Russian Journal of General Chemistry, Vol. 73, No. 3, 2003, pp. 344–349. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 3, 2003, pp. 370–375.
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Molecular and Electrooptical Characteristics of Poly(1-trimethylsilyl-1-propynes) with Varied Chain Regularity

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Received October 30, 2002

Abstract—Samples of a disubstituted polyacetylene, poly(1-trimethylsilyl-1-propyne), containing on the average 60% of *cis*-C=C bonds and prepared with $NbCl_5$ as catalyst were studied by means of Kerr effect measurements in solution and molecular hydrodynamics methods. The resulting data were correlated with the properties of the sample prepared with another catalytic system, $TaCl_5$/BuLi. Samples prepared under different catalytic conditions were found to have much different electrooptical properties. It was concluded that the $TaCl_5$/BuLi catalyst allows preparation of polymers with longer continuous sequences of monomeric units of the same isomeric structure as compared with those obtained with $NbCl_5$.

Disubstituted polyacetylenes, poly(1-trimethylsilyl-1-propynes), prepared by catalytic synthesis with Group V element halides as catalysts are of practical importance as film-forming polymers with excellent gas-separating properties [1–4]. Earlier a correlation between the microstructure of poly(1-trimethylsilyl-1-propyne) chains, their morphology, and gas-transfer properties of the polymeric films was found [5, 6]. However, detailed structure regularity studies on poly(1-trimethylsilyl-1-propynes) by means of X-ray diffraction are hampered by the amorphism of these polymers. This characteristic feature makes poly(1-trimethylsilyl-1-propynes) interesting to study in solution by optical and electrooptical methods sensitive to ordering of chemical bonds in macromolecules, including Kerr effect measurements. The Kerr effect depends on the anisotropy of optical polarizability and polarity of macromolecules and thus allows certain conclusions as to the regularity of their chain structure [7, 8].

By Kerr effect studies on solutions of fractions of disubstituted polyacetylenes, poly(1-trimethylsilyl-1-propyne [7], and poly(1-trimethylgermyl-1-propyne) [8], we established a correlation between the Kerr constant and the structure regularity of macromolecules of this class of polymers, associated with the formation in the course of their catalytic synthesis of sufficiently long regular-composition sections (including up to 20 monomeric units [8]) on the background of a generally statistical distribution of the *cis* and *trans* forms of conjugated carbon–carbon bonds in the polymeric chains [4].

The present study is a continuation of our research into electrooptical and conformational characteristics of poly(1-trimethylsilyl-1-propynes) [7, 9, 10] on an example of the samples synthesized with use of a new catalyst and differing from those examined earlier in the average ratio of *cis*- and *trans*-C=C bonds.

The aim of the work was to study the equilibrium Kerr effect in solutions of the samples synthesized with a niobium salt, $NbCl_5$, as catalyst and to compare their molecular characteristics with those of the poly(1-trimethylsilyl-1-propyne) prepared with the $TaCl_5$/BuLi catalytic system.

Table 1 presents the synthesis conditions and the average ratios of *cis* and *trans*-C=C bonds in the samples studied, as determined by ^{13}C NMR spectroscopy.

Figure 1a demonstrates the plots of the rate of shifting of the sedimentation boundary $\Delta\ln X$ vs. time Δt for solutions of sample no. 4 in cyclohexane. From the slopes of the plots we determined sedimentation coefficients $S = \omega^{-2}(\Delta\ln X/\Delta t)$, where ω is the angular speed of the ultracentrifuge rotor. For all the samples studied, the concentration dependences of sedimentation coefficients were found to fit the approximate linear relationship $S^{-1} = S_0^{-1}(1 + k_s c + ...)$ which is commonly used for calculation of the sedimentation

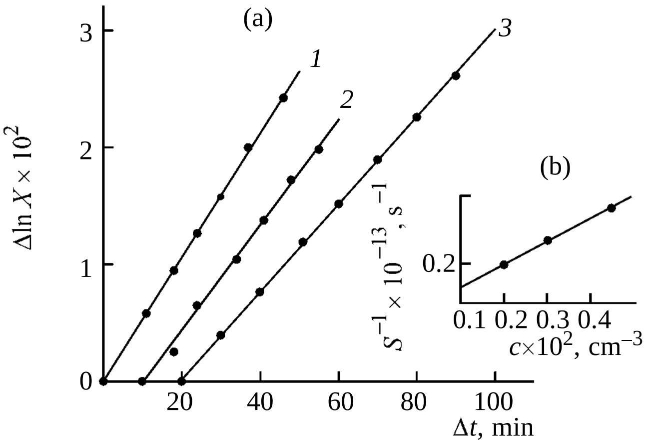

Fig. 1. (a) Rate of shifting of the sedimentation boundary $\Delta\ln X$ vs. time Δt for (*1*–*3*) three concentrations of solutions of sample no. 4 in cyclohexane and (b) concentration dependence of the sedimentation coefficient S^{-1} for this sample.

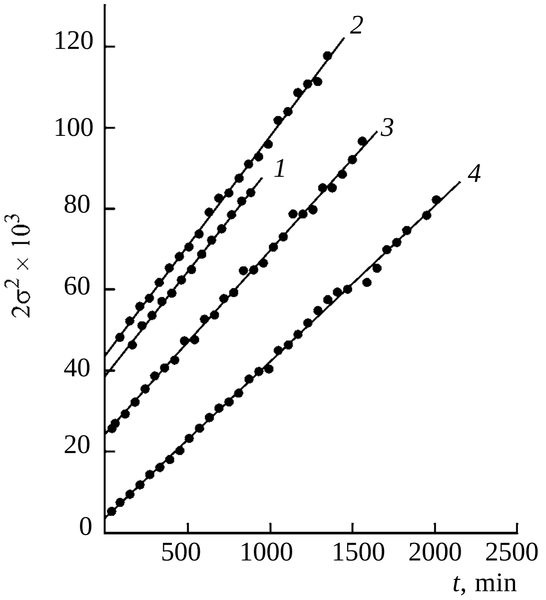

Fig. 2. Plots of diffusion boundary variance $2\sigma^2$ vs. time t for sample nos. 1–4 in cyclohexane. Here and in Figs. 3 and 5, the plot numbers correspond to the sample numbers in Table 2.

coefficient S_0 at $c \to 0$ [11]. Figure 1b represents the corresponding experimental concentration dependence of S^{-1} for sample no. 4.

Figure 2 shows the plots of the double variance $2\sigma^2$ of the diffusion boundary vs. time t for sample nos. 1–4, whose slopes were used to determine the diffusion coefficients $D = (1/2)(d\sigma^2/dt)$. The diffusion coefficients D_0 in Table 2 were obtained with account for the concentration dependence of D. From the experimental sedimentation coefficients S_0 and forward diffusion coefficients D_0 (Table 2) of the polymer samples we estimated their molecular weights [Eq. (2)].

Figure 3 shows the concentration dependences of specific viscosity η_{sp}/c from which, by Eq. (3), we determined the intrinsic viscosities [η] and Higgins constants k'. The Higgins constants k' reflecting the thermodynamic state of the polymer–solvent system [11] are given in Table 2. Comparing the [ν] values and their corresponding k' values we can see that toluene is the thermodynamically “poorest” solvent for sample nos. 1–4, which, in turn, practically rules out volume effects on the electrooptical properties of sample nos. 1–4 in this solvent [12].

It can be noted that the molecular weights of the poly(1-trimethylsilyl-1-propynes) prepared with $NbCl_5$ are rather high [$(159–490) \times 10^3$], and, hence, the reaction temperature has no significant effect on the degree of polymerization of the samples. The use of another catalyst for the synthesis of poly(1-trimethylsilyl-1-propyne) (Table 2, sample no. 5) allows the molecular weight of the polymer to be substantially increased.

The electrooptical Kerr effects of solutions of the poly(1-trimethylsilyl-1-propyne) samples in all the solvents used in the present work are positive, proportional to the squared electric field strength, and exceed the solvent contribution to the observed birefringence.

Figure 4 represents typical plots of birefringence Δn vs. squared electric field strength E^2 for solutions of sample no. 1 in carbon tetrachloride. Fig. 5 gives

Table 1. Reaction conditions and average contents of *cis*-C=C bonds in the samples studied

Sample no.	Solvent/ catalyst[a]	Reaction temperature, °C	α, %[b]
1	Toluene/$NbCl_5$	80	60
2	Toluene/$NbCl_5$	25	60
3	Toluene/$NbCl_5$	0	60
4	Toluene/$NbCl_5$	–10	70
5	Toluene/$TaCl_5$/BuLi	–10	40

[a] Monomer : catalyst molar ratio 50 : 1. [b] α is the content of *cis*-C=C bonds in the polymer.

Table 2. Intrinsic viscosities [η], Higgins constants *k*', specific electrooptical Kerr constants *K* of the samples in toluene (C_7H_8), carbon tetrachloride (CCl_4), and cyclohexane (C_6H_{12}), and their diffusion coefficients D_0, sedimentation coefficients S_0, and molecular weights *M*

Parameter	Sample no. 1[a]			Sample no. 2			Sample no. 3			Sample no. 4			Sample no. 5[b]		
	C_7H_8	CCl_4	C_6H_{12}	C_7H_8	CCl_4	C_6H_{12}	C_7H_8	CCl_4	C_6H_{12}	C_7H_8	CCl_4	C_6H_{12}	C_7H_8	CCl_4	C_6H_{12}
[η], $cm^3 g^{-1}$	62	96	91	46	84	79	70	92	91	60	105	151	650	–	667
k'	1.27	0.41	0.45	1.21	0.40	0.49	1.11	0.42	0.44	1.17	0.35	0.11	0.45	–	0.26
$K \times 10^{10}$, $cm^5 g^{-1} \cdot (300 V)^{-2}$	1.3	2.1	1.2	0.5	1.0	0.7	0.8	1.5	0.9	1.4	2.1	–	5.2	–	5.8
$D_0 \times 10^7$, $cm^2 s^{-1}$			2.15			2.24			1.87			1.52			0.70
$S_0 \times 10^{13}$, s			–			3.96			4.76			6.06			7.54
$M \times 10^{-3}$			159			190			274			492			1160

[a] The molecular weight of sample no. 1 was calculated from the diffusion and viscometry data by the equation $M = 100 \times (A_0 T)^3/([\eta]\eta_0^3 D_0^3)$ at an average experimental hydrodynamic invariant A_0 of 3.31×10^{-10} g cm^2 s^{-2} $3deg^{-1}$ $mol^{-1/3}$. [b] Sample no. 5, unlike sample nos. 1–4, is insoluble in CCl_4.

the concentration dependences of specific Kerr constant for sample nos. 1–4 in toluene. The *K* values extrapolated, in accordance with Eq. (4), to zero concentrations of the samples in various solvents, are given in Table 2.

As can be seen, the Kerr constants *K* of sample nos. 1–4 in carbon tetrachloride are slightly higher than those in toluene and cyclohexane, which stems from a disparity in the internal field factors which measure the difference in the strengths of the external field and the field acting on the molecule in the solution and responsible for the observed electrooptical effect [see Eq. (4)]. In accordance with this equation, the relative *K* values of sample nos. 1–4 in each of the solvents studied remain almost invariable. The *K* values of sample nos. 1–4 in toluene, carbon tetrachloride, and cyclohexane vary only slightly both from solvent to solvent and from sample to sample in the same solvent. For the samples studied in the present work the *K* values vary from 0.5×10^{-10} (sample no. 2) to 1.4×10^{-10} cm^5 g^{-1} $(300\ V)^2$ (sample no. 4) in toluene. These *K* values are substantially lower than the corresponding Kerr constant in the

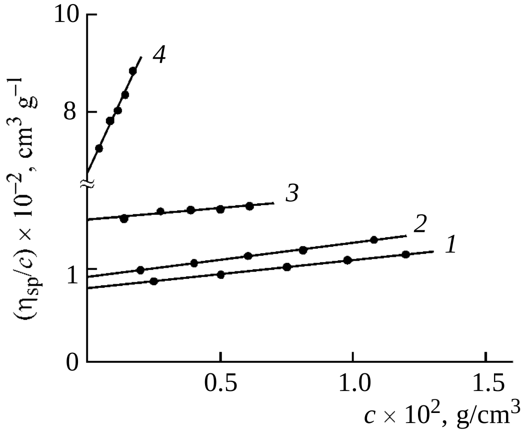

Fig. 3. Plots of viscosity η_{sp}/c vs. concentration of solutions of sample nos. 1–4 in cyclohexane.

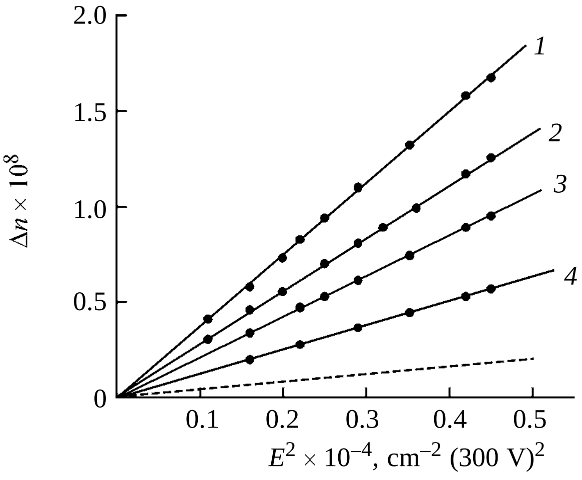

Fig. 4. Plots of birefringence Δn vs. squared electric field strength E^2 for solutions of sample no. 1 in carbon tetrachloride at concentrations of (*1*) 1.41, (*2*) 0.984, (*3*) 0.693, and (*4*) 0.429×10^{-2} g cm^{-3}. The dotted line shows the same plot for the solvent.

same solvent for the sample with a 40 : 60% average *cis/trans*-C=C ratio, prepared with $TaCl_5$/BuLi as catalyst. (Table 2, sample no. 5). According to our previous data for another sample synthesized with $TaCl_5$/BuLi and examined by fractions [7], the specific Kerr constants of toluene solutions of the fractions vary from 5 to 12.5×10^{-10} cm^5 g^{-1} $(300\ V)^{-2}$, whereas the molecular weights of these fractions span the range $(325–1040) \times 10^3$ and also relate to the Gaussian chain length range [11].

Thus, we revealed substantial differences in the electrooptical characteristics of the poly(1-trimethylsilyl-1-propyne) samples prepared with different catalysts. Obviously, the latter exert a marked effect on the microstructure and, as a consequence, molecular properties of the polymers.

The reason for such strong differences in the Kerr constants K of polymer samples having similar chemical composition and molecular weights falling into the Gaussian chain length range, where K should not depend on the molecular weight of the polymer [12], is to be looked for in different degrees of intramolecular ordering of chemical bonds in macrochains or, more specifically, different degrees of regularity of addition of monomeric units in only one of their possible isomeric forms in the course of polymer synthesis under different catalytic conditions. It is such structural differences of macromolecules that the electrooptical Kerr effect is sensitive to [12, 13].

As we showed earlier [8], the K values of disubstituted polyacetylenes depend on the presence in their structure of fairly long regular sequences of *trans*- or *cis*-C=C bonds which are kinetic units of these polymeric chains that tend to independently orient on exposure to electric field in solutions. This stems from a direct relation between K and the optical polarizability anisotropy and dipole moment of the kinetic unit of the chain, according to Eq. (1) [12].

$$K = \frac{2\pi N_A (n_0 + 2)^2 (\varepsilon_0 + 2)^2 \rho_0}{1215 kTn_0 M} \times \Delta a \left[2\Delta a + \frac{\mu^2}{kT}(3\cos^2\beta - 1) \right]. \quad (1)$$

Here k is the Boltzmann constant, N_A is the Avogadro number, M is the molecular weight of an independently oriented unit of the chain, Δa and μ are the optical polarizability anitropy and constant dipole moment of the unit, respectively, β is the angle between the direction of the dipole moment and the strongest optical polarizability axis of the selected fragment of the chain, and n_0, ε_0, ρ_0 are the refractive index, dielectric constant, and density of the solvent.

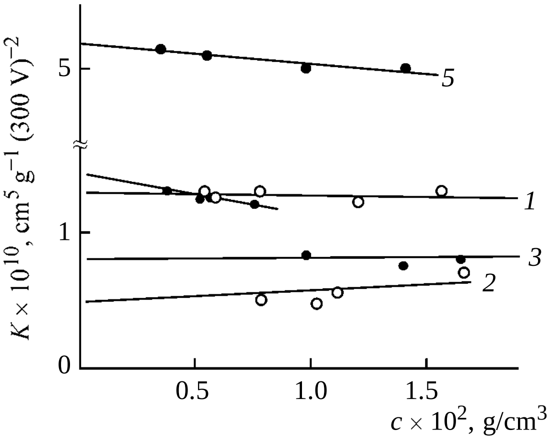

Fig. 5. Concentration dependences of specific Kerr constant K for solutions of sample nos. 1–5 in toluene.

As shown in [8], the polarity of the regular portion of the poly(1-trimethylsilyl-1-propyne) chain is directly related to its length. This determines the electrooptical properties of this class of polymers. The difference in the electrooptical properties of samples prepared with different catalysts is indicative of the presence in their chains of various-length sequences with the same configuration of the C=C bonds. The experimental data on the electrooptical properties of poly(1-trimethylsilyl1-propyne) samples with similar average *cis/trans*-C=C ratios but prepared under different catalytic conditions give us grounds to state that the $TaCl_5$/BuLi catalytic system allows preparation of polymers with a higher degrees of regularity (i.e., with a greater number of monomeric units incorporated in blocks of regular structure) than the $NbCl_5$ catalyst.

EXPERIMENTAL

Four unfractionated samples of poly(1-trimethylsilyl-1-propyne) prepared with $NbCl_5$ as catalyst without any source of counter ions added to the reaction mixture were studied. Varying the reaction temperature in the range 0–80°C had no effect on the average content of the *cis* structures in sample nos. 1–3 whose average *cis/trans*-C=C ratio was 60 : 40%. As the reaction temperature was brought down to –10°C, the content of *cis* structures (sample no. 4) tended to increase.

Sample no. 5 was prepared by the procedure described in [9].

The *cis/trans*-C=C ratio in the polymers was determined from the ^{13}C NMR spectra of solutions of poly(1-trimethylsilyl-1-propynes) in $CDCl_3$, recorded on a Bruker MSh-300 (75.47 MHz) instrument as described in [14]. The molecular weights of the polymer samples were determined by the diffusion–sedimentation method in cyclohexane [12, 15].

High-rate sedimentation was studied on an MOM-3180 ultracentrifuge in a single-section cuvette at a rotor speed of 40×10^3 rpm. Detailed procedures for sedimentation boundary and forward diffusion measurements are described in [15]. The sedimentation coefficients S were calculated from the shift of the sedimentation boundary X with time.

The forward diffusion was studied on a Tsvetkov diffusometer by a classical method that involves forming a boundary between the solution and solvent and its recording at certain intervals by means of a polarization interferometer [12, 15]. A conventional algorithm of diffusion data treatment was used [15].

The molecular weights M of the samples were calculated from their D_0 and sedimentation coefficients S_0 by the Svedberg formula [12, 15].

$$M = RTS_0/(1 - \nu\rho_0)D_0. \quad (2)$$

Here R is the universal gas constant, T is the absolute temperature, ν is the specific partial volume of the polymer in the solution (the experimental ν value for sample no. 1 in cyclohexane is 0.995 $cm^3\ g^{-1}$), and ρ_0 is the density of the solvent.

Intrinsic viscosity measurements were carried out in cyclohexane, toluene, and carbon tetrachloride to meet the thermodynamic conditions in solvents used for electrooptical studies. The intrinsic viscosities $[\eta]$ of the samples were determined from Higgins plots [15].

$$\eta_{sp}/c = [\eta] + k'[\eta]^2c + \ldots \quad (3)$$

Here $\eta_{sp}/c = (\eta - \eta_0)/c\eta_0 = (t - t_0)/ct_0$, η and η_0 are the viscosities of the solution and the solvent, respectively, t and t_0 are the flow time of the solution and the solvent in the Ostwald viscometer.

The electrooptical Kerr effect in solutions was studied in pulse electric field, square pulse time 100–200 ms, cell voltage 0–1 kV. The measurements were performed in a glass cell with parallel-plate titanium electrodes (length 2 cm, plate spacing 0.05 cm). The Kerr effect was measured by the photoelectric method with use of low-frequency modulation of elliptic light polarization by the compensation procedure described in [12]. The source was a He–Ne laser (λ 6328×10^{-8} cm), and the compensator was a thin mica plate with an intrinsic phase difference of 0.01–2π.

The specific Kerr constants were calculated by Eq. (4).

$$K = \lim_{\substack{E \to 0 \\ c \to 0}} [(\Delta n - \Delta n_0)/E^2c]. \quad (4)$$

Here $(\Delta n - \Delta n_0)$ is the difference in the birefringences in electric field of a solution of a substance under examination at concentration c and of the solvent, respectively, and E is the electric field strength.

Viscosity, sedimentation, and diffusion measurements were performed at 25±0.1°C, and electrooptical measurements, at 21±0.1°C.

ACKNOWLEDGMENTS

The work was financially supported by the *Integratsiya* Special Federal Program (project no. 326.38).

The authors are grateful to N.A. Mikhailova and I.Yu. Ruzmaikina for their participation in this work.

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