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Refraction of amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropylvinyl ether within a telecommunication wavelength ranges near 1300 and 1550 nm

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Abstract: Amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropyl vinyl ether were synthesized by ultrahigh pressure method without using of initiators. By applying spectroscopic refractometry method, authors measured the refraction (refractive index $n(\lambda)$ and material dispersion $dn(\lambda)/d\lambda$, where λ is a wavelength of optical copolymers radiation) within a telecommunication wavelength ranges near λ = 1300 and 1550 nm. It is shown that it have low values of $n(\lambda)$ and small material dispersion $dn(\lambda)/d\lambda$. Synthesized copolymers can be used as a cladding of silica fibers for high-speed optical information transmission systems, as well as a cladding of waveguides made of fluorine-containing electro-optical polymers for high-speed light modulators.

Keywords: amorphous perfluorinated polymers, ultrahigh pressure polymerization, refraction, refractive index, dispersion.

Introduction

Amorphous perfluorinated polymers with high transparency, low refractive index $n(\lambda)$ and low dispersion $dn(\lambda)/d\lambda$ within a "telecommunication" wavelength ranges λ near 1300 and 1550 nm, are promising for use in various devices for high-speed optical information transmission [1-4], for example, as a cladding of light-guiding silica fibers. At the same time, the high

transparency of perfluoropolymers provides a low attenuation coefficient for optical signals during its propagation along silica fiber, and low dispersion of refractive index provides a wide wavelength range and high data transfer rates (which can reach several Tb/s per channel) along one single-mode fiber [**5**]. In addition, perfluorinated polymers are characterized by higher chemical resistance and are more resistant to elevated temperatures than their hydrocarbon compatibles, since C-F bond in the polymer molecule is stronger than C-H bond.

Although various types of amorphous perfluorinated homo- and copolymers have been developed in a lab environment (see, for example, [6], US-patents and patents of European Patent Society [7-9]), the assortment of commercially produced and, therefore, available materials of this type is very limited. Amorphous perfluoropolymers, as far as we know, are industrially produced by only a few companies, such as DuPont (Teflon AF type polymers), Asachi Glass Co. (polymers Cytop) and Solvay Co. (polymers Hyflon AD).

This is due to complex technological process of synthesis, low yield of useful product, and, as a consequence, high cost of such polymers. In Russia, to create similar products, the method of thermal polymerization at ultrahigh pressure, developed by Institute of Organic Chemistry of Russian Academy of Sciences, is used. This method makes it possible to synthesize polymers from almost all currently known perfluorinated monomers, including those that, due to steric hindrances, under normal conditions do not enter into reaction of radical polymerization. Earlier, the perfluorostyrene homopolymer was synthesized using ultrahigh pressure (6.8 - 20 ths. atm.) [10]. Hereafter, this method was the first to synthesize amorphous homopolymers of hexafluoropropylene [11] and perfluoroisopropyl vinyl ether [12], as well as copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropyl vinyl ether [13]. In this paper, the refraction (refractive index $n(\lambda)$ and dispersion $dn(\lambda)/d\lambda$) of these copolymers within a telecommunication wavelength ranges near λ = 1300 and 1550 nm are studied for the first time. It is shown that these substances have low values of $n(\lambda)$ and $dn(\lambda)/d\lambda$) (lower than that of quartz), which makes it possible to use them as a cladding of silica fibers in the systems of high-speed optical transmission of information, as well as for formation of cladding for waveguides from fluorine-containing electro-optical polymers for high speed light modulators.

Synthesis of amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropylvinylether at ultrahigh pressure, and study of their properties

To obtain these copolymers, we used monomers perfluoro-2,2-dimethyl-1,3-dioxol D1 and perfluoropropylvinyl ether E1 produced by P&M Invest Co. [14] (see Fig. 1).

These monomers are transparent colorless liquids, the degree of their chemical purity was more than 98%.

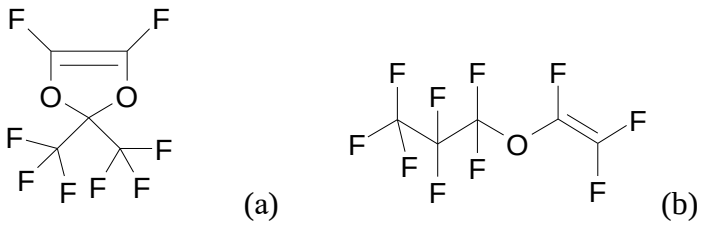


Figure 1. *Perfluorinated monomers: perfluoro-2,2-dimethyl-1,3-dioxol D1 (a), perfluoropropylvinyl ether E1 (b), used for synthesis of copolymers.*

This synthesis was carried out at a pressure of 13.5 ths. atm. and a temperature of 55°C for 15 days without any initiators. The monomers were preliminarily distilled under argon atmosphere to remove dissolved oxygen, which is known to be an inhibitor of radical polymerization reaction. After that, the monomers at a given molar ratio were poured into 2.5 cm^3 teflon ampoule, which was tightly closed with teflon lid and placed in die mold. To ensure the tightness of reaction volume, the fluoroplastic gaskets were used. The synthesis scheme for copolymers is shown in Fig. 2.

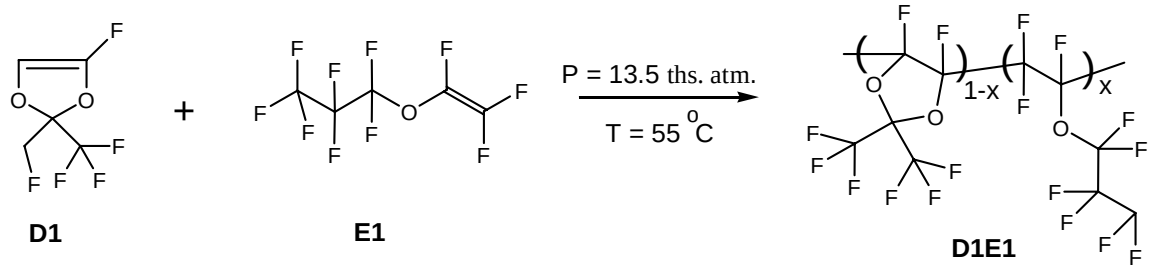


Figure 2. *Synthesis scheme and fragment of perfluorinated copolymer D1E1 structure prepared by ultrahigh pressure method. x is molar concentration of perfluoropropylvinylether E1 in the copolymer.*

Process of radical copolymerization of monomers D1 and E1, accompanied by shrinkage of reaction mixture, was controlled by punch displacement in the mold. On completing of reaction, the obtained copolymer was unloaded from ampoule and kept under vacuum at a temperature of 100°C until constant weight. Herewith, the residual monomers and light volatile by-products of this reaction were removed from copolymer. In Fig. 3 shows a typical NMR spectrum of synthesized copolymer D1E1 in perfluorobenzene, obtained via Bruker AM-300 spectrometer (282.40 MHz for ^{19}F). The ratio of integrated intensities of CF_3 - groups of dioxole (-82.7 ppm) and ether (-84.8 ppm) chain fragments showed that the molar concentration of perfluoropropyl vinyl ether in

the copolymer is x » 0.39. The yield of useful product, defined in terms ratio of copolymer weight (after it holding in vacuo at 100°C) to monomer mixture weight of reaction ampoule, was 69%.

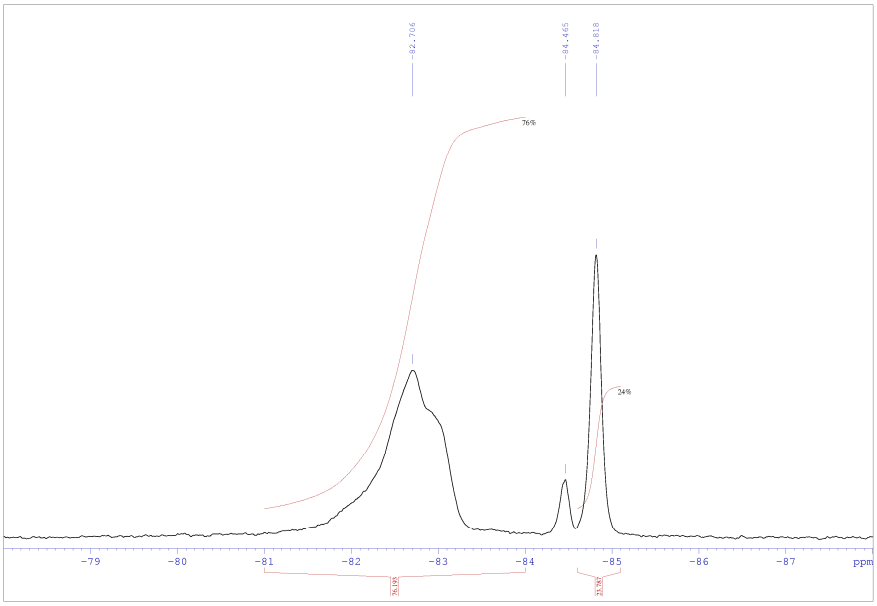


Figure 3. *NMR spectrum of D1E1 copolymer with x » 0.39, synthesized by ultrahigh pressure method. This spectrum was obtained via Bruker AM-300 spectrometer (282.40 MHz for ^{19}F) in perfluorobenzene.*

Structural diagnostics of D1E1 perfluorinated copolymers was carried out by wide-angle X-ray scattering method via Rigaku Miniflex600 diffractometer (Cu, l = 1.54184 Å). In Fig. 4 shows a typical diffraction pattern obtained for D1E1 copolymer with x = 0.39 within the scattering angle range 2q from 5 to 100 deg. It is seen that this diffraction pattern does not contain sharp peaks, but has wide “halos” near 2q ≈ 10, 14 and 40 deg. The absence of sharp peaks indicates that this copolymer is amorphous.

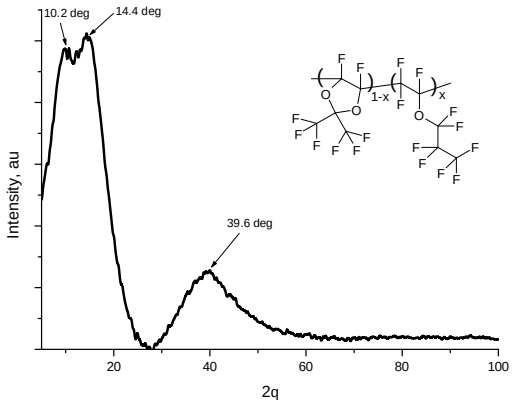


Figure 4. *Diffraction pattern of perfluoro-2,2-dimethyl-1,3-dioxole- and perfluoro-propylvinyl ether copolymers with x » 0.39, measured via Rigaku Miniflex600 diffractometer. q is angle of incidence X-ray beam to sample.*

To estimate the molecular weight of D1E1 copolymer, the average hydrodynamic diameter of macromolecular globules in perfluorodecline was measured. Measurements were performed by dynamic light scattering method via Brookhaven particle/protein analyzer while illumination of sample by 640 nm laser beam. In Fig. 5 shows a typical histogram of globule size distribution. From Fig. 5 it follows that the average size of these globules is 18 nm, i.e. D1E1 copolymer can be classified as a high molecular weight substance.

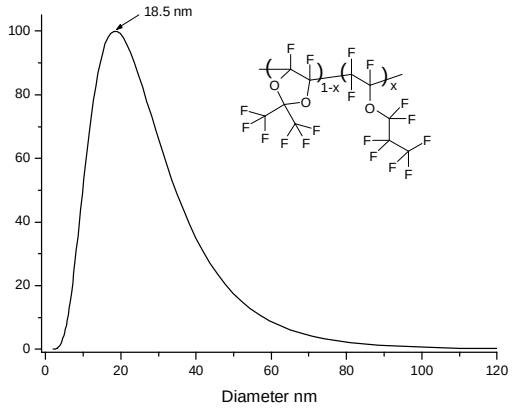


Figure 5. *Histogram of macromolecular globules size distribution of D1E1 copolymer with x = 0.39, measured by dynamic light scattering method in perfluorodecalin.*

Investigation of refraction amorphous of perfluorinated copolymers near l =1300 and 1550 nm using spectroscopic refractometry method

Measurement of refractive index n *n*(l) and dispersion d*n*(l)/dl (where l is the wavelength of optical radiation) of perfluoro-2,2-dimethyl-1,3-dioxole- and perfluoropropylvinyl ether copolymers was carried out via spectroscopic refractometric complex made based on multi-wavelength refractometer DR-M2/1550 manufactured by Atago Co. (Japan). This refractometer was equipped with InGaAs CCD camera C10633 (HAMAMATSU), sensitive within a wavelength range of 900-1600 nm. The light source was 250 W halogen lamp located in the immediate vicinity of entrance slit of M266 monochromator (Solar Laser Systems, Belarus). The special multi-core fiber-optic cable was connected to output slit of this monochromator, including 7 quartz optical fibers with diameter of light-guiding core equal 1.0 mm. At the end of this cable, facing to output slit of monochromator, the cores were arranged in the form of line parallel to entrance slit. At the other end of cable, which was used to illuminate the sample applied to the working face of measuring prism of refractometer, the cores were arranged in a form of circle.

This design provided the efficient collection of monochromatic radiation, which made it possible to measure the refractive index of copolymers at a telecommunication wavelength ranges near l = 1300 and 1550 nm [15].

Note that values of *n* obtained via DR-M2/1550 refractometer on n_D -scale (l = 589.3 nm) must be converted into “true” values of refractive index n_l using following relationship [15]:

$$\sin(b) = \pm n_D \cos(a) \mp \sqrt{N_D^2 - n_D^2}\sin(a) \quad , \qquad (1)$$

$$n_l = \sqrt{N_l^2 - \sin^2(b)}\sin(a) \pm \sin(b)\cos(a) \quad . \qquad (2)$$

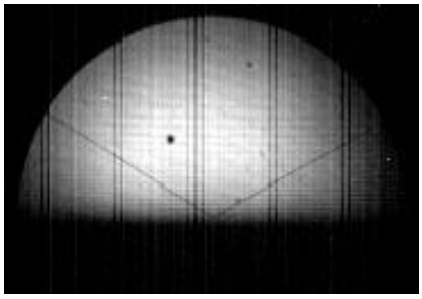
Here b is the angle that outermost beam forms relative normal to output face of measuring prism, ND is refractive index of measuring prism material at a wavelength of 589.3 nm, a is refracting angle of prism, N_l is dispersion dependence of prism material. The upper and lower signs in the formulas (1), (2) fit the cases when outermost beam emerging from measuring prism is deflected towards the refracting angle of prism or towards to opposite direction, respectively.

Refracting angle of measuring prism a = 63 0 0¢ 2¢¢ ± 3¢¢ and its refractive index N_D = 1.74064 ± 0.00002 were measured via GS-5 spectroscopic goniometer. Dispersion dependence N_l of prism material in IR spectrum was approximated by Cauchy dispersion formula, i. e.:

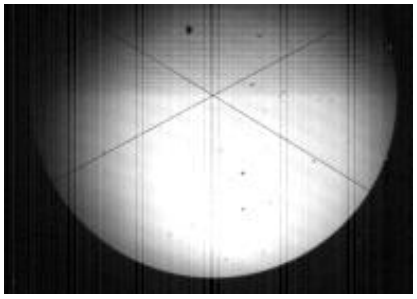
$$N_l = P_1 + P_2/l^2 + P_3/l^4 \, , \qquad (3)$$

where these coefficients *P* were assumed to be equal to P_1= 1.6934; P_2 = 2.7´ 10^4 nm^2; P_3 = -5.1´ 10^9 nm^4.

When measuring the refractive index of D1E1 copolymers, the illumination of sample deposited at the measuring prism of DR-M2/1550 refractometer was carried out both through the illumination prism and from the side of measuring prism (see Fig. 6). The results of measurement were averaged.



a)



b)

Figure 6. *View of crosshair and light/shade boundaries in the field of view of InGaAs camera when measuring the refractive index of D1E1 copolymer with x = 0.39 at a wavelengths l = 1275 nm (a) and 1550 nm (b). Highlighting of sample applied to measuring prism of refractometer was carried out through illuminating prism (a) and from the side of measuring prism (b).*

In Fig. 7 shows the dependences of refractive index *n*(l) for amorphous perfluorinated D1E1 copolymer with a molar concentration of ether x = 0.39 within a telecommunication wavelength ranges near 1300 and 1550 nm. The spectral width of illuminating radiation, determined by the width of monochromator slits, was 5.8 nm when measured near 1300 nm, and 8.7 nm - near 1550 nm. From Fig. 7 it follows that refractive index of copolymer lies within limits of *n* = 1.3160 - 1.3165 (in spectral range of *n* = 1250 - 1350 nm), and within t limits of *n* = 1.3159 - 1.3160 (in the spectral range 1500 - 1600 nm). From Fig. 7 that the refractive index of the copolymer lies in the range n = 1.3160 - 1.3165 in the range 1250 - 1350 nm and n = 1.3159 - 1.3160 in the range 1500 - 1600 nm. These values are significantly lower than the refractive indices of quartz n = 1.447 and n = 1.444 near 1300 and 1550 nm, respectively [16]. Thus, copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropyl vinyl ether can be used as a cladding of silica fibers for high-speed optical data transmission systems.

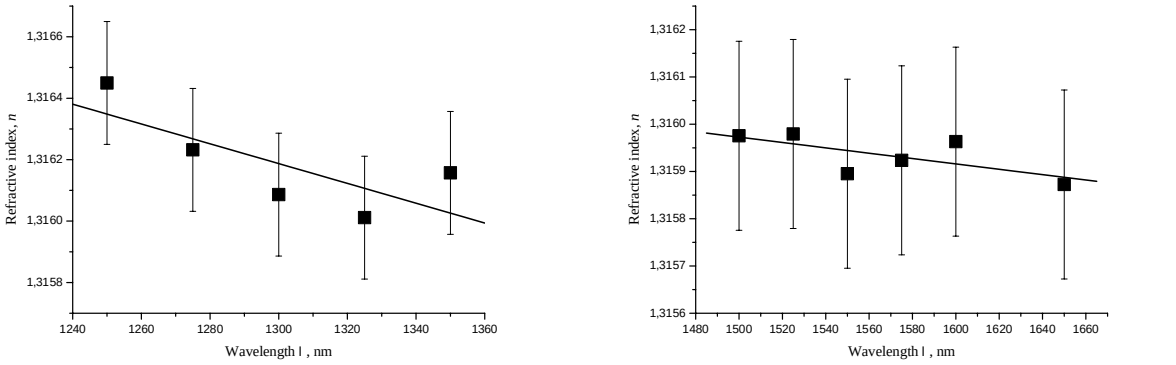


Figure 7. *Squares is dependences of refractive index n(l) for perfluorinated D1E1 copolymer with x = 0.39 near l = 1300 nm (a) and l = 1550 nm (b), and solid lines is average dispersion dn(l)/dl obtained by linear interpolation of n(l).*

From Fig. 7 it follows that dispersion of refractive index of perfluoro-2,2-dimethyl-1,3-dioxole- and perfluoropropylvinylether copolymers with x = 0.39 is d*n*(l)/dl = -3.2´ 10^{-6} nm^{-1} within a range 1250 - 1350 nm, and -6.2´ 10^{-7} nm-1 - within a range 1500 - 1600 nm, which is lower than dispersion of quartz d*n*(l)/dl = -1,13´ 10^{-5} nm^{-1} and -1,20´ 10^{-5} nm^{-1} [16] in the corresponding spectral regions. Low d*n*(l)/dl values provide a low pulse spreading rate over long sections of

optical fiber, which allows to increase the signal repetition rate and, consequently, the data transfer rate.

Results and Discussions

Amorphous fluorine-containing polymeric materials have high optical transparency within the telecommunication wavelength ranges near λ = 1300 and λ = 1550 nm and therefore are promising for creation of various fiber-optic and integrated-optical devices. In such devices, IR radiation propagates along the light-guiding core (quartz fiber or polymer waveguide) due to effect of total internal reflection at the core/cladding interface, and refractive index of cladding should be less than the refractive index of light-guiding core. It is known that fluorine-containing monomers and polymers have a very low refractive index *n*. So, the refractive index of monomer-fluoroacrylates in form CH_2=CH-COO-CH_2-$(CF_2)_m$-CF_3, m = 3, 5, 7, with fluorination degree of 64 - 77% is *n* » 1.33 near λ = 1550 nm [15]. Therefore, to form the cladding, the polymers with *n* < 1.32 should be used. This paper shows that amorphous perfluorinated copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropylvinyl ether have a low refractive index (less than 1.3165 near λ = 1300 nm, and less than 1.3160 near λ = 1550 nm), as well as a low material dispersion, and therefore suitable for creating a cladding of waveguides from fluorine-containing acrylic polymers. It can also be used as cladding for silica fibers and waveguides made from fluorine-containing electro-optical polymers with covalently attached chromophores in the side chain [17].

Conclusion

Amorphous copolymers of perfluoro-2,2-dimethyl-1,3-dioxole and perfluoropropyl vinyl ether were synthesized by ultrahigh pressure method (13.5 ths. atm.) without using of initiators. By applying the spectroscopic refractometry method, the refractive index and dispersion of copolymers were measured within a telecommunication wavelength ranges near λ = 1300 and λ = 1550 nm. It is shown that refractive index of these copolymer with a molar concentration of ether x = 0.39 lies within a range of *n* = 1.3160 - 1.3165, within the range of *n* = 1250 - 1350 nm and within the range of *n* = 1.3159 - 1.3160 (within a spectral range of 1500 - 1600 nm), its dispersion is $dn(\lambda)/d\lambda = -3.2 \cdot 10^{-6}$ nm^{-1} and $-6.2 \cdot 10^{-7}$ nm^{-1}, respectively. These values are lower than refractive index and dispersion of quartz in the corresponding spectral ranges. Thus, the synthesized copolymers are promising for use as a cladding of silica fibers in high-speed optical information

transmission systems. It can also be used as cladding for waveguides made from fluorine-containing acrylic and electro-optical polymers to create high-speed integrated-optical light modulators.

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