

A PENTABLOCK POLYMER FORMING CORE-SHELL STRUCTURES

POLÍMEROS PENTABLOQUES QUE FORMAN ESTRUCTURAS "CORE-SHELL"

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In order to elucidate the interplay between hydrophobic and hydrophilic forces as well as electrostatic interactions for a polymer in an aqueous environment, we recently designed a new pentablock polymer, with the configuration ABCBA. This is a linear chain, where two hydrophobic blocks (B) have been attached to each side of a hydrophilic segment (C), and with negatively charged groups (A) at the ends of the chain. In this system there will be a competition between the attractive forces of the hydrophobic blocks, the repulsion between the charged groups, and the tendency for the hydrophilic group to maximize the interaction with the surrounding water. The polymer was made in two versions, with different lengths of the hydrophilic block, having 34 and 77 segments, respectively. We observed that the physical properties of the system are highly dependent on the length of this C block. A sharp and highly reproducible temperature-induced transition, related to changes in chain conformation, is seen at a temperature around 37 °C. The reason for this behavior, as well as the robustness of the transitions discussed.

Con el objetivo de dilucidar la relación entre las fuerzas hidrofóbicas e hidrofílicas, así como de las interacciones electrostáticas para un polímero en ambiente acuoso, hemos diseñado recientemente un nuevo polímero penta-bloque, con la configuración ABCBA. Se trata de una cadena lineal, donde se han unido dos bloques hidrofóbicos (B) a cada costado de un segmento hidrofílico (C), y que posee grupos cargados negativamente (A), en los extremos de la cadena. En este sistema hay una competencia entre las fuerzas atractivas de los bloques hidrofóbicos, la repulsión entre los grupos cargados, y la tendencia del grupo hidrofílico a maximizar la interacción con el agua circundante. El polímero se obtuvo en dos versiones, con diferentes longitudes del bloque hidrofílico de 34 y 77 segmentos, respectivamente. Las propiedades físicas del sistema dependen fuertemente de la longitud del bloque C. Se observa una fuerte transición inducida por temperatura altamente reproducible, alrededor de los 37 °C, relacionada a cambios en la conformación de la cadena. Se discute la causa de este comportamiento, así como la robustez de la mencionada transición.

PACS: Polymer solutions flow properties, 47.57.Ng; structure of polymer solutions, 61.25.he; preparation of polymers, 81.05.g

INTRODUCTION

A fascinating property of so-called amphiphilic block copolymers is their ability to self-assemble into micelles, vesicles, and gels of various morphologies. This can occur as a response to environmental stimuli, e.g. by incorporating temperature-responsive blocks [1]. The term amphiphilic here refers to the different properties represented by two distinct blocks along the same chain, here hydrophilic ("water-friendly") and hydrophobic ("water-unfriendly") blocks. These polymers belong to an important class of materials with a large number of applications, including drug delivery systems, adaptive lubricants, and "smart" surface coatings [2-7]. Most of the previous studies on water-soluble copolymers have been focused on diblock and triblock systems [8-14]. However, we have recently started working with copolymers with up to five well-defined blocks along the chain (pentablock polymer), which opens up for a more complex range of interactions and behaviors in the system.

We here look specifically at results obtained on a ABCBA pentablock copolymer with different lengths of the hydrophilic

C-block (cfr. Figure 1). It consists of one hydrophilic *poly(ethylene glycol)* block (PEG, block C), two thermo-sensitive *poly(-Nisopropylacrylamide)* blocks (PNIPAAm, block B), and an anionic *poly(4-styrenesulfonic acidsodium)* (PSSS, block A) block at both ends of the copolymer chain.

A B C B A
PSSS-*b*-PNIPAAm-*b*-PEG-*b*-PNIPAAm-*b*-PSSS

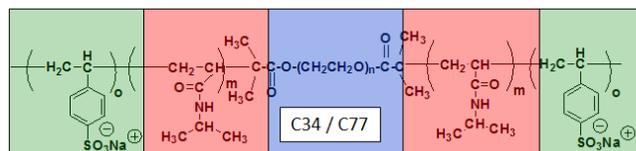


Figure 1: Schematics of the pentablock polymer used in this work. The color codes refer to hydrophobic (red), hydrophilic (blue), and charged groups (green). Here the repetition numbers for the A/B blocks are 12/63 (C34) and 14/65 (C77), respectively.

PNIPAAm is employed here since it is a highly sensitive thermoresponsive polymer that is able to associate and

contract above its so-called lower critical solution temperature (LCST) of ca. 32 °C, when being alone in solution [15]. The charged block at both ends of the chain are here introduced as an extra element of control in the system. It will amongst other factors ensure a high degree of solubility of the copolymer in water. Since the B-block becomes hydrophobic at a certain temperature, one may expect this block to combine with similar blocks from other chains and expel water, thus forming a nano-sized micellar structure.

It is of interest here to look at what kind of forces are expected to be present in this system. For polymer chains dissolved in water, there is usually a fine balance between several forces -all around or slightly higher than $k_B T$ - that determine the actual conformation of the chain. In the case of the polymer chain studied here, we expect there to be a contribution from hydrophobic forces (entropy change for water), hydrophilic (e.g. hydrogen bonds with water molecules), Coulombic (due to the charged end groups), as well as the contribution to entropy (positive ΔS) upon any liberation of counterions from the polymer. Thus a conformational change as that depicted schematically in Figure 2 may be induced by one of these contributions dominating slightly over the others for an individual segment (monomer), and being strongly amplified by the fact that the polymer chain contains a large number of segments.

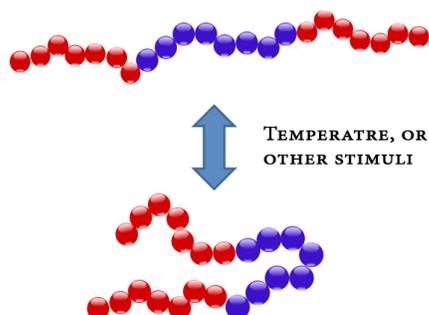


Figure 2. Simple schematics of conformational change for a polymer chain with hydrophobic (red) and hydrophilic (blue) segments.

This paper presents a summary of recent results obtained with this system, and will emphasize how the length of the PEG block has a large impact on the temperature-induced viscosity and structure of the polymer. We also discuss the reversibility and cyclability of this behavior. More background information on this system can be found in ref. [16].

RESULTS AND DISCUSSION

In order to elucidate the association behavior in polymer systems, measurement of turbidity can be very useful as an initial step. Figure 3 shows how an extremely abrupt transition is observed for this system at a temperature around 37 °C upon heating, for both chain lengths studied. The rise of the turbidity with increasing temperature indicates the formation of condensed structures, sufficiently large to scatter light. When the hydrophobic blocks of several chains interact and assemble, these will at elevated temperature contract strongly in order to avoid water exposure if there is a sufficient number

of hydrophobic segments present.

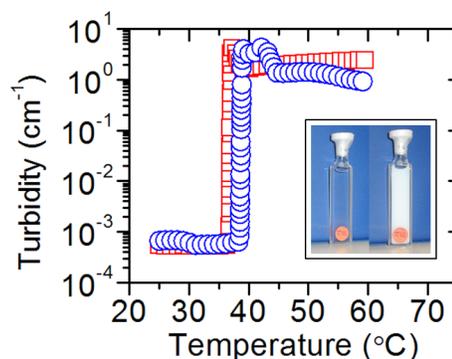


Figure 3. Change of turbidity vs. temperature for the C34 (red squares) and C77 (blue circles) system (4 wt.%). Inset: visual appearance at 25 °C and 50 °C for C34.

Also visual inspection of the system reveals that upon heating it becomes highly turbid (see inset Figure 3). Note that these changes were found to be fully reversible, thus the original character is regained upon cooling below the threshold. A series of new measurements, obtained after those presented in ref. [16] and during an extended period of several months, have shown that the heating/cooling process can be repeated nearly indefinitely without any observable loss in material properties. This behavior is actually not so common in soft-matter systems, where loss of reversibility and aggregation/ageing is seen very often. We believe that the main reason for this important property for the present system is the use of heavily charged end blocks, which stabilize the system and introduce a marked robustness in its behavior.

To gain further insight into this system, shear viscosity measurements were performed. A shear flow tends to bring polymer chains close to each other faster than from Brownian motion, thereby speeding up the assembly. This phenomenon is known as “orthokinetic” aggregation and it frequently appears in solutions or suspensions of sticky moieties at low shear rate. At high shear rate, on the other hand, the large association complexes are foreseen to break up under the influence of high shear stresses. The effects of temperature and shear rate on the viscosity of the system are illustrated in Figure 4. A much stronger temperature dependence of the viscosity is found for C77 than for C34, and an incipient shear rate effect is observed at high temperatures for C77, whereas no effect can be discerned for C34. This result clearly shows that interconnected and thus effectively larger species are formed in solutions of C77 at elevated temperatures, while only non-connected assemblies are formed in the C34 system. This interconnection between assemblies is provided by the long C-block. We may note here the dramatic viscosity increase (more than a factor 100) for the system with the longest central block upon a change in temperature. Also this change has now been found to be reproducible after long periods of repeated use.

We furthermore performed small-angle neutron scattering

(SANS) measurements on this system to gain insight about structural changes at the nanoscale. For both C34 and C77 we observe a dramatic change in the SANS pattern with increasing temperature. The low- q scattering increases more than a factor of ten, demonstrating that a significant structural reorganization takes place in the size regime probed by SANS. At 30 °C, i.e. below the threshold temperature, there is only weak scattering, as expected for a polymer that exists mainly as individual unfolded chains (unimers). We may here make use of the so-called Debye model [17] i.e. the form factor (P), developed for a flexible linear polymer chain in solution, where the scattering function is given by

$$P(x) = 2[e^{-x} + x - 1] / x^2, \quad \text{with } x = (qR_G)^2.$$

Here q is the scalar of scattering vector, $q = (4\pi / \lambda) \sin \theta$, where λ is the neutron wavelength and θ is the scattering angle.

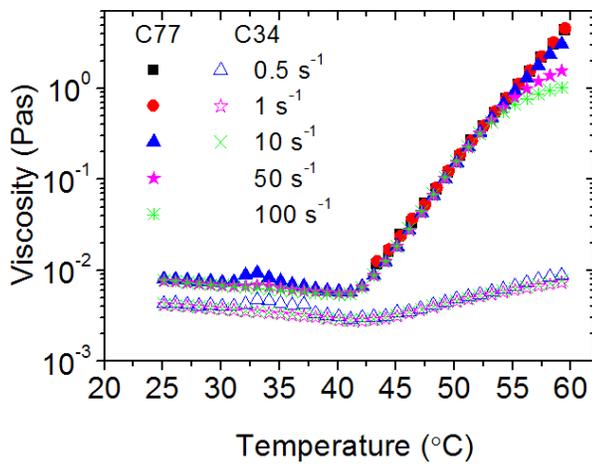


Figure 4. Viscosity dependence on temperature and shear rate, as well as on the length of the hydrophilic block for the two variants of the polymer chain.

This model results in a value for the radius of gyration (RG) of the unimer equal to 29 Å, or ca. 3 nm (the scattering from C34 and C77 at 30 °C cannot be distinguished in this respect). For the high temperature dataset the shape of the SANS data, including the suppression of the scattering at low q -values, encourages the use of a core-shell model [18] to fit the data. Due to the presence of charges it is necessary to include a Coulomb interaction in the model.

When using the core-shell form factor together with a screened Coulomb interaction potential [19] we obtain a good fit for the C77 polymer (as seen in Figure 5), giving an average core radius of 89 Å, and a shell thickness of 37 Å. This would correspond to an overall particle diameter of 252 Å, or ca. 25 nm. In this calculation we have employed the already known values of the D₂O scattering length density and the dielectric constant, i.e. $6.3 \times 10^{-6} \text{ Å}^{-2}$ and 78, respectively. For the short PEG-chain polymer (C34) the model fit shown in Figure 5 deviates from the data at the lowest q -values, most likely due to the existence of a population of larger particles whose size cannot be determined within this q -range.

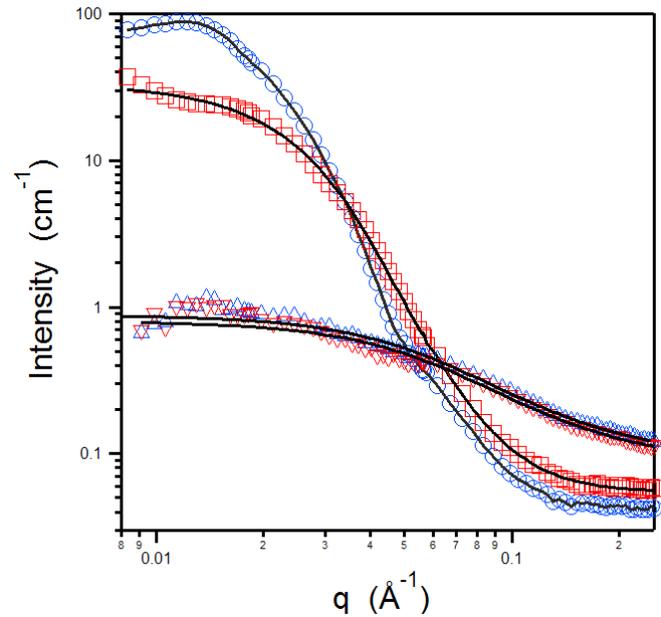


Figure 5. SANS patterns for C34 (red squares) and C77 (blue circles) at 50 °C and at 30 °C (triangles).

Overall, the SANS study shows clearly how these chains assemble to form core-shell particles upon a temperature increase above the transition, which was found to be at ca. 37 °C.

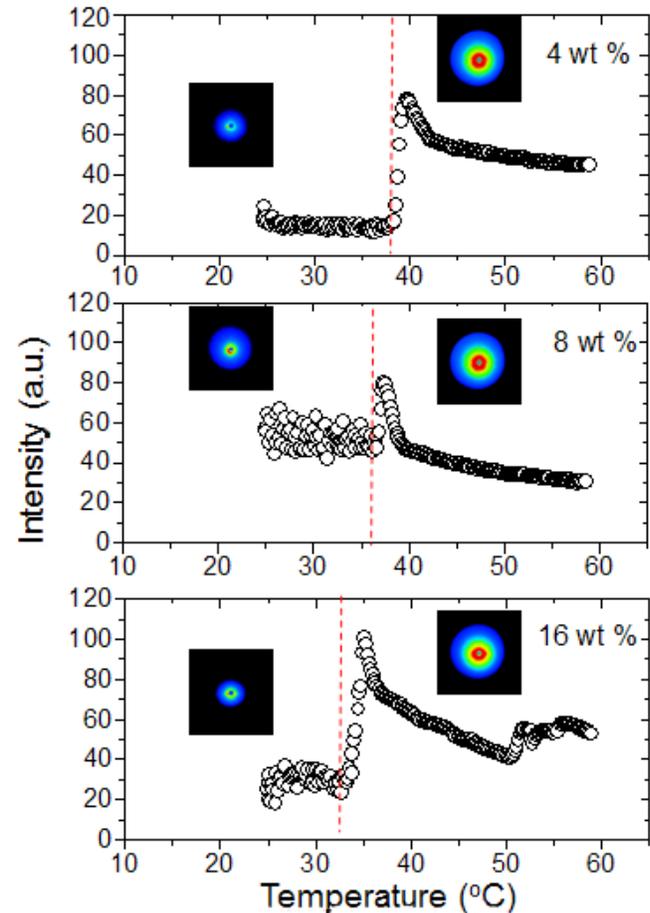


Figure 6: Small angle light-scattering (SALS) intensity vs. temperature for three different concentrations of the C34 system; 4, 8, and 16 wt.%. The insets show the 2D SALS patterns at low temperature and at the peak of the transition.

We have recently also studied the effect of polymer concentration on the behavior of this system. It is found that the transition temperature can be moved down in steps upon an increase in concentration. This is illustrated in Figure 6, where the change in light scattering intensity was used to probe the system through the transition region.

It can here be seen how the initial transition temperature just above 37 °C (4 wt.%) is shifted towards 35 °C and subsequently to 32 °C for the 8 and 16 wt.% systems, respectively. However, the increased concentration will also have strong influence on the polymer chain conformation and interaction between chains, effects that need further studies to be clarified in detail.

CONCLUSIONS

We have revisited our recent studies on thermoresponsive polymers, with a particular focus on a pentablock system (ABCBA). It is shown how a highly abrupt transition from extended chains to globular entities can be induced by proper combination of hydrophilic and hydrophobic elements. Repeated studies have shown that this behavior is not only fully reversible, but shows no signs of ageing even over extended periods of time. We have reason to believe that the incorporation of charged end groups is an important element in this respect. The well-defined changes observed in opacity together with the cyclability could be of interest in connection with e.g. adaptable surface layers without the need for external (e.g. electrical) connections.

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