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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Effect of 1,1,5-Trihydroperfluoropentanol and Formulations Based on It on the Structure of Oriented Polycaproamide Fibers

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Abstract—Polycaproamide fibers, unmodified and modified with 1,1,5-trihydroperfluoropentanol and its formulations with copper diacetate bis(ε-caprolactamate) or *N,N*-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,3-benzenediurea, were studied by X-ray diffraction.

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Polycaproamide (PCA) belongs to the group of fiber-forming polymers which form the base of cord fabric [1] and many textile materials [2]. The molecular and crystal structure of PCA was examined in numerous studies [3–11]. It was found that PCA is partially crystalline. Three crystal modification of PCA (α, β, and γ) are known [3, 4, 7]. The total degree of crystallinity and the phase composition of PCA are largely determined by the method and conditions of sample forming. For PCA fibers, the contribution of the amorphous phase is, as a rule, insignificant, whereas in PCA films formed from solutions in formic acid the amorphous phase prevails [4].

The structure of PCA fiber is affected by chemical treatment [12, 13], thermal activation [14], mechanical activation [15], and treatment with low-temperature plasma [16, 17]. It is known [8] that introduction of moisture into PCA affects differently, depending on its amount, the state of supramolecular formations in amorphous areas. This leads to plasticization and antiplasticization phenomena. At low moisture concentrations in PCA (up to 1.6%), plasticization is observed, whereas further moistening (up to 5.5% moisture content) leads to antiplasticization, which is associated with difficult penetration of molecules into ordered regions. The X-ray diffraction pattern of a freshly formed thread is characterized by a diffuse halo with no pronounced evidences of orientation. It corresponds to the amorphous or finely crystalline state of the polymer of the mesomorphic structure. As the thread is moistened, a stable crystalline structure of the α-modification is formed (two clearly separated rings in the X-ray pattern), with pronounced axial orientation [18].

Storozhakova et al. suggested polyfluorinated alcohols (PFAs) of the general formula $H(CF_2CF_2)_nCH_2OH$ as PCA modifiers [19–25]. Molecules of these compounds actively interact with the PCA macromolecule owing to the presence of proton-donor HO and HCF_2 groups (the latter groups become acidic owing to strong electron-withdrawing effect of the fluorine atoms) and a perfluorinated chain. At a fivefold excess of the polyfluorinated alcohol, PCA fully dissolves with a noticeable exothermic effect [19, 20].

Quantum-chemical calculations of intermolecular interactions for PCA modified with PFA revealed increased bond order between associated groups, suggesting enhancement of hydrogen bonds –NH•••O=C< between the adjacent macromolecules under the influence of PFA even at relatively low PFA concentrations (one PFA molecule per several PCA macromolecules) [21, 22].

Modification of the PCA fiber with 1,1,5-trihydroperfluoropentanol (TPFP) and formulations based on it makes the polymer more resistant to both photochemical and thermal degradation [22, 23]. Introduction of microamounts of PFA into PCA films in the step of their forming [24] leads to an increase in the content of the crystalline α-phase and in the size of ordered domains.

The goal of this study was to examine by X-ray diffraction the effect of TPFP and formulations based

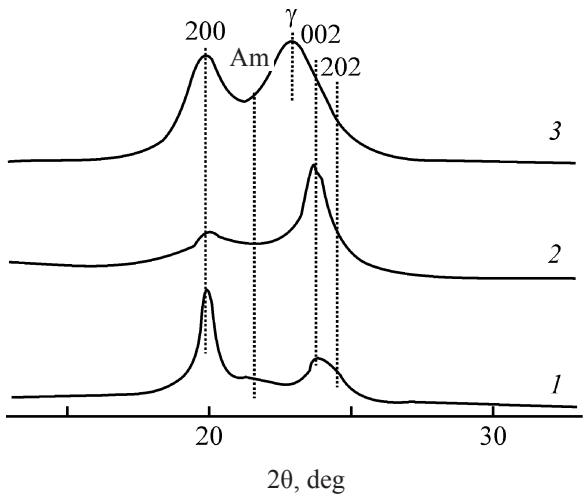

Fig. 1. Experimental diffraction patterns (reflection mode) of various samples of unmodified polycaproamide. (2θ) Bragg angle; the same for Figs. 2–5. (*1*) Film cast from solution in formic acid, (*2*) bar prepared by powder pressing, and (*3*) commercial fiber. The positions of the three major reflections of the α-modification (Miller indices), major reflection of the γ-modification (γ), and amorphous halo (Am) are indicated.

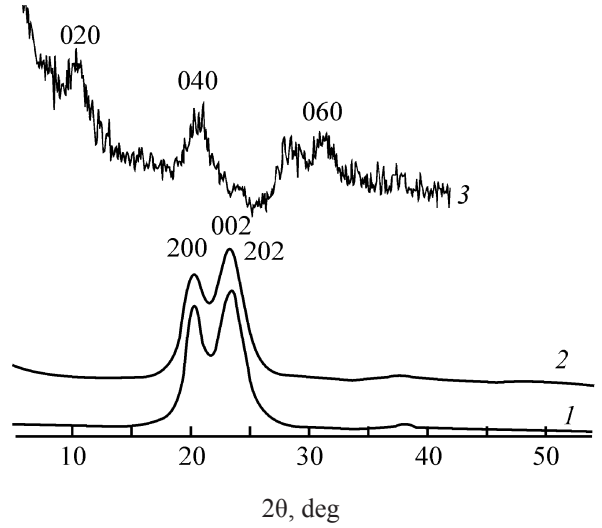

Fig. 2. Experimental X-ray diffraction patterns of fibers of unmodified polycaproamide, taken in different geometries: (*1*) reflection mode (diffraction vector is perpendicular to fiber axis), (*2*) transmission mode with vertical fiber orientation (diffraction vector is perpendicular to fiber axis), and (*3*) transmission mode with horizontal fiber orientation (diffraction vector is parallel to fiber axis).

on it, containing as second component copper diacetate bis(ε-caprolactamate) (CDBC) or *N,N*-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,3-benzenediurea (TMBDU), on the structure of oriented PCA fibers.

EXPERIMENTAL

1,1,5-Trihydroperfluoropentanol (TPFP) and CDBC or TMBDU were introduced into PCA in accordance with [21] using a vacuum drum-type drier rotating at a rate of 4 rpm. After adding TPFP (~3×10^{-3} wt %) or TPFP with the same amount of CDBC or TMBDU to the granulate, the drying (residual pressure 1.6 kPa, temperature 115°C) was performed to a moisture content of no more than 0.013%.

Analysis for fluorine was performed with a Bruker AXS X-ray photofluorescence analyzer. Samples for tests were pellets 40 mm in diameter and 25 mm high. All the tests were performed in comparison with the initial materials.

The forming and extension of PCA fiber from the granulate were performed in succession with a PP-600I no. 4 spinning frame (forming) and a KV-150-Ich 32 machine (extension) at 95°C, draw ratio 4.40.

The breaking load and relative elongation at break of PCA fiber were determined in accordance with GOST (State Standard) 6611.0–73 and 6611.4–73.

The diffraction patterns of PCA fibers, including a commercial sample (1) and samples containing TPFP and formulations based on it were taken with a DRON-3 automated diffractometer in the Bragg–Brentano (reflection mode) and Debye–Scherrer (transmission mode) geometries, at the following parameters: $Cu_{K\alpha}$ radiation (λ=1.5418 Å), graphite monochromator on the secondary beam, generator operating at 36 kV × 20 mA, θ/2θ scanning, angle step 0.05 deg, scanning rate 1 deg min–1.

Structural-morphological features of PCA-based materials are largely determined by the conditions of sample preparation. The diffraction samples of unmodified PCA samples (nonoriented film, bar, fiber) are shown in Fig. 1. As already noted, the morphology and phase composition of polycaproamide depend on the sample preparation procedure (Fig. 1). Nonoriented polycaproamide films prepared from a solution in formic acid are partially crystalline, with prevalence of monoclinic α-modification. The crystallites are preferentially oriented so that the crystallographic axis b (coinciding with the axis of the macromolecular backbone) is parallel to the film plane, whereas crystallographic axis a (coinciding with the direction of formation of the strongest hydrogen bonds between carbonyl and amide groups of adjacent molecules) is perpendicular to it.

The monolithic samples prepared by pressing of polycaproamide powder also contain amorphous and α-crystalline components. However, in this case the crystallite morphology is quite different. Apparently, under the influence of mechanical strain, hydrogen-bonded layers of macromolecules (crystallographic plane ab) are oriented perpendicular to the direction of external mechanical load, i.e., parallel to the most developed plane of the sample. In the diffraction pattern recorded in the reflection mode (diffraction vector is perpendicular to the sample plane), this is expressed (Fig. 1) in redistribution of reflection intensities: Instead of 002 line, which is the most intense for the film, the 200 line becomes prevalent (direction of van der Waals packing of H-bonded macromolecular layers). Along with changes in the crystallite morphology, monolithic samples are characterized by lower degree of crystallinity and smaller size of ordered regions (the diffraction lines are broader) compared to the films.

Polycaproamide fibers contain, along with α-modification, also the fraction of considerably less ordered γ-modification. In addition, the fibers exhibit virtually ideal axial texture: The fiber axis coincides with the molecular axis of the macromolecule, i.e., crystallographic axis b. As a result, in the diffraction curve taken in the transmission mode, at horizontal orientation of the fibers (diffraction vector is parallel to fiber axis), only 0k0 reflections bearing information on the periodicity along the molecular axis are manifested (Fig. 2). Apparently, crystallographic axes a and c do not have preferential directions.

Introduction into PCA fiber of microamounts of TPFP and formulations based on it leads to considerable changes in the physicochemical properties of the fiber [21–23]. We examined the effect of microamounts of TPFP and its formulations with 3.8×10^{-2} wt % CDBC or 3.5×10^{-2} wt % TMBDU on the supramolecular structure of PCA fiber. The fluorine content of the fiber was estimated by X-ray fluorescence analysis at 10^{-3} wt % (Fig. 3). It should be noted that the fairly volatile polyfluorinated alcohol is largely preserved in the polymer structure after granulation and fiber forming under the conditions of high treatment temperatures (255°C) and considerable shear stresses in the course of extrusion and casting.

The effect of PCA modification on the physicomechanical properties was examined with fibers prepared through the melt [22]. Introduction of TPFP exerts a plasticizing effect: The breaking elongation increases by 35% on the average. This fact shows that the TPFP-modified PCA threads are highly elastic.

Table 1. Preservation of strength in the course of UV-induced ($\lambda > 300$ nm) oxidative degradation of PCA fiber modified with CDBC–TPFP formulation (data in numerator) in comparison with the unmodified PCA fiber (data in denominator)

Irradiation time, h	Residual strength	Residual breaking elongation
	%	
146	100 100	100 100
288	90 72	96 90
411	85 45	83 52

High-temperature processing of PCA is accompanied by depolymerization and formation of ε-caprolactam (CL) and oligomers. These products of PCA degradation are present in the PCA fiber, deteriorating its quality and primarily decreasing the fiber strength and its resistance to heat and light. The presence of catalytic amounts of the copper modifier in the system favors the reaction of TPFP with CL formed in the course of depolymerization. The use of copper-containing complexes in combination with TPFP also leads to formation of additional bonds between macromolecules [26].

Indeed, addition of 3.8×10^{-2} wt % CDBC–TPFP formulation exerts a stabilizing effect against UV irradiation (Table 1). Comparison of the results of testing the new copper-containing formulation (TPFP–CDBC) and commercially used stabilizer, 2,2-bis(p-phenylenam inophenoxy)diethyl ether (N1) (Table 1), shows that our formulation exhibits a high photostabilizing effect. For example, for PCA modified with the copper-containing formulation, the residual strength after UV irradiation for

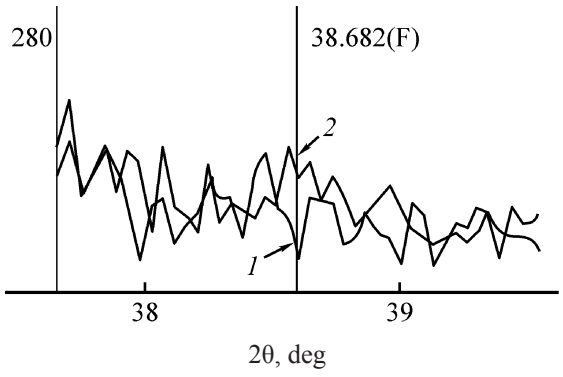

Fig. 3. X-ray fluorescence spectrum plotted against the angle of the turn of the analyzer crystal in the region of the FKα1,2 line of the pressed PCA sample. Sample: (*1*) initial and (*2*) modified with polyfluorinated alcohol.

411 h is 85%, and the residual breaking elongation, 83%, whereas for unmodified PCA these parameters amount to 45 and 52%, respectively.

Also, thermolysis at 200°C of PCA fibers modified with the copper complex in combination with TPFP occurs with an induction period: The strength of the fiber does not change during the first hour of heating (Table 2). After heating for 2 h at 200°C, the residual strength of the fiber is 87%, against 81% for the unmodified PCA.

To reveal possible mechanisms of the effect of the modifying additives, [TPFP, copper diacetate bis(ε-caprolactamate), TMBDU radical inhibitor], we performed an X-ray diffraction study of a series of unmodified and modified fibers. The results of measurements in the reflection mode (Bragg–Brentano geometry) are shown in Fig. 4. All the diffraction patterns

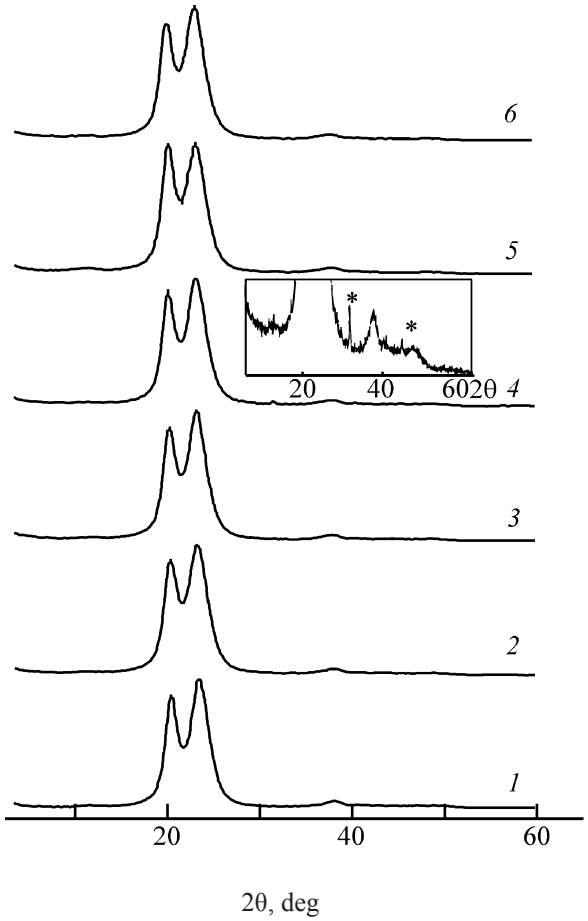

Fig. 4. Experimental diffraction patterns (reflection mode) of modified polycaproamide fibers: (*1*) commercial PCA, (*2*) PCA + TPFP, (*3, 4*) PCA + TPFP + CDBC, (*5*) PCA + TPFP + TMBDU, and (6) aged commercial PCA. Additional reflections belonging to the copper-containing modifier are shown in the insert.

Table 2. Preservation of the strength of PCA fibers modified with CDBC–TPFP formulation (data in numerator) in comparison with the PCA fibers stabilized with N1 (data in denominator). Heating at 200°C for 2 h

Heating time, h	Residual strength, %
Before heating	100/100
1.0	100/93
1.5	90/85
2.0	87/81

are qualitatively similar, i.e., X-ray diffraction in this geometry appears to be insensitive to structural effects of the modifier. Minor changes are observed only for one of two samples: there appear narrow reflections (see insert in Fig. 4) belonging, most probably, to the copper complex or a product of its chemical evolution. In addition, slight redistribution of the intensities of the major PCA reflections is observed for the sample modified with TPFP and TMBDU radical inhibitor. It should be noted that, for PCA films cast from solutions in formic acid, we observed the concentration-dependent effect of TPFP on the morphology, expressed in redistribution of the intensities of diffraction reflections.

Nevertheless, structural effects of introducing microamounts of polyfluorinated alcohols can be clearly

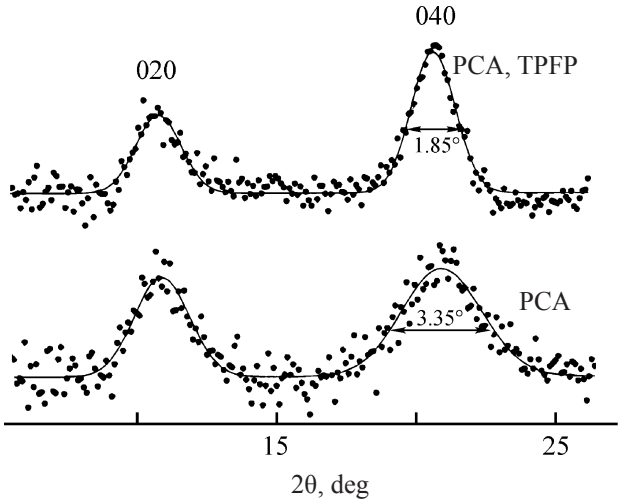

Fig. 5. Profile analysis of diffraction patterns of unmodified polycaproamide and of polycaproamide modified with PFS-2 polyfluorinated alcohol, recorded in the transmission mode with horizontal fiber orientation. Points are experimental data, and solid lines show fitting by two Gaussian functions.

traced in the diffraction pattern recorded in the transmission mode at horizontal fiber orientation (diffraction vector is parallel to fiber axis) (Fig. 5). According to the data obtained, introduction of TPFP into the fiber leads to certain narrowing of 020 and especially 040 reflections, suggesting an increase in the size of the ordered region in this crystallographic direction. Evaluation of the coherent scattering region size by the Selyakov–Scherrer formula [25] gives the values of ~25 and 50 Å for the unmodified and modified fiber, respectively.

CONCLUSIONS

(1) Structural reorganization of the macromolecular system under the influence of microamounts of polyfluorinated alcohols in the course of preparation of polycaproamide fiber leads to certain narrowing of 020 and especially 040 reflections, suggesting an increase in the size of the ordered region in this crystallographic direction.

(2) Orientation extension of the modified polycaproamide fiber in the presence of microstructures formed by molecules of polyfluorinated alcohol enhances the heat resistance of the fiber.

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