Solution Properties of Poly(2-ethylhexyl acrylate) in Theta-Solvents

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ABSTRACT

Unperturbed dimensions of poly(2-ethylhexyl acrylate) using direct measurements in theta-solvents and graphical procedures for viscosity data in good solvents are determined. Calculated conformational parameters confirmed the flexible character of poly(2-ethylhexyl acrylate), having increased stiffness due to its long side chain.

Key Words: unperturbed dimensions, poly(2-ethylhexyl acrylate), conformational parameters, theta-solvents

INTRODUCTION

In a good solvent the dimensions of polymer coils are extended by interactions with the solvent. In order to evaluate the unperturbed dimensions, these interactions operating between the polymer chain and the solvent have to be eliminated. This may be done in two ways:

–determination of the unperturbed parameters in a theta-solvent (under theta-conditions these interactions are cancelled).

–determination of some perturbed parameters and extrapolation of their values to the unperturbed state using some of the existing theories.

Comparatively little work [1–4] has been done on poly(2-ethylhexyl acrylate) solutions, especially at the theta-conditions, where according to our knowledge direct measurements in theta-solvents are still missing. Recently Bohdanecký and Netopilík [5], when analyzing observed anomalies in characterizing the theta-state of flexible macromolecules with long alkyl side groups, have recommended methods for unperturbed dimensions determination which are more sensitive than the simple logarithmic plot of intrinsic viscosity [η] vs. molecular weight [M], and also they are based on theories which take into account different factors (long-chain branching, chain thickness and excluded volume) affecting the hydrodynamic properties. In the present contribution the unperturbed dimensions of poly(2-ethylhexyl acrylate) have been determined in theta-solvents and the effect of side chain length on solution properties, using these methods, is discussed.

EXPERIMENTAL

Linear samples of poly(2-ethylhexyl acrylate) were prepared by solution polymerization at 12 °C. The obtained fractions were characterized by methods of light scattering, osmometry and viscometry.

The details of the methods employed are followed as in previous published report [4]. The
theta-temperature for the case of single theta-solvent was established from the temperature dependence of the second virial coefficient, $A_2$, as a temperature where $A_2=0$.

The composition of the theta-solvent mixture was determined by the Elias titration method to the first cloud point and by extrapolation of their concentration dependence to pure polymer [6].

**RESULTS AND DISCUSSION**

**Measurements in Theta-Solvents**

According to the solubility tests n-alcohols and higher ketones acted as theta-solvents for the studied polymer. As a single theta-solvent n-propanol at $\theta_{A_2=0}=32.5 \, ^\circ\text{C}$ was applied. The determined composition of the theta-mixture butanone/isopropanol at 25 $^\circ\text{C}$ was 25/75 by volume.

For random polymer coils in the non-draining regime, the intrinsic viscosity $[\eta]$ under theta-conditions should be proportional to the square root of the molecular weight.

$$[\eta] = K_0 M^{1/2} \quad (1)$$

$$K_0 = \phi (\bar{R}_0^2 / M)_x^{3/2} \quad (2)$$

where $\phi$ is the Flory viscosity constant ($\phi=2.6 \times 10^{21}$ if the intrinsic viscosity is expressed in deciliters per gram).

The ratio of the unperturbed mean square end to end distance, $\bar{R}_0^2$, and the molecular weight in the random coil limit, $(\bar{R}_0^2 / M)_x$, is related to the Kuhn statistical segment length by the equation:

$$l_k = M_c (\bar{R}_0^2 / M)_x \quad (3)$$

where $M_c$ is the mean molecular weight per unit contour length and for polymer studied in this paper:

$$M_c = (m_0/2.5) \times 10^6 \, \text{cm}^{-1} \quad (4)$$

where $m_0$ is the molecular weight of the monomeric unit.

The proportionality of $[\eta]$ to $M^{1/2}$ is frequently used as a criterion of theta-conditions since it is easier experimentally to apply than any other.

The results of the viscometric measurements in both theta-systems are summarized in Table 1. The data in Table 1 give the following Mark-Houwink-Sakurada relations based on refs [4] and [5].

<table>
<thead>
<tr>
<th>$M_n \times 10^{-6}$</th>
<th>n-propanol</th>
<th>butanone/isopropanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.15</td>
<td>1.61</td>
<td>1.66</td>
</tr>
<tr>
<td>3.18</td>
<td>1.27</td>
<td>1.30</td>
</tr>
<tr>
<td>2.70</td>
<td>1.17</td>
<td>1.20</td>
</tr>
<tr>
<td>1.96</td>
<td>0.99</td>
<td>1.00</td>
</tr>
<tr>
<td>0.85</td>
<td>0.66</td>
<td>0.67</td>
</tr>
</tbody>
</table>

which confirm that both systems are very close to theta-conditions and after applying the proportionality of $[\eta]$ to $M^{1/2}$ the criterion $K_0=7.2 \times 10^{-4}$, valid for both studied theta-systems, is obtained.

The anomalies observed for some polyacrylates with long side groups (n-dodecyl, n-cetyl), where for $A_2=0$, the exponent of Mark-Houwink-Sakurada equation differs from 0.5 [7, 8], are not found for the studied macromolecules, suggesting that the critical side chain length in observing such anomalies should exist.

**Measurements in Good Solvents**

Bohdačeký and Netopilík [5] in their analysis of anomalies observed for some polymers, with long side groups, have employed three different
methods of plotting intrinsic viscosity data. Two of them result from the theory of the worm-like chain model, where according to recent theories of intrinsic viscosity based on this model [9, 10] the exponent in Mark-Houwink-Sakurada equation should be constant over a broad range of chain lengths, and equal to 1/2 only if reduced chain diameter, d_r (i.e. the ratio of the chain diameter, d, and the Kuhn segment length, l_K), is close to 0.4.

As poly(2-ethylhexyl acrylate) macromolecules do not exhibit the dependence of their solution properties on chain thickness for the determination of the unperturbed dimensions we have applied only the third method i.e., Burchard-Stockmayer-Fixman plot, based on the following equation [11, 12].

$$[\eta]/M^{1/2} = K_0 + c_p BM^{1/2}$$

(5)

where $c_p$ is a numerical and B is a characteristic of the polymer-solvent interaction.

This method has been proposed to eliminate the excluded volume effect by extrapolating the intrinsic viscosity data to $M^{1/2}=0$. The existence of a minimum in this plot at low values of M indicates $d_r > 0.4$. On the contrary, plateaux and/or maxima at high molecular weights are indication of long-chain branching.

The application of this method to the viscosity data in good solvents [4] is shown in Figure 1. The linear character of the presented dependencies in Figure 1 is indicative of an excluded volume effect, and influences of long-chain branching and chain thickness are absent. The unperturbed dimensions of poly(2-ethylhexyl acrylate) are practically independent of the solvents used and the obtained value, $K_0 = 7.3 \times 10^{-4}$, is very close to the value determined in theta-systems, as well with value obtained by Penzel and Goetz [2] by applying the same procedure for their THF solutions.

The conformational parameters $l_K$ and $C_w$ are computed from the $K_0$ values by means of Equations (2), (3) and (6).

$$C_w = (R_0^2 / M)_w m_y/2 l_b^2$$

(6)

where $C_w$ is the characteristic ratio (in the random coil limit), $l_b = 1.5 \times 10^{-8}$ cm is the length of the main-chain C-C bond.

The obtained values $C_w = 17.5$ and $l_b = 31 \times 10^{-8}$ cm confirm, that poly(2-ethylhexyl acrylate) macromolecules are typical flexible polymers with increased stiffness due to their relatively long side chain.

CONCLUSION

To determine the unperturbed dimensions of poly(2-ethylhexyl acrylate), the direct measurements in theta-solvents and graphical procedures for viscosity data in good solvents are employed. But as the dimensions of polymer coils are extended by interactions with the solvent, these interactions operating between the polymer chain and the solvent are eliminated.

The method adopted for studying poly(2-ethylhexyl acrylate) is through the determination of unperturbed dimensions in theta-conditions where so far direct measurements in theta-solvents have not been reported.
REFERENCES