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INCREASING THE OPTICAL TRANSPARENCY OF AMORPHOUS COPOLYMERS OF PERFLUORINATED DIOXOLES AND VINYL ETHERS USING XENON DIFLUORIDE

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Abstract: The amorphous perfluorinated polymers are promising for the creation of integrated optical devices operating in the near infrared (IR) spectrum due to their high optical transparency in this spectral range. During the synthesis of copolymers from perfluorinated dioxoles and vinyl ethers by radical copolymerization under ultrahigh pressure (10-14 thous. atm.), side chemical reactions (for example, the opening of the dioxolane ring) can occur. Subsequent interaction of the products of these reactions with air moisture leads to formation of carboxyl substituents - (C=O)-OH in the macromolecule, and, as a result, to increase in polymer absorption coefficient. Using the copolymer of perfluoro-2-methyl-2-ethyl-1,3-dioxol and perfluoro-n-propyl vinyl ether as an example, we showed that their treatment with xenon difluoride leads to fluorodecarboxylation of - (C=O)-OH groups and increases the optical transparency of copolymer in near IR range.

Keywords: amorphous perfluorinated polymers, copolymers, fluorodecarboxylation, xenon difluoride, light guide films.

Introduction

The amorphous perfluorinated polymers possess a higher optical transparency in the near IR-spectrum than its hydrocarbon analogues [1, 2]. This is due to the fact that the replacement of light hydrogen atoms in the macromolecule by heavier fluorine atoms result to a shift of vibrational absorption bands towards longer wavelengths and, as a consequence to an appearance of "transparency spectral windows" in the range of 1–7 μm [1]. Therefore, the amorphous

perfluoropolymers, such as TeflonAF (DuPont), Cytop (Asahi Glass), Hyflon AD (Solvay), are promising for creation of various integrated optical devices operating in this spectral range, in particular, in the "telecommunication" C - range wavelengths 1530 - 1565 nm [2, 3].

The synthesis of perfluorinated polymers can be carried out from the corresponding monomers without using of radical polymerization initiators under ultrahigh pressure [4]. Such synthesis may be accompanied by side reactions, for example, the copolymerization of dioxols and ethers can lead to the opening of the dioxolane ring, with formation of the group $-C(=O)-F$ [4]. Subsequent hydrolysis of this group upon interaction with air moisture is accompanied by formation of carboxyl substituents $-(C=O)-H$ in the side chain of copolymer [4], which increases its absorption coefficient in the near IR-range. In this article it was shown that treatment with xenon difluoride leads to decrease in number of carboxyl groups in a copolymer and to increase in its optical transparency.

Fluorodecarboxylation of dioxol- and ether-based perfluoropolymers

The copolymers of $(D_3)_{1-x}(E_1)_x$ ($0 < x < 1$) perfluoro-2-methyl-2-ethyl-1,3-dioxole (D_3) and perfluoro-n-propyl vinyl ether (E_1) were synthesized using ultra high pressure method. The fragment of copolymer structure is shown in the insert to Fig. 1. The resulted substances are amorphous. Their intrinsic viscosity, measured using HVROC-S viscometer (RheoSense Inc.), was $[\eta] \approx 0.048$ ml/mg. IR absorption spectra were measured using Shimadzu 8400S FTIR spectrometer. For this purpose, by centrifugation on the KBr substrates from solutions of $(D_3)_{1-x}(E_1)_x$ in perfluorodecalin were formed films 12–18 μm thick. These samples were heated at 165 °C for 12 hours to completely removing the solvent. After that, the IR transmittance $T(\lambda)$ through the structure "film/substrate" was measured. The transmission spectrum of the film with copolymer $(D_3)_{0.5}(E_1)_{0.5}$ is shown in Fig. 1 (see Curve 1).

As can be seen from Fig. 1, the most intense absorption band of $(D_3)_{0.5}(E_1)_{0.5}$ copolymer, due to fundamental vibration frequency ν_1 of C–F bonds, is located near 1250 cm^{-1} [1]. The first harmonic ν_2 of this bond, according to [1], is located near 2490 cm^{-1} . In Fig. 1 this harmonic corresponds to the strip centered at 2481 cm^{-1} . The vibration harmonic ν_1 of C–H bonds lies near 2950 cm^{-1} [1] and is weakly expressed (absorption band near 2944 cm^{-1} , see Fig. 1), which indicates the presence of only a very small amounts of residual hydrogen atoms in the copolymer macromolecule.

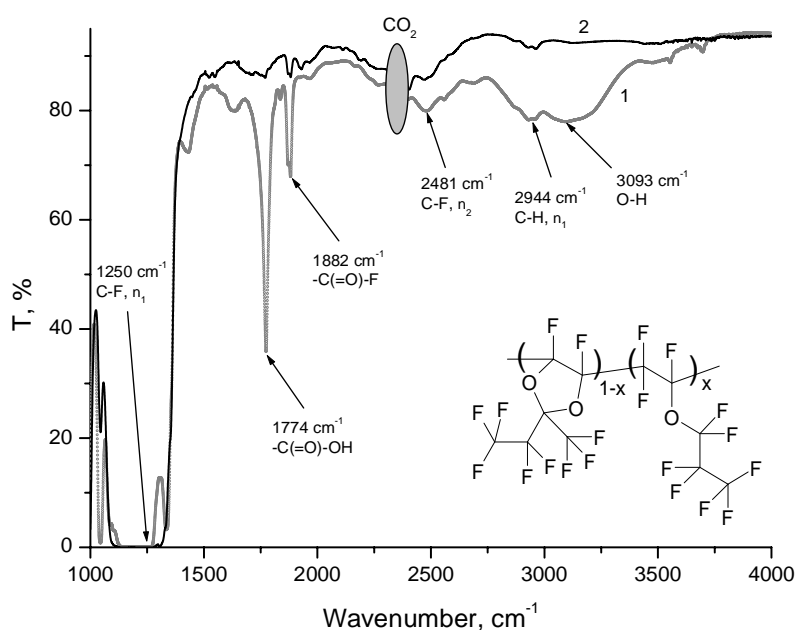
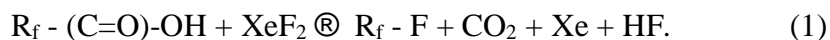


Figure 1. The transmission spectrum of the film of copolymer $(D_3)_{0.5}(E_1)_{0.5}$ at the KBr substrate (Curve 1). The Curve 2 is for same copolymer, but treated by XeF_2 . In the side insert is shown the fragment of copolymer structure, where x is the molar concentration of ether units in the macromolecule.

The absorption band centered near 3093 cm^{-1} is apparently due to coupled vibrational stretching of O–H bonds in carboxyl groups [5]. In addition, the spectrum contains the intense absorption lines centered at 1774 and 1882 cm^{-1} . The spectral line at 1774 cm^{-1} is due to coupled vibrations of the C=O atoms in the $-(\text{C}=\text{O})\text{-OH}$ group, and the spectral line at 1882 cm^{-1} can be associated with the vibrations of these atoms in the $-(\text{C}=\text{O})\text{-F}$ group [5].

The presence of carboxyl groups, as well as H atoms in the copolymer macromolecule leads to decrease in its optical transparency in the near IR spectrum, including in the C range. In order to fluorodecarboxylate the copolymer, we used the xenon difluoride XeF_2 , which is one of the most active fluorinating agents. The Curve 2 in Fig. 1 represents the transmission spectrum of $(D_3)_{0.5}(E_1)_{0.5}$ copolymer treated using XeF_2 . This treatment was carried out as follows. The copolymer was dissolved in perfluorodecalin with concentration of 10–12 %, resulting solution was placed in a Teflon ampoule and XeF_2 crystals were added there. After that, the solution was stirred on a magnetic stirrer at $65\text{ }^\circ\text{C}$ for 24 hours. A copolymer film treated with xenon difluoride was formed at the KBr substrate in the same manner and under the same conditions as for copolymer film that was not subjected to fluorodecarboxylation. From a comparison of Curves 1 and 2, it follows that the XeF_2 treatment leads to the disappearance of the absorption line centered near 1774 cm^{-1} and the band near 3093 cm^{-1} . As a result, the optical transparency of copolymer in the

near IR spectrum increased. A possible scheme for the interaction of XeF₂ with carboxyl groups in the copolymer macromolecule is described by equation [6].



We believe that the process of fluorodecarboxylation using xenon difluoride is also possible for copolymers from other perfluorinated dioxoles and ethers. The copolymer (D₃)_{0.5}(E₁)_{0.5} obtained as a result of XeF₂ treatment is capable of film formation and can be used to create waveguide waveguide arrangements for integrated optics.

Conclusions

Using the amorphous perfluorinated copolymer of perfluoro-2-methyl-2-ethyl-1,3-dioxole and perfluoro-n-propyl vinyl ether as an example, it was demonstrated that its treatment using xenon difluoride leads to an increase in its optical transparency in the near IR wavelength range (due to quantity reduction of carboxyl groups in the macromolecule and increase its degree of fluorination). The resulting copolymers are capable of film formation and can be used to create various elements of integrated optical devices.

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