Dipole Structure and Electrooptical Properties of Poly-N-vinylpyrrolidone in Nonaqueous Solvents

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Abstract—Electrooptical Kerr effect and dielectric polarization were studied for poly-N-vinylpyrrolidone solutions in chloroform and in mixed chloroform–CCl₄ solvent. The results were compared with those for an analogue of the monomeric unit of poly-N-vinylpyrrolidone, low-molecular-weight compound N-methylpyrrolidone.

Poly-N-vinylpyrrolidone (PVP) is one of the major synthetic polymers used in medicine and pharmacology; it exhibits extremely valuable properties. PVP is biologically inert, fairly stable thermally and chemically, nontoxic for living bodies, and capable of complexing with diverse compounds in aqueous media. This made PVP suitable for extensive use in production of drugs, medical preparations, and cosmetics [1].

\[-CH₂-CH⁻ \]

PVP

Studies of the properties of biologically active molecular complexes of PVP with fullerene C₆₀ [2] and PVP derivatives with covalently bound C₆₀ [3] revealed a very strong dependence of the electrooptical properties of these compounds on their composition and type of bonding between fullerene and PVP. However, there are no published data on specific features of the electrooptical behavior of PVP in solutions. Therefore, we studied the Kerr effect of PVP in nonaqueous media. The solvents were chosen so as to eliminate the influence of aggregation phenomena and enable correlation of the molecular structure of PVP, which has been extensively studied by various methods [1], with the electrooptical properties of PVP and its derivatives.

In this study, we analyzed by the methods of electrooptical Kerr effect and dielectric polarization two PVP samples with different molecular weights (MWs) (Table 1) in chloroform and mixed 1 : 1 (by volume) chloroform–carbon tetrachloride (CCl₄) solvent. The PVP-1,2 samples were synthesized at the Institute of Macromolecular Compounds, Russian Academy of Sciences. The analogue of the monomeric unit of PVP, N-methylpyrrolidone (MP) produced by Sigma 50760, was studied by the Kerr effect method in chloroform.

Table 1. Specific electrooptical Kerr constants \( K \), specific dielectric polarizations \( \mu_2/M \) for MP and PVP-1,2 in organic solvents, and optical polarizability anisotropy \( \Delta b \) for the PVP monomeric unit

<table>
<thead>
<tr>
<th>Sample</th>
<th>( M )</th>
<th>( K \times 10^{10}, \text{cm}^{2} \text{g}^{-1}(300 \text{ V})^{-2} \text{ in chloroform} )</th>
<th>( K \times 10^{10}, \text{cm}^{2} \text{g}^{-1}(300 \text{ V})^{-2} \text{ in chloroform–CCl}_4 )</th>
<th>( \mu_2/M \times 10^{36}, \text{D g}^{-1} \text{ in chloroform–CCl}_4 )</th>
<th>( \Delta b \times 10^{25}, \text{cm}^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>99.1</td>
<td>+1.75</td>
<td>–</td>
<td>0.167</td>
<td>–</td>
</tr>
<tr>
<td>PVP-1</td>
<td>10000</td>
<td>−0.80</td>
<td>−0.2</td>
<td>0.022</td>
<td>−10</td>
</tr>
<tr>
<td>PVP-2</td>
<td>38000</td>
<td>−0.82</td>
<td>−0.2</td>
<td>0.025</td>
<td>−10</td>
</tr>
</tbody>
</table>

* Determined in [4] by the birefringence method for the homologous series of samples and fractions of PVP in benzyl alcohol solutions.
Evlampieva et al.

Fig. 1. Variation of the birefringence $\Delta n$ with the squared electric field intensity, $E^2$, for PVP-1 sample in mixed chloroform--CCl$_4$ solvent at solution concentration, g cm$^{-3}$, of (1) 6.14 $\times$ 10$^{-2}$ and (4) 3.85 $\times$ 10$^{-2}$. Straight lines (1) and (3) correspond to the solvent. Straight lines (3) and (4) are shifted along the ordinate axis by 1.5 $\times$ 10$^{-8}$.

Fig. 2. Variation of the birefringence $\Delta n$ of MP with the squared electric field intensity $E^2$ in chloroform at concentration, g cm$^{-3}$, of (1) 30.5 $\times$ 10$^{-2}$, (2) 18.3 $\times$ 10$^{-2}$, (3) 17.3 $\times$ 10$^{-2}$, (4) 9.8 $\times$ 10$^{-2}$, (5) 4.6 $\times$ 10$^{-2}$, and (6) 0.00.

Fig. 3. Concentration dependences of the specific Kerr constant $K$ for (1) PVP-1,2 samples in chloroform, (2) PVP-1 sample in the mixed chloroform--CCl$_4$ solvent, and (3) MP in chloroform.

The birefringence of solutions subjected to pulse electric field ([Kerr effect], hereinafter, birefringence in electric field, BE) was measured by the compensation method [5] at rectangular pulse duration of 1 ms. The parameters of the setup and the measurement cell corresponded to those described in [6]. The equilibrium (i.e., independent of the frequency and duration of electric pulses) electrooptical properties of the samples were characterized by the specific Kerr constant $K$

$$K = \lim_{E \to 0} (\Delta n - \Delta n_0)/E^2 c.$$

Here, $(\Delta n - \Delta n_0)$ is the difference between the birefringences of the solution of concentration $c$ and of the solvent, and $E$, the electric field intensity in the measurement cell.

In the solvents used, PVP exhibited a minor negative intrinsic (minus the contribution from the solvent) electrooptical effect proportional to the squared electric field intensity, in accordance with the Kerr law for molecular-dispersed media. Figure 1 shows the plots of the optical birefringence $\Delta n$ against the squared electric field intensity, $E^2$, for PVP-1 sample. It is seen that the difference in $\Delta n$ between the solution and solvent is small, though exceeding the measurement error. Figure 2 shows the same dependences for MP solutions in chloroform. Since the electrooptical Kerr effect is positive for MP and negative for chloroform, the sign of the electrooptical effect of the solution changed with the MP concentration in chloroform (Fig. 2).

The specific Kerr constant of the samples was determined, in accordance with Eq.(1), from the $K = f(c)$ plot (Fig. 3). Here, each $K$ value is the slope of the $\Delta n = f(E^2)$ plot estimated at a certain concentration of the solution. Thus, for PVP-1 sample we obtained the Kerr constants $K = -0.80 \pm 0.07 \times 10^{-10}$ g$^{-1}$ cm$^5$ (300 V)$^{-2}$ in chloroform and $K = -0.20 \pm 0.05 \times 10^{-10}$ g$^{-1}$ cm$^5$ (300 V)$^{-2}$ in the mixed solvent. These constants were identical, within the experimental error, to those of the second sample,