ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 3, pp. 677–685. © Pleiades Publishing, Ltd., 2009.
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IR-Spectroscopic Examination of Polytetrafluoroethylene and Its Modified Forms

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Received February 1, 2008

Abstract—The results of IR-spectroscopic examinations of the molecular and supramolecular structure of polytetrafluoroethylene and polymer materials thereof were summarized. It was shown that, upon heat, mechanical, and other treatment, as well as under radiation exposure, polytetrafluoroethylene preserves its chain-helical conformation, and the resulting modified forms consist of crystalline and amorphous phases in a ratio depending on the history of the sample. The degree of the structural ordering in the polymer decreases with increasing temperature and pressure. The formation of branched moieties and short macromolecules with double bonds ($-CF=CF_2$) in the terminal groups is specific for the process caused by thermal and radiation-induced degradation. The oxidation of the polymer macromolecules requires applying high irradiation doses and heating samples in an oxygen or air atmosphere.

DOI: 10.1134/S1070363209030499

INTRODUCTION

Polytetrafluoroethylene has a number of unique properties and is the subject of much investigation by different techniques. In the recent years, much progress has been achieved in development of new forms of polytetrafluoroethylene, free from drawbacks of the basic polymer. Such materials include, in particular, powdered forms of polytetrafluoroethylene. The structure and properties of the modified forms and, hence, their specific applications are largely determined by their preparation technology [1–8]. This necessitates thorough examination of each product obtained by a new method.

Here, we present the results of IR-spectroscopic examinations of the molecular and supramolecular structures of polytetrafluoroethylene and of some materials thereof.

Molecular Structure of Polytetrafluoroethylene and Materials Thereof

Naturally, the characteristic spectroscopic properties of polytetrafluoroethylene should also be exhibited by its modifications (powders, films, granules, threads). For this reason, we will first briefly characterize the vibrational spectra of the base material and then analyze the spectral changes induced by modification of the polymer.

The vibrational spectrum of polytetrafluoroethylene is typically analyzed theoretically in terms of the structural model in which its unit cell contains one molecular chain C_nF_{2n+2} [9]. Such model implies the following symmetry types for the optically active group vibrations: four A_1 modes, three A_2 modes, eight E_1 modes, and nine E_2 modes. Among them, A_2 and E_1 vibrations are IR-active, and A_1, E_1, and E_2 vibrations, Raman-active. Figure 1 shows a typical IR spectrum of commercial polytetrafluoroethylene, fluoroplastic-4

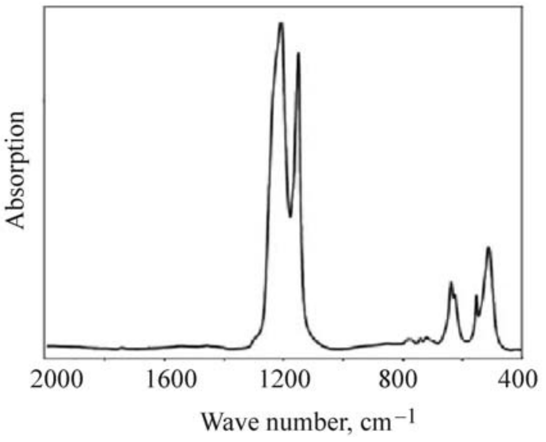


Fig. 1. IR absorption spectrum of F-4 commercial polytetrafluoroethylene.

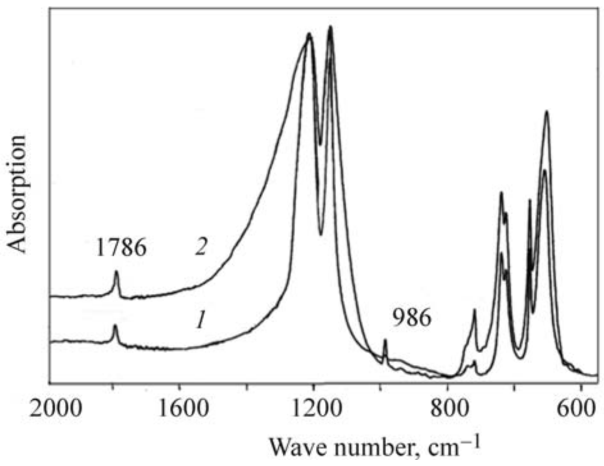
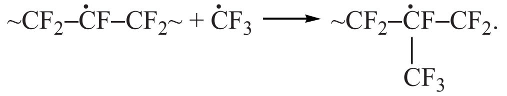


Fig. 2. IR absorption spectrum of Forum sample (*1*) before and (*2*) after stress application.

(F-4). It is seen that the IR spectrum is fairly simple, owing to a simple chemical structure of the polymer macromolecules $(–CF_2–)_n$. The most intense bands are those associated with stretching vibrations of CF_2 groups (1211 and 1154 cm^{-1}) and ν(CC) vibration manifested as an inflection at ~1233 cm^{-1}. The region below 650 cm^{-1} corresponds to bending and out-of-plane vibrations of CF_2 groups: Wagging vibrations $\gamma_\omega(CF_2)$ are manifested at 639 cm^{-1}, and bands at 555 and 516 cm^{-1} are associated with bending and rocking vibrations of the CF_2 groups, respectively.

Modification of polytetrafluoroethylene by different techniques (radiation, electron, and laser exposure, as well as heat and mechanical treatment) and in various media causes the polymer to pass to dispersed, ultradispersed, or a different state (threads, wool, granules). The IR spectra of such items preserve the bands associated with C–F and C–C stretching vibrations, CCC and CF_2 bending vibrations, and out-of-plane vibrations of the CF_2 groups, individual moieties, and the entire chain [5, 10–12] even at high radiation doses. This suggests that the external impact does not cause exhaustive destruction of the molecular chain of polytetrafluoroethylene. Nevertheless, there exist sound reasons to presume that, in many cases, changes occur at the molecular level. For example, radiation exposure of polytetrafluoroethylene results in C–C and C–F bond scission, yielding radicals [13–17] promoting macromolecular chain crossing, branching, or formation of moieties from shorter chains. The resulting new groups exhibit their intrinsic bands it the vibrational spectra, and can be recorded, when in sufficient amount.

The quantum-chemical calculations [18] showed that the IR spectra of polytetrafluoroethylene are sensitive to defects in its structure, associated with $–CF–CF_3$ groups arising in the side chains:



$$\sim CF_2-\dot{C}F-CF_2\sim + \dot{C}F_3 \longrightarrow \sim CF_2-\underset{\overset{|}{CF_3}}{\dot{C}F}-CF_2.$$

This characteristic group in the macromolecular chain is manifested as a band at 986 cm^{-1}. The IR spectrum of commercial polytetrafluoroethylene samples does not contain bands in this area. At the same time, the IR spectrum of Forum ultradispersed powder (Fig. 2), prepared by thermo gas dynamic treatment of F-4 [19], contains a distinct band at 986 cm^{-1} [10, 20, 21]. Similar bands were also observed in the IR spectra of irradiated polytetrafluoroethylene samples in a number of experimental studies [13, 22–26] (Fig. 3). Notably, mechanical treatment (stress, impact) causes the band at 986 cm^{-1} in the IR spectra of Forum to grow in intensity [20]; in irradiated samples the same effect is caused by increasing the radiation dose [27] and temperature [17].

Also, the IR spectra of irradiated polytetra-fluoroethylene samples often contain a band at 1786 cm^{-1}. It is always observed in the IR spectrum of Forum powder (see Fig. 2). According to relevant quantum-chemical data, the band at 1786 cm^{-1} in the IR spectra of C_nF_{2n} chain molecules is associated with vibrations of the terminal $–CF=CF_2$ groups [28]. This suggests the presence of these groups in the molecular chains of Forum polymer and irradiated polytetrafluoroethylene samples. The fact that the number of these groups is

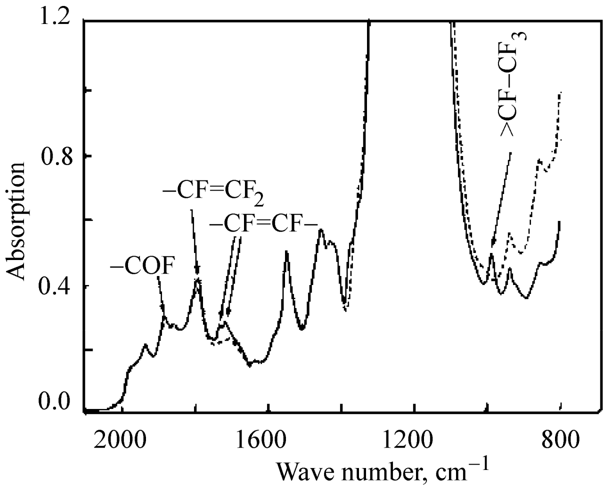


Fig. 3. IR absorption spectrum of polytetrafluoroethylene irradiated in a vacuum at a dose of 1 MGy.

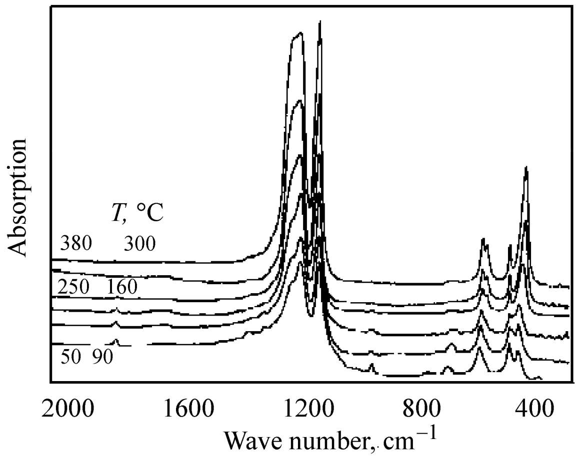


Fig. 4. IR absorption spectrum of the fractions obtained by sublimation of Forum sample at different temperatures.

sufficient for recording the corresponding band suggests that the samples comprise shorter macromolecules than does untreated polytetrafluoroethylene.

Interestingly, thermogravimetric examinations [3] showed that the mass loss onset for Forum powder was observed at temperatures as low as 50°C. Buznik et al. [3] attributed such behavior to the presence in the powder of phases with different heat resistances, associated with the difference in the molecular weights of the macromolecules of these phases. This allows partitioning the Forum product into stable fractions. Our spectroscopic data [21] suggest that the fractions differ in the structure of the macromolecules, as evidenced by intensities of the bands of fractions, observed in the IR spectra at 1786 and 985 cm^{-1} (Fig. 4). Both these bands are characterized by fairly high intensities in the IR spectra of the fractions isolated at temperatures within 50–100°C. The intensity of these bands in the IR spectra of the fractions obtained at 200–250°C is appreciably lower, and above 300°C, negligible. This suggests that the low-molecular-weight fractions consist of short branched chains with side >CF–CF$_3$ and terminal –CF=CF2 groups. The fractions isolated at higher temperatures are characterized by a smaller number of branched moieties and longer chains, which makes their structure close to that of polytetrafluoroethylene at temperatures above 300°C.

Notably, mechanical load (stress, impact) and heat treatment of the material does not affect the position and shape of the band at 1786 cm^{-1} in the IR spectrum of Forum. This suggests that the structure of the terminal group remains unchanged and that terminal and side groups do not affect each other.

A different situation is observed in the case of irradiation of Forum. We found [29] that, upon electron exposure of the sample in air at 40–100 mrad doses, virtually all the bands in the spectra are preserved. Hence, these radiation doses do not cause degradation of the polymer-chain structure of the material. At the same time, within 1700–1900 cm^{-1}, very weak bands are observed at 1778 and 1885 cm^{-1} (Fig. 5), lacking in the IR spectra of nonirradiated samples. New bands in the IR spectra of polytetrafluoroethylene samples irradiated in air were also observed in several experimental studies [22, 24–27]. The band at 1885 cm^{-1} is typically interpreted as due to terminal carbonyl groups in the corresponding structures. The band at 1786 cm^{-1} observed in the IR spectra of nonirradiated Forum samples is shifted upon irradiation by 7 cm^{-1} to lower frequencies (to 1778 cm^{-1}), irrespective of the radiation dose. The band at 1778 cm^{-1} is assigned to vibrations of the double bond, specifically to the terminal olefin group –CF=CF$_2$. The vibrations of the >C=CF$_2$ groups in side branches are manifested as lower-frequency bands (~1750 cm^{-1}); the C=C vibrations inside the chain are IR-inactive or are manifested as very weak bands [30]. As suggested by quantum-chemical calculations [30], one reason to shifting of the band at 1786 cm^{-1} to 1778 cm^{-1} can be found in electron density redistribution due to appearance in the chains of different, e.g., carbonyl groups, or of peroxide radicals. Oxidation of Forum, i.e., the appearance in the chains of oxygen-containing

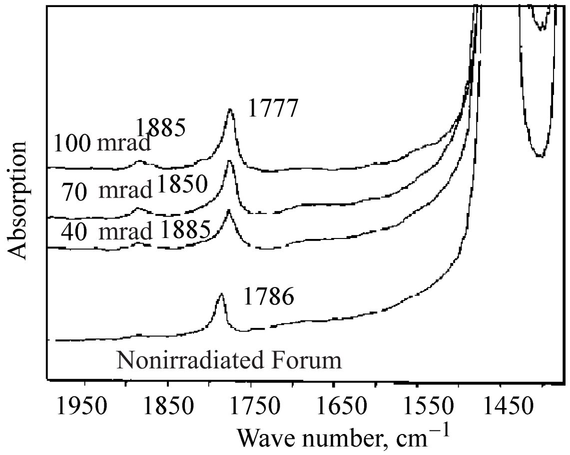


Fig. 5. IR absorption spectra of irradiated Forum samples.

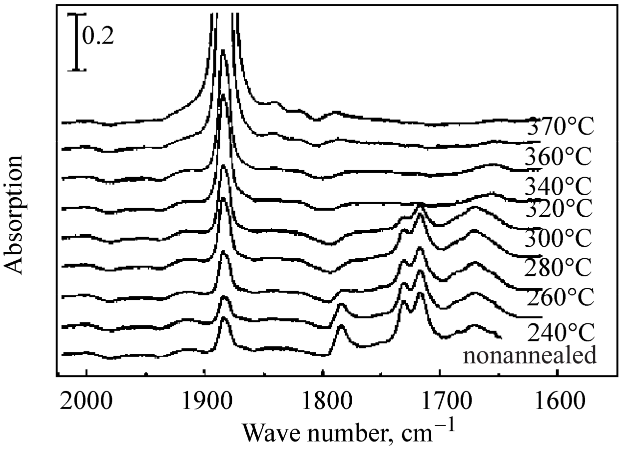


Fig. 6. Differential absorption spectra of nonannealed and annealed (at different temperatures) polytetrafluoroethylene sample irradiated at a dose of 2 MGy at 365°C.

groups or radicals, can be presumed with a good reason, considering the specific irradiation conditions (radiolysis in air). Formation of stable peroxide radicals in the Forum macromolecules upon irradiation was confirmed by ESR data [31]. Detailed analysis of the band at 1778 cm^{-1} shows that it is asymmetric (see Fig. 5) with an inflection at 1785 cm^{-1}, which suggests that the structure contains chains both with olefin and carbonyl groups and with the olefin group only at the end of the macromolecules, like in the nonirradiated material.

The appearance of the band at 1786 cm^{-1} in the IR spectra of the irradiated samples of commercial polytetrafluoroethylene (F-4) even at a low dose of 0.1 MGy, not only in a vacuum but also in air, is characteristic for this material [22–27]. An increase in the dose to 1 MGy for polytetrafluoroethylene in a vacuum causes this band to grow in intensity, which suggests degradation of the polymer. Analysis of the IR spectra of the irradiated samples revealed formation of new groups in the polymer chains, each characterized by its corresponding band whose intensity varies with the radiation dose. It was found [32–35] that, along with the already mentioned bands at 1786 and 986 cm^{-1}, the IR spectra of the samples irradiated at high doses often contain bands at 1730, 1717, and 1671 cm^{-1}. Relevant quantum-chemical calculations [28, 30] suggest that the latter should be assigned to –CF=CF– (1730 and 1717 cm^{-1}) and –CF=C< (1671 cm^{-1}) vibrations.

The IR spectra of the polytetrafluoroethylene samples irradiated in air at high doses (~3 MGy) contain, along with the band at 1885 cm^{-1}, bands at 1810 and 1780 cm^{-1} [36]. It can be naturally presumed that, at high radiation doses, the resulting radicals react with atmospheric oxygen, especially in the presence of water vapor. The bands at 1810 and 1780 cm^{-1} were assigned to vibrations of the –COOH groups [34], as validated by quantum-chemical calculations for model $C_nF_{2n}O$ molecules and by the experimental data reported by Lappan et al. [27]. Those experiments involved annealing of the irradiated samples with the aim to elucidate the structure of the moieties formed from oxidation in irradiated polytetrafluoroethylene. It was shown that, irrespective of the radiation dose, the band associated with the –CF=CF$_2$ vibrations decreases in intensity in the IR spectra of polytetrafluoroethylene; at the same time, a band is observed at 1884 cm^{-1}, whose intensity varies with the annealing temperature (Fig. 6). Upon annealing at 280°C of the sample irradiated at 1 MGy, the band associated with the –CF=CF$_2$ vibrations disappeared owing to the following process:

$$–CF_2–CF=CF_2 + O_2 \rightarrow {\sim}CF_2–COF + COF_2.$$

It should be noted that bands at 1730, 1717, and 1671 cm^{-1} also disappear upon annealing at 320°C.

The IR spectra showed that the radiation-induced changes in the structure of polytetrafluoroethylene are due not only to chain scission and formation of short macromolecular chains but also to formation of branched structures or chain crossing. The relative number of side and terminal groups, as well as of branches was estimated from the intensities of the corresponding bands, and it was found that, at identical radiation doses, the number of the side –CF–CF$_3$

groups and –CF< branched moieties exceeds that of the $–CF=CF_2$ and –COF terminal groups [36]. This suggests that, under irradiation, branching is preferred over chain scission into short macromolecules.

Electron or ultraviolet radiation exposure at high doses in a nitrogen atmosphere can yield amide groups $–CONH_2$ and NH_4F groups in the polytetrafluoroethylene chain [7, 22, 37]. The bands assigned to NH_4F groups disappear upon heating the sample to 100°C in a vacuum, and weak bands at 1768 and 1567 cm^{-1} associated with vibrations of amide groups are preserved.

Thus, the IR-spectroscopic data for polytetrafluoroethylene samples modified by different techniques suggest that the treatment can modify the chemical structure of the polymer, namely, result in formation of intramolecular double bonds, side branches, and terminal groups of various compositions. To summarize, degradation of polytetrafluoroethylene typically yields the $–CF=CF_2$ terminal group; oxidation of polytetrafluoroethylene, i.e., formation of terminal –COF or $–CONH_2$ groups, requires high radiation doses, as well as special oxidizing media for the reactions and annealing of the samples.

Specific Features of the Supramolecular Structure of Polytetrafluoroethylene and Materials Thereof

Numerous studies suggest that treatment modifies the morphology and supramolecular structure of polytetrafluoroethylene, even if it preserved its chemical structure [12, 38–41]. The IR spectra are sensitive to such modifications [42], thereby providing information on the structure of the modified forms of the polymer.

Crystallininty and Amorphism in Polytetrafluoroethylene

A polymer can have amorphous structure, contain intermediate ordered domains like long segments of individual macromolecules, mesomorphous formations, domains with various types of ordering, and be comprised of totally crystalline phase. The amorphism is often due not only to defectiveness of the macromolecule but also to a decrease in the degree of crystallinity, caused by physical factors, e.g., existence of potential internal rotation barriers and potential minima for certain conformations. The ordered domains in the polymer can be quantitatively characterized by the degree of crystallinity. To this end, IR-spectroscopic examinations utilize bands whose intensity varies with the crystallinity of the polymer. It is accepted that the regular ordering-sensitive bands are indicative of the presence of a regular chain, i.e., of an ordered sequence of the monomer units. True crystallinity-sensitive bands are associated with interaction between vibrations of the neighbor chains in the crystal lattice.

The above-said is absolutely true of polytetrafluoroethylene [43]. Higgs [44] showed that the optical density of the band at 780 cm^{-1}, observed in the IR spectra of this polymer, linearly increases with decreasing degree of crystallinity of the sample. This band was suggested for estimation of the degree of ordering of the structure of polytetrafluoroethylene [9]. Along with a number of other bands at 700–800 cm^{-1}, this band was assigned to vibrations of the molecular chains in the amorphous phase. Melting of the polymer causes the bands in this area to substantially grow in intensity. The bands at 640, 625 and 516 cm^{-1} are interpreted as regular ordering- [9] and also as crystallinity-sensitive bands. Melting causes the intensity of the bands at 625 and 516 cm^{-1} to decline to zero, and one wide band appears at 640 cm^{-1}; the intensity of these bands changes jumpwise at phase transition temperatures, as determined crystallographically. The half-width of the band at 516 cm^{-1} changes jumpwise at 20°C [40], which, according to structural examinations, corresponds to a phase transition in crystalline polytetrafluoroethylene [4].

Comparison of the IR spectra of fluoroplastic-4 and Tomflon powdered sample prepared by fast electron bombardment of polytetrafluoroethylene, followed by mechanical treatment [38, 43] shows that the shapes of the bands corresponding to the amorphous phase are identical (Fig. 7). The spectra of F-4 and Tomflon in this region coincide; the intensity ratios of the bands corresponding to the crystalline (503–512 cm^{-1}) and amorphous (778 cm^{-1}) phases are also close. This suggests identical amorphous disordering in these samples. The spectrum of Forum exhibits a different pattern in the region corresponding to the amorphous phase. In particular, one wide flat-top band is observed instead of bands at 740 and 720 cm^{-1}, and the signal at 778 cm^{-1} is lacking. Clearly, the amorphous phases and, consequently, the disordering in F-4, Tomflon, and Forum differ in nature.

The degree of crystallinity of polytetrafluoroethylene can be estimated both from Raman [45] and

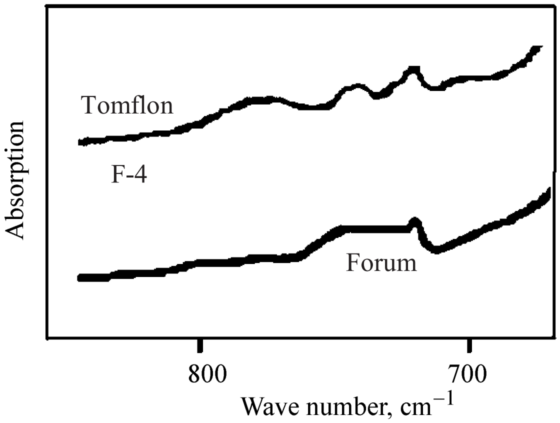


Fig. 7. IR absorption spectrum of F-4, Tomflon, and Forum samples at 700–800 cm^{-1}.

IR [46, 47] spectra. In the latter case, this can be illustrated by the data reported by Yang [47] who applied IR spectroscopy to examine the change in the ratio of the crystalline to amorphous fractions in the structure of the polymer, induced by annealing at different temperatures (Fig. 8). No additional bands were observed in the IR spectra of annealed samples, but there was a change in the intensity ratio of the bands at 850–400 cm^{-1}. Those data suggest [47] that the crystallinity of the sample decreases with increasing annealing temperature. Our studies of the temperature dependence for polytetrafluoroethylene with the use of the spectral band at 514 cm^{-1} [31] allowed the same conclusion.

Of much interest are the data reported by Usui et al. [48] who examined the temperature dependence for the IR reflection spectra of polytetrafluoroethylene films deposited onto an aluminum plate surface. Those experiments involved analysis of the intensities of the bands associated not only with libration vibrations of the CF_2 groups (850–400 cm^{-1}) but also with C–F stretching vibrations. It was shown that, with increaseing temperature from 81 to 265°C, the bands at 1258 and 1170 cm^{-1} tend to decrease in intensity and are shifted to lower frequencies. The corresponding modes belong to E_1 symmetry (dipole moment oscillations perpendicular to the polymer chain axis). At the same time, the bands with A_2 symmetry (dipole moment oscillations parallel to the chain axis), appear at 644 and 524 cm^{-1} and grow in intensity. Masetti et al. [49] interpreted this effect as due to enhanced disordering in the structure of crystalline polytetrafluoroethylene, specifically to the fact that, in the film deposited at low temperatures, the molecular chains are aligned parallel to the substrate surface, but lose this predominant orientation with increasing temperature.

As to Forum material, it does not preserve the structural integrity upon heating, as mentioned above. The IR spectra showed that the fractions isolated at different temperatures differ not only in the molecular, but also in the supramolecular, structure [21]. Within 800–400 cm^{-1}, both the band intensities and shapes are different for the fractions. In the IR spectra of low-temperature fractions this region contains a fairly

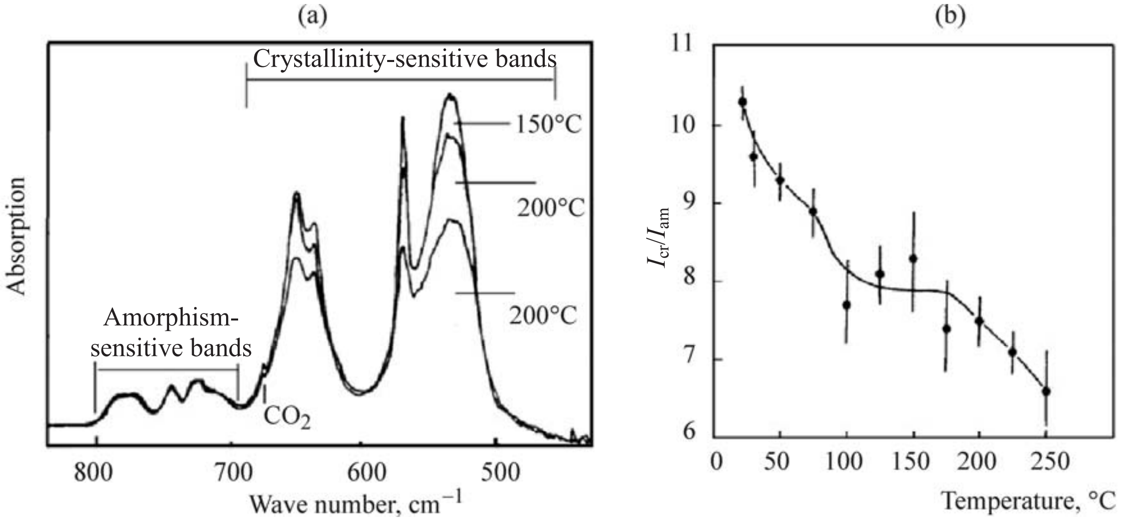


Fig. 8. (a) IR absorption spectra of polytetrafluoroethylene at 400–800 cm^{-1} upon annealing and (b) variation of the intensity ratio of the crystallinity- (516 cm^{-1}) and amorphism-sensitive (738 cm^{-1}) bands.

intense broad band with a maximum at 748 cm^{-1} (see Fig. 4). In the spectra of the fractions obtained at 100–160°C the intensity of the high-frequency component tends to decrease, and at 250°C a flat-top band is observed at 748–720 cm^{-1}. If the bands at 700–800 cm^{-1} are assigned to vibrations associated with the amorphous structure, it is possible to identify three types of samples: highly amorphous fractions obtained at 50–100°C; fractions obtained at 100–160°C, which are also fairly amorphous, but with the amorphism of a nature different from that in low-temperature fractions; and high-temperature, mainly crystalline, fractions. The above-said can be ascertained by comparing the intensities of the bands corresponding to the amorphous and crystalline phases in the samples (516 cm^{-1}) [21].

Helical Conformation and Packing of Polytetrafluoroethylene Macromolecules

As known, the molecular chains in polytetrafluoroethylene assume a helical conformation. The IR spectra of this polymer, as well as of materials thereof, typically exhibit a prominent doublet at 640 and 625 cm^{-1} (see Fig. 1). Brown [40] showed that the intensity ratio of these bands is variable: Upon heating the sample the band at 625 cm^{-1} grows, and the band at 640 cm^{-1}, decreases in intensity. This was attributed to the change in the helical conformation of the macromolecules and their packing [9]. It is believed that the band at 625 cm^{-1} characterizes the structural defects, i.e., the chain segments that are the sites of transitions between the left- and right-handed helices, and the band at 640 cm^{-1} is associated with a regular helix occurring in the polytetrafluoroethylene structure. Hence, an opposite effect (enhancement of the conformational ordering) with decreasing temperature should be expected. Indeed, IR-spectroscopic examinations of polytetrafluoroethylene and Forum material showed [31, 50] that the band at 625 cm^{-1} decreases in intensity with decreasing temperature and has negligible intensity at liquid nitrogen temperature (Fig. 9).

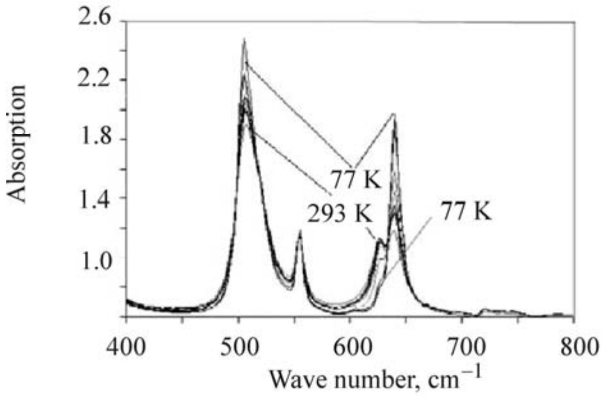


Fig. 9. IR absorption spectra of Forum sample at temperatures within 293–77 K.

The bands at 640 and 625 cm^{-1} are manifested as a prominent doublet in the IR spectrum of the Forum powder at room temperature [21]. The same is true of the IR spectra of its high-temperature fractions, which are highly crystalline, as shown above. The spectra of low-temperature fractions in the region of interest are characterized by one asymmetric band with a maximum at 648 cm^{-1}. With increasing temperature of isolation of the fraction this band is shifted to lower frequencies, to 640 cm^{-1} (at 230°C), which position remains unchanged upon subsequent heating of the polymer. An inflection appears in the low-frequency wing of the band, which virtually jumpwise turns to a shoulder, and upon heating to 200°C, to a band with the maximum at 625 cm^{-1}. Analysis of the peak intensity ratio for the bands of interest in relation to the temperature of isolation of the fraction revealed three segments. The first segment at temperatures within 50–110°C is associated primarily with fractions in which the molecular chain helices have twists in the same direction. Within 110–290°C, the structures of the fractions contain chain segments which are the sites of transitions between the right- and left-handed helices. The conformation of the fractions isolated above 300° C is close to that of the initial polymer. It should be noted that, in the IR spectra of the low-temperature fractions, the position of the band attributed to wagging vibrations (typically observed at 640 cm^{-1}) is by 8 cm^{-1} higher. This fact can be explained by the difference in the helix twist angles, associated with the presence of branched moieties or terminal olefin groups. Notably, the position of the band at 640 cm^{-1} remains unchanged in the IR spectra, in which bands associated with vibrations of these groups are lacking.

X-ray examinations showed that, at high pressures, polytetrafluoroethylene changes from helical to planar conformation. This causes significant changes in the relevant selection rules. For example, in the case of helical conformation of polytetrafluoroethylene, three A_2 symmetry modes are active (516, 640, 1210 cm^{-1}), among which two modes (640 and 1210 cm^{-1}) originate from inactive modes in the planar configuration. These conformational changes induced by high pressures should be manifested in IR spectra, and, indeed, they were revealed by Brown [40]: Specifically, the bands at 1210 and 640 cm^{-1} in the spectrum of a polytetrafluoroethylene sample significantly decreased in intensity.

CONCLUSIONS

The presented data demonstrate the capabilities of IR spectroscopy in examination of the structure of polytetrafluoroethylene and its modified forms. Changes in the molecular structure, induced by treatment of the polymer, are detected from appearance in the IR spectra of new bands which are not superposed with the bands of the basic polymer and are easily identifiable even when with low intensities. Polytetrafluoroethylene preserves its chain-helical conformation upon heating, as well as upon radiation, mechanical, and other exposures.

Commercial polytetrafluoroethylene and most of its modified forms consist of ordered (crystalline) and disordered (amorphous) phases. The quantitative ratio of these phases depends on the history of the sample. The degree of ordering of the polymer structure tends to decrease with increasing temperature and pressure. As shown by IR spectra, thermal degradation yields branched macromolecules and terminal groups with double bonds ($–CF=CF_2$). Radiation-induced degradation requires very low radiation doses (0.1 MGy) and also yields branched macromolecules and short chains with $–CF=CF_2$ terminal groups. At the same time, oxidation of the polymer macromolecules requires high radiation doses and annealing in an oxygen atmosphere or in air.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project no. 06-03-32185a) and Far-Eastern Branch, Russian Academy of Sciences (project no. 06-I-P8-008).

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