# ELECTROOPTICAL AND HYDRODYNAMIC PROPERTIES OF THE MACROMOLECULES OF THIRD-GENERATION CYLINDRICAL DENDRIMERS WITH DENDRONS BASED ON L-ASPARGIC ACID.

N.V. Tsvetkov*, I.A. Martchenko*, L.N. Andreeva**, S.V. Bushin**
*Department of Physics, Saint Petersburg State University, ul. Ulyanovskaya 1, 198904, Saint Petersburg, Petrodvorets, Russia
**Institute of Macromolecular Compounds of Russian Academy of Sciences, Bolshoi Pr, 31, 199004, Saint Petersburg, Russia
ilyamartch@mail.ru

Samples of third-generation cylindrical dendrimers with molar masses ranging in the interval 20000…60000 have been studied by the methods of equilibrium and non-equilibrium electrical birefringence, molecular hydrodynamics and optics. Dispersion dependences indicate that the macromolecules undergo reorientation in external electric fields due to their constant dipole moments. It was found that the absolute values of Kerr and flow birefringence constants exceed the values obtained for analogous dendrimers of lower generations. The mechanism of reorientation has proven to be strongly dependent on the physical and chemical properties of the solvent. In chloroform solutions, the studied dendrimers align to the microwave-frequency electric fields according to large-scale mechanism. In dichloroacetic acid solutions, the observed reorientation mechanism is low-scale, which is explained by degradation of intermolecular hydrogen bonds. Terminal dendritic substituents of the macromolecules have experimentally proven to be oriented mainly along the main polymer chain.
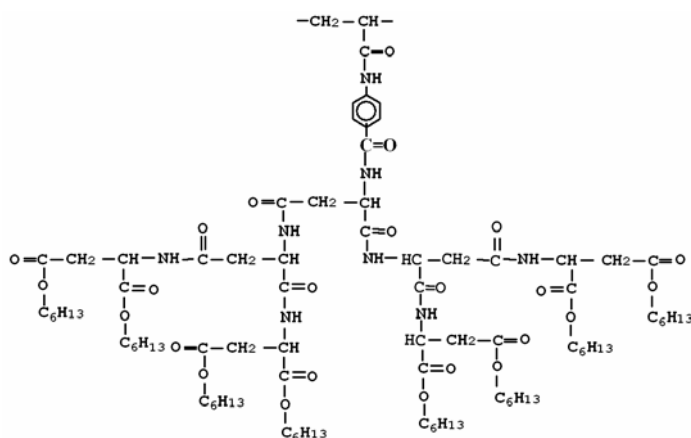
A great interest in recent years is devoted to dendrimers that include amino acids as their main chains [1] or side dendrons [2]. Such polymers may find applications in pharmaceutics and in genetical research because of their probable biological activity. In present work, samples of third-generation cylindrical dendrimers have been studied by methods of electrical birefringence (in rectangular-pulsed and sinusoidal-pulsed electric fields) and molecular hydrodynamics and optics.

Structure of a monomer unit (with molar mass of 1656) is outlined on Fig. 1.

Such a molecule experiences multiple intermolecular hydrogen bonds. The synthesis has been performed by means of radical polymerization. Solutions of analogous dendrimers of first and second generations have been studied earlier [3, 4].

Methods

Electric birefringence. A Kerr cell equipped with two titanium electrodes was filled with the studied solution. The gap between the electrodes was equal to $d=0,030\pm0,005\ cm$, the length of the electrodes along the light path was equal to *3 cm*. A He-Ne laser generated the wavelength $\lambda=632.8\ nm$. The elliptic rotating compensator had the path difference $\Delta\lambda/\lambda=0.01$. The Kerr constant at a certain frequency of the external electric field E is:

$$K_\upsilon = \frac{\Delta n - \Delta n_0}{cE^2}$$

Mean relaxation times $\tau=1/(2D_r)$ may be found when analyzing the dispersion curves, according to the expression: $\tau=1/\omega_n$, where $\omega_n=2\pi v_m$ is the frequency corresponding to the half-decay of the dispersion.

Flow birefringence. A titanium dynamooptimeter with the height of *3 cm* and the rotor's diameter of *3 cm* was filled with the solution. The gap between the concentric cylinders was *0.024 cm*. The elliptic rotating compensator had the path difference $\Delta\lambda/\lambda=0.035$. The optical shear coefficient $\Delta n/\Delta\tau$ is given by:

$$\frac{\Delta n}{\Delta \tau} = \frac{\Delta n_p - \Delta n_0}{g(\eta - \eta_0)},$$

where $\Delta\tau$ is a shear stress, g is a shear rate in the gap, η and η_0 are the viscosities of a solution and a solvent respectfully.

Isothermal diffusion methods were used to measure the translational diffusion coefficients. A polarization diffusometer was equipped with a glass cell that had the length of 3 cm along the light path. The average increment of refractive indexes was equal to $(dn/dc)_{aver}=0.062$.

Results and discussion

Fig. 2 illustrates the equilibrium electric birefringence data for solutions of cylindrical dendrimers. In the studied strength range, these obtained plots are straight lines obeying the Kerr law. The results obtained with methods of non-equilibrium electric birefringence are illustrated with Fig. 3 that shows the dependences of birefringence Δn on the squared electric field E^2, for the sinusoidal-pulsed fields at different frequencies. Analogous dependencies have been obtained for every studied sample at varied concentrations.
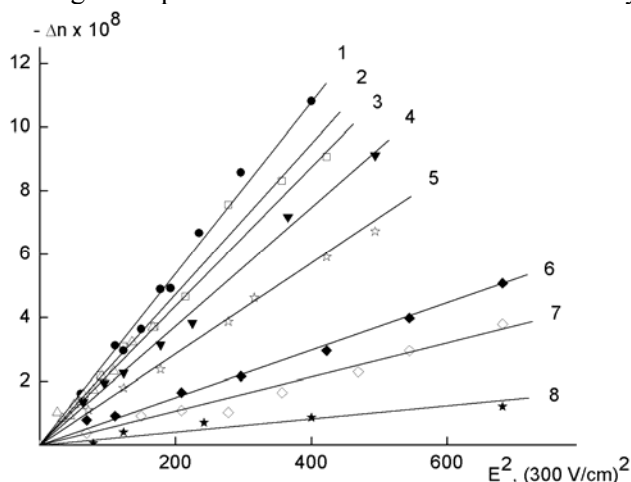

Fig. 2. Dependences of birefringence Δn on the square of rectangular-pulsed electric field E^2 for the chloroform solution of P3-3 sample at the mass concentrations $c = 2.88 \cdot 10^{-2}$ g/cm³ (1), $c = 1.67 \cdot 10^{-2}$ g/cm³ (2), $c = 1.10 \cdot 10^{-2}$ g/cm³ (3), $c = 0.75 \cdot 10^{-2}$ g/cm³ (4), $c = 0.52 \cdot 10^{-2}$ g/cm³ (5), $c = 0.17 \cdot 10^{-2}$ g/cm³ (6), $c = 0.09 \cdot 10^{-2}$ g/cm³ (7), for pure chloroform (8).
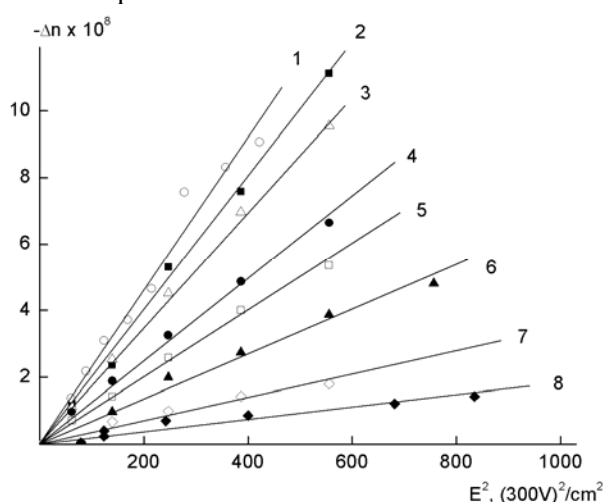
Fig. 3. Dependences of birefringence Δn on the square of sinusoidal-pulsed electric field E^2 for the chloroform solution of P3-3 sample at the mass concentration $c = 2.88 \cdot 10^{-2}$ g/cm³. The plot includes data for the fields of frequencies of 0 Hz (1), 13 kHz (2), 21 kHz (3), 60 kHz (4), 100 kHz (5), 200 kHz (6), 600 kHz (7), and data of pure chloroform (8).

The specific Kerr constants were calculated using the said data. Fig. 4 displays the dispersion curves for a sample at varied concentrations. Fig. 5 shows the dispersion curves for different samples at a minimum researched concentration.
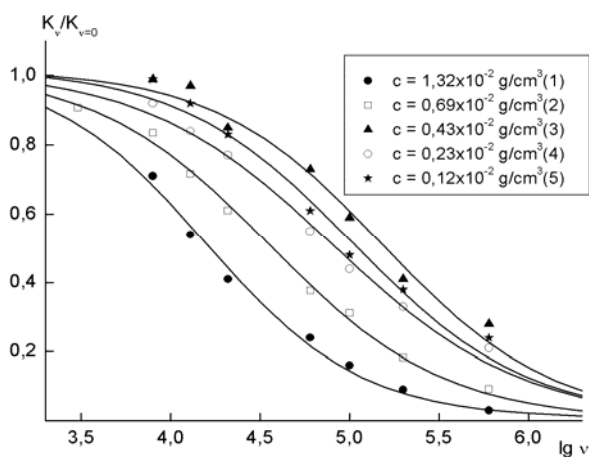

Fig. 4. Dispersion curves of specific Kerr constant $K_\nu/K_{\nu \to 0}$ for the chloroform solutions of P3-5 sample at mass concentrations $c = 1.32 \cdot 10^{-2}$ g/cm³ (1), $c = 0.69 \cdot 10^{-2}$ g/cm³ (2), $c = 0.43 \cdot 10^{-2}$ g/cm³ (3), $c = 0.23 \cdot 10^{-2}$ g/cm³ (4), $c = 0.12 \cdot 10^{-2}$ g/cm³ (5).
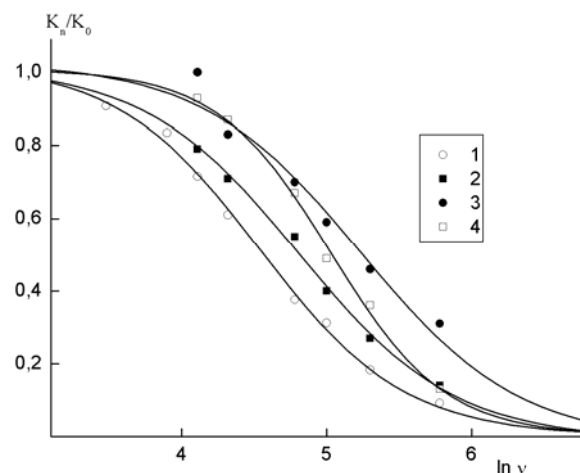
Fig. 5. Dispersion curves of specific Kerr constant $K_\nu/K_{\nu \to 0}$ for the chloroform solutions of polymers P3-5 (1), P3-3 (2), P3-1 (3), P3-2 (4), at the least studied concentrations.

Dispersion dependences of the samples decay virtually to zero which indicates that the electric birefringence in solutions is explained by the constant dipole moments of the molecules. Relaxation time $\tau = 1/(2D_r)$, molar mass M and intrinsic viscosity $[\eta]$ have a relation expressed by $M[\eta]\eta_0 D_r = FRT$, where D_r is a rotational diffusion coefficient with respect to short axis of a molecule, F is a model parameter that characterizes the dimensions and the conformation of a molecule. For rigid molecules the values of F range from 0.13 for a rod to 0.42 for a spherical particle.

The values of F for molecules in chloroform solutions never exceeded 0.1, which corresponds to a rigid rod. It was shown that the values of F for studied samples in DCA seriously exceed the corresponding values for chloroform solutions and the theoretically possible value 0.42 for kinetically rigid molecules.

The calculated flow birefringence constants exceed the values obtained for dendrimers of lower generations. This growth is most likely connected with the increased number of anisotropic groups and the increased rigidity of a macromolecule.

The values of translational diffusion coefficients, measured experimentally, were used to calculate the values of translational friction factors f of a single particle. Conformation of the main polymer chain is supposed to be close to rod-like because of the relatively low polymerization degrees. The Fujita's expression [5] for the friction factors of spherocylindrical particles is given by:

$$f = \frac{3\pi\eta_0 L}{\ln L/d + Q(d/L)},$$

where $Q(d/L)$ is the power series for the parameter d/L that is given by the expression:

$$Q(d/L) = 0.3863 + 0.6863 \cdot (d/L) - 0.06250 \cdot (d/L)^2 - 0.01042 \cdot (d/L)^3 - 0.000651 \cdot (d/L)^4 + 0.0005859 \cdot (d/L)^5 + \dots$$
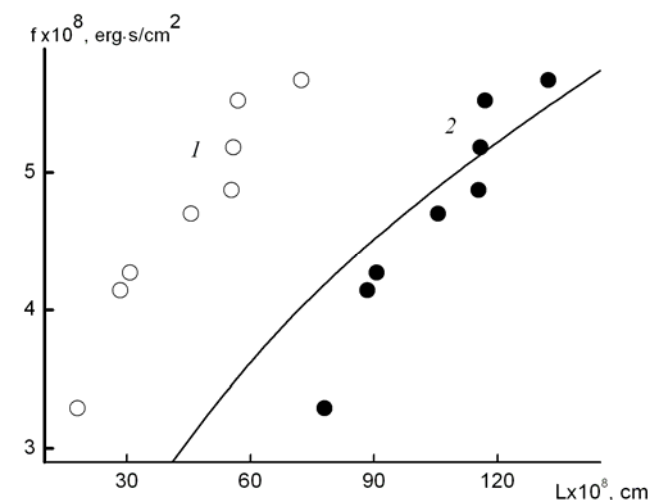
where d is the diameter of the sperocylinder and L is its length. Approximation of f in dependence of the length of a polymer chain L has shown that the Fujita formulas cannot describe the experimental data at any reasonable values of the diameter of molecules (Fig. 6).

Fig. 6. Dependence of the translational friction factors on the linear dimensions of a molecule. The data was obtained with the method of translational isothermal diffusion. The curves show the best fit with theoretical expressions for rigid spherocyliners.

However, if all experimental data is displaced *60 Å* to the right, a good correlation between theory and experiment is achieved (Fig. 6). This fact is evidence that the linear dimensions of macromolecules are exterior of the corresponding lengths of polymer chains. Intermolecular interactions force terminal dendrons (attached to "first" and "last" chain segments) to be oriented along the polymer chain, not normally to it.

Conclusions

All of the studied samples show close Kerr and flow birefringence constants that exceed the corresponding values for the samples of first and second generations. This fact may be related to increased equilibrium rigidity and increased optical anisotropy of a monomer unit.

Dispersion dependences show that the macromolecules undergo reorientation in external electric fields because of their constant dipole moments. The mechanism of reorientation is strongly dependent on the physical and chemical properties of the solvent. In chloroform solutions, the studied macromolecules align to the microwave-frequency electric fields according to large-scale mechanism. In other words, carbochain polymers acquire high kinetic rigidity when side dendritic substituents are attached to the main chain. However, for dichloroacetic acid solutions, the macromolecules undergo reorientation according to low-scale mechanism.

The difference in the reorientation mechanism is explained by degradation of intermolecular hydrogen bonds caused by molecules of dichloroacetic acid.

Terminal dendritic substituents have proven to be oriented mainly along the main chain.

References
1. C.C. Lee, J.M.J. Frechet. Macromolecules. **39**. *No. 2*, 476-481. (2006). 2. *M. Mondeshki, G. Mihov, R. Graf, H.W. Spiess, K. Mullen, P. Papandopulos, A. Gitsas and G. Floudas*. Macromolecules. *No. 26*, 9605-9613. (2006). *3. Бушин С.В., Цветков Н.В., Андреева Л.Н., Беляева Е.В., Иванова В.О., Безрукова М.А., Гирбасова Н.В., Билибин А.Ю.* // Высокомолек. соед. А. Т. 2005. 47.№2. С.315-324. *4. Бушин С.В., Андреева Л.Н., Гирбасова Н.В., Безрукова М.А., Алябьева В.П., Цветков Н.В., Билибин А.Ю.*// Высокомолек. соед. 2007 (в печати). *5. Yamakawa H., Fujii M.* // Macromolecules. 1973. V.6. N.3. *P.407.*