

RESPONSIVE COPOLYMER MICROGEL MORPHOLOGY

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The Flory temperature-induced volume transition theory for responsive copolymer microgels in the approximation of homogeneous polymer network was developed and applied for the case of random copolymer of poly(vinylcaprolactam) (PVCL)-*co*-poly(N-isopropylacrilamide (PNIPAAm)). The most probable morphological parameters were selected from the hydrodynamic radius temperature dependence measured by photon correlation spectroscopy and Flory equation of state for each of the homopolymer microgels. Our approach relays on the morphology parameters measured independently for homopolymer microgels made from PVCL and PNIPAAm as components of the copolymer microgel.

Key words: Temperature-induced volume transition of microgels, Flory theory, Random copolymer microgel morphology.

1. INTRODUCTION

Responsive microgels which swell or deswell in response to specific environmental stimuli (i.e., pH, temperature, solute concentration, solvent composition, ionic strength, light, or electric field) are of technological interest as bioseparation matrices, bioreactors, superabsorbents, chemical sensors, and chemical transducers [1,2]. Special interest is focused on the microgels based on polymers, which have a lower critical solution temperature (LCST) near the temperature of the human body. The temperature-responsive nature of these polymers leads to a variety of biological applications. Microgels made from these polymers have been considered as drug delivery devices, materials for tissue engineering and materials for preventing surgical adhesion. Poly(N-isopropylacrilamide) (PNIPAAm) is the most widely studied microgel and has a LCST of 34 °C [3]. It is biocompatible and materials based on this polymer can be potentially used in biomedical applications.

In order to better exploit the technological promise of responsive materials, an improved understanding of the impact of the underlying morphologies on the gel swelling responses to various stimuli is required. Indeed, the ability to predict changes in the microgel particle size (and thus the water content and the pore size) according to the local microstructure and chemical composition of the microgel would facilitate the design and synthesis of optimized microgels for specific applications. Recently, Flory temperature-induced volume transition theory for homopolymer microgels [4] was generalized for the case of bimodal heterogeneous morphology [5,6]. The most probable morphological parameters were selected from the microscopic and thermodynamic constraints imposed by ¹H transverse relaxation NMR and Flory equation of state in the approximation of a homogeneous morphology.

In this work we are extending the Flory swelling/deswelling volume transition theory of microgels in the approximation of homogeneous crosslink distribution of the copolymer polymer network. As an example this approach was applied to characterize quantitatively the morphology of PVCL-PNIPAAm random copolymer microgels.

2. THEORY

The major assumption of the Flory-Rehner gel swelling theory [7] is that the free energy change on swelling consists of two contributions, the energy of mixing and the free energy of elastic deformation, which are assumed to be separable and additive, i.e.,

$$\Pi_{mix} = -\frac{N_A k_B T}{v_S} \left[\phi + \ln(1 - \phi) + \chi \phi^2 \right] \quad (1)$$

and

$$\Pi_{elastic} = \frac{N k_B T}{V_0} \left[\left(\frac{\phi}{2\phi_0} \right) - \left(\frac{\phi}{\phi_0} \right)^{1/3} \right]. \quad (2)$$

In the above equations N_A is the Avogadro number, k_B is the Boltzmann constant, $v_S = 1.81 \times 10^{-5} \text{ m}^3$ is the molar volume of D_2O , which is our solvent, χ is the Flory parameter, ϕ is the polymer volume fraction in the particle, N is the number of subchains in a microgel particle and $V_0 = 4\pi R_{H0}^3 / 3$.

The equilibrium is achieved when the total osmotic pressure is equal to zero, i.e.,

$$\Pi = \Pi_{mix} + \Pi_{elastic} = 0. \quad (3)$$

The Flory-Rehner state equation for homopolymer microgel in the homogeneous approximation is, as reported before [6],

$$T_{\Pi=0} = \frac{A\Theta\phi_0^2 \left(\frac{R_{H0}}{R_H} \right)^6}{\frac{v_S N}{N_A V_0} \left[\frac{1}{2} \left(\frac{R_{H0}}{R_H} \right)^3 - \left(\frac{R_{H0}}{R_H} \right) \right] - \phi_0 \left(\frac{R_{H0}}{R_H} \right)^3 - \ln \left(1 - \phi_0 \left(\frac{R_{H0}}{R_H} \right)^3 \right) + \left(A - \frac{1}{2} \right) \phi_0^2 \left(\frac{R_{H0}}{R_H} \right)^6 - \chi_1 \phi_0^3 \left(\frac{R_{H0}}{R_H} \right)^9}. \quad (4)$$

The parameter which accounts for the polymer-polymer and water-polymer interactions is the Flory parameter, χ , which is also responsible for the collapse of the microgel particle. This is why in order to account for the net interaction of copolymer and water solution, we have modified this parameter following the work of Oh and Bae [8] by separating the interaction into χ_{AC} of A -type segment and solvent C and χ_{BC} between B -type segment and solvent C .

We consider in the following that the system is a statistical copolymer of A and B monomers. We neglect the interaction between A and B segments, considering that their interaction with the solvent is predominant. Therefore, the copolymer interaction parameter has the following form,

$$\chi_{copol} = w\chi_{AC} + (1 - w)\chi_{BC}, \quad (5)$$

where

$$\chi_{XC} = \frac{1}{2} - A_{XC} \left(1 - \frac{\Theta_{XC}}{T} \right) + \phi \chi_{1XC}, \quad (6)$$

with $X = A$ or B , A_{XC} is the second virial coefficient and w is the mole fraction of the A polymer which is 0.5 for both our systems in the investigated PVCL-PNIPAAm system. The Θ -temperatures of the polymer-solvent system are denoted by Θ_{XC} ; for $T = \Theta_{XC}$, $\chi_{XC} = 0.5$ and the second virial coefficient A_{XC} becomes zero.

For a microgel that swells isotropically, we can write,

$$\frac{\phi}{\phi_0} = \left(\frac{R_{H0}}{R_H} \right)^3, \quad (7)$$

where we choose R_H (R_{H0}) and ϕ (ϕ_0) as the particle size and volume fraction in the swollen (deswollen) state.

The temperature dependence of the microgel size is accounted for through the temperature dependence of χ . By introducing Eqs. (5) and (7) into Eq. (4), we obtain an explicit equation of state relating the temperature with the hydrodynamic radius R_H for the copolymer microgel in the homogeneous approximation, i.e.,

$$T_{H=0} = \frac{\phi_0^2 \left(\frac{R_{H0}}{R_H} \right)^6 [wA_{AC}\Theta_{AC} + (1-w)A_{BC}\Theta_{BC}]}{\frac{v_s N}{N_A V_0} \left[\frac{1}{2} \left(\frac{R_{H0}}{R_H} \right)^3 - \left(\frac{R_{H0}}{R_H} \right) - \phi_0 \left(\frac{R_{H0}}{R_H} \right)^3 - \ln \left(1 - \phi_0 \left(\frac{R_{H0}}{R_H} \right)^3 \right) + \left[wA_{AC} + (1-w)A_{BC} - \frac{1}{2} \right] \phi_0^2 \left(\frac{R_{H0}}{R_H} \right)^6 - [w\chi_{AC} + (1-w)\chi_{BC}] \phi_0^3 \left(\frac{R_{H0}}{R_H} \right)^9}. \quad (8)$$

For a microgel made of a homopolymer, i.e., $\chi_{AC} = \chi_{BC}$ and $w = 1$, Eq. (8) becomes Eq. (4) for homopolymer microgel.

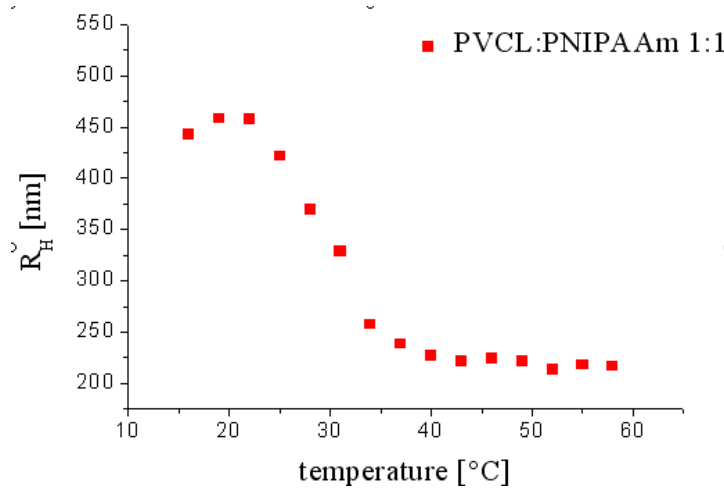


Fig. 1a – Hydrodynamic radius measured by photon correlation spectroscopy of copolymer microgel PVCL-PNIPAAm 1:1 versus temperature.

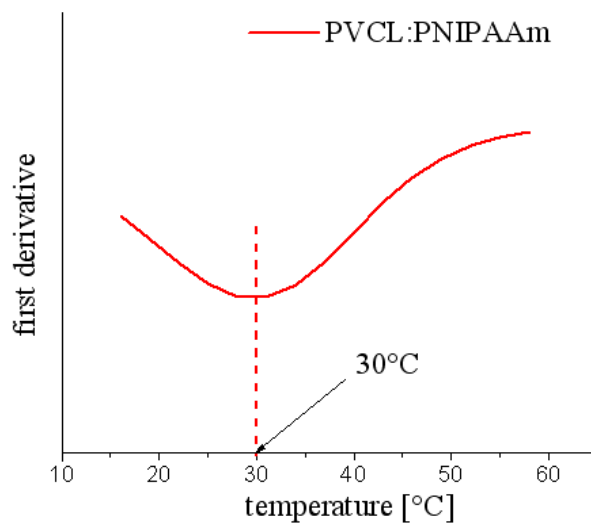


Fig. 1b – First-order derivatives of the volume size-temperature curve (Fig. 1a) showing the volume transition temperature.

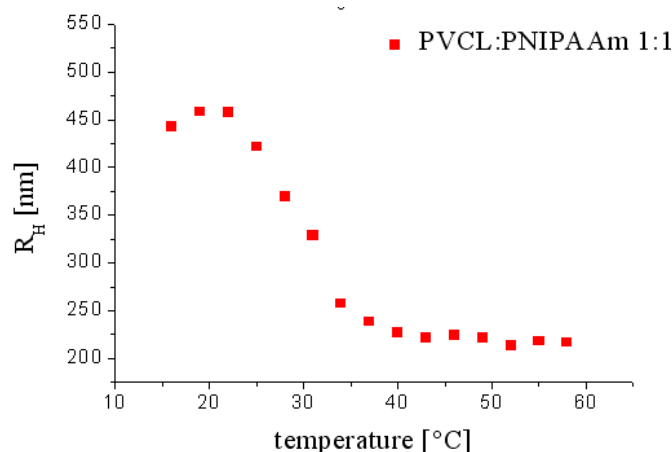


Fig. 2 – Size-temperature data from DLS for PVCL and PNIPAAm homopolymer microgels fitted with equation of state (Eq. 4) in the homogeneous morphology approximation (solid line).

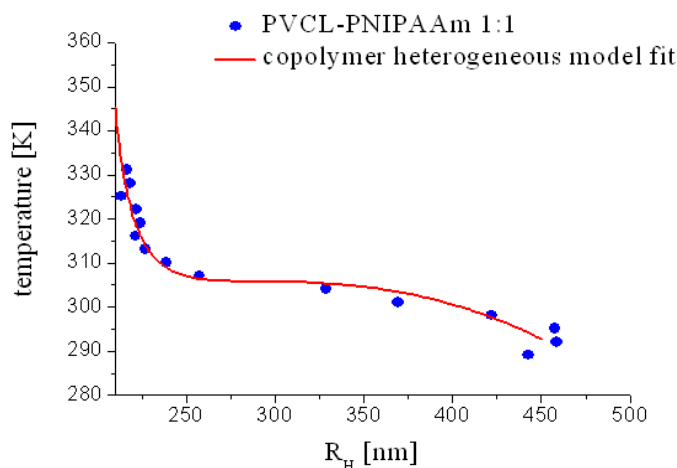


Fig. 3 – Size-temperature data from DLS for copolymer microgel PVCL-PNIPAAm 1:1 fitted with equation of state (Eq. 8) in the homogeneous morphology approximation (solid lines).

3. RESULTS AND DISCUSSION

3.1. Temperature-Induced Volume Transition by Dynamic Light Scattering

Microgels made from the homopolymers PVCL and PNIPAAm as well as copolymer PVCL-PNIPAAm with the molar ratio of 1:1 were prepared based on the procedure described in Ref. [5,6]. The temperature dependence of the hydrodynamic radius was measured using dynamic light scattering (DLS). Figure 1a shows the temperature-dependent swelling of the PVCL-PNIPAAm copolymer microgel that has a volume transition temperature of ~ 30 °C as can be seen from the first-order derivatives of the temperature transition curves (Fig. 1b). Homopolymer microgels made of PVCL and PNIPAAm as individual components of the copolymer microgel have volume transition temperatures at about 32 and 34°C, respectively (*vide infra*).

3.2. Microgel Structural Parameters for Homopolymer Microgels Using the Homogeneous Flory model

We have used the homopolymer microgel systems of each component, i.e., PVCL and PNIPAAm in order to obtain the temperature transition parameters that we will need for the copolymer systems

investigation. We have fitted the DLS temperature-transition data with the Flory equation of state for homopolymer microgels Eq. 4 (see Fig. 2). Since the volume fraction in the deswollen state ϕ_0 for these polymeric microgels is unknown, we performed different fits for different values of ϕ_0 in the range 0.2-0.9, leaving N , A , Θ and χ_1 as free parameters. In order to choose the best set of values, we can compare these results with independent values of the microgel parameters. For instance, we can estimate the number of subchains in the microgel particle by considering that each crosslink molecule connects two subchains. As a result $N = 2N_A V_0 c$, with c the molar concentration of the crosslinker used in the synthesis process. The parameter set that agrees best with this assumption are shown in Table 1 for the two homopolymer microgels. Figure 2 also shows the homogeneous model (Eq. 4) best fits of the DLS data for PVCL and PNIPAAm microgels.

Table 1

Results from the size-temperature fit by the homogeneous Flory theory morphology approximation for PVCL and PNIPAAm homopolymer microgels

	PVCL	PNIPAAm
ϕ_0	0.75	0.9
N	9.64×10^5	1.86×10^5
Θ	307.23	318.05
A	-2.45	-5.42
χ_1	0.48	1.00

3.3. Morphology Characterization of Copolymer Microgels Using the Flory Swelling Theory

After having determined the parameters for the homopolymer systems we can investigate the copolymer microgel morphology using Flory equation of state in the uniform cross-link distribution approximation. To this purpose we use Eq. (8) to fit the data obtained by dynamic light scattering with the purpose of finding relevant microgel structural parameters (Fig. 3). Moreover, some of the microgel parameters obtained above for the homopolymer were useful for calculating the structural parameters for the copolymer network morphology. For instance, we use in a good approximation the quantities A , Θ and χ_1 determined before for each homopolymer system (PVCL and PNIPAAm) for determining the structural parameters of the copolymer system. Hence, the morphological parameters for the copolymer PVCL-PNIPAAm 1:1 microgel are shown in Table 2.

Table 2

Results for the size-temperature fit for the copolymer system, considering the best-fit results of the homogeneous model

	PVCL-PNIPAAm 1:1
ϕ_0	0.88
N	1.81×10^7

It is important to notice that microgel systems experience different deswelling degree of the original size. The deswelling degree can be defined by the ratio of the hydrodynamic radius at 25°C with the collapsed microgel particle size at 60°C. This quantity takes the values of 1.36, 0.42, and 2.04 for PVCL, PNIPAAm, and PVCL-PNIPAAm 1:1 microgels, respectively. The behaviour of PVCL and PVCL-PNIPAAm 1:1 microgels is similar and different from that of PNIPAAm microgel. This fact can be explained by the fact that the Flory interaction parameter between polymer chains and solvent for PVCL and PVCL-PNIPAAm 1:1 are similar. This can be easily seen from the data of Table 1 and Eqs. (5) and (6).

In this paper, the swelling theory of microgel in the approximation of homogeneous morphology was generalized for the case of copolymer networks. The most probable values for the microgel morphology parameters, i.e., ϕ_0 , N , θ , A , and χ_1 for the case of PVCL-PNIPAm 1:1 system were established using (i) the size-temperature dependence measured using photon correlation spectroscopy, and (ii) the morphology parameters for homopolymer PVCL and PNIPAm microgels. The number of subchains N for the copolymer microgel is much larger compared to the homopolymer microgels that probably shows that the assumption of a homogeneous morphology is a crude approximation. Generalization of Flory theory for the case of heterogeneous morphology of responsive microgels made from copolymers will be published elsewhere. In this case the crosslink density is different in the core and corona of microgel.

REFERENCES

1. A.Z. PICH, H.J.P. ADLER, *Composite aqueous microgels*, Polym. Intern., **56**, pp. 291–307, 2009.
2. B.R. SAUNDERS, N. LAAJAM, E. DALY, S. TEOW, X. HU, R. STEPTO, *Microgels: from responsive polymers colloids to biomaterials*, Adv. Colloid Interface Sci., **147–148**, pp. 251–262, 2009.
3. M. KARG, T. HELLWEG, *New “smart” poly(NIPAM) microgels and nanoparticle microgel hybrids: properties and advances in characterization*, Curr. Opin. Coll. Int. Sci., **14**, pp. 438-, 2009.
4. P.J. FLORY, *Principles of Polymer Chemistry*, Cornell University Press, London 1953.
5. S. SCHACHSCHAL, A. BALACEANU, C. MELIAN, D.E. DEMCO, T. ECKERT, W. RICHTERING, A. PICH, *Polyampholyte microgels with anionic core and cationic shell*, Macromolecules, **43**, pp. 4331–4339, 2010.
6. A. BALACEANU, D.E. DEMCO, M. MÖLLER, A. PICH, *Microgel heterogeneous morphology reflected in temperature-induced volume transition and 1H high-resolution transverse relaxation NMR. The case of poly(N-vinylcaprolactam) microgel*, Macromolecules, **44**, pp. 2161–2169, 2011.
7. P.J. FLORY, J. REHNER, *Statistical mechanics of cross-linked polymers networks*, J. Chem. Phys., **11**, pp. 521–527, 1943.
8. K.S. OH, Y.C. BAE, *Swelling behavior of submicron gel particles*, J. Appl. Polym. Sci., **69**, pp. 109–114, 1998.

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