

Hydrodynamic, optical and electrooptical properties of hyper-branched macromolecules with side dendrons based on L-aspartic acid

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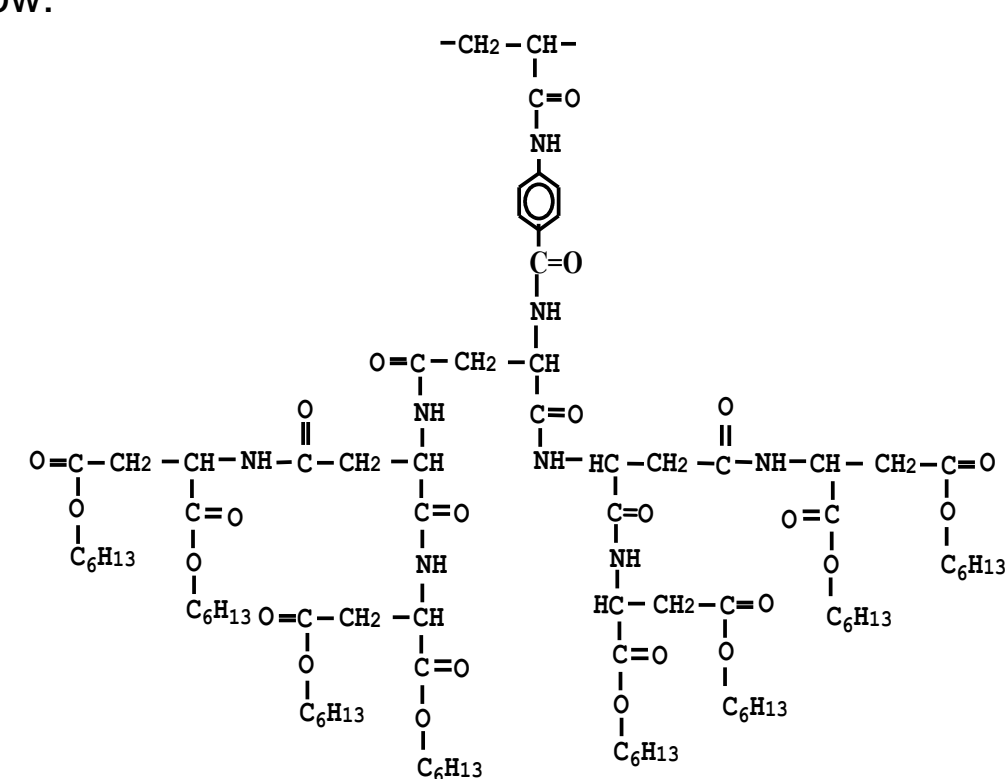
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Introduction, object of study

Samples of third-generation cylindrical dendrimers with molar masses ranging in the interval 20000...60000 have been studied by methods of electrical birefringence (in rectangular-pulsed and sinusoidal-pulsed electric fields), molecular hydrodynamics and optics.

The structure of a monomer unit (with the molecular mass of 1656) is shown below:



The synthesis has been performed by means of radical polymerization. Solutions of analogous dendrimers of first and second generations have been studied earlier [1, 2].

Methods

Hydrodynamic methods

Determination of hydrodynamic characteristics and conformational analysis of the macromolecules under investigation were carried out with the methods of viscometry, DLS, translational diffusion, and sedimentation.

Electric birefringence

A Kerr cell was equipped with two titanium electrodes separated by the gap of $d = 0.030 \pm 0.005$ 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 $\Delta\lambda = 0.01$. The Kerr constant at a certain frequency is given by:

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

Mean relaxation times $\tau = 1/(2D_r)$ may be found when analyzing the dispersion curves, according to the expression:

$$\tau = \frac{1}{\omega_m}$$

where $\omega_m = 2\pi\nu_m$ is the frequency corresponding to the half-decay of the birefringence dispersion.

Relaxation times $\tau = 1/(2D_r)$, molecular masses M and intrinsic viscosities $[\eta]$ have a relation expressed by:

$$M[\eta]D_r = FRT,$$

where D_r is a diffusion coefficient of rotation with respect to short axis of a molecule, F is a model parameter that characterizes the dimensions and the conformation of a molecule, and for rigid molecules ranges from 0.13 for a rod to 0.42 for a spherical globule.

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 $\Delta\lambda = 0.035$. The measurements were made with a photoelectric sensor. The optical shear coefficient $\Delta n/\Delta\tau$ is given by:

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

Experimental results

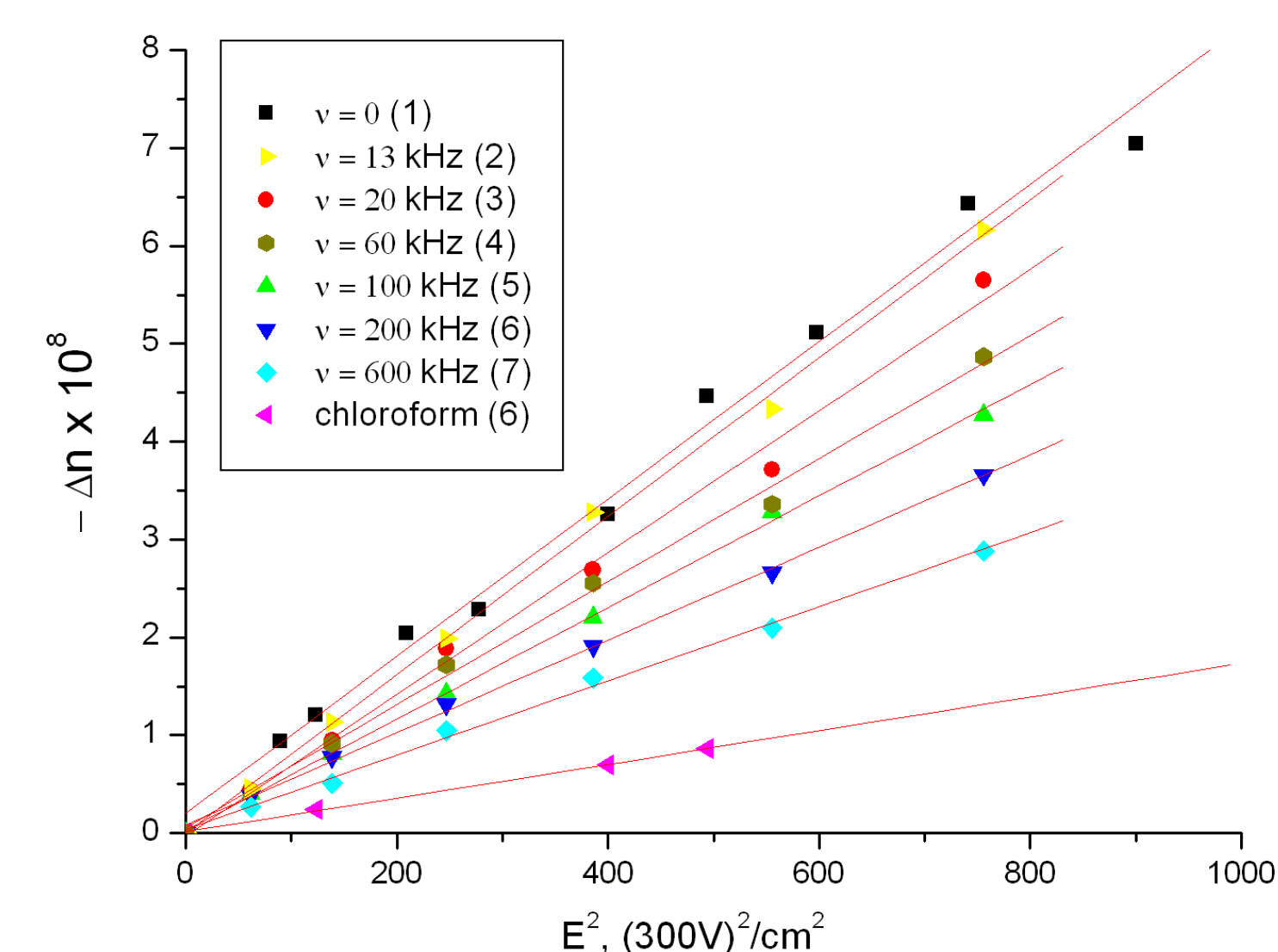


Fig. 1. Dependences of birefringence Δn on the square of sinusoidal-pulsed electric field E^2 for the chloroform solution of P3-1 sample at the mass concentration $c = 0.27 \cdot 10^{-2}$ g/cm³. The plot includes data for the rectangular-pulsed (0 Hz) electric field (1), sinusoidal fields with frequencies of 13 kHz (2), 20 kHz (3), 60 kHz (4), 100 kHz (5), 200 kHz (6), 600 kHz (7), and data of pure chloroform (8).

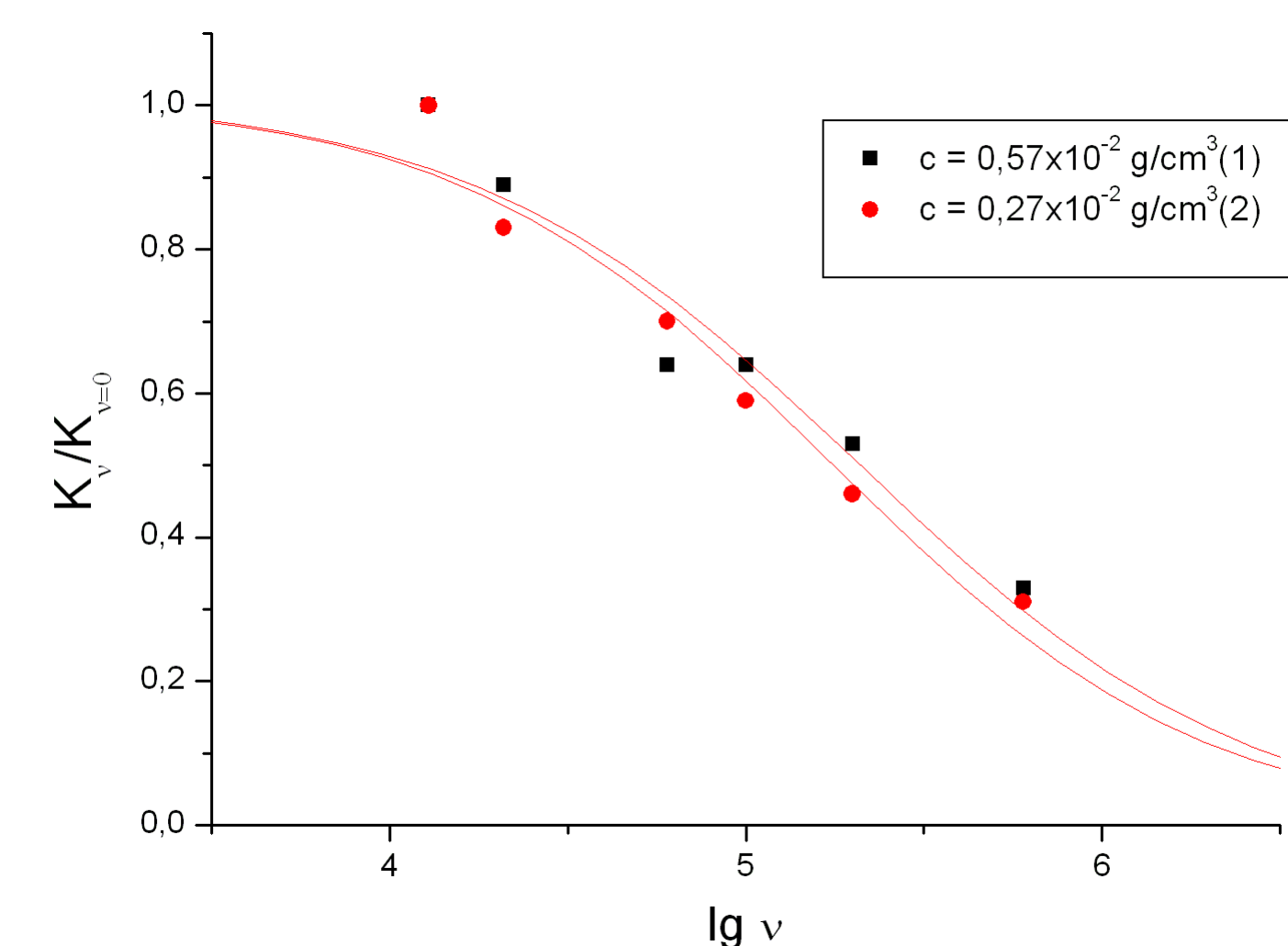


Fig. 3. Dispersion curves of specific Kerr constant $K_v/K_{v(0)}$ for the chloroform solutions of P3-1 sample at mass concentrations $c = 0.57 \cdot 10^{-2}$ g/cm³ (1), $c = 0.27 \cdot 10^{-2}$ g/cm³ (2).

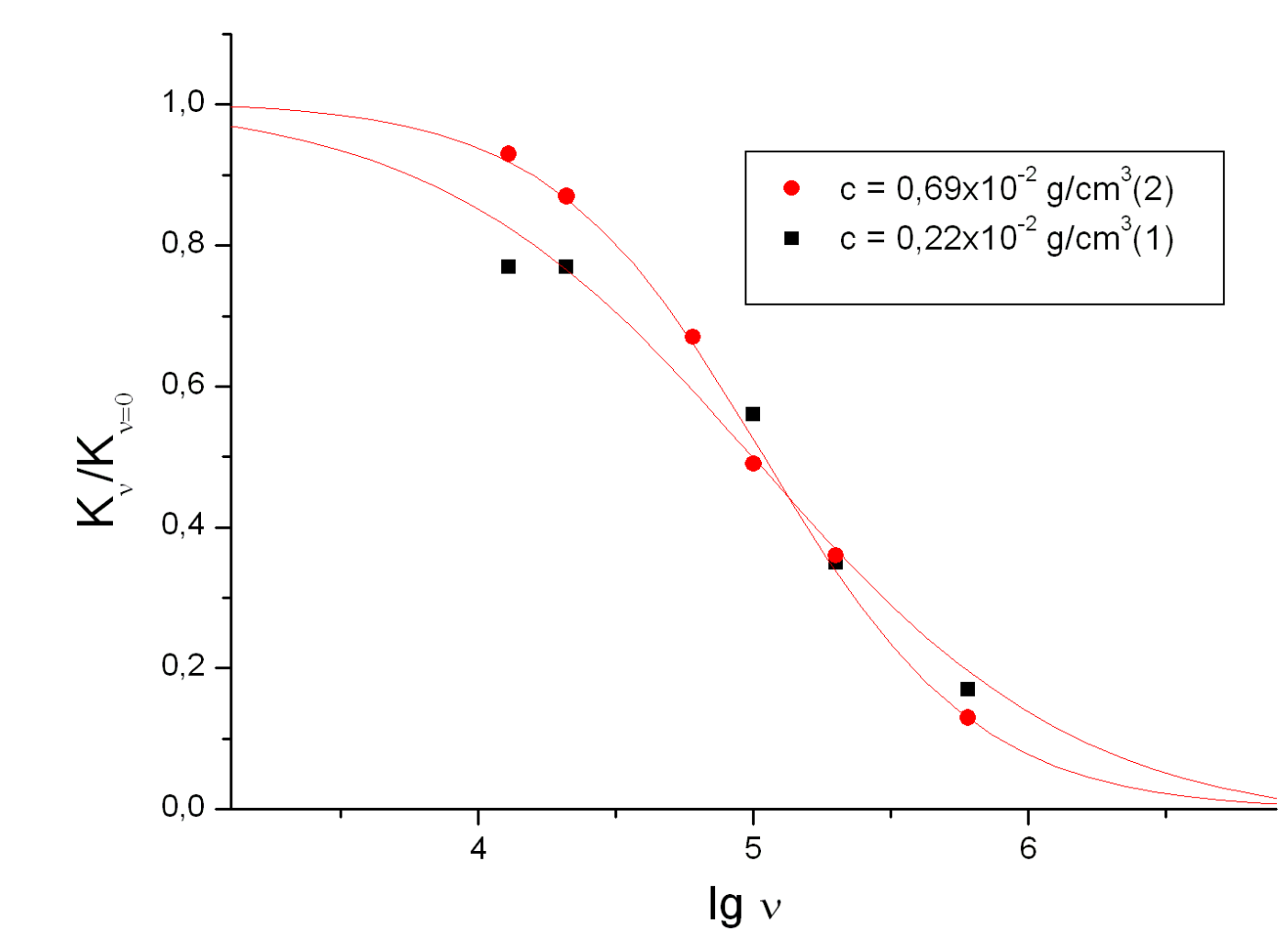


Fig. 5. Dispersion curves of specific Kerr constant $K_v/K_{v(0)}$ for the chloroform solutions of P3-2 sample at mass concentrations $c = 0.69 \cdot 10^{-2}$ g/cm³ (1), $c = 0.22 \cdot 10^{-2}$ g/cm³ (2).

Experimental results

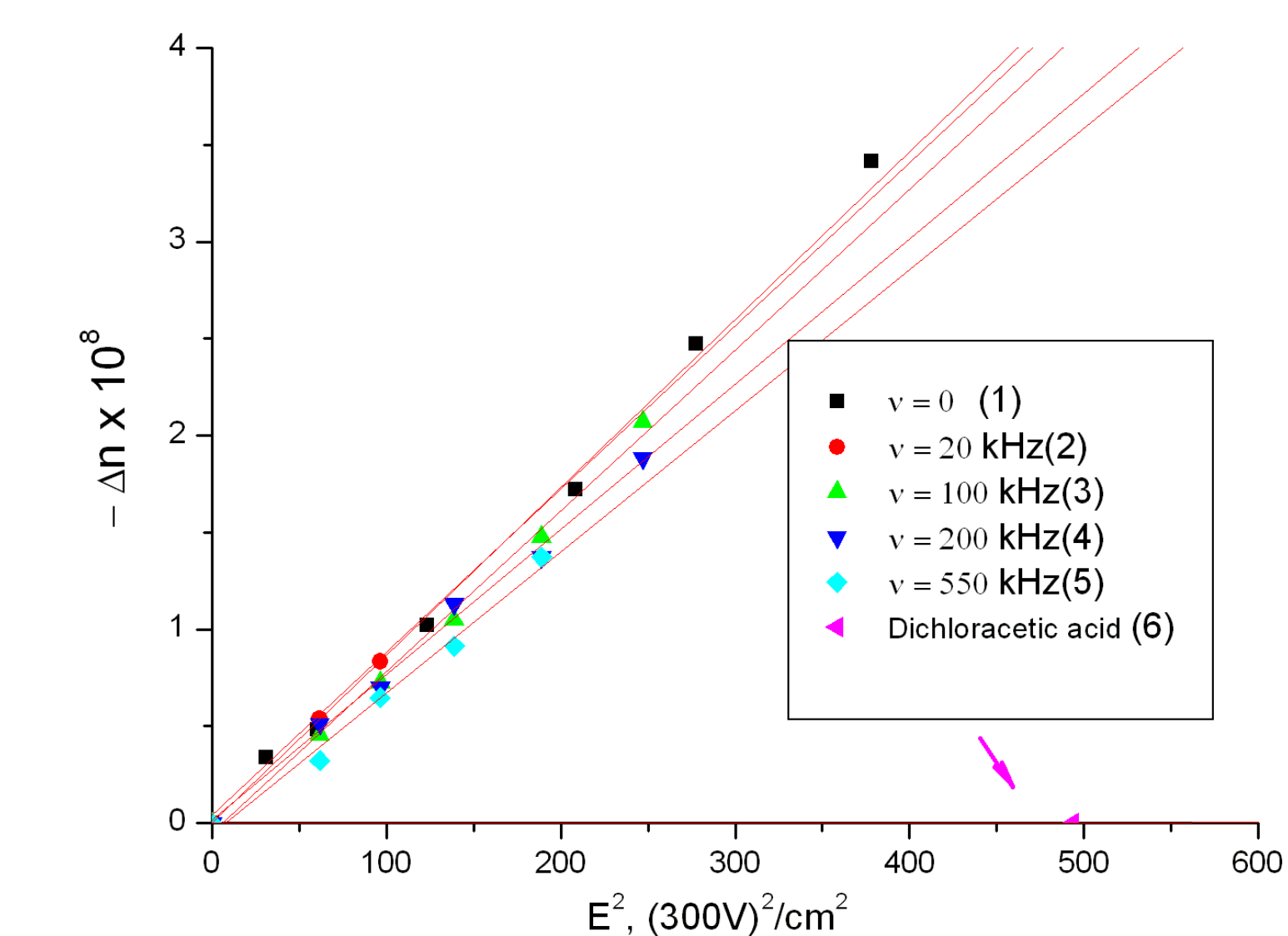


Fig. 2. Dependences of birefringence Δn on the square of sinusoidal-pulsed electric field E^2 for the dichloroacetic acid solution of P3-1 sample at the mass concentration $c = 0.84 \cdot 10^{-2}$ g/cm³. The plot includes data for the rectangular-pulsed (0 Hz) electric field (1), sinusoidal fields with frequencies of 20 kHz (2), 100 kHz (3), 200 kHz (4), 550 kHz (5), and data of pure dichloroacetic acid (6).

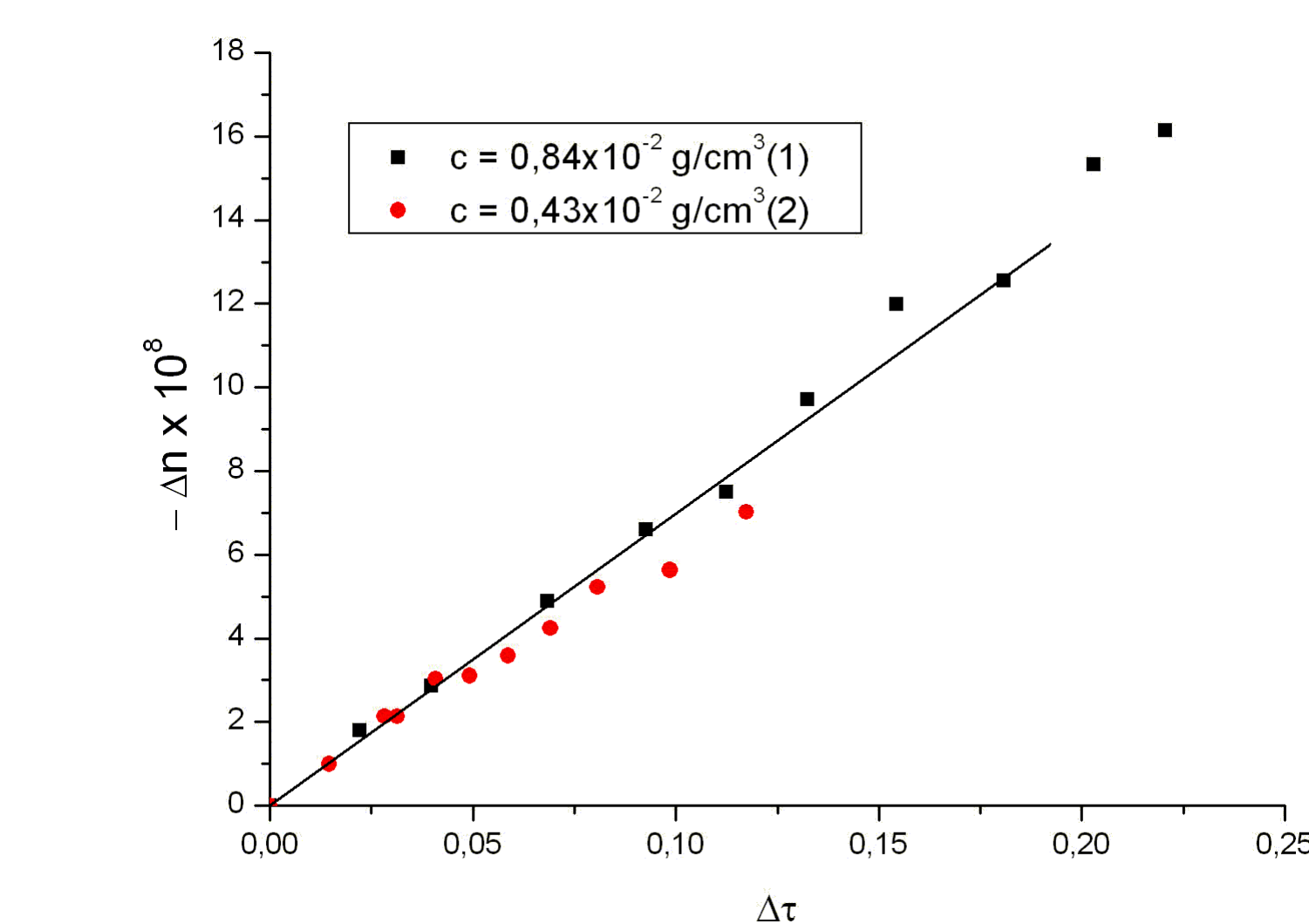


Fig. 4. Dependence of the birefringence on the shear stress $\Delta\tau$ for the dichloroacetic acid solutions of P3-2 samples at mass concentrations $c = 0.84 \cdot 10^{-2}$ g/cm³ (1) and $c = 0.43 \cdot 10^{-2}$ g/cm³ (2).

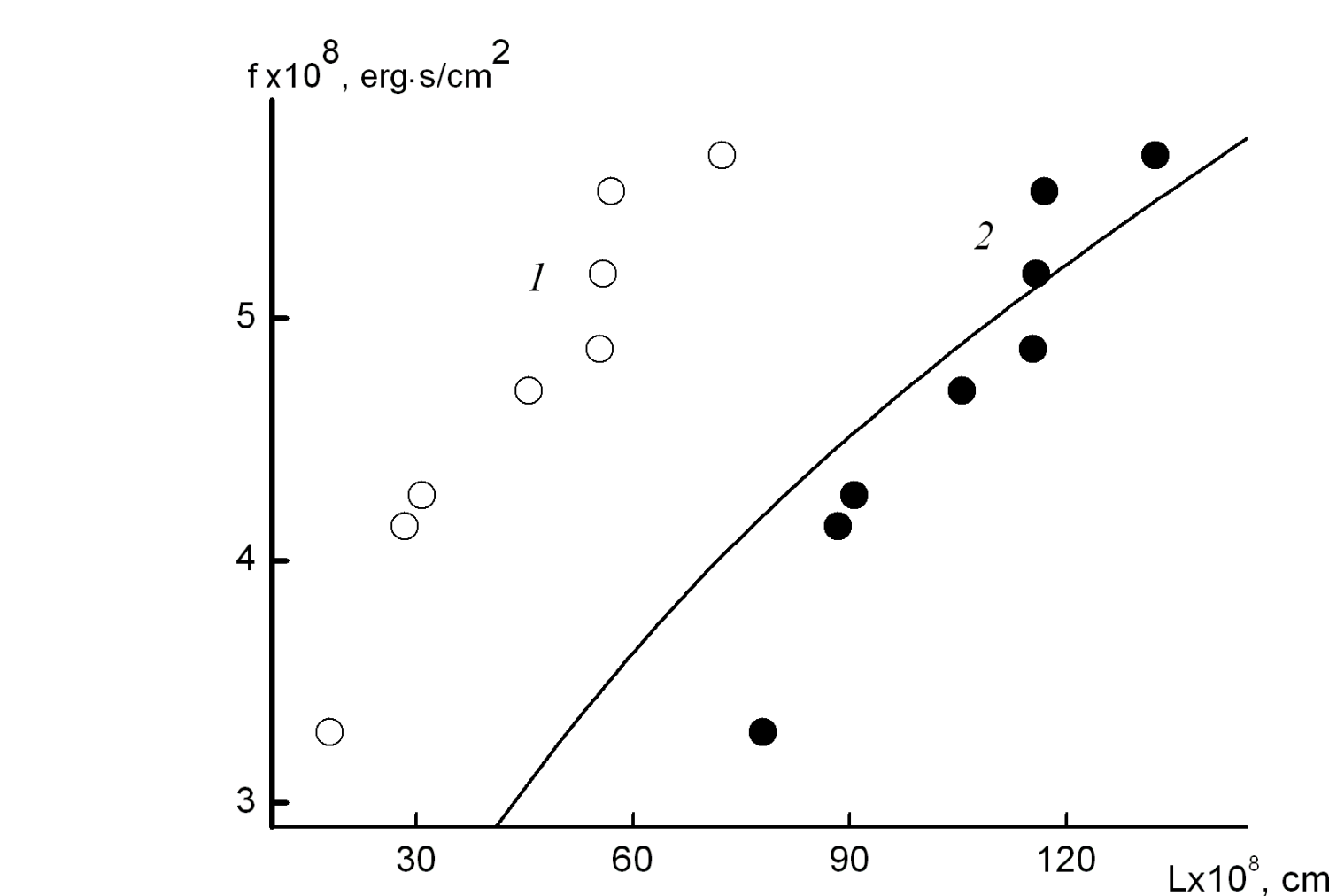


Fig. 6. Dependence of the translational friction factors on the linear dimensions of a molecule. The data was obtained with diffusion methods. The data was fitted with the Fujita's expression [3] for the friction factors of spherocylindrical particles. (1) is the data for the calculated length of main polymer chains, (2) is the same data increased with 60Å to achieve best fitting with the theory.

Discussion and conclusions

Dispersion dependences indicate that the macromolecules undergo the reorientation in external electric because of their constant dipole moments which causes the electric birefringence in their solutions.

Estimated coefficients F that describe the spatial conformation of a molecule, have shown that the mechanism of reorientation of studied samples 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. 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.

The Kerr constants ($-100 \dots -300 \cdot 10^{-10}$ g²/cm²(300 V)⁻²) and the flow birefringence constants ($-50 \dots -200 \cdot 10^{-2}$ s²/cm/g) 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 intrinsic viscosities of samples and their translational diffusion coefficients in dependence on molar masses allowed outlining the Mark-Kuhn-Houwink equations:

$$D = 6.17 \times 10^{-5} M^{-0.4}$$

$$[\eta] = 1.09 \times M^{0.24}$$

The low power indexes in both equations (below 0.5) indicate that the particles approach to having spherical shape and being non-draining.

Analysis of the translation diffusion factors indicate 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.

The table includes various parameters of the studied set of samples

In chloroform solutions											
No	[η], dl/g	D _r × 10 ⁷ , cm ² /s	D _{tr,ck} × 10 ⁷ , cm ² /s	S × 10 ¹³ , s	M _w	M _{SD}	M _{th}	Δn/Δc × 10 ¹¹ , g ² /cm ² (300 V) ⁻²	K × 10 ¹⁰ , g ² /cm ² (300 V) ⁻²	τ × 10 ⁶ , s	F
1	0.16	7.3		-7.8		76500		-170	-(170-560)	2.4	0.06
2	-		7.5 ± 0.3		60300						
3	0.14	8					59000	-165	-(250-330)	0.8	0.11
4	0.12	8.5					58600	-220	-(210-270)	1.2	0.06
5	0.12		8.8 ± 0.2			48200	51000				
6	0.14	9.7					32500	-205	-(160-295)	6	0.01
7	0.14	10		8.3 ± 0.3		30500	30000	-170	-(185-260)	1.2	0.04
8	0.11	12.6					19000	-150	-(170-560)	2	0.01
In dichloroacetic acid solution											
3	0.08						59000	-70	-(90-115)	<-0.2	>3.3
4	0.08						58600	-65	-(105-125)	<-0.1	>6.5
7	0.10						30500	-68			

References

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