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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Poly(propylene glycols) as Effective Additives to the Sol-Gel Process in Fabrication of Antireflection Coatings onto Silica Glass

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Abstract—Possibility of obtaining mesoporous silicon dioxide antireflection coatings with low refractive index (1.20–1.277) by using additions of poly(propylene glycols) with various molecular masses in a sol-gel process was examined. It was demonstrated that the optimal concentration of poly(propylene glycols) in the sol, at which a sol-gel process followed by heating of a sample yields a transparent film with a maximum light transmission of 98.3–99.0%, depends on the average molecular mass of the additive.

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Multilayer coatings are widely used in blooming of optical articles. These coatings are deposited by vacuum techniques [2] and a sol-gel method [2–4]. The sol-gel method is simpler in practice and can be used to deposit coatings onto large optical elements.

New opportunities in fabrication of antireflection coatings are opened up by production of nanoporous (mesoporous) silicon oxides with low refractive indices (1.20–1.30) by modern versions of the sol-gel technique: (1) matrix synthesis of mesoporous silicates and aluminosilicates in the presence of surfactants [5, 6]; (2) synthesis of porous materials on the basis of bridged polysesquioxanes [7]; and (3) synthesis of mesoporous silicates in the presence of non-surfactant organic compounds [8].

It has been shown previously that addition of organic acids, derivatives of organic acids [9], carbochain polymers, statistical copolymers [10], and oligoesters [11] to the sol-gel process results in deposition of antireflection coatings on silicate glass. The coatings are transparent thin films (~100 nm) that are composed of mesoporous silicon dioxide and have low refractive index (1.23–1.34). Silicate glass with a double-side single-layer coating has the maximum transmittance of 98.0–99.0% for light incident onto the glass at an angle of 0°. Without the coating, the maximum transmittance of this glass is only 91.0%. The organic compounds studied [9–11] are not surfactants or amphiphilic block-copolymers and the sol-gel technique for deposition of mesoporous silicon dioxide can be regarded as belonging to version (3).

The aim of this study was to examine the possibility of deposition of mesoporous silicon dioxide antireflection coatings with low refractive index (1.23–1.30) by using poly(propylene glycol) oligomers with various molecular masses in the sol-gel process.

EXPERIMENTAL

Tetraethoxysilane (TEOS) was hydrolyzed by the procedure described in [10]. A 1.0-ml portion of TEOS and 5.0 ml of isopropanol were placed in a 50-ml glass vessel and water (in a 4 : 1 molar ratio with respect to TEOS) and hydrochloric acid (3.0×10^{-3} mol per mole of TEOS) were added. After the reaction mixture was agitated with a magnetic stirrer for 1–4 h, a solution of polypropylene glycol (PPG) in isopropanol was introduced into the reaction mixture and it was agitated

Effect of the PPG MM on the blooming capacity of film coatings

PPG MM	n	Optical thickness, nm	Maximum transmission, %	λ_{max}, nm	Optimal PPG concentration, %
425	1.280	114	98.3	500	2.0
725	1.260	118	98.5	472	2.0
1000	1.270	117	98.7	503	2.0
2000	1.250	134	98.8	540	2.5
2700	1.225	132	98.7	495	2.5
3500	1.200	128	99.0	508	3.2

at room temperature for additional 1 h. The mixture was diluted with isopropanol to a concentration of 1.0 wt % in terms of SiO_2.

Poly(propylene glycol) with various molecular masses (MM) (PPG-425, PPG-725, PPG-1000, PPG-2000, PPG-2700, PPG-3500) was purchased from Aldrich. Silicate glass slides (refractive index 1.506) served as substrates.

The coatings were deposited onto silicate glass in the same way as it was done in [10]. Their optical transmission was determined in the spectral range 200–1100 nm on a Perkin–Elmer Lambda 25 spectrometer.

The optical thickness of the films and their refractive index was determined with an LEF-3M1 ellipsometer.

Figure 1 shows optical transmission curves of uncoated slides and those with double-side single-layer coatings based on mesoporous silicon dioxide and produced by the sol-gel method in the presence of various PPG concentrations: (a) PPG-425, (b) PPG-725, (c) PPG-1000, (d) PPG-2000, (e) PPG-2700, and (f) PPG-3500.

The uncoated glass has the maximum transmission of 91.1% at wavelengths of 515–520 nm (curve *1*), with the transmission steadily decreasing to 83.3% as the wavelength shifts into the near-IR region. The glass does not transmit UV light with wavelengths shorter than 325 nm. Transparent coatings composed of mesoporous silicon dioxide with addition of PPG-425 (see Fig. 1a) make the optical transmission of the glass higher (the blooming effect is observed) in the spectral range 350–1100 nm (curves *2*–*5*). The blooming effect depends on the PPG-425 concentration in the sol: its magnitude first increases, passes through a maximum, and then starts to decrease as the additive concentration is raised. The maximum transmission of 98.3% is observed at 500 nm at the optimal additive concentration of 2.0 wt % (curve *3*). The optical thickness of the film is 114 nm, and its refractive index, 1.28 (see table).

The blooming effect is also observed for mesoporous silicon dioxide coatings obtained by the sol-gel method in the presence of various concentrations of other poly(propylene glycols): PPG-725, PPG-1000, PPG-2000, PPG-2700, and PPG-3500 (see Figs. 1b–1f and table).

The above examples indicate that the previously developed [12] EISA method (evaporation-induced self-assembly, self-organization of nanostructures, caused by evaporation of the solvent) for matrix synthesis of mesoporous silicon dioxide transparent coatings can be modified by replacing surfactants and amphiphilic block-copolymers with the well-known and readily available polypropylene glycol oligomers. In the process, a very low refractive index can be obtained: 1.20–1.28 for a transparent film composed of mesoporous silicon dioxide (see table). As follows from the Lorentz–Lorenz formula, the content of air in nanopores of the film is 40–57 vol %.

Analysis of the experimental data in the table suggests the following. First, addition of PPG-2700 and PPG-3500 oligomers results in the formation of mesoporous films of silicon dioxide with the minimum refractive indices of 1.225 and 1.20. Accordingly, the maximum transmission of light by glass slides covered with these films is observed: 98.7 and 99.0%.

It follows from the known formulas $\lambda/4 = n_f d_f$ and $n_f = \sqrt{n_g}$ (λ is the wavelength of light at which the transmission is at a maximum; n_f, refractive index of a film with 100% antireflection effect; d_f, film thickness; and n_g, refractive index of the glass, equal to 1.506)

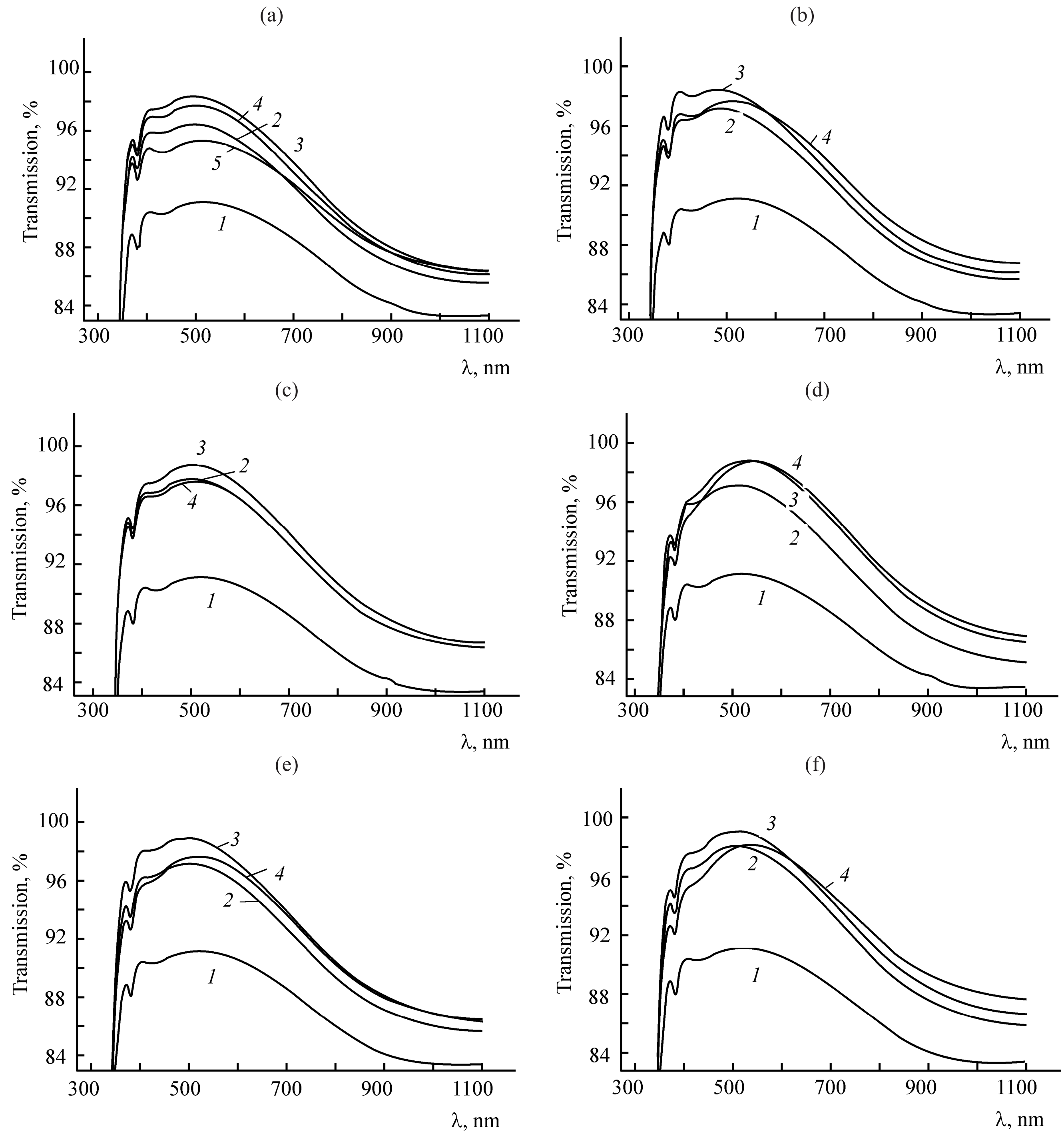

Fig. 1. Effect of additives on the blooming capacity of single-layer double-side coatings on glass. (λ) is wavelength. Additive: (a) PG-425, (b) PPG-725, (c) PPG-1000, (d) PPG-2000, (e) PPG-2700, and (f) PPG-3500. (*1*) Coating-free glass; additive content (wt %): (a) (*2*) 1.5, (*3*) 2.0, (*4*) 2.5, (*5*) 3.0; (b) (*2*) 1.5, (*3*) 2.0, (*4*) 3.0; (c) (*2*) 1.5, (*3*) 2.0, (*4*) 3.0; (d) (*2*) 1.5, (*3*) 2.2, (*4*) 2.5; (e) (*2*) 2.0, (*3*) 2.5, (*4*) 3.0; and (f) (*2*) 1.5, (*3*) 3.2, (*4*) 5.0.

that $n_f \leq 1.227$ for λ of 100% transmission. The last condition is only satisfied by mesoporous films produced by the sol-gel method in the presence of the optimal concentrations of PPG-2700 and PPG-3500. However, the maximum transmission of glass slides with the given film coatings is substantially lower than 100%: 98.7 and 99.0%. Probably, this is due to presence of light-absorbing impurities in the silicate glass, that diminish the maximum transmission by 1%. This is indicated by curve 1 describing the transmission of glass slides without film coatings (see Figs. 1a–1f). The theoretical maximum transmission at λ = 515–520 nm of a glass with a refractive index of 1.505 must be about 92.0% and, in the case under consideration, 91.%, i.e., by 1% lower than the theoretical value because of the impurities that make lower the transmission of light by the glass.

Second, it follows from the data in the table that the refractive index of mesoporous silicon dioxide films decreases from 1.277 to 1.20 as the average molecular mass of PPG increases from 425 to 3500. The optimal concentration of the additive in the sol-gel process grows from 2.0 to 3.2 wt %. The maximum light transmission by glass slides with film coatings also increases from 98.3 to 99.0% as the refractive index of mesoporous silicon dioxide decreases. It follows from the Lorentz–Lorenz formula that a porous silicon dioxide film with a refractive index of 1.28 contains 40 vol % air, and that with a refractive index of 1.20, 57 vol %.

It can be assumed that the size of nanopores and their total volume that predetermine the decrease in the refractive index of a film, depend on the ratio between the concentrations of TEOS and PPG. As this ratio decreases, i.e., the PPG concentration in the sol grows, it would be expected that the size and total volume of nanopores increases and, accordingly, the refractive index of a film decreases and the transmission of light by a coated glass slide becomes higher, and just this behavior is observed experi-mentally (see table and Figs. 1a–1f). However, the nanopores in the films can only grow in size to a certain limit equal to wavelengths in the spectral range under study. As the pore size approaches this limit, a steep rise in light scattering and, consequently, a decrease in transmission of the glass slide with a coating would be expected.

Two optical phenomena, blooming of glass with coatings having low refractive index and light scattering by the coatings, affect the transmission of light by a samples in opposite ways, and, therefore, the optimal PPG concentrations (2.0–3.2 wt %), at which the maximum blooming effect is recorded (transmission 98.3–99.0%, see Figs. 1a–1f), are observed in all the cases under study.

Interestingly, use of a PPG with an average molecular mass of 3500 in the sol-gel process at the optimal concentration of 3.2 wt % makes it possible to obtain porous films containing up to 57 vol % of air and exhibiting the strongest blooming effect.

CONCLUSIONS

(1) Poly(propylene glycol) oligomers (MM 425–3500) can be used as an organic additive to a silicon dioxide sol, which predetermines spontaneous microseparation of the inorganic and organic phases in the formation of a gel as a thin transparent film on the silicate glass surface.

(2) In “burning-out” of the organic phase from the gel at 500°C in air, a transparent film of nanoporous silicon dioxide is formed on the glass surface. The film has a low refractive index (1.20–1.277) and exhibits a strong blooming effect.

(3) The organic additive has the optimal concentration of 2.0–3.2 wt % in the sol.

(4) The refractive index of nanoporous silicon dioxide films decreases from 1.277 to 1.20 and the optimal concentration of the additive grows from 2.0 to 3.2 wt % as the average molecular mass of polypropylene glycol increases from 425 to 3500.

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