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SPECIFIC TECHNOLOGICAL PROCESSES

Heat-Resistant Polyfunctional Materials for Microelectronics: Hydrodynamic, Optical, and Conformational Properties of Si-Containing Poly(*ortho*-Hydroxy Amide)

L. I. Rudaya[a]*, I. A. Strelina[b], O. V. Okatova[b], M. A. Bezrukova[b], M. N. Bol'shakov[b], A. Yu. Marfichev[b], G. K. Lebedeva[b], and S. M. Ramsh[a]

[a] *St. Petersburg State Technological Institute (Technical University), Moskovskii pr. 26, St. Petersburg, 190013 Russia*
**e-mail: 9241890@mail.ru*
[b] *Institute of Macromolecular Compounds, Russian Academy of Sciences, Bolshoi pr. 31, St. Petersburg, 199004 Russia*

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Abstract—Polycondensation of a mixture of diamines, 3,3'-dihydroxy-4,4'-diaminodiphenylmethane and bis-(3-aminopropyl)dimethylsiloxane taken in a 3 : 2 molar ratio, with isophthaloyl chloride was used to synthesize a silicon-containing poly(*ortho*-hydroxyamide) POA-Si exhibiting an increased adhesion to such substrates as Si, SiO_2, quartz, glass, and glass-ceramics. The polymer was separated by the fractional precipitation method into seven fractions and its polydispersity was evaluated. The degree of intramolecular orientation ordering (Kuhn segment) was determined and Mark–Kuhn–Houwink equations were derived, which can be used to determine the molecular masses of the newly synthesized samples.

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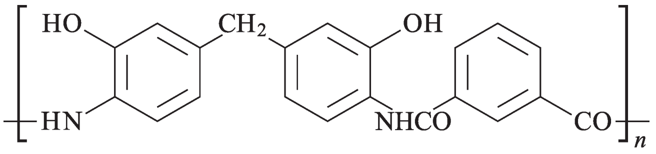
It is known that aromatic poly(*ortho*-hydroxyamides) (POA) and poly(benzoxazoles) PBO formed in the polydehydration of the former are used as heat-resistant polymeric binders for microelectronics [1]. The product formed in polycondensation of 3,3'-dihydroxy-4,4'-diaminodiphenylmethane and isophthalic acid chloride, POA (I), was used, with addition of hydrophobic light-sensitive solubility inhibitors, derivatives of 2,1-diazonaphthalenone, to create a heat-resistant photoresist that can be used to form solid or microprofiled thermally stable thin-film protective dielectric coatings [2–4].



POA (I)

The photoresist proved itself to be good not only as an interlayer insulator and protective coating, but also as a component for nanocomposites with good dielectric properties [5], luminescent and laser-sensitive coatings [6, 7], composites serving to form a matrix triad of light filters for liquid-crystal displays, and as a means of device protection from microwave radiation [8, 9].

The process in which a microprofiled protective layer is formed and its properties and quality are largely determined by the chemical structure, molecular-mass distribution, and thermodynamic and conformational properties of molecular chains in the polymeric binder contained in the photoresist. For POA (I), the hydrodynamic and conformational characteristics were studied, and Mark–Kuhn–Houwink equations were derived on the basis of experimental data and then used to determine its molecular mass (MM). The molecular-mass distribution (MMD) in polymer samples can be controlled by choosing synthesis conditions. This distribution must be such that, on the one hand, the thermal stability of films formed on its basis is provided and, on the other hand, the films remain soluble in

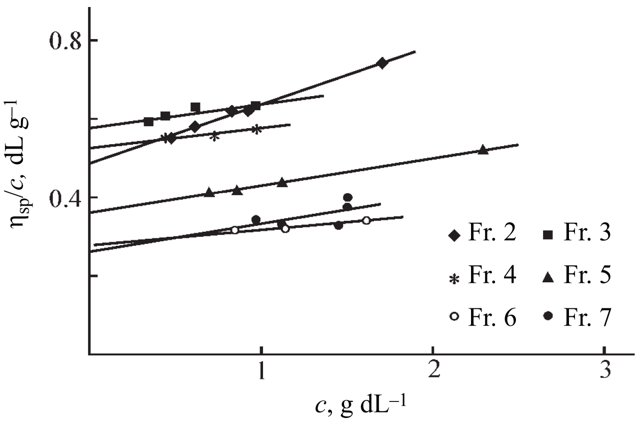


Fig. 1. Dependence of η_{sp}/c on c for fractions of the copolymer POA-Si (II) in DMAA.

aqueous-alkaline solutions when a microprofile is formed after the exposure.

Materials based on POA (I) form heat-resistant strong-adhesion films on the following substrates: Al_2O_3, aluminum, sapphire, GaAs, Al/Si, Cr/Si, Au/Si, Ni/Si. However, the adhesion of the films to silicon-containing substrates (Si, SiO_2, quartz, glass, glass-ceramic) is lowered, which results in the flaking and cracking of the films, especially in the case of their thermal treatment. It is more appropriate to use for substrates of this kind copolymers including both aromatic and Si-containing fragments. The synthesis, physicochemical properties, and electrical characteristics of such a polymer, POA-Si (II), were described in [4]. The reaction of polycondensation of isophthaloyl chloride and two diamines, 3,3'-dihydroxy-4,4'-diaminodiphenylmethane and bis-(3-aminopropyl)dimethylsiloxane (taken in a 3 : 2 molar ratio), was performed similarly to the synthesis of POA (I). Because the chemical natures of the diamines entering into the reaction are different, then, naturally, the MMD and the conformational parameters of POA-Si (II) may differ from those for POA (I).

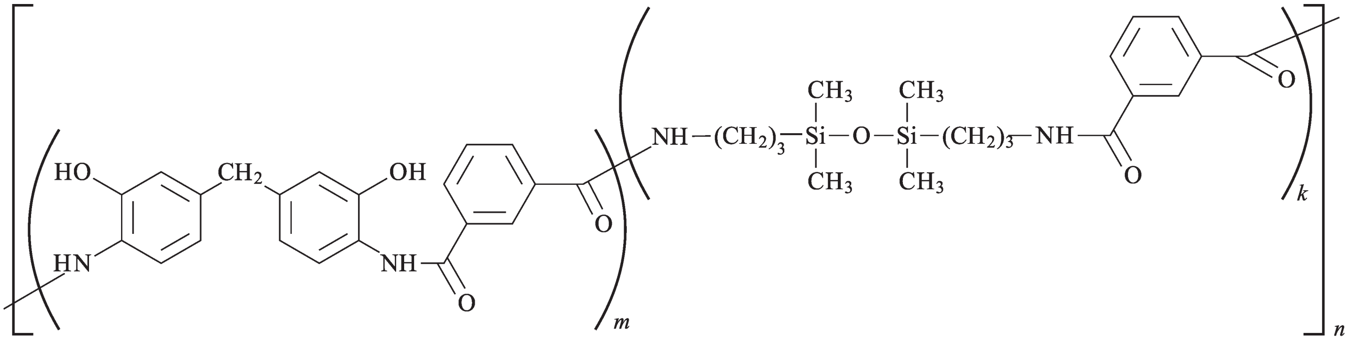
The goal of our study was to examine the hydrodynamic, optical, and conformational characteristics of POA-Si (II): determine the MM of fractions of the copolymer; evaluate its polydispersity; calculate from experimental data the Kuhn segment, which characterizes the degree of intramolecular orientation ordering, and parameters of the Mark–Kuhn–Houwink equation for the presently unknown viscometric and diffusion data. This is important for understanding, controlling, and optimizing the technological processes performed when microprofile layers and protective coatings are deposited.

EXPERIMENTAL

Synthesis of POA-Si (II). Isophthaloyl chloride (IPC) from Sigma Aldrich (CAS 99-63-8) was used without any preliminary purification. Epychlorohydrin (ECH) from Sigma Aldrich (CAS 106-89-8) and bis-(3-aminopropyl) dimethylsiloxane were distilled prior to being used. POA-Si (II) was produced by the polycondensation reaction of a mixture of diamines, 3,3'-dihydroxy-4,4'-diaminodiphenylmethane and bis-(3-aminopropyl) dimethylsiloxane (taken in a 3 : 2 molar ratio), and IPC dissolved in dimethylacetamide (DMAA) with amount of moisture not exceeding 0.05% by the procedure reported in [4] (Scheme 1).

Procedure for fractionation of POA-Si (II). To choose the precipitating agent, we preliminarily performed precipitation of POA-Si (II) from a solution in DMAA with carbinol, isopropanol, and ethanol. Ethanol

Scheme 1.



POA-Si (II)
$m = 0.6$; $k = 0.4$

was found to be the most efficient for the fractional precipitation of this polymer from solution.

A 3.11-g portion of POA-Si (II) was dissolved in 70 mL of DMAA, and the solution was cooled to (–5 ± 2)°C. Ethanol cooled to (–5 ± 2)°C was added to the resulting solution from a dropping funnel. A stable finely dispersed precipitate appeared only upon addition of 88 mL of the precipitating agent. The resulting suspension was allowed to stay for 24 h, and then the solution was separated from the precipitate by decantation. The precipitate was treated with ethanol to remove the remainder of DMAA and dried in a vacuum-desiccator. The yield of the first fraction was 0.34 g (10.9%) (fraction 1). The isolation and treatment of the subsequent fractions from the solution being fractionated were performed similarly. The weights of the resulting fractions are listed in Table 1. The total weight m_0 of all the fractions was 2.84 g. The first fraction was found to be nearly insoluble in DMAA.

All the hydrodynamic and optical studies were carried out in DMAA. The research procedures were described in [10, 11, 13].

Viscometry. The viscosity of solutions of the copolymer fractions were measured in an Ostwald capillary viscometer. The flow time of the solvent was 70 s. The characteristic viscosities [η] of the solutions were found (Fig. 1) by the Huggins extrapolation $[\eta] = \lim_{c\to 0}(\eta_{sp}/c)$, where c is the solution concentration, and $\eta_r = \eta/\eta_0$ is the ratio between the solution viscosity η and that of the solvent, η_0.

The translational diffusion was examined with a Tsvetkov polarization diffusion meter [10, 11] by the classical method in which a boundary is formed between a solution and a solvent, and the position of this boundary is recorded at certain intervals of time. The study was carried out in a metallic cuvette with a teflon insert having thickness of 2 cm along the light path. The variance $\overline{\sigma^2} = (Q/H)^2/2\pi$ was calculated by the method of the maximum ordinate H and area Q (Q is the area under the diffusion curve, and H, its maximum ordinate).

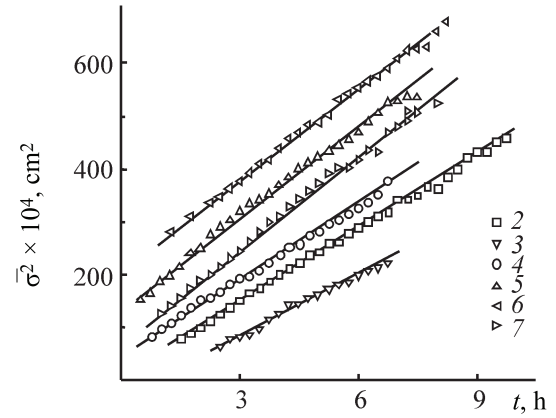


Fig. 2. Variance $\overline{\sigma^2}$ of the diffusion boundary vs. time t. The digits at the symbols correspond to fraction numbers in Table 1.

The diffusion coefficients D of the fractions were found from the slope ratios of linear time dependences of the variance $\overline{\sigma^2}$ of the diffusion boundary (Fig. 2) by the formula

$$D = (1/2)\partial\overline{\sigma^2}/\partial t. \tag{1}$$

The diffusion coefficients found at so low concentrations were taken to be the values D_0 extrapolated to the zero concentration.

The values obtained for [η] and translational diffusion coefficient D are listed in Table 1.

Table 1. Results of hydrodynamic and optical studies of fractions of POA-Si (II) copolymer in DMAA

Fraction	Fraction weight Δm_M, mg	MM	[η], dL g^{-1}	k'	$D \times 10^7$, cm^2 s^{-1}	dn/dc	$\Delta n/\Delta\tau \times 10^{10}$, cm s^2 g^{-1}
1	340						
2	1180	7000	0.48	0.64	6.4	0.19	
3	370	10300	0.57	0.17	5.3	0.18	14.1
4	200	6300	0.53	0.16	7.1	0.19	
5	250	5300	0.36	0.54	7.7	0.18	17.9
6	170	6200	0.30	0.52	7.8	0.21	
7	330	4500	0.26	1.07	8.1	0.19	15.0

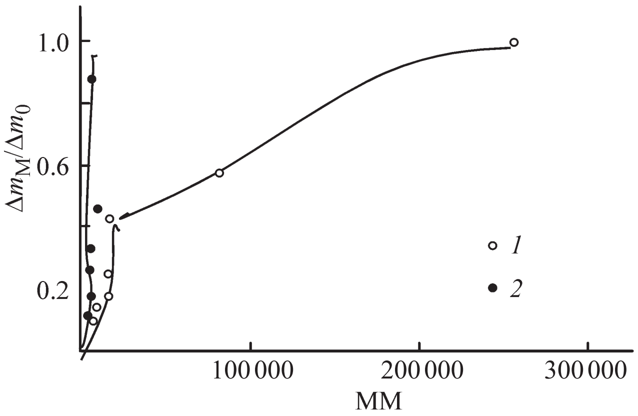


Fig. 3. Integral molecular-mass distribution of (*1*) POA (I) and (*2*) POA-Si (II) samples according to the results of a fractional rectification.

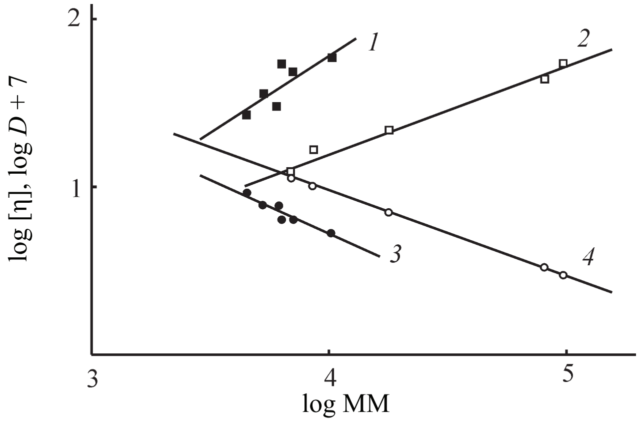


Fig. 4. Logarithmic dependence of (*1, 2*) characteristic viscosity [η] and (*3, 4*) diffusion coefficient on MM for (*1, 3*) POA-Si(II) and (*2, 4*) POA (I) fractions in DMAA.

Flow birefringence (Maxwell effect) (FB). Measurements were made in a titanium dynamo-optimeter at a wavelength $\lambda = 550$ nm. The rotated elliptical compensator had a relative path-length difference $\Delta\lambda/\lambda = 0.032$. For the copolymer fractions, measurements were made at solution concentrations $c \approx (1\text{–}1.5) \times 10^{-2}$ g cm^{-3}. So low solution concentrations, at which the condition $c[\eta] < 1$ is satisfied, made it possible to take as the optical shear coefficient of the dissolved polymer, [n]/[η], the values $(\Delta n/\Delta\tau) = (\Delta n_{sol} - \Delta n_0)/[g(\eta - \eta_0)]$. Here, Δn_{sol} and Δn_0 are, respectively, the birefringence values observed for, respectively, solutions and solvent; $\Delta\tau = g(\eta - \eta_0)$, excess shear stress; *g*, flow rate gradient; and η and η_0, solution and solvent viscosities, respectively.

RESULTS AND DISCUSSION

Hydrodynamic properties. The dependence $\eta_{sp}/c = f(c)$ is described by the equation $\eta_{sp/c} = [\eta] + k'[\eta]^2c$. The coefficient *k*' is the Huggins parameter characterizing the polymer–solvent interaction, which is independent of the molecular weight for the given system. In a θ-solvent (thermodynamically ideal) [10], $k' \approx 0.5$, this parameter being larger in a poor solvent and 0.2–0.3 in a good solvent. For the given copolymer, the scatter of *k*' values is in all probability determined by the different compositions of the copolymer fractions.

The molecular masses of the fractions were found from the results obtained in measurements of the characteristic viscosity [η] and translational diffusion coefficients $D_0 = kT/f$ (*f* is the friction coefficient of a macromolecule) by using the relation

$$M_{D[\eta]} = (A_0/\eta_0 D_0)^3 (T^3/[\eta]) \quad (2)$$

at a hydrodynamic invariant $A_0 = 3.2 \times 10^{-10}$ erg/K [10, 12].

As follows from the data in Table 1, the isolated fractions of POA-Si (II) have rather close MMs. This is indicative of a very narrow MMD of the sample. Figure 3 shows integral MMD curves for POA (I) and for the copolymer under study. In POA (I), 46% is constituted by low-molecular fractions (MM ≤ 20 000), and more than 50%, by a macromolecular fraction (MM ~260 000). For the POA-Si (II) copolymer, the content of the macromolecular (insoluble) part does not exceed 12%.

Figure 4 plots on the log–log scale the dependences of the characteristic viscosity [η] and diffusion *D* on molecular weight $M_{D\eta}$ for the fractions under study of POA-Si (II) copolymer. For comparison, the dependences for the earlier examined POA (I) are shown.

To these dependences correspond the Mark–Kuhn-Houwink equations

$$[\eta] = 0.013 \times M^{0.92}, \text{ cm}^3\text{ g}^{-1}; \quad (3)$$

$$D = 1.9 \times 10^{-4} M^{-64}, \text{ cm}^2\text{ s}^{-1}. \quad (4)$$

The exponents in the Mark–Kuhn–Houwink equations obtained for POA-Si (II) somewhat exceed those previously obtained for POA (I) (0.53 for viscometry and –0.52 for diffusion). This indicates that macromolecules of POA-Si (II) copolymer in DMAA are larger in size than POA (I) molecules in the same solvent. This is also evidenced by the higher characteristic viscosities for the copolymer fractions, compared with [η] for POA (I)

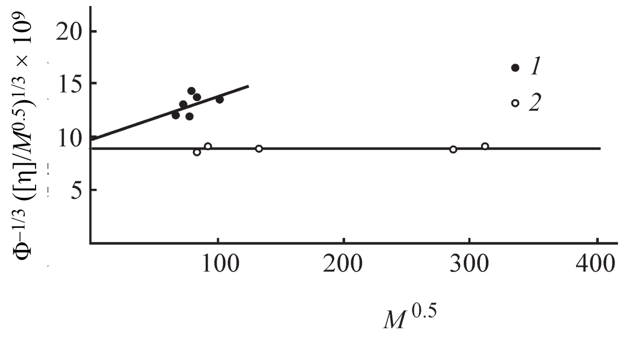


Fig. 5. Dependence of $\Phi^{-1/3}$ $([\eta]/M^{0.5})^{1/3}$ on $M^{0.5}$ for (*1*) POA (I) and (*2*) POA-Si (II) in DMAA.

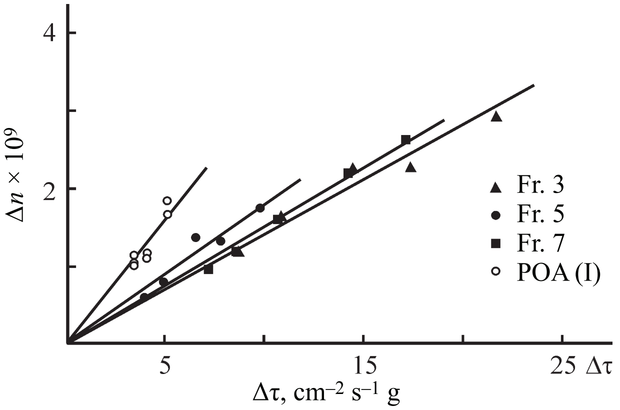


Fig. 6. Dependence of the birefringence Δ*n* on the shear stress for POA (I) and POA-Si (II) copolymer in DMAA.

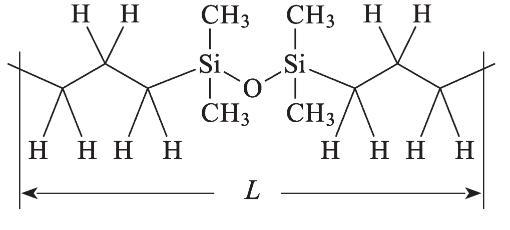
fractions with about the same MMs. This may be due to the intramolecular interaction (repulsion, incompatibility) of siloxane + methylene groups and POA units, which leads to "swelling" of macromolecules. Equations (3) and (4) can be used to find the molecular masses of the fractions obtained for the copolymer of the given composition from their characteristic viscosities [η] or from the translational diffusion coefficient measured in DMAA.

To evaluate the equilibrium rigidity of molecules, the Stockmayer–Fixman extrapolation procedure [14] is performed as

$$\Phi^{-1/3}([\eta]/M^{0.5})^{1/3} = (A/M_L)^{0.5}[1 + 0.17B(M_L/A)^{3/2}M^{0.5}], \quad (5)$$

where, $\Phi = 2.2 \times 10^{21}$ is the Flory parameter; *A*, length of the statistical Kuhn segment, *M*, molecular weight; and M_L, mass of a unit chain length.

As the unit chain length M_L is taken the average value for the copolymer composition $0.6_{POA}/0.4_{SiO}$ = $(M_{LPOA}) \times 0.6 + (M_{LSiO}) \times 0.4$. The mass of the chain unit length, $M_{LPOA} = 21.2 \times 10^8$ mol cm^{-1}. For the $-(CH_2)_3-Si(CH_3)_2-O-Si(CH_3)_2-(CH_2)_3-$ fragment (its structure is shown), the mass of the unit chain length was calculated for a straightened chain with valence angles preserved.



The mass of the repetitive part is calculated and divided by its length. The chain length can be calculated by using the valence angles and bond lengths or by, e.g., Hyper Chem software. We obtain the value $M_{LSiO} = 216/12.5 \times 10^{-8} = 17.3 \times 10^8$ mol cm^{-1}. With these values, we have for the copolymer, $M_{LPOA\text{-}Si} = (21.2 \times 0.6 + 17.3 \times 0.4) \times 10^8$ mol cm^{-1} = 19.64×10^8 mol cm^{-1}. The $\Phi^{-1/3}$ $([\eta]/M^{0.5})^{1/3} = 9.9 \times 10^{-9}$ intercept on the ordinate axis [equal to $(A/M_L)^{0.5}$] was used to find the Kuhn segment length *A* = 19.0 Å. This value nearly coincides (within the measurement accuracy) with *A* = 17.0 for POA (I).

Laminar flow birefringence (Maxwell effect) is determined by the optical, conformational, and hydrodynamic properties of dissolved noninteracting macroscopic particles (macromolecules).

For systems in which the refractive indices of the polymer (n_k) and solvent (n_s) are different, the characteristic birefringence can be represented as a sum of three terms [10, 13]:

$$[n]/[\eta] = [n]_i/[\eta] + [n]_f/[\eta] + [n]_{fs}/[\eta]. \quad (6)$$

The first term is the contribution due to the intrinsic optical anisotropy of molecules, given for a Gaussian chain by the Kuhn relation [10]:

$$\frac{[n]_i}{[\eta]} = \frac{4\pi(n_s^2 + 2)^2}{45kTn_s}(\alpha_1 - \alpha_2)_i, \quad (7)$$

where $(\alpha_1 - \alpha_2)_i$ is the intrinsic optical anisotropy of the segment, and *T* is temperature.

The second term in Eq. (6), the macroscopic form effect, is represented as the relation

$$\frac{[n]_f}{[\eta]} = \frac{0.058\Phi(n_s^2 + 2)^2(n_k^2 - n_s^2)^2}{\pi\rho^2 N_A RTn_s^3} \times \frac{M}{[\eta]}, \quad (8)$$

Table 2. Polarizability difference of the segment ($\alpha_1 - \alpha_2$) and anisotropy β of a unit chain length of the copolymer and its components

Polymer/copolymer/components	$(\Delta n/\Delta\tau) \times 10^{10}$, cm s^2 g^{-1}	A, Å	$(\alpha_2–\alpha_2) \times 10^{25}$, cm^3	$\beta \times 10^{17}$, cm^2
POA (I)	30.0	17.0	375	22.0
–(CH_2–CH_2)–[a]		20.8	50	2.4
–Si(CH_3)$_2$–O–[a]		14	4.7	0.34
POA-Si (II)	14.1–17.9	19.1	176–224	9.3–11.7

[a] Data taken from [15].

where Φ is the Flory coefficient, and ρ is the density of the polymer. A characteristic feature of the contribution made by the effect of macroform to $[n]/[\eta]$ is that it depends on the MM of the polymer. For the most macromolecular fraction, $[n[/[\eta] \approx 1 \times 10^{-10}$ cm s^2 g^{-1}, which is comparable with the error in $(\Delta n/\Delta\tau)$ measurements.

The third term in Eq. (6), $[n]_{fs}/[\eta]$, the microform effect is determined by the MM of the segment, M_s, and by the function of the axial ratio $(L_2 - L_1)_s$:

$$\frac{[n]_{fs}}{[\eta]} = \frac{(n_s^2 + 2)^2(n_k^2 - n_s^2)^2}{180\pi RT n_s^3\rho} \times \frac{M_s}{[\eta]}(L_2 - L_1)_s, \qquad (9)$$

For flexible-chain polymers, to which the copolymer under study belongs, the microform effect is also rather small and its contribution to the observable FB can be disregarded.

Thus, the observed birefringence $[n]_i/[\eta] \approx (\Delta n/\Delta\tau)_{sol}$ is due to the intrinsic optical anisotropy of molecules, which is determined for a Gaussian chain by the Kuhn relation (7).

Figure 6 shows the $\Delta n = f(\Delta\tau)$ dependences for the starting POA (I) and several fractions of the copolymer. It follows from the plots that the $(\Delta n/\Delta\tau)$ ratio for the copolymers is approximately twice smaller than that for the starting POA (I).

This is in a good agreement with the additivity principle of the optical anisotropy for macromolecules [12]. According to this principle, the anisotropy of a unit chain length for the three-component system, $\beta = \beta_1 Z_1 + \beta_2 Z_2 + \beta_3 Z_3$, where β is the anisotropy of a unit chain length of the copolymer and its components, Z is the molar fraction of a component, and subscripts 1, 2, and 3 belong to different components of the copolymer, represented in Table 2. The values of β_2 and β_3 for components 2 and 3 were taken from [15].

In the initial composition POA (I)/POA-Si (II) = 0.6/0.4, with 1.5 monomer units –SiO– and 3 –CH_2–CH_2–CH_2– units contained in 0.4, i.e., the molar components are distributed as 0.6/0.27/0.13. Then, $\beta = \beta_1 Z_1 + \beta_2 Z_2 + \beta_3 Z_3 = (0.6 \times 22.0 + 0.272.4 + 0.13 \times 0.34) \times 10^{-17}$ cm^2 = 13.89×10^{-17} cm^2.

A similar calculation shows that the best coincidence of the experimental values of β is obtained at a molar fraction of the most anisotropic component Z_{1POA} of 0.5 ± 0.05.

CONCLUSIONS

(1) The reaction of polycondensation of a mixture of diamines, 3,3'-dihydroxy-4,4'-diaminodiphenylmethane and bis-(3-aminopropyl)dimethylsiloxane, with isophthaloyl chloride yielded the POA-Si copolymer. The method of fractional precipitation was used to separate the polymer into 7 fractions. Birefringence data indicate that the composition of the fractions under study (molar ratio between the diamines) is close to the composition taken when performing the synthesis.

(2) The molecular masses of POA-Si fractions were found from the results of diffusion-viscometric measurements. The Mark–Kuhn–Houwink equations were obtained for the viscometric and diffusion data. In contrast to the previously studied POA (I), all the fractions have rather small molecular masses, and the sample itself is characterized by a very narrow molecular-mass distribution. Despite the insignificant decrease in the thermal stability of POA-Si(II) as compared with POA, just the narrow molecular-mass distribution may favor synthesis of strong-adhesion films with more uniform thicknesses and electrical characteristics on silicon-containing substrates.

(3) The introduction of the bis-(3-aminopropyl) dimethylsiloxane fragment led to a significant increase in the size of POA-Si macromolecules, compared with that for POA. This may be due to the intramolecular interaction (repulsion, incompatibility) between bis-(3-aminopropyl)dimethylsiloxane units and the aromatic constituent in the copolymer. However, the lengths of the statistical Kuhn segments nearly coincide for both polymers within the experimental error: $A = (18 \pm 2)$ Å.

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REFERENCES

1. Sheng-H. Hsiao and Liang-R Dai, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, vol. 37, no. 13, pp. 2129–2136.
2. RF Patent 2 379 731 (publ. 2010).
3. RF Patent 2 549 532 (publ. 2015).
4. Lebedeva, G.K., Bazhenova, A.S., Rudaya, L.I., et al., *Russ. J. Appl. Chem.,* 2016, vol. 89, no. 10, pp. 1647–1654.
5. RF Patent 2 478 663 (publ. 2012).
6. RF Patent 2 505 579 (publ. 2014).
7. RF Patent 2 522 604 (publ. 2014).
8. RF Patent 2 404 446 (publ. 2010).
9. RF Patent 2 373 246 (publ. 2009).
10. Tsvetkov, V., Eskin, V., and Frenkel, S., *Structure of Macromolecules in Solutions.* London: Butterworths, 1970, p. 490.
11. Lavrenko, V.P., Gubarev, A.S., Lavrenko, P.N., et al., *Zavod. Lab.*, 2013, vol. 79, no. 7, part 1, p. 33.
12. Tsvetkov, N.V., *Rigid Chain Polymers*, New York: Plenum Press, 1989.
13. Tsvetkov, V. and Andreeva, L., *Adv. Polym. Sci.*, 1981, vol. 39, pp. 95–207.
14. Stockmayer, W.N. and Fixman, M.*, J. Polym. Sci. Part C: Polym. Symp.*, 1963, vol. 1, no. 1, pp. 137–140.
15. Tsvetkov, V.N., Andreeva, L.N., and Tsvetkov, N.V., *Anisotropy of Segments and Monomer Units of Polymer Molecules in Polymer Handbook,* Grulke, E., Brandrup, J., and Immergut, E.H., Eds., New York: Willey and Sons, 1998, vol. VII, pp. 745–763.