High Pressure Induced Coil-Globule Transitions of Smart Polymers

A. Kirpach[1], *D. Adolf*[2]

Summary: In current work time-resolved optical spectroscopy (TROS) has been used to study coil-globule transitions monitored by the local segmental dynamics of anthracene labeled poly (*N*-isopropymethacrylamide), PNIPMAM as a function of pressure (0.1 MPa–200 MPa) over a temperature range of 283 K to 333 K. The positions of temperature-induced transition were observed to be independent on molecular weight of polymer at low pressures. The positions of pressure-induced transition were observed to be dependent on molecular weight of polymer at temperatures below LCST at atmospheric pressure. Double globule-coil-globule transition was observed to occur with pressure increasing at temperatures nearly above LCST. All these results along with values of intrinsic viscosity evaluated from values of correlation times measured for globules formed at different pressure/temperature conditions suggest the different mechanisms of compactisation governed by pressure and temperature and, correspondently, the different types of final structures. At low pressures with temperature increasing the compact, well-packed globules are forming via initial interactions between neighboring parts of polymer chain and further collapse. Relatively loosened particles are forming with pressurizing at low temperatures. Interaction between remote along the chain units takes part from the first stage of globule formation. And finally, rather solvated and irregularly twisted particles are forming at high pressure and high temperatures, i.e. at conditions, when both processes are involved.

Keywords: coil-globule transition; high pressure; local dynamics; smart polymers

Introduction

Studies of local dynamics of polymer chains in solution afford valuable insight into the structure-property relationships of polymers. Motions at the microscopic level on the scale of a few repeat monomer units are sensitive as to the chemical structure of those repeat units, as to inter- and intramacromolecular interactions. Intramolecular interactions are changing dramatically when polymer chain undergoes a coil-globule transition and, correspondently, it is manifesting in change of the rate of molecular mobility.

So-called 'smart' (e.g. stimuli responsive) polymers undergo coil-globule transition in aqueous solution with heating. Such polymers based on poly(alkylacrylamides) and poly(alkylmethacrylamides) have been a focus of increasing activity in polymer physics an chemistry during the past decade. Within these families the best investigated polymer is poly (*N*-isopropymethacrylamide), PNIPMAM. Such interest stems from the fact, that the transitions of smart thermoresponsive polymers occur nearly physiologically important temperature of 310 K (37 °C), which promises a wide range of application from flocculation to drag release. On the other hand, these polymers are bearing the similar hydrophobic and

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proton-donor and proton-acceptor groups as a polypeptides. This fact makes such smart polymers to be simple but valuable models of proteins and polypeptides.

Time-resolved optical spectroscopy (TROS) methods were successfully applied to the study of relaxation behaviour of these polymers undergoing transition in aqueous solution with temperature increasing at atmospheric pressure. The sensitivitity of TROS allows ultra dilute solutions to be employed thereby allowing measurements to monitor intramolecular issues within chain collapse before the onset of interchain aggregation.

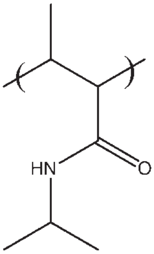
Suprisingly, the role of pressure was not so widely adressed to the study of smart behaviour of synthetic polymers. The only few resent works were devoted to determination cloud points only of polymer solutions under pressure. At the same time, within the biophysics community, the pressure variable has been employed widely to study conformational events such as chain folding/misfolding due to this variable's ability to induce the transition impossible to achieve at normal pressure conditions, to stabilize intermediates within the transition and to resolve histeresys. However, this area is still very immature especially in comparison to what is known regarding temperature chained molecule dynamics and conformational transitions.

Recently the relaxation behaviour of synthetic polymers in organic solutions of good thermodynamic quality and in a bulk state was studied under pressure. The next logic and inherent step is to study the transitions between these two states in case of coil-globule transition, especially if experience in study of such transitions at atmospheric pressure using TROS was successful. This manuscript describes the investigation of pressure and temperature induced coil-globule transitions of poly (*N*-isopropymethacrylamide), PNIPMAM monitored by TROS.

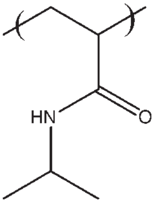
Materials and Methods

Polymers and Polymer Solutions

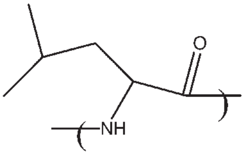
From chemical point of view PNIPMAM is vinyl homopolymer differing from PNIPAM by the presence of methyl group attached to a backbone.



PNIPAM



PNIPMAM



poly(leucine), PLeu.

PNIPMAM and PNIPAM chemical structures are closed to those of such polypeptides poly(leucine), PLeu.

Anthracene labeled PNIPMAM samples were synthesized in Institute of Macromolecular Compounds of Russian Academy of Science. Synthesis and fractioning are described in several papers[1–3]. Molecular weights (M) of the fractions were estimated by viscometry in ethanol and water and and were found to be 50×10^3 Dalton and 140×10^3 Dalton. Polydispersity of fractions was found to be $M_w/M_n = 1.4–1.6$ using sedimentation. Each polymer chain contains one anthracene chromophore per 1000 monomer units located in side chain. The chain is covalently bonded to the anthracene chromophore's 9 position allowing its $S_0 \rightarrow S_1$ electronic transition dipole moment to be oriented mainly perpendicular to the chain backbone.

Local polymer dynamics are monitored through changes in the spatial orientation of this transition dipole as discussed further in the following sections.

We used extremely dilute aqueous solutions of polymers to prevent possible aggregation. Concentration of polymer did not exceed 0.01 mg/ml.

High Pressure Cell

Details of the high pressure cell have been described in previous manuscripts[4–6]. This paper reports data taken at temperatures ranged from 283 to 333 K and at pressures ranged from 0.1 to 200 MPa.

Experimental Technique and Data Fitting

Both the time-resolved optical spectroscopy technique[4–6] and associated equipment[7] employed in this study have been described in detail elsewhere. To summarize, the measurement is sensitive to a time-dependent anisotropy, $r(t)$, calculated from the vertical and horizontal fluorescence emission decays, $I_{||}(t)$, and $I_{\perp}(t)$, via

$$r(t) = \frac{I_{||}(t) - I_{\perp}(t)}{I_{||}(t) + 2I_{\perp}(t)} \qquad (1)$$

The anisotropy decays were fit to an empirical biexponential function with fitting parameters A, B, τ_1, and τ_2.

$$r(t) = A\exp(-t/\tau_1) + B\exp(-t/\tau_2) \qquad (2)$$

Distortions in the data introduced by the finite width of the laser pulse (~5 ps) and the response of the detection equipment were deconvolved via iterative impulse reconvolution[8]. Reduced χ^2 values for these fits were typically no larger than 1.15. The biexponential fits are used solely to characterise the shape of the anisotropy decays and no further significance is given to the fit parameters. An average correlation time, τ_c, representing the overall time scale of the monitored segmental dynamic was determined using

$$\tau_c = \frac{1}{r_0}\int_0^{\infty} r(t)dt \qquad (3)$$

where r_0 is the fundamental anisotropy and τ_c values are determined via integration of the biexponential fits. Measurements at atmospheric pressure yielded r_0 values for labeled polymethyl alkylamides in the range 0.32 ± 0.02 in good agreement with values for other anthracene-labelled polymer solutions[4,5]. Additionally, all reported τ_c values within this manuscript have an associated error of ±10%.

Correction of Pressure Induced Birefringence

Undesired polarisation scrambling is present within the experiment due to the pressure-induced birefringence of the quartz windows. Contributions of this effect to $I_{||}(t)$ and $I_{\perp}(t)$ are corrected via the method of Paladini and Weber[9]. The scrambling correction factor, γ, is determined at a pressure P as

$$\gamma(P) = \frac{[1 - (r_0^{obs}(P)/r_0(P_{atm}))]}{3} \qquad (4)$$

where $r_0^{obs}(P)$ is observed value of the fundamental anisotropy at a pressure P and $r_0(P_{atm})$ is the fundamental anisotropy at atmospheric pressure, P_{atm}. Value of r_0^{obs} decreases to no less then 0.2 over the experimental range of pressure and corrected r_0^{obs} values fall within a window of 0.33 ± 0.02 for all values of temperature and pressure employed within this study.

Results and Discussion

Temperature Induced Transition of PNIPMAM at Atmospheric Pressure

It can be seen, that below the transition point local dynamics follows “normal” Arrhenius type of behaviour, which means that correlation times are decreasing with heating. At this pre-transition conditions polymer chain exists as a flexible coil. At 43–44 °C a dramatic increasing of correlation times occurs which marks the conformational transition of PNIPMAM from open coil to a compact, slow moving globular structure. For both samples transition occurs at approximately same temperatures, which corresponds to observation of many authors reported very weak molecular weight dependencies of transition position (or even absence at all[10]) for variety of smart polymers.

The difference in values of correlation times for polymers of two different molecular weights is much more pronounced at post-transition state. It could mean that polymer of higher molecular weight forms more perfect, better packing globule, were local dynamics is more restricted. These results are in good agreement with those obtained for this polymer of different molecular weights by Anufrieva et all [2,3] using different fluorescence techniques. Steady-state polarised luminescent experiments shown the cooperative increasing of hindrance of intramolecular dynamics of PNIPMAM is narrow region of temperature. The increase of values of relaxation times corresponds to increase of local concentration non-polar groups monitored by the luminescent probe sensitive to hydrophilic environment. The independence of position of transition on molecular weight of polymer was interpreted as the fact that interaction of neighbouring alkyl groups, increasing with heating, play role of initiator for structure compactisation. The value of 5 cm^3/g of intrinsic viscosity, estimated from plateau region of relaxation times confirmed the fact of compactisation. On the other hand, these results correspond to results of colorimetric and diffusion measurements and size-exclusion chromatography[1] confirming PNIPMAM compactization at heating. Stokes radii R_s's, diffusion coefficients D's and heat capacities c_p's were determined for PNIPMAM polymers of molecular weight from 11.2×10^3 to 370×10^3 Dalton at 23 °C and 50 °C. These values were found to be correspondent to those known for unfolded and proteins native of corresponding molecular weights.

Similar conformational transition in water with temperature increasing was monitored for more flexible and better-studied PNIPAM using TROS and other complementary spectroscopic techniques, as quenching of fluorescence, excimer formation and fluorescence probe experiments, for acenaphthylene-labelled[11–13] polymer and for pyrene-labelled[14,15] polymer. It was shown, that local dynamics, quenching constant, probe solubilization and excimer formation are changing dramatically suggesting compactization of polymer chain in water at 32 °C. This results were compared with those, obtained in methanol, were PNIPAM exist in coil state in the same experimental range of temperature. However, using more concentrated solutions as in present study, authors[11–15] presumed two-stage mechanism of PNIPAM behaviour nearly critical point. The first step involves intramolecular coil collapse. This is followed by intermolecular aggregation between collapsed coils.

For this polymer undergoing transition around 32 °C cloud point[16,17] the change of size was measured by Wang[18] using light scattering technique. Exploring extremely dilute aqueous solution (6.7×10^{-4} mg/ml) of monodisperse ($M_w/M_n < 1.05$) high molecular weight ($M_w = 1.3 \times 10^7$ g/mol = Dalton) sample the author observed monomolecular transition manifesting in changes of radii of hydration and hydrodynamic radii of PNIPAM chain. The average chain density of the fully collapsed globule was estimated as 0.34 g/cm^3. Light hysteresis observed between heating and cooling of this sample was attributed to formation on crumpled coil and molten globule between the random coil and the collapsed globule states.

Effect of Pressure on Temperature Induced Transition

Figure 2 reveals examples of pressure effect on temperature-induced transition of PNIPMAM polymers. It can be seen that for both samples transition exists within pressure range of 0.1–100 MPa and does not exist at 200 MPa. At high pressure conditions local dynamics of polymer is hindered in all region of temperature studied, which corresponds to globular state. Transition of low molecular weight sample, monitored at

100 MPa is shifted to higher temperature in comparison with that observed at normal pressure. Contrary, transitions of high molecular weight sample, monitored at 0.1 and 100 MPa are merged. We will try to give explanation of such kind effects in next sections.

Effect of Water Viscosity

It is well known fact that dependence of local dynamics on solvent viscosity could be described as power low, $\tau \sim \eta^{\alpha}$. Degree α can be estimated from Figures 1, 2 replotted as $\ln \tau$ versus $\ln \eta$ for all pressures and temperatures. In this work the viscosity values for all experimental points were generated using Harris's system of equations[19].

It was found that for pre-transition state correlation time is proportional to viscosity, i.e. $\alpha = 1$, at pressure ranged from 0.1 to 200 MPa. Whereas for globule state local dynamics does not obey to this low. For post-transition state $\alpha = 0.64$ for low molecular weight sample and $\alpha = 0.56$ for high molecular weight sample.

Pressure Induced Transition

Figure 3 reveals results confirming existence pressure-induced transitions of PNIPMAM polymers at temperature conditions were transition does not occur at atmospheric pressure, i.e in 10–35 °C region. It can be seen, that pressure does not influence significantly on values of correlation times at pressurising from 0.1 to 100 MPa. After that local dynamics is slowing dramatically reaching plateau region at pressures higher then 160 MPa. Again, values of correlation times, characterising globule state, are significantly higher for higher molecular weight sample. And for this sample transitions occur at lower pressures then transitions of low molecular weight PNIPMAM. Such pressure induced transitions, monitored by any relaxation methods, were not reported in literature before.

It was interesting to compare these results to those obtained by pressurising at temperatures higher then transition point at atmospheric pressure. Figure 3 illustrated such efforts. It can be seen, that there are no any transitions at 55 °C. Local dynamics is remaining to be hindered in

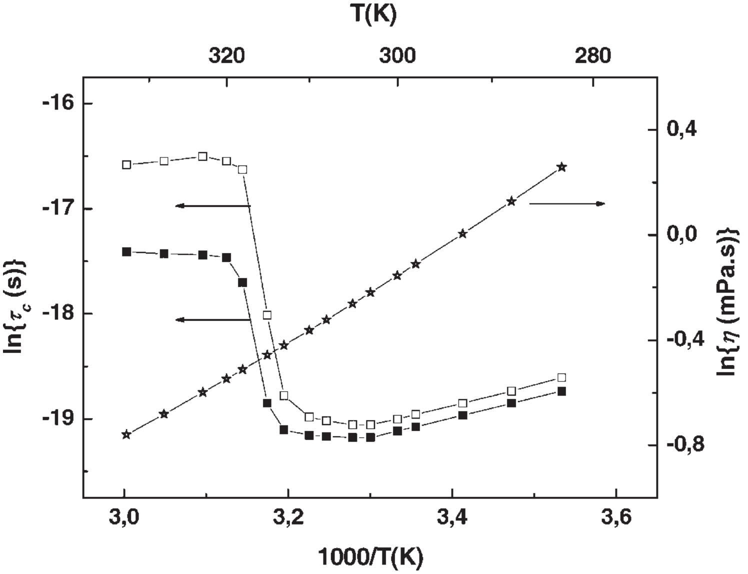


Figure 1.
The temperature dependence (i.e. Arrhenius format) of PNIPMAM correlation times at 0.1 MPa for samples of $M = 50 \times 10^3$ Dalton (closed squares) and $M = 140 \times 10^3$ Dalton (open squares). Stars correspond to water viscosity at 0.1 MPa.

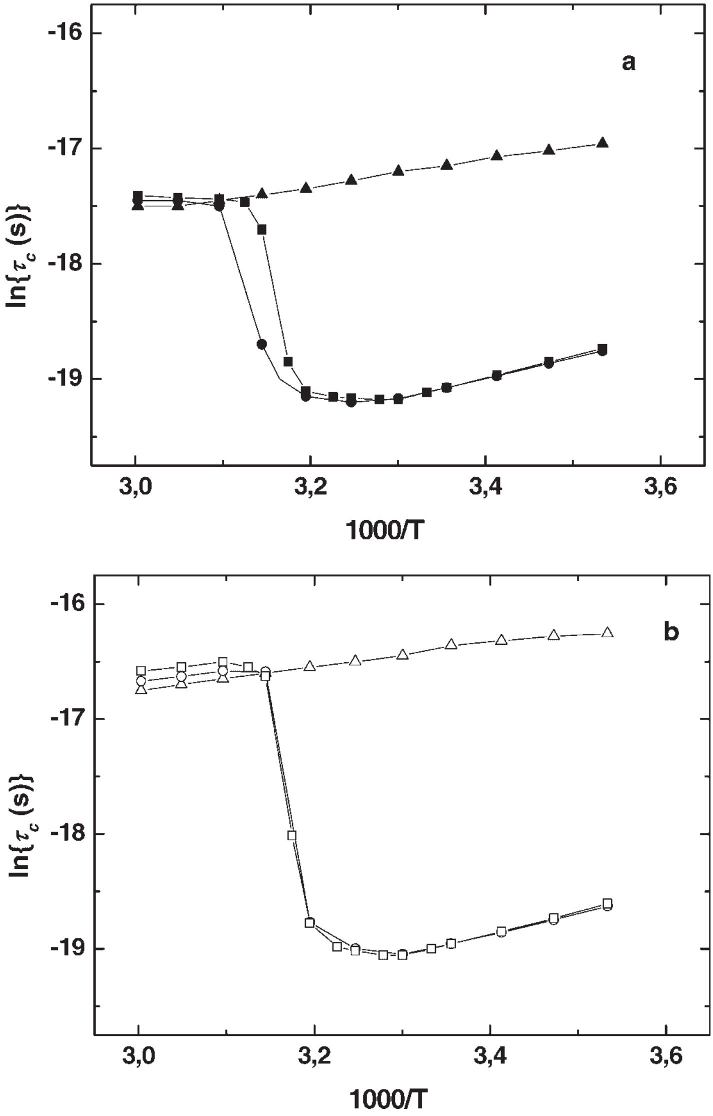


Figure 2.

Arrhenius plots of PNIPMAM correlation times at pressures of 0.1 MPa (squares), 100 MPa (cycles) and 200 MPa (triangles) for samples of M = 50 × 10^3 Dalton (closed symbols, (a)) and M = 140 × 10^3 Dalton (open symbols, (b)).

whole experimental range, which confirms globule state for both samples.

At 45 °C correlation times fall down dramatically from the first steps of pressurising, reach the plateau region at middle pressures, and then they are increasing again. It suggests that it is possible to induce double-stage transition of smart polymers by pressurising solution at temperatures nearly higher LCST point. In this case polymer is unfolding from globule to coil first and collapsing to globule again with further pressurising.

Significant difference between such double-stage transitions can be observed for samples of different molecular weights. The second stage for low molecular weight sample is located in nearly the same region

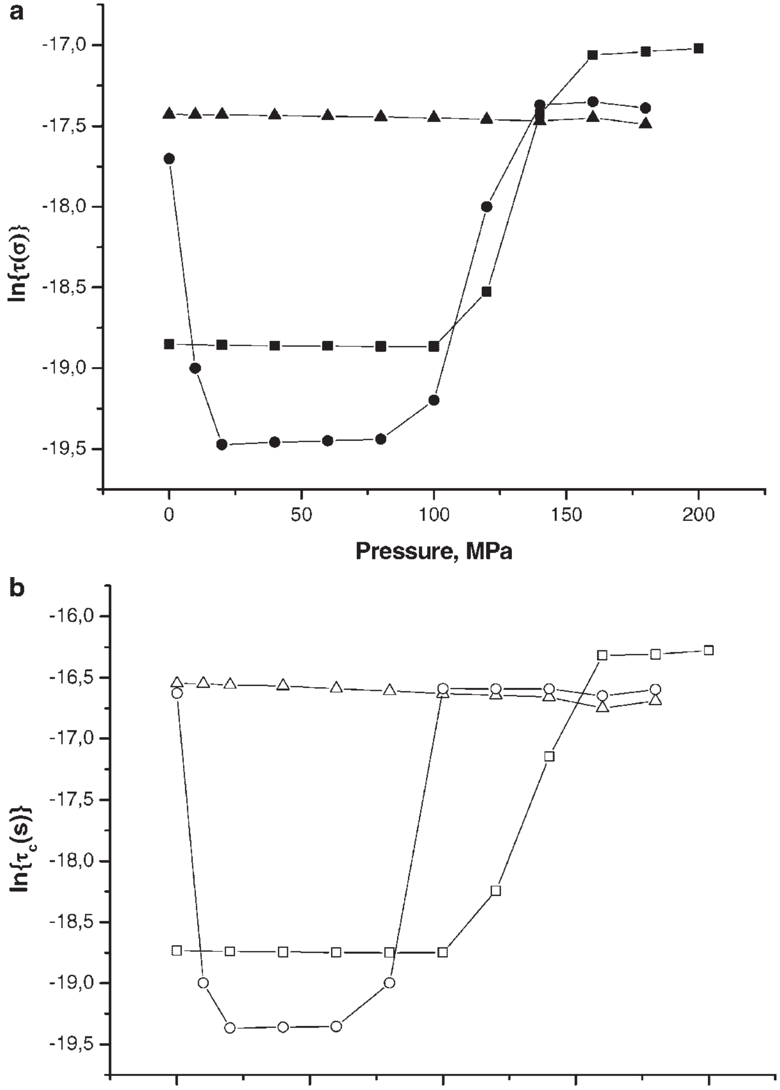


Figure 3.
Pressure dependencies of PNIPMAM correlation times at temperatures of 15 °C (squares), 45 °C (cycles) and 55 °C (triangles) for samples of $M = 50 \times 10^3$ Dalton (closed symbols, (a)) and $M = 140 \times 10^3$ Dalton (open symbols, (b)).

of pressures as for one-stage transitions. For high molecular weight sample the situation is different. The second stage of transition at 45 °C is significantly shifted to the side of lower pressures in comparison with single transitions at temperatures lower temperature transition point.

Pressure-Temperature Phase Diagram

Analysis of whole set of experimental data plotted versus temperature and pressure permits us to imagine phase diagrams for both samples. These diagrams are represented within Figure 4. They look like parts of ellipsoid curves and inside area corre-

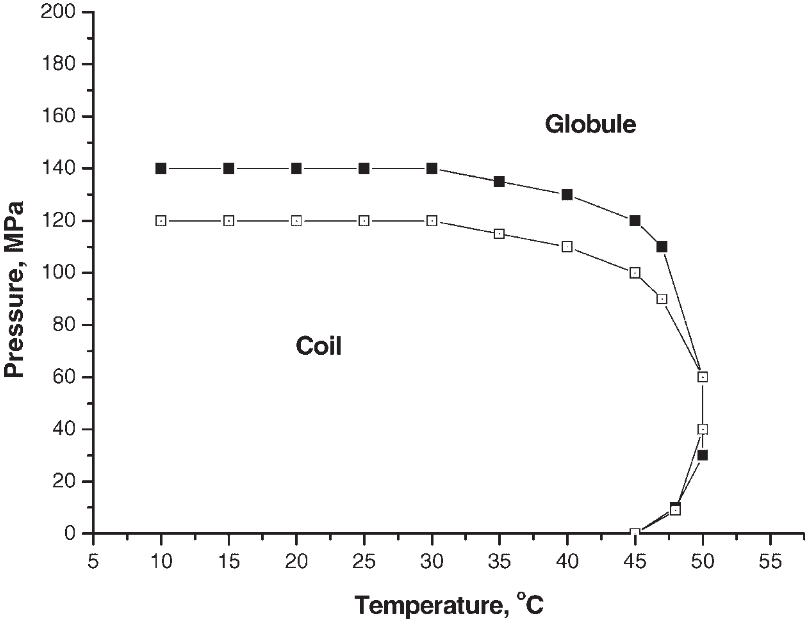


Figure 4.
Pressure-Temperature phase diagram for PNIPMAM samples of $M = 50 \times 10^3$ Dalton (closed squares) and $M = 140 \times 10^3$ Dalton (open squares).

sponds to coil state, whereas outside region represents the globule state. Such kind of data description permits us to answer a questions arises from previous sections. In particular, it reflects the facts that temperature points of transitions are slightly dependent on molecular weight, while pressure points are very sensitive to them. It explains the fact that double-stage pressure-induced transitions can be detected at temperatures nearly above 45 °C.

It can be seen, why temperature shift of transition was observed for low molecular weight sample and it was not detected for high molecular weight sample at pressure of 100 MPa. On the other hand, the much more pronounced pressure shift of second stage of transition of high molecular weight sample at 45 °C could be explain by the difference of curvatures at temperatures higher LCST. Kunugi [16,17] reported similar P-T ellipses obtained within pressure-temperature study of cloud points for PNIPAM.

In general, the fact, that the positions of temperature-induced transitions monitored by local dynamics are independent on molecular weight of polymer, indicates that these compact structures consist of local structured regions formed via the interaction of adjacent chain units. On the other hand, the sensitivity of dynamics to the positions pressure-induced transition suggests that collapse occurs with interaction between monomer units remote along the chain as well. It is obvious, that at high pressures and high temperatures the mixed transition containing both of these processes is observed.

Account of Rotation of Macromolecule as a Whole and Role of Viscosity

All previous analysis of the correlation times versus temperature at fixed values of pressure and versus pressure at fixed values of temperature for the PNIPMAM demonstrates that when pressure or temperature conditions vary, polymer undergoes a cooperative structural transition in narrow range of temperature or pressure. This process corresponds to compactisation of polymer coil to the globular structure. When the temperatures at fixed pressures and pressures at fixed temperatures reach critical points, the dependencies of correlation times versus varied parameter reach a plateau. This suggests the appearance of a new relaxation process with time comparable to τ_c. This process is related to a rotational mobility of a macromolecule as a whole and is characterised by the time τ_{wh} as the polymer coil is compacted by the effect of pressure or temperature. Previously the similar approach was used for interpretation of relaxation data describing coil-globule transitions of polymers at atmospheric pressure[2,3,20,21].

For researchers using TROS it means that at post-transition state they collect fluorescence anisotropy decay data corresponding to *observed* correlation time τ_{obs} which is a real superposition of two times as

$$r/r_0 = \exp(-t/\tau_{loc}) * \exp(-t/\tau_{wh}), \tag{5}$$

were τ_{loc} is a correlation time characterising local dynamics of polymer chain in globular state.

It means that

$$1/\tau_{obs} = 1/\tau_{loc} + 1/\tau_{wh}, \tag{6}$$

There are two notes here, which can be kept in mind. The first is that it is impossible to resolve the local dynamics from rotation as a whole within one TROS experiment. The second note is that the representation of τ_{obs} in form of eq. (6) assumes that all three correlation times obey Kramer's law in post-transition state. On the other hand, all these correlation times somehow depend on viscosity of water anyway.

Assuming a power low of viscosity effect on correlation times one can modify eq. (6) to form

$$(\eta^{\alpha}/\eta_0)\tau_{obs} = (\eta^{\beta}/\eta_0)\tau_{loc} + (\eta/\eta_0)\tau_{wh}, \tag{7}$$

where η_0 is a reference viscosity.

For $\eta_0 = 1$, which is closed to viscosity of water at 20 °C and 0.1 MPa, the simplified form of eq. (7) can be achieved

$$\eta^{\alpha}/\tau_{obs} = \eta^{\beta}/\tau_{loc} + \eta/\tau_{wh}. \tag{8}$$

The value of 1 of viscosity dependence coefficient for rotation of globule as a whole was chosen according to well-known formula[22,23]

$$\tau_{wh} = 1.2\ \eta[\eta]M/RT, \tag{9}$$

were $[\eta]$ is the intrinsic viscosity, M is molecular weight of polymer and R is the universal gas constant.

Analysis of our data in spirit of eq. (8) shows that for temperature induced coil-globule transitions of PNPMAM at fixed pressures viscosity power law coefficient α is about 0.64–0.66 for low molecular weight sample and it is about 0.56–0.58 for high molecular weight sample. In this case for the equal values of τ_{wh} and τ_{loc} correlation times reduced to reference viscosity η_0, described above, the empirical approach gives the values of β within a region from 0.45 to 0.47 for low molecular weight sample and from 0.36 to 0.38 for high molecular weight sample. It, firstly, suggests that local dynamics of polymer in globule state very week depends on viscosity of solvent. It seems a reasonable conclusion, because, actually, we monitor the motion of polymer segments presumably located on the surface of globule. If it is true, the environment of kinetic segment should control this local motion and these neighbours do not consist of water molecules only but of polymer monomers packed into globular state as well. Secondly, the fact that viscosity dependence of local dynamics on water viscosity is stronger for high molecular weigh sample, suggests that higher molecular weight polymers are able to collapse to better packed globules. Unfortunately, we cannot estimate the values of α and β coefficients for globular state from dependencies describing pressure induced transition at fixed temperatures. Slopes of $\ln\tau$ versus $\ln\eta$ are negligible or even absent. The reason for that is in the fact that water viscosity is changing on few percent only in our experimental range of pressure, whereas it is changing on hundreds percent with temperature increasing. We can say only that these coefficients are of the same order as those determined from temperature dependencies, or even less. It suggests that local kinetic segments located on globules formed by pressure are mostly surrounded by polymer monomers rather then by molecules of water.

Intrinsic Viscosity of Globules

Using eq. 9 it is possible to estimate intrinsic viscosity for post-transition states. The results of this analysis are represented within Table 1. The values of $[\eta]$ were estimated as from τ_{obs} , as from correlation times reduced to the viscosity of water equal to 1, $\tau_{obs}\eta = 1$.

It can be seen that $[\eta]$ values characterising globules formed within temperature induced transitions at atmospheric pressure are of 6 cm^3/g for low molecular weight sample and of 5 cm^3/g for high molecular weight sample. They are closed to values of intrinsic viscosity reported for natural proteins[24], forming rigid compact spherical particles. Rather more loosened globules characterising by $[\eta]$ values of 6–7 cm^3/g are obtained by pressurising polymer solutions at low temperatures. And relatively high $[\eta]$ values of 14–18 cm^3/g were obtained for compact structures formed at high pressure and high temperature conditions. These values suggest that PNIPMAM polymers form either very asymmetrical particles, or very solvated, irregularly twisted particles at these conditions. In all cases values of intrinsic viscosity are lower for high molecular weight sample, which indicates that it is able to collapse into more compact structures rather then low molecular weight polymer.

Conclusion

Time-resolved optical spectroscopy has been employed to study coil-globule transitions monitored by the local segmental dynamics of anthracene labelled poly (*N*-isopropymethacrylamide), PNIPMAM as a function of pressure (0.1 MPa–200 MPa) over a temperature range of 283 K to 333 K. The positions of temperature-induced transition were observed to be independent on molecular weight of polymer at low pressures. The positions of pressure-induced transition were observed to be dependent on molecular weight of polymer at temperatures below LCST at atmospheric pressure. Double globule-coil-globule transition was observed to occur with pressure increasing at temperatures nearly above LCST. All these results along with values of intrinsic viscosity evaluated from values of correlation times measured for globules formed at different pressure/temperature conditions suggest the different mechanisms of compactisation governed by pressure and temperature and, correspondently, different types of final structures. At low pressures with temperature increasing the compact, well-packed globules are forming via initial interactions between neighboring parts of polymer chain and further collapse. Relatively loosened particles are forming with pressurizing at low temperatures. Interaction between remote along the chain units takes part from the first stage of globulesation. And finally, rather solvated and irregularly twisted

Table 1.
The intrinsic viscosities $[\eta]$ determined from eq. 9 using unreduced and reduced to $\eta = 1$ mPa.s values of correlation time.

Temperature, K	Pressure, MPa	$M = 50000$		$M = 140000$	
		$[\eta]$ from τ_{obs}, cm^3/g	$[\eta]$ from $\tau_{obs}{}^{\eta=1}$, cm^3/g	$[\eta]$ from τ_{obs}, cm^3/g	$[\eta]$ from $\tau_{obs}{}^{\eta=1}$, cm^3/g
288	200	8.4	7.7	6.3	5.8
328	200	12.3	18.0	9.8	13.6
328	0.1	6.5	6.0	5.6	5.2

particles are forming at high pressure and high temperatures, i.e. at conditions, when both processes are involved.

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