Original Contributions

Halogenated poly-(N-vinylcarbazoles): flexibility and viscometric constants

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Abstract: N-vinylcarbazole, 3-Cl-N-vinylcarbazole, and 3-Br-N-vinylcarbazole were homopolymerized via radical polymerization. Several monodispersed samples of respective polymers were obtained by fractionation and their intrinsic viscosities were measured in tetrahydrofurane at 25 °C. The viscometric constants K and a, the monomeric unit projection length b, and the flexibility parameter λ were determined using the gel permeation chromatography technique to determine the elution volume Ve and apply a newly derived relationship between the flexibility parameter and molecular weight. The presence of halogen atoms in the carbazole group of PNVC varies the value of b and, consequently, the rigidity of the polymer.

Key words: 3-Cl-N-vinylcarbazole; 3-Br-N-vinylcarbazole; monomeric unit projection length; viscometric constants

1 Introduction

The flexibility of a polymer is established by the value of the parameter $\lambda = q/h$, where q is the persistence length and h the monomeric unit projection length, which can be determined by conformational analysis or using techniques capable to give information about chain polymer dimensions [1].

In the present paper, we deal with the deduction of h by means of the gel permeation chromatography (GPC) technique. For that aim, we will only use the elution volume value of the pic of the chromatogram obtained for each fraction. Samples shall fit the requirements of being monodispersed and fulfilling the universal calibration method [2]; their intrinsic viscosities must be measured under the same conditions as in the GPC experiments.

2 Experimental

Poly-N-vinylcarbazole (PNVC), poly-3Cl-N-vinylcarbazole (PNVC-Cl), and poly-3Br-N-vinylcarbazole (PNVC-Br) were synthesized via radical polymerization [3] and fractionated in a benzene-methanol solution at 25 °C following the fractionated precipitation method.

A column set of pore size 500, 10^3, 10^4, 10^5, and 10^6 Å was established in a Waters-GPC Model 150 LC to obtain the elution volume Ve for each monodispersed fraction in tetrahydrofurane (THF) at 25 °C. The calibration curve for this column set was obtained by elution of seven polystyrene standards.

The intrinsic viscosities [η] were measured in a Ubbelohde-type capillary viscometer in tetrahydrofurane (THF) at 25 °C. To assure the required accuracy, measurements were conducted in a constant temperature bath regulated within ± 0.02 °C. Corrections for kinetic energy were taken into account. The resulting [η] and Ve values are listed in Table 1.

3 Results and discussion

Using values of the Mark-Houwink-Sakurada (MHS) constants ($K = 1.60 \times 10^{-4}$ and $a = 0.70$) for PS [2] in THF at 25 °C, the resulting universal calibration curve was

$$\log([\eta] M) = 15.725 - 0.307 Ve.$$  (1)
Table 1. Data obtained from viscometry and GPC techniques

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(Ve)</th>
<th>([\eta])</th>
<th>(M)</th>
<th>(\lambda)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNVC-FR1</td>
<td>34.54</td>
<td>0.533</td>
<td>2.54 x 10^5</td>
<td>5.98</td>
</tr>
<tr>
<td>PNVC-FR2</td>
<td>35.29</td>
<td>0.440</td>
<td>1.81</td>
<td>5.75</td>
</tr>
<tr>
<td>PNVC-FR3</td>
<td>35.89</td>
<td>0.381</td>
<td>1.37</td>
<td>5.57</td>
</tr>
<tr>
<td>PNVC-FR4</td>
<td>36.43</td>
<td>0.317</td>
<td>1.12</td>
<td>5.42</td>
</tr>
<tr>
<td>PNVC-FR5</td>
<td>36.98</td>
<td>0.262</td>
<td>9.29 x 10^4</td>
<td>5.27</td>
</tr>
<tr>
<td>PNVC-FR6</td>
<td>37.50</td>
<td>0.259</td>
<td>6.46</td>
<td>5.13</td>
</tr>
<tr>
<td>PNVC-FR7</td>
<td>38.51</td>
<td>0.205</td>
<td>4.00</td>
<td>4.87</td>
</tr>
<tr>
<td>PNVC-FR8</td>
<td>40.14</td>
<td>0.157</td>
<td>1.65</td>
<td>4.47</td>
</tr>
<tr>
<td>PNVC-FR9</td>
<td>41.91</td>
<td>0.092</td>
<td>8.07 x 10^3</td>
<td>4.08</td>
</tr>
</tbody>
</table>

The hydrodynamic volume \([\eta]/M\) is related to the radius of gyration \(r\) by

\[
\langle r^2 \rangle^{1/2} = \left( \frac{[\eta]M}{\phi_0} \right)^{1/3} .
\]  

(2)

Assuming that polymers adopt coiled conformation, \(r\) can be related to the flexibility parameter \(\lambda\) \([5]\) by

\[
\lambda = \frac{\langle r^2 \rangle M_0}{2b^2M} .
\]  

(3)

By introducing Eq. (2) into Eq. (3), we can write the \(\lambda\) parameter as function of the hydrodynamic volume as

\[
\lambda = \left( \frac{[\eta]M}{\phi_0} \right)^{2/3} \frac{M_0}{2b^2M} .
\]  

(4)

By substituting for PS both the monomeric molecular weight \(M_0\) and monomeric unit projection length \(b = 2.57\) Å \([6]\) in Eq. (4), as well the corresponding molecular weights \(M\) and intrinsic viscosities of each PS standard, \(\lambda\) values were determined, and a plot of \(\lambda\) values vs \(Ve\) led to the linear relationship

\[
\log \lambda = 1.554 - 0.023 Ve .
\]  

(5)

Equation (5) directly provides flexibility for any monodispersed polymer sample knowing its \(Ve\). In this way, Eq. (5) represents a particular calibration curve for any monodispersed sample kit in one column set at fixed conditions. When the column set is replaced, another standard sample is used or experimental conditions are modified. Again another single linear relationship between \(\log \lambda\) and \(Ve\) should be found. Anyway, the intercept and slope of this straight line only depend on instrumental factors.

Moreover, replacing \([\eta]\) by \(KM^a\) in Eq. (4) and applying logarithms, it becomes

\[
\log \lambda = \log \frac{M_0}{2b^2M} + \frac{2}{3} \log K + \frac{2a - 1}{3} \log M ,
\]  

(6)

where unknown parameters \(a\), \(K\), and \(b\) can be obtained according to Eq. (6) by plotting \(\log \lambda\) vs \(\log M\) and \(\lambda\) can be obtained from Eqs. (1) and (5) respectively, whether \(Ve\) and \([\eta]\) have previously been determined. \(\phi_0\) is Flory's constant.

Now we will check the above with PNVC, PNVC-C1, and PNVC-Br. \(Ve\), \([\eta]\), \(M\), and \(\lambda\) values are listed in Table 1. Plotting \(\log \lambda\) vs \(\log M\) according to Eq. (6), a straight line for each polymer was obtained (Figs. 1-3). Derived values of \(a\), \(K\), and \(b\) for respective polymers are listed in Table 2.

Regarding these results, it could occur that a halogen atom linked to the aromatic structure of the repeated unit contributes increasing polymer rigidity, which in this case is not significantly manifested on \(a\) and \(K\) values; however, \(b\)-values are actually different. For this reason, the three different straight lines are closed, but they cannot be interpreted overlapped or offset from a mean value.

The values of \(a\), \(K\), and \(b\) obtained for PNVC are in good agreement with bibliographic data.

Table 2. Values of \(a\), \(K\), and \(b\) obtained by applying Eq. (6) to data of \(M\) and \(\lambda\) for PNVC, PNVC-C1, and PNVC-Br

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(a)</th>
<th>(K \times 10^4) (cm³/g)</th>
<th>(b) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PNVC</td>
<td>0.66</td>
<td>1.24</td>
<td>2.77</td>
</tr>
<tr>
<td>PNVC-C1</td>
<td>0.66</td>
<td>1.22</td>
<td>3.01</td>
</tr>
<tr>
<td>PNVC-Br</td>
<td>0.67</td>
<td>0.90</td>
<td>3.05</td>
</tr>
</tbody>
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