

Fluorinated Monomers and Polymers with Specific Properties for Integrated Optics and Photonics

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Nowadays, fluorinated polymeric materials are increasingly used in integrated optics owing to their high functionality and manufacturability [1–4]. As distinct from hydrocarbon polymers, fluorinated polymers have lower absorption in all three telecom wavelength ranges near 0.85, 1.3, and 1.55 μm .

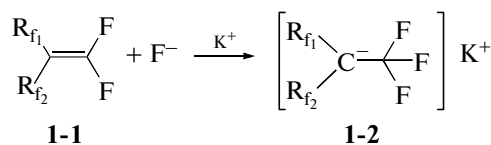
This is caused by the fact that the stretching vibration overtones of the C–F bonds are shifted toward longer wavelengths as compared with the C–H overtones responsible for the absorption in the given spectral ranges [5]. Yet another specific feature of fluorinated monomers is the low refractive index (n_D). The copolymerization of fluorinated and non-fluorinated monomers makes it possible to vary the refractive index of the composition in wide ranges, which is important for fabrication of waveguides with a specified numerical aperture. Finally, fluorinated polymers are more thermostable and more resistant to degradation, color change, etc. This is due to the fact that the C–F bond energy is much higher than the C–H bond energy.

Monomers for producing integrated optical devices (for example, optical waveguides) should have some specific properties. First, they should have high optical transparency in the working range of the spectrum. Second, monomers should be rather active in the process of radical photopolymerization since waveguides are fabricated by UV photolithography. This is associated with the fact that the cross-sectional dimensions of waveguides are very small: their height and width

range from a few to several tens of microns. Third, monomers with high and low refractive indices intended to be the components of the compositions for the light-guiding core and the waveguide cladding should readily copolymerize with each other.

This work is aimed at synthesizing new fluorinated monomers exhibiting the above set of useful properties and at studying the possibility of using them for fabrication of polymer waveguides.

As is known, perfluoroolefins **1-1**, unlike the non-fluorinated analogues, react with KF to form metastable reactive carbanions **1-2**. This is attested by a multitude of chemical transformations on their basis; in addition, they have been detected by ^{19}F NMR [6]. The primary addition of the fluoride ion to the double bond of a perfluoroalkene followed by stabilization of the resulting carbanion with the potassium cations occurs smoothly in polar solvents with high solvation ability (Scheme 1).



Scheme 1.

It has been shown that the perfluoroalkyl carbanion can be sometimes stabilized with an organic carbocation rather than an inorganic counterion (K^+ , Cs^+ , etc.) [7]. Reactions with intermediate formation of polyfluorocarbanions occupy a prominent place in the chemistry of fluoroolefins [8–10]. Their in situ generation in the reaction mixture in the presence of various electrophilic agents, such as diazo compounds, α -oxides, sultones, isocyanates, sulfenyl chlorides, and alkyl halides, enables the synthesis of new organofluorine compounds and monomers for polymer chemistry [11].

Using the commercially available perfluoroolefin 1,1,1,3,4,4,5,5,5-nonafluoro-2-(trifluoromethyl)-2-

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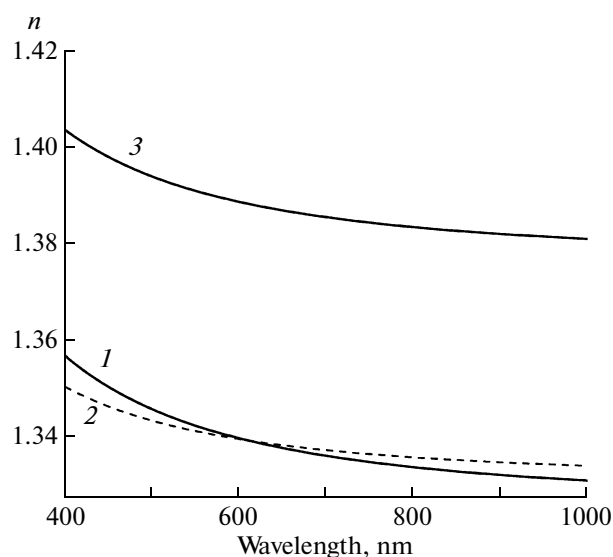
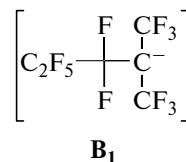


Fig. 1. Refractive index (n) of fluorinated monomers (1) **2-6**, (2) **3-3**, and (3) **4-3** in the telecom wavelength ranges near 0.85, 1.3, and 1.55 μm .

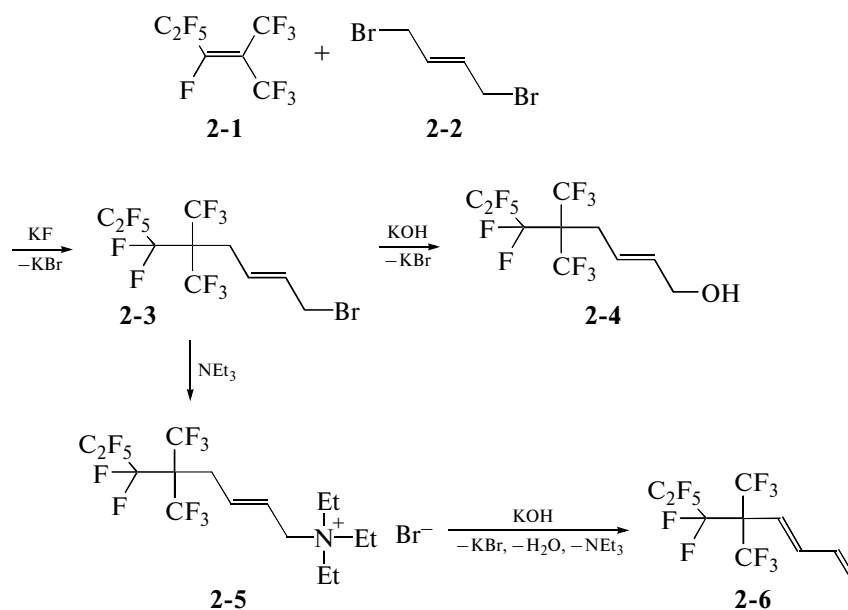
pentene (**2-1**) and 1,4-dibromo-2-butene (**2-2**), we attempted to develop the general methodology of synthesis of previously unknown 1-perfluoroalkyl-1,3-butadienes (**2-6**) (Scheme 2). It is worth noting that, as distinct from acrylates, butadiene and its derivatives have not been heretofore used for creating optical waveguides. Nevertheless, the suggested synthetic scheme promised the synthesis of new highly fluorinated monomer **2-6** meeting the requirements on the

chemical composition of waveguides with specific properties.

Indeed, the reaction of olefin **2-1** with bromide **2-2** in the presence of anhydrous KF in dry dimethylformamide yields (*E,Z*)-1-bromo-6,6,7,7,8,8,8-heptafluoro-5,5-bis(trifluoromethyl)-2-octene (**2-3**). However, despite the long-term boiling, the yield of **2-3** does not exceed 45%. It turned out that the introduction of 5–10 mol % CsF considerably decreases the reaction time (15–16 h) and increases the yield of the target product to 70%. It is likely that cesium fluoride favors the formation of perfluorocarbanion **B₁**, which is the intermediate of this reaction.



We faced difficulties when we tried to accomplish next steps of Scheme 2. The dehydrobromination of compound **2-3** in an alkaline medium is accompanied by a dominating side reaction. In particular, the reaction of **2-3** with KOH yields a mixture of products rather than the desired (*E,Z*)-6,6,7,7,8,8,8-heptafluoro-5,5-bis(trifluoromethyl)-1,3-octadiene (**2-6**). According to chromatography mass spectrometry and ¹H NMR data, the major product in this mixture is (*E,Z*)-6,6,7,7,8,8,8-heptafluoro-5,5-bis(trifluoromethyl)-2-octen-1-ol (**2-4**). It is evident that, under the given conditions, nucleophilic substitution of OH group for the bromide ion occurs instead of dehydrobromination.



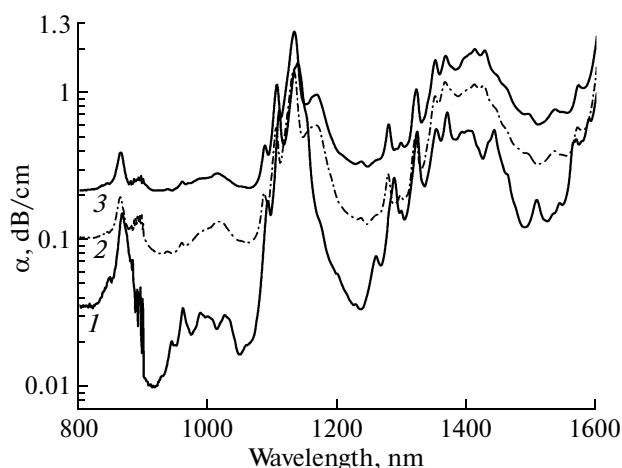


Fig. 2. Absorption factor $\alpha(\lambda)$ of fluorinated monomers (1) 2-6, (2) 3-3, and (3) 4-3 in the telecom wavelength ranges near 0.85, 1.3, and 1.55 μm .

Therefore, we forced to use an alternative route for accomplishing the dehydrobromination of 2-3 and, thus, somewhat changed the planned scheme of synthesis. It is known that the treatment of quaternary ammonium salts with aqueous solutions of alkali metal hydroxides on moderate heating (to 60°C) smoothly leads to the elimination of trialkylammonium bromide to give the double bond [12]. To synthesize the starting quaternary salt, heptafluorobromoalkene 2-3 was reacted with triethylamine. The reaction of these reagents in dry acetone at room temperature gave crystalline (*E,Z*)-*N,N,N*-triethyl-6,6,7,7,8,8,8-heptafluoro-5,5-bis(trifluoromethyl)-2-octene-1-ammonium bromide (2-5) in high yield. Salt 2-5 thus obtained was treated with a 10% KOH solution at 60°C, which resulted in elimination of the ammonium group with simultaneous double bond isomerization. After the treatment of the reaction mixture and fractionation of the resulting distillate, diene 2-6 was obtained in 75% yield. The overall yield of 2-6, as calculated for initial 2-1, was 41%. Compound 2-6 is a colorless liquid with bp 146–147°C/760 mmHg, density $d^{20} = 1.528$, and refractive index $n_D^{20} = 1.3403$. The liquid is insoluble in water and soluble in organic solvents.

The structure of 2-6 has been confirmed by ^1H and ^{19}F NMR, mass spectrometry, and elemental analysis. The ^1H NMR spectrum of compound 2-6 in CDCl_3 (a Bruker AM300 spectrometer operating at 300.13 MHz, chemical shifts were referenced to TMS) shows the signals of CH protons (5.80, 6.50, and 6.91 ppm) and CH_2 protons (5.52 ppm). The ^{19}F NMR spectrum of octadiene 2-6 in CDCl_3 (the same spectrometer operating at 282.4 MHz, chemical shifts were referenced to CFCl_3) shows the characteristic signals of two CF_2 groups at -125.14 and -110.75 ppm and the signals

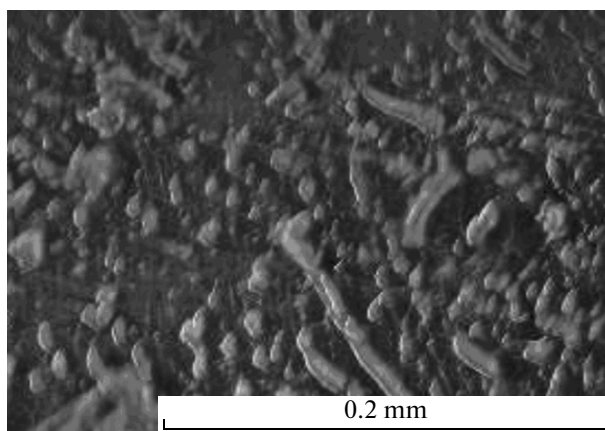
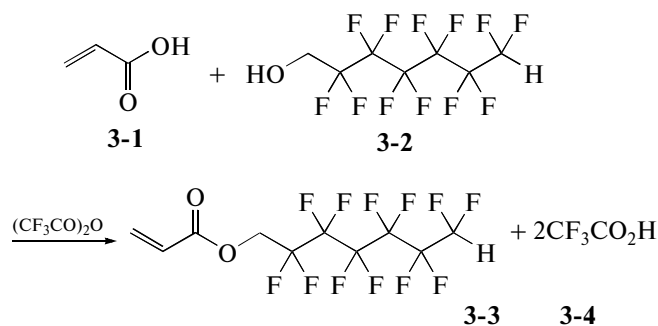


Fig. 3. SEM image of the surface of the copolymer of octadiene 2-6 and of diacrylate 4-3 (5 mol %).

arisen from nine fluorine atoms at -82.89 ppm (CF_3) and -65.35 ppm (2CF_3).

The mass spectrum of 2-6 (a Finnigan MAT INCOS 50 quadrupole mass spectrometer, direct insertion probe, electron impact ionization, 70 eV) shows the molecular ion peak at 372 $[\text{M}]^+$ and the characteristic peaks of the products of destruction of compound 2-6 at $m/z = 203^+$ ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{C}(\text{CF}_3)_2$, 169^+ (C_3F_7), and 69^+ (CF_3).

To obtain copolymers with octadiene 2-6 of different composition, we also synthesized highly fluorinated acrylates (Schemes 3 and 4).



Scheme 3.

It is worth noting that 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptyl acrylate (3-3) and 2,2,3,3,4,4,5,5-octafluoro-1,6-hexadiyl diacrylate (4-3) have been previously synthesized for purposes unrelated to application in fiber optic electronics [13, 14]. However, the described method of their synthesis did not ensure the purity required for monomers for fabrication of light guides. Therefore, we needed to find a new method of their synthesis. Applying the procedure suggested in [15] for synthesis of other acrylates, where trifluoroacetic anhydride was used as the condensing

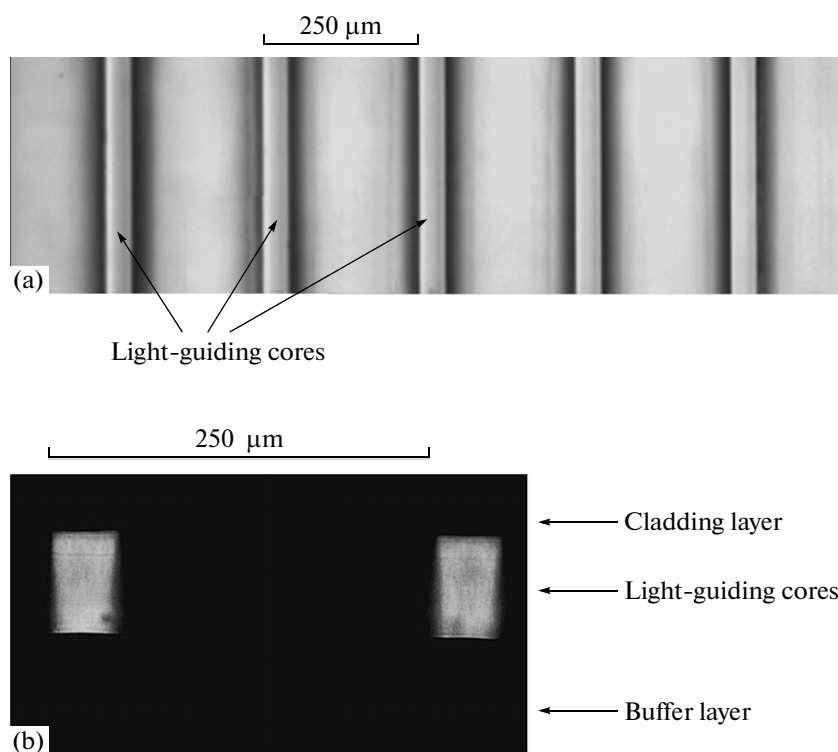
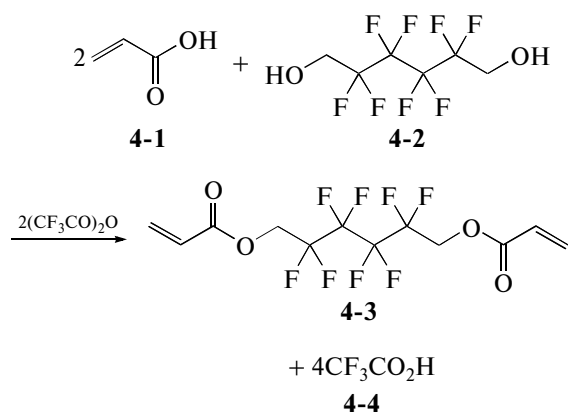


Fig. 4. Photograph of the array of polymer waveguides on a silicon substrate fabricated by contact UV lithography. (a) Top view before covering the waveguides with a cladding layer and (b) end view after the formation of the cladding layer.

agent, we obtained target acrylate **3-3** and diacrylate **4-3** of purity ~99% (Scheme 4).



Scheme 4.

The optical properties of the synthesized fluorinated monomers in the telecom wavelength ranges were studied. The refractive indices of monomers **2-6** (1), **3-3** (2), and **4-3** (3) were measured on an IRF454-B2M refractometer (Fig. 1) and the absorption factors, on a Shimadzu UV3600 spectrophotometer (Fig. 2).

Figure 1 shows that the refractive indices have normal dispersion in the visible and near-IR spectral ranges. The refractive indices (n_D) at the wavelength 589.3 nm are 1.3403 for octadiene **2-6** (1), 1.3400 for

acrylate **3-3** (2), and 1.3892 for diacrylate **4-3** (3). The absorption factors of monomers **2-6**, **3-3**, and **4-3** near 1.5 μm are 0.12, 0.33, and 0.61 dB/cm, respectively (Fig. 2).

The synthesized monomers were used for preparation of copolymers of different composition. Before proceeding to a laborious process of fabricating waveguides from monomers **2-6**, **3-3**, and **4-3**, we carried out their bulk free-radical copolymerization and studied the optical properties of the resulting copolymers.

We studied the effect of the initiator and copolymerization conditions (reaction time, temperature, initiator concentration) on the yield and properties of the copolymers. The optimal conditions for the synthesis were found to be 70°C, the reaction time of 12–16 h, and 1.5 wt % of benzoyl peroxide.

Octadiene **2-6** (the fluorination degree 72.2%) and acrylate **3-3** (the fluorination degree 66.7%) are transparent and infinitely miscible liquids, which is a necessary condition for fabricating polymer waveguides by contact UV photolithography. The ratio of **2-6** and **3-3** units was varied from 3 : 7 to 7 : 3. The resulting copolymers are transparent rubbery substances. Their structure has been confirmed by elemental analysis and IR spectroscopy. We have demonstrated that the introduction of 5 mol % of diacrylate **4-3** (the fluorination degree 44.4%) into the above monomer mixture and

its subsequent copolymerization leads to materials with the density and hardness sufficient for processing and the optical transparency in telecom wavelength ranges.

Scanning electron microscopy (SEM) of the sample surface has shown that the copolymer of octadiene **2-6** and 5 mol % diacrylate **4-3** as a cross-linking agent has a network structure (Fig. 3). The absorption factor of this copolymer near 0.85 μm is 0.05 dB/cm.

From mixtures of monomers **2-6**, **3-3**, and **4-3**, we prepared compositions with high and low refractive indices capable of photopolymerization. For fabricating light-guiding cores, composition no. 1 composed of these monomers taken in the ratio 0.15 : 0.75 : 0.1 with $n_D = 1.3569$ was used. For the buffer and cladding layers, composition no. 2 with the monomer ratio 0.25 : 0.65 : 0.1 and $n_D = 1.3466$ was used. For initiation of the radical polymerization, 1.5% of Irgacure-651 initiator was introduced into the compositions. In the course of photopolymerization, shrinkage of the compositions occurs, which is accompanied by some increase in the refractive index. Inasmuch as the difference between the refractive indices of the light-guiding core and the cladding of the waveguide determines its numerical aperture (which is an important characteristic), we measured n_D of the copolymers synthesized from compositions no. 1 and no. 2. Measurements were taken with a Metricon-2010 prism coupler at λ 633 nm. The copolymer obtained from composition no. 1 has $n_D(633 \text{ nm}) = 1.409$, and for the copolymer from composition no. 2, $n_D(633 \text{ nm}) = 1.405$. Thus, the difference between the refractive indices of the light-guiding rod and the cladding is 0.04, which corresponds to the numerical aperture of 0.2.

The fabrication of polymer wave guides by contact UV photolithography involved three steps. First, a buffer polymeric layer with the low refractive index was created on a substrate. Then, light-guiding rods of waveguides were fabricated on the buffer layer by illuminating the layer of the liquid composition through a photomask. Finally, the light-guiding cores were covered with a polymer layer with the low refractive index. Figure 4 shows the photographs of polymeric waveguides fabricated by this method on a silicon substrate with the use of compositions no. 1 and no. 2. The ends of the waveguides in Fig. 4b were obtained by chipping the silicon plate. As is seen, the waveguide width is 40 μm , the height is 80 μm , and the distance between light-guiding cores is 210 μm .

Thus, we have synthesized new fluorinated monomers exhibiting high optical transparency in the telecom wavelength ranged near 0.85, 1.3, and 1.5 μm . The optical properties of the monomers (refractive

index, absorption factor) have been studied. The bulk free-radical copolymerization of the monomers has been carried out, and the optimal conditions for copolymerization have been determined. Compositions with high and low refractive indices capable of photopolymerization have been created. Multimode polymer waveguides on a silicon substrate have been fabricated from these compositions by UV photolithography.

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