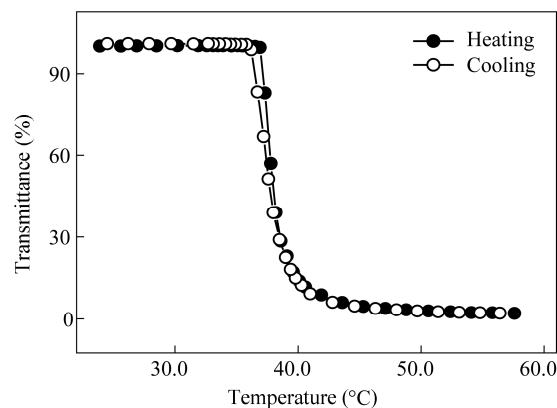


Fig. 5 Change in transmittance during a heating-and-cooling cycle

The poly(AM-*co*-DAM) concentration is fixed at 1.0 mg/mL and the molar fraction of DAM (f_{DAM}) is 0.49.

Figure 6 shows the temperature dependence of specific heat capacity (C_p) in a heating-and-cooling cycle, where either the heating or cooling rate is 1.0 K/min. It can be seen that the curve is asymmetrical in the heating process, which might be induced by the competition between the intrachain contraction and interchain association during heating^[36]. That is, the collapse of chains before or after the interchain aggregation at a certain heating rate would lead to an asymmetrical curve^[36]. The chains collapse and aggregate simultaneously only when the heating rate is low enough. For the same reason, the curve is asymmetrical or even becomes bimodal in the cooling process.

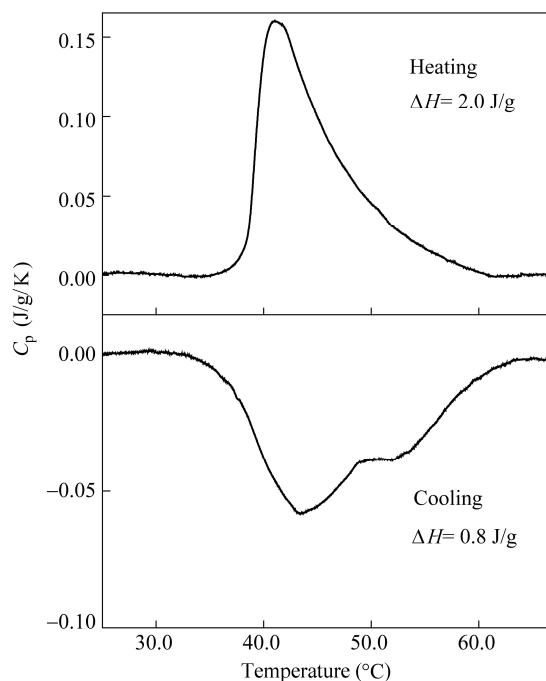


Fig. 6 Temperature dependence of the specific heat capacity (C_p) of poly(AM-*co*-DAM) in a heating-and-cooling cycle

The molar fraction of DAM (f_{DAM}) is 0.49 and the polymer concentration is 20.0 mg/mL.

Clearly, we also can not observe the hysteresis in the cooling process. The transition temperature in the cooling process is even some higher than that in the heating process, indicating that the chains in the aggregates are readily dissolved because the interactions between the polymer segments can be easily overcome by the segment-water interactions. The transition temperature measured by MicroDSC is somewhat higher than those measured by turbidimeter and DLS. This is because the aggregation or dissolution of the chains is slower than the scanning rate, leading to a higher apparent transition temperature.

The enthalpy change (ΔH) of poly(AM-co-DAM) can be obtained from Fig. 6. Obviously, it is far less than that for PNIPAM^[38]. As we know, the dehydration involved in the intrachain contraction and interchain association upon heating is an endothermic process, which will increase ΔH . The formation of additional hydrogen bonds in the collapsed state is an exothermic process, thereby it reduces the ΔH ^[38]. The steric hindrance of the large side groups in DAM units would prevent the chains from forming the additional hydrogen bonds. Therefore, the small ΔH in the heating process is attributed to the low extent of dehydration of the chains induced by the introduction of hydrophilic AM units into the copolymer. Note that ΔH in the cooling process is smaller than that in heating process in that the dissolution of the aggregates from their shell to the core is slower than the cooling, and the chains inside the aggregates still associate even they are cooled to a certain temperature in the time we examined.

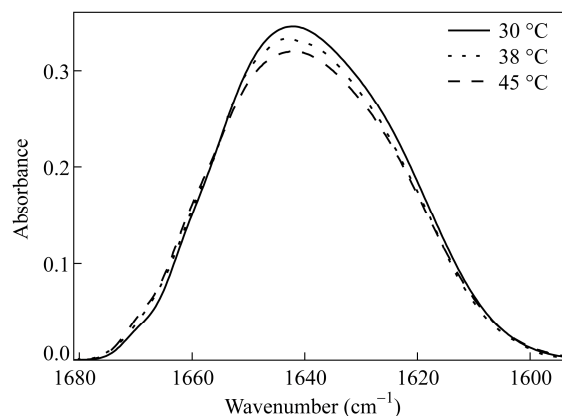
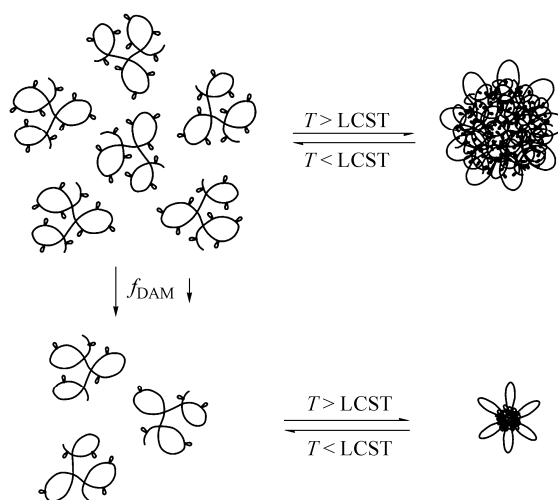


Fig. 7 FTIR spectra of poly(AM-co-DAM) in D₂O (20.0 mg/mL) in the range of 1590–1680 cm⁻¹ at different temperatures (The molar fraction of DAM (f_{DAM}) is 0.49.)



Scheme 2 Temperature induced aggregation of poly(AM-co-DAM) chains

Figure 7 shows FTIR spectra of poly(AM-*co*-DAM) in the range of 1590–1680 cm^{-1} at different temperatures, where the change of the amide I band ascribed to the stretching vibration of C=O groups is related to the additional hydrogen bonding^[39]. We do not show other bands since they are independent of temperature. D₂O instead of H₂O is used to measure the FTIR spectra because the bending mode at 1640 cm^{-1} for water moves to 1200 cm^{-1} for D₂O and it does not overlap with the bands centered at 1654 cm^{-1} and 1643 cm^{-1} for amide I of poly(AM-*co*-DAM) chains in solution^[39]. A broad band ranging from 1590 cm^{-1} to 1680 cm^{-1} is observed owing to the overlapping of the amide I bands from DAM unit and AM unit. As reported before^[39], the amide I band has a blue or red shift if C=O group forms a hydrogen bond with N–H group or water. Here, the amide I band involves three components, *i.e.*, component one assigned to free C=O groups without hydrogen bonding, component two assigned to the C=O groups forming hydrogen bonds with N–H groups, and component three assigned to the C=O groups coupled with water molecules. The shoulder at about 1665 cm^{-1} is attributed to the C=O groups forming hydrogen bonds with N–H groups. As temperature increases, the intensity slightly varies, indicating that C=O species do not form additional hydrogen bonds with N–H groups in the collapsed state. In other words, C=O groups can form hydrogen bonds with N–H groups in the collapsed state of poly(AM-*co*-DAM) with the same level as those in the swelling state. Namely, no additional hydrogen bonds is formed^[32, 33, 36, 37]. This is why we did not observe a hysteresis. It is possible that the steric hindrance of the large side group in DAM unit impedes the formation of the hydrogen bonds. In short, the aggregation of poly(AM-*co*-DAM) chains are reversible. The temperature induced aggregation of poly(AM-*co*-DAM) is illustrated in Scheme 2.

CONCLUSIONS

In conclusion, we have investigated the LCST behavior of poly(AM-*co*-DAM) chains, where the corresponding homopolymers are thermally insensitive. The copolymer composition and concentration have significant effects on the aggregation behavior. No hysteresis can be observed during the heating-cooling process because the copolymer chains cannot form additional hydrogen bonds in the collapsed state due to the steric hindrance of the large side groups in DAM units.

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