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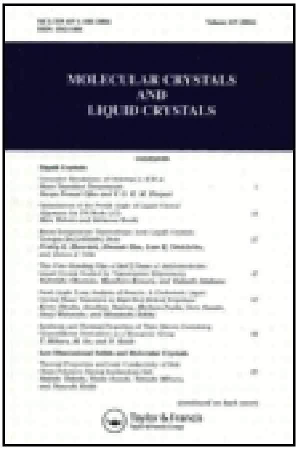

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Optical and Conformational Properties of LC Cellulose Derivatives in Dilute Solutions

Tatjana V. Filippova[a], Horst Dautzenberg[b] & Irina N. Shtennikova[a]

[a] Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoi pr. 31, Saint-Petersburg, 199004, Russia

[b] Universitat Potsdam WIP-Forschungsgruppe fur Polyelektrolyt-komplexstrukturen, Kantstrrasse 55, D-14513, Teltow, Germany

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[a]*Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoi pr. 31, Saint-Petersburg, 199004 Russia and* [b]*Universitat Potsdam WIP-Forschungsgruppe fur Polyelektrolyt-komplexstrukturen, Kantstrrasse 55, D-14513 Teltow, Germany*

To analyze the influence of structure of the cellulose derivatives on the mesomorphic behavior it was carried out the investigation of their molecular properties in dilute solutions. Flow birefringence and intrinsic viscosity of cellulose derivatives were studied. The optical anisotropy and equilibrium rigidity of polymer chain were determined. The investigated cellulose derivatives are characterized by the high equilibrium rigidity. It was established that their molecules have the conformation of a kinetically rigid coil. It was shown that the values and sign of flow birefringence and correspondingly the optical anisotropy of monomer units depends on the structure of side substitutes and are influenced by the solvent nature and thermodynamical quality of polymer solution.

Keywords: cellulose derivatives; flow birefringence; intrinsic viscosity

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INTRODUCTION

Recently the interest in rigid-chain polymers has particularly increased in connection with the possibility of using them for obtaining polymeric liquid crystals (LC) [1].

The experimental investigations of LC polymers in dilute solutions have shown that their hydrodynamic properties are influence by draining effect and weakening of hydrodynamic interaction that is a direct result of the high equilibrium rigidity of their chains whose Kuhn segment length exceeds that of typical flexible-chain polymers. The studies of flow birefringence in rigid-chain polymer solutions have suggested that the conformations of their molecules can differ greatly varying from a rod to a Gaussian coil with increasing molecular weight. The conformational characteristics of rigid-chain LC molecules can be described most adequately by the wormlike chain model [2].

All these considerations may be applied to such natural compounds as the derivatives of cellulose which hydrodynamic and optical properties are studied here. They have shown themselves typical rigid-chain polymers. It is their high equilibrium rigidity that favors the formation of the lyotropic mesomorphic structure in the concentrated solutions [3].

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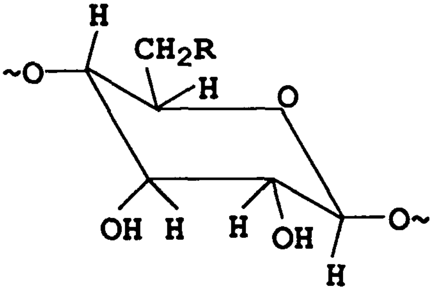
EXPERIMENT

The experiments were performed on series of cellulose derivatives of the following structure:



R_1 - OSO_3Na
R_2 - $COONa$
R_3 - OCH_2-C_6H_5
R_4 - OC_2H_5
R_5 - CONH-PO-$(OC_6H_5)_2$
R_6 - COCH-$(C_6H_5)_2$
R_7 - CO-C_6H_5
R_8 - CONH-C_6H_5

Hydrodynamic and optical properties of cellulose derivatives are studied in dilute solutions using flow birefringence and viscometry.

Birefringence Δn was measured by visual optical instrument [2] with compensator phase difference $\delta = 0.035\ \lambda$, where $\lambda = 5460$ Å is light wavelength. Measurements were carried out in metal dynamooptimeter with an internal rotor (the height of rotor is 3 cm along the beam, the gap between the rotor and the stator was 0.026 cm). The shear rate gradient was less than critical and flow was laminar.

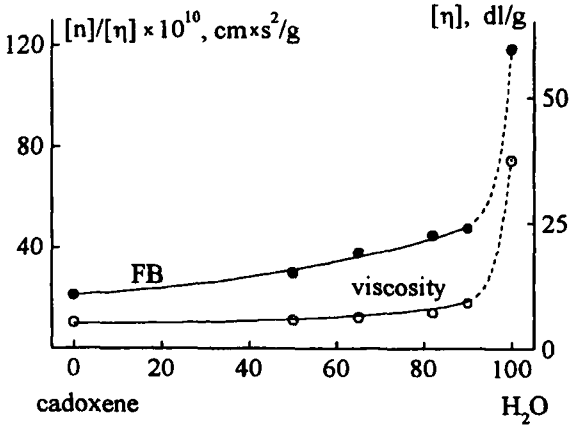


FIGURE 1. Flow birefringence [n]/[η] and intrinsic viscosity [η] for R_2 ($M=3.7\times10^5$, DS=1.05) depending solvent composition.

TABLE 3. Kuhn segment length A for R_2 in different solvents.

Solvent	A, Å
Cadoxene	130 ± 20
Cadoxene+H_2O(1:1)	170 ± 20
Cadoxene+H_2O(1:10)	180 ± 20
2n NaOH	200 ± 20
0.5n NaOH	300 ± 30
2n NaCl	330 ± 30
0.5n NaCl	350 ± 30

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TABLE 2. Characteristics of optical and hydrodynamic properties of cellulose derivatives in dilute solutions

Polymer	Solvent	$M\times10^{-5}$	$[\eta]\times10^{-2}$	$[n]/[\eta]\times10^{10}$
R_1	cadoxene	1.7	5.3	20
	3N NaOH			13
R_2	cadoxene	3.7 - 0.4	5.3 - 0.5	25
	cadoxene+H_20		7.5 - 0.6	33
R_3	dioxane	0.3	0.6	25
R_4	dioxane	0.8	2.5	30
R_5	dioxane	10.0	4.9	49
R_6	dioxane	2.3	2.6	82
R_7	dioxane	4.74	5.7	- 35
R_8	dioxane	1.72	3.4	- 128

tent in the solvent leads to the formation of intramolecular hydrogen bonds. Secondly, it is necessary to consider the possibility of electrostatic swelling of macromolecules with decrease in cadoxene concentration. Consequently, these effects change equilibrium rigidity of macromolecules investigated [4]. TABLE 3 shows the change of Kuhn segment length A with the variation of solvent composition or solvent nature.

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RESULTS AND DISCUSSION

The values of intrinsic viscosity, Huggins constant and characteristical flow birefringence [n]/[η] for cellulose sulfate (R_1) shown in TABLE 1 evidence that the k_H and [n]/[η] values do not depend on molecular weight and substitution degree. Hence, the influence of solvent nature is observed: the flow birefringence of R_1 in cadoxene is higher then that in aqueous solvents.

TABLE 2 shows the molecular weight and optical characteristics of cellulose derivatives under investigation. It should be noted that all samples investigated have sufficiently large molecular weights M, which are in Gaussian region. Consequently, we may compare the [n]/[η] values obtained for different cellulose derivatives.

It is seen that the side chain structure changes the flow birefringence. The including of phenylene cycles in the side chain especially through amide or ester group brings to high [n]/[η] values and to the change in sign (R_7, R_8).

For carboxymethyl cellulose (R_2) we compare properties of cadoxene – water solvents with different composition. In mixed solvents the flow birefringence is higher then in cadoxene. In FIGURE 1 it is shown the flow birefringence and intrinsic viscosity dependence on the solvent composition. It is possible that there are two reasons for the growth of both [η] and [n]/[η]. Firstly, the increase of water con-

Viscometry measurements were carried out in Ostwald viscometer. Intrinsic viscosities $[\eta]$ and Huggins constant k_H were calculated from the dependencies $\eta_{sp}/c = f(c)$. (c is solution concentration and η_{sp} is related viscosity.)

TABLE 1. Hydrodynamic and optical properties of R_1 in solutions.

Sample	DS	Solvent	$[\eta]\times 10^{-2}$	k_H	$[n]/[\eta]\times 10^{10}$
1	0.5	cadoxene	3.15	0.30	20 ± 2
2	0.5	cadoxene	2.75	0.36	20 ± 2
3	0.4	cadoxene	5.30	0.33	20 ± 2
		3n NaOH	5.10	0.40	13 ± 2
4	0.4	cadoxene	4.20	0.38	20 ± 2
5	0.4	cadoxene	3.87	0.30	20 ± 2
6	0.4	cadoxene	2.90	0.36	20 ± 2
		3n NaOH	3.10	0.22	13 ± 2
7	0.4	cadoxene	2.46	0.45	20 ± 2
8	0.4	cadoxene	2.00	0.90	20 ± 2
9	0.4	cadoxene	1.45	0.48	20 ± 2
		3n NaOH	1.66	0.34	13 ± 2
10	0.4	cadoxene	0.80	0.33	20 ± 2
11	0.4	cadoxene	0.60	0.42	20 ± 2
12	0.2	cadoxene	3.4	0.67	20 ± 2

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CONCLUSIONS

Flow birefringence and viscometry experimental data show that cellulose and cellulose derivatives macromolecular conformation presents itself as draining Gaussian coil with rather high equilibrium rigidity (A > 100Å).

The nature of the solvent used in experiment do influence the optical, hydrodynamic and conformational properties of investigated macromolecules.

The equilibrium rigidity (Kuhn segment length) of cellulose and cellulose derivatives depends on side chain structure, degree of substitution and solvent nature. High intramolecular orientational order and crystal-like behavior of these macromolecules and ability to form lyotropic liquid crystals served as a basis for technology development and manufacturing of new liquid-crystal materials.

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