Available online at www.sciencedirect.com
ScienceDirect
Materials Science and Engineering C 28 (2008) 811 – 815
MATERIALS SCIENCE & ENGINEERING C
www.elsevier.com/locate/msec

Structural transition of a homopolymer in solvents mixture

Moez Guettari *, Adel Aschi, Riadh Gomati, Abdelhafidh Gharbi

Laboratoire de Physique de la Matière Molle, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Tunisia

Abstract

The present work is aimed at studying the thermodynamic behaviour of a polymer in solvents mixture. Dynamic light scattering is used to measure the hydrodynamic radius of polyvinylpyrrolidone ($M_w = 360{,}000$ g/mol), in water/methanol solvents mixture, versus the mixed solvents composition at 25 °C. Then, we show that the polymer conformation adopts the Coil–Globule–Coil structure when the methanol molar fraction X_A is varied. This transition is attributed to solvent quality change which result from water and methanol complex formation. The polymer contraction rate calculated for each composition takes its maximum value at $X_A = 0.17$. Hildebrand theory assuming the solvents mixture as an equivalent solvent was used to analyze the change in mixed solvents quality. These changes can be attributed to dispersive forces in solvents mixture.

Keywords: Polymer solution; Hydrodynamic radius; Mixed solvents; Dynamic light scattering; Hildebrand

1. Introduction

The conformation of a synthetic or biological macromolecule depends on his intrinsic and extrinsic proprieties. The intrinsic proprieties are the results of chemical structure establishing inter and intra-monomers bonding like hydrogen-bonding, electrostatic interactions… On the other part, the extrinsic proprieties are governed by the macromolecules concentration and their interactions with solvent molecules. Other thermodynamic parameters like as temperature play an important role in the stability of the solution and macromolecular conformation. The relationship between such interactions and the physical or structural proprieties were well studied [1–3]. However, the behaviour of macromolecules in solvents mixture is not well understood although this topic is attractive in practical and fundamental domains [4–13]. The changes in extrinsic proprieties are governed by interactions between solvents molecules/polymer segments and between solvents molecules. By conductivity and viscosity measurements, Tong et al. [5] showed a transition of ionizable polymers from polyelectrolyte to ionomer type behaviour driven by mixed solvents polarity. By small-angle neutron scattering and swelling experiments, Naoki et al. [6] found that Poly(12-acryloyloxydodecanoic acid-co-acrylic acid) gels exhibit different swelling behaviours and disorganization processes of organized structures depending on the kind of mixed solvents (aqueous and organic solvent: proionic acid/1-propanol). Gateau et al. [9] have modified the colloidal structure of asphaltene by adding a polar solvent to toluene. By density measurements, Smith [12] studied protein volume changes on cosolvent denaturation. Keshmirizadeh et al. [7] developed a theoretical approach based on hard sphere model to explain change on solvents mixture activity of a polymer solution. The polyvinylpyrrolidone (PVP) is a neutral polymer, which is soluble in water and organic solvents like methanol. On the other part, the water–methanol mixture properties, which were studied at 25 °C, display large deviations from ideal mixture behaviour [15,16]. Particularly, an excess of dielectric constant and dynamic viscosity with respect to ideal behaviour was disclosed. These phenomena are attributed to the strong dipolar interactions between water and alcohol molecules. In this work, we prospect the PVP behaviour in water–methanol mixture by using dynamic light scattering. Indeed, we study the variation of the macromolecules hydrodynamic radius versus the methanol molar fraction X_A. Then we deduce from the experimental

---

* Corresponding author. Fax: +216 71 885 073.
E-mail address: gtarimoez@yahoo.fr (M. Guettari).

0928-4931/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.msec.2007.10.025

results the kind of interactions between solvents molecules and polymer segments. Finally, we calculate the mixed solvents polymer interaction parameter by using Hildebrand theory.

2. Theoretical background

According to thermodynamic analysis, the polymer solution properties are described by the Flory–Huggins theory. Based on lattice model, the free energy of mixing polymer and solvent is expressed for neutral polymer as [17]:

$$\frac{\Delta G_{\mathrm{m}}}{k_{\mathrm{B}}T} = n_{\mathrm{p}}\ln\phi + n_{\mathrm{s}}\ln(1-\phi) + \chi_{\mathrm{ps}}n_{\mathrm{s}}\phi \tag{1}$$

where ϕ, n_{p} and n_{s} are respectively the volume fraction of polymer in solution, number of polymer molecules and number of solvent molecules. χ_{ps} represents the polymer solvent interaction, it is a dimensionless free-energy parameter that contains both entropy and enthalpy terms:

$$\chi_{\mathrm{ps}} = \chi_{\mathrm{S}} + \chi_{\mathrm{H}} \tag{2}$$

where χ_{S} and χ_{H} are respectively the entropic and enthalpy contribution in polymer solvent interaction parameter. Solvent quality and polymer conformation depend on the interaction parameter value. Thus, a low value of χ_{ps} ($\chi_{\mathrm{ps}}<0.5$) means a good solvent in which the polymer takes a coil conformation. When $\chi_{\mathrm{ps}}=0.5$, interactions polymer/solvent molecules disappear, in this case polymer can be described like an ideal chain, it is the theta state. The last case ($\chi_{\mathrm{ps}}>0.5$) corresponds to poor solvent where the polymer takes a globular conformation (it may not be soluble in such a case). The enthalpy contribution to polymer solvent interaction parameter can be expressed by the following equation:

$$\chi_{\mathrm{H}} = \left(\frac{V_{\mathrm{s}}}{RT}\right)A_{\mathrm{sp}} \tag{3}$$

where V_{s} is the molar volume of the solvent, (cm^3 mol^{-1}), R is the universal gas constant, (cal mol^{-1} K^{-1}), T is the temperature (K), A_{sp} is a term depending on the solubility parameters of the solvent and the polymer respectively: δ_{s} and δ_{p} (cal/cm^3)$^{1/2}$. For non-polar system A_{sp} takes the form [22]:

$$A_{\mathrm{sp}} = \left(\delta_{\mathrm{s}} - \delta_{\mathrm{p}}\right)^2 \tag{4}$$

According to Hildebrand and Scott theory [18], the solubility parameter δ of a substance, which is a measure of molecular interaction, is defined by the relation:

$$\delta = \left(\frac{\Delta E_{\mathrm{LV}}}{V_{\mathrm{M}}}\right)^{\frac{1}{2}} \tag{5}$$

where ΔE_{LV} is the molar energy of vaporization per cm^3 and V_{M} is the molar volume of substance. Hansen et al. [23] assume the solubility parameter δ to result from three contributions: δ_{d}, δ_{p} and δ_{h} which are related respectively to the dispersive, polar and hydrogen-bonding interactions, so as these parameters verify the relationship:

$$\delta^2 = \delta_{\mathrm{d}}^2 + \delta_{\mathrm{p}}^2 + \delta_{\mathrm{h}}^2 \tag{6}$$

In the cases of water and methanol solvents, these parameters take the values indicated in the following table (Table 1):

Table 1
Hansen parameters of water and methanol at 25 °C [14]

Substance (M Pa$^{1/2}$)	Water	Methanol
δ_{d}	15.5	15.1
δ_{p}	16	12.3
δ_{h}	42.4	22.3
δ	47.9	29.7

If both solvent molecules and polymer segments interact, A_{sp} is defined using the two-composition solubility parameters [19]:

$$A_{sp} = \left(\delta_{\mathrm{sd}} - \delta_{\mathrm{pd}}\right)^2 + \left(\delta_{\mathrm{sp}} - \delta_{\mathrm{pp}}\right)^2 \tag{7}$$

δ_{sd}, δ_{pd}, δ_{sp}, and δ_{pp} are respectively the dispersion (subscript d) and polar (subscript p) parts of solubility parameter of solvent (subscript s) and polymer (subscript p). On the other hand, the solubility parameter of solvents mixture δ_{sm} can be calculated from the parameter of each solvent noted by 1 and 2 by the following equation [19]:

$$\delta_{\mathrm{sm}} = \delta_{\mathrm{s1}}\phi_{\mathrm{s1}} + \delta_{\mathrm{s2}}\phi_{\mathrm{s2}} \tag{8}$$

where δ_{sm} is the Hansen parameter of mixture (dispersion, polar or hydrogen-bonding part), δ_{s1} and δ_{s2} are the Hansen parameter of the pure solvent noted by 1 and 2, ϕ_{s1} and ϕ_{s2} are the volume fraction of solvent 1 and 2 in the mixture. The molar volume of the mixture V_{sm} is calculated by the following equation:

$$V_{\mathrm{sm}} = \frac{V_{\mathrm{s1}}V_{\mathrm{s2}}}{V_{\mathrm{s1}}\phi_{\mathrm{s1}} + V_{\mathrm{s2}}\phi_{\mathrm{s2}}} \tag{9}$$

Where V_{s1} and V_{s2} are the volume molar of solvent 1 and 2. The volume fraction of solvent 1 is calculated from the molar fraction X_{s1} in the mixture:

$$\phi_{\mathrm{s1}} = \frac{\left(\frac{\rho_{\mathrm{sm}}}{\rho_{\mathrm{s1}}}\right)}{1 + \frac{(1-X_{\mathrm{s1}})M_{\mathrm{s2}}}{X_{\mathrm{s1}}M_{\mathrm{s1}}}} \tag{10}$$

where ρ_{s1} and ρ_{sm} are respectively solvent and solvents mixture density, $M_{\mathrm{s1(2)}}$ is the solvent 1(2) molar mass. The volume fraction of solvent 2 is calculated by using the equation:

$$\phi_{s2} = 1 - \phi_{s1} \tag{11}$$

By combining Eqs. (3–11), the Flory parameter χ_{smp} describing the interaction between polymer and solvents mixture takes the form:

$$\chi_{\mathrm{smp}} = \left(\frac{V_{\mathrm{s1}}V_{\mathrm{s2}}}{RT(V_{\mathrm{s1}}\phi_{\mathrm{s1}} + V_{\mathrm{s2}}\phi_{\mathrm{s2}})}\right)\left[\left(\delta_{\mathrm{smd}} - \delta_{\mathrm{pd}}\right)^2 + \left(\delta_{\mathrm{smp}} - \delta_{\mathrm{pp}}\right)^2\right] \tag{12}$$

This equation permits predicting quantitatively the solvents mixture quality at a given composition and fixed temperature. It depends on the physical proprieties of both solvents and polymer. The molar volume of a solvent $V_{\mathrm{s1(2)}}$ can be calculated from its molar mass $M_{\mathrm{s1(2)}}$ and density $\rho_{\mathrm{s1(2)}}$ by the following equation:

$$V_{\mathrm{s1(2)}} = \frac{M_{\mathrm{s1(2)}}}{\rho_{\mathrm{s1(2)}}} \tag{13}$$

In fact, this approach has been reported by Suh et al. [25], in the case of solvent/non-solvent mixture. Here, we adopt this