

Peculiarities of Phase and Supermolecular Structure of Graft Copolymers of Polycaproamide with Poly(methacrylic Acid)

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SYNOPSIS

The structure of graft copolymers of PCA with PMAA obtained by the methods of chemically initiated liquid-phase grafting polymerization has been investigated with the use of electron microscopy, electron-probe microanalysis, and X-ray radiography. The concentration profiles of the graft copolymer distribution along the fiber cross section and diffusion coefficients of the monomer solutions correlated with the kinetics of the graft layer penetration inside the polymeric matrix have been determined. The concentration profile of the graft polymer distribution has been shown to have drops down to the zero level. Grafting proceeds both in the amorphous regions and on the surface of imperfect crystals. The structure of the graft layer, in which the segregated chains of graft PMAA constitutes the dispersed medium and the PCA inclusions represent the dispersed phase, has been found to be heterogeneous.

INTRODUCTION

In recent years the chemical methods of initiating the grafting polymerization have received much attention.^{1,2} Of particular interest are graft copolymers of polycaproamide (PCA) with polymethacrylic acid (PMAA) since such a method of modifying the PCA fibers and films makes it possible to regulate their hygroscopicity and electrofiableness within a wide range as well as to obtain cation-exchange fibrous sorbents and ion-selective membranes.^{3,4}

It has been shown in numerous investigations of the properties of graft copolymers of polyethylene, polypropylene, and polystyrene obtained by radiation and chemical methods⁵ that, to a great extent, these properties are determined by structural and morphological characteristics of these polymeric systems, namely, by the sizes and the character of the graft layer distribution in the polymeric support, their supermolecular and phase structure.

However, the publications in this field mainly concern the structure of graft copolymers obtained upon radiative initiation of grafting polymerization.⁶

At the same time, the data on the structure of PCA copolymers obtained by the method of chemical initiation are practically absent.⁷

The purpose of the present work is the study of structural morphological and phase characteristics of the structure of graft copolymers of PCA with PMAA obtained by the method of chemically initiated liquid-phase grafting polymerization.

EXPERIMENTAL

PCA fibers with spinneret draft were employed for grafting polymerization. Molecular mass of PCA was 22,000, the crystallinity degree, according to X-ray structural analysis, was 40, and the disorientation angle was equal to 28°. For grafting, freshly distilled MAA, $d_0^{20} = 1.0157$, $n^{20} = 1.4315$, recrystallized $K_2S_2O_8$, $Na_2S_2O_3 \cdot 3H_2O$, and $CuSO_4 \cdot 5H_2O$ (chemically pure grade) were used.

Synthesis of Graft Copolymers

Grafting polymerization was performed in aqueous solution of methacrylic acid (MAA) at concentration 0.696 mol/L. The redox system $K_2S_2O_8$ - $Na_2S_2O_3$ -

Cu^{2+} allowing one to obtain the graft copolymer of PCA with PMAA without the formation of homopolymer was used as the initiator.⁹ The amount of the graft copolymer was determined gravimetrically and by a chemical method (with respect to the content of the $-\text{COOH}$ group). The films of polymeric mixtures of PCA and PMAA to study the thermodynamic compatibility were prepared from PCA and PMAA solutions in dimethyl sulfoxide.

Electron-Probe X-Ray Spectral Microanalysis

The method of contrasting the MAA carboxyl groups was used to identify the character of the graft polymer distribution along the cross section of the fiber. The samples were placed in the AgNO_3 aqueous solution (0.1 mol/L) at 25°C for 24 h. then the samples were washed in distilled water to separate from excess salt and dried to constant weight. The Ag^+ ions concentration in the samples was determined according to the procedure described in Ref. 9. The conditions for contrasting were chosen as a result of preliminary investigations with the use of PMAA films. Special experiments have shown that during the period of 24 h the reaction of substitution of the H^+ ions for Ag^+ ions proceeds steadily along the entire thickness of the film. The same parameters of substitution as in model systems are exhibited in the case of graft copolymers of PCA with PMAA. Experimental dependence of the intensity of characteristic X-ray radiation of the Ag on their concentration in the sample was obtained in this case. This dependence was further used as the reference concentration for plotting the concentration profiles.

To study the structural characteristics of graft copolymers, the modified samples were placed in epoxy resin; after solidification of the latter the sample was cross-cut on an LKB-3100 ultramicrotome; then the end face surface was contrasted. The procedure of preparing the cross sections for their examination on a JSM-U3 microscope was similar to that described in Ref. 10. The size of the generation some of X-ray radiation upon given conditions of microanalysis was equal to $1.2\ \mu\text{m}$. Heterogeneities along the section thickness did not exceed the cross sectional size of the generation zone of X-ray radiation.

The method of structural etching by selective solvent—hexafluoroisopropanol (HFIP)—was employed to identify the supermolecular structure of the PCA–PMAA graft copolymer. The preliminary experiments have shown that HTIP selectively dissolves the PCA phase which does not enter into the reaction.

Transmission Electron Microscopy

Analysis of the structural–morphological characteristics of the graft layer structure was made with the use of the method of single-stage carbon–platinum replicas, examining them on a transmission electron microscope, Model EM-30I. The method of structural etching in plasms of high frequency oxygen discharge was used to identify the supermolecular phase arrangement of the graft layer. The discharge frequency was equal to 10 MHz. The oxygen pressure was 0.02 torr. The electron energy in the etching zone did not exceed 4 eV.

X-Ray Structural Analysis

The study of the structure of the PCA–PMAA graft copolymers was performed by the method of X-ray structural analysis at big and small angles on DRON-I, DRON-3, and KRM-I devices equipped with a nickel filter, Cu K_α radiation.

Sorption Method

Diffusion of MAA and its aqueous solutions were studied on a Mac-Ben vacuum balance and by the traditional gravimetric method. Kinetic curves of sorption are Fickian ones, which allowed the determination of the MAA diffusion coefficients.¹¹ In the case of the gravimetric method, the inaccuracy was equal to 0.0002%.

RESULTS AND DISCUSSION

Figures 1 and 2 give the concentration profiles of the graft PMAA distribution in the modified PCA samples obtained under similar conditions of grafting polymerization. As is seen, the character of the concentration profile differs in principle depending on the degree of grafting (ω). At low degrees of grafting ($\omega = 9\%$), the concentration profile has a concave shape and is satisfactorily described by Fick's equation. At this stage of the grafting process, the graft polymer gradually penetrates into the matrix depth. Simultaneously, the PMAA concentration near the boundary region gradually increases.

At $\omega > 30\%$, the stepwise concentration profile with practically constant concentration of the graft polymer in the surface layer is formed. This profile has a comparatively extended diffusion tail spreading towards the fiber core. In this case, some increase in the fiber diameter is observed.

The absolute concentration of PMAA increases with a further increase of the amount of the graft

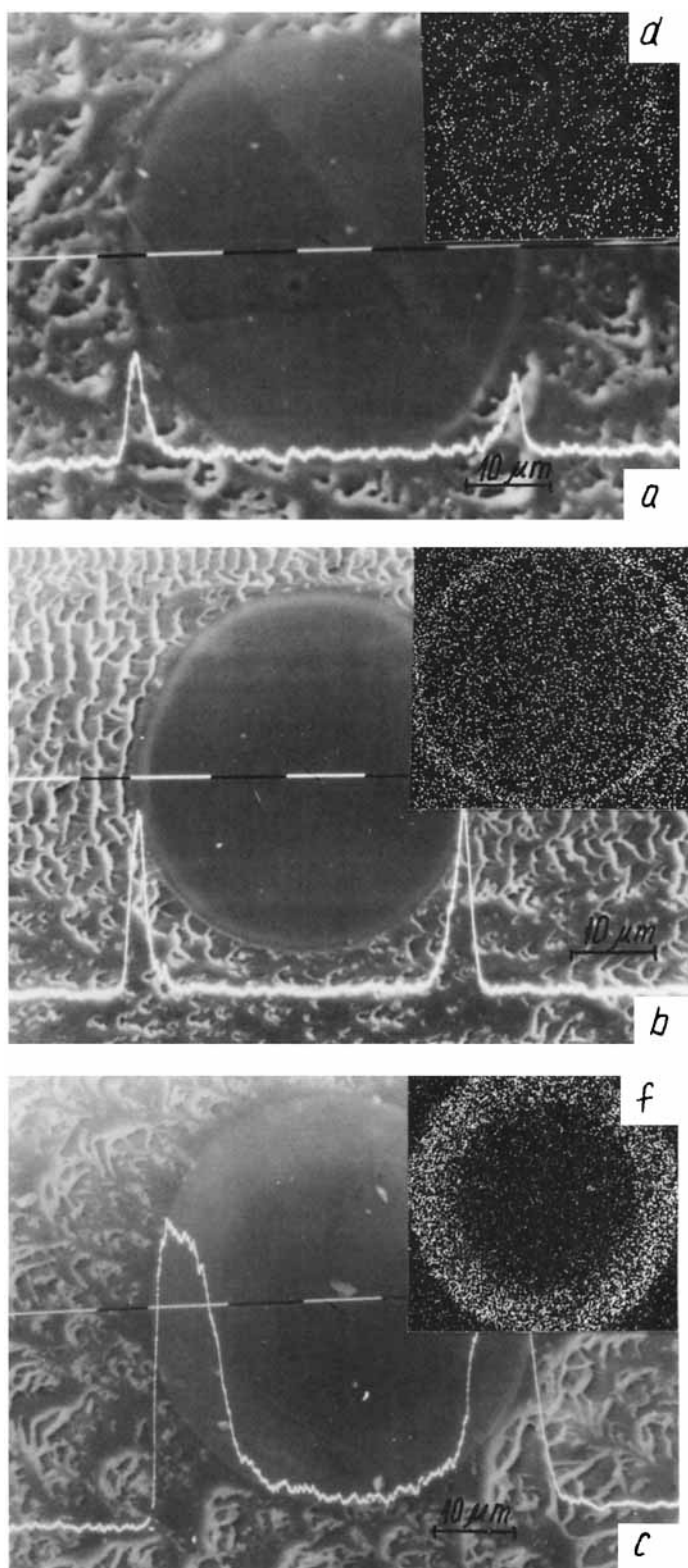


Figure 1 Microphotographs of cross sections of modified PCA fibers with concentration profiles of PMAA distribution in PCA (a, b, c) and in the rays of characteristic radiation of Ag (d, e, f). ω : (a, d) 9.7%; (b, e) 30.7%; (b, f) 57.2%.

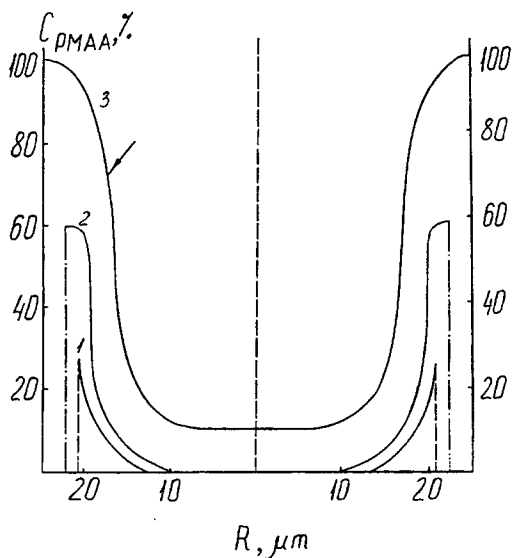


Figure 2 Changes in the sizes the concentration profile depending on the degree of PMAA grafting. ω : (1) 9.7%; (2) 30.7%; (3) 57.2%.

polymer ($\omega > 50\%$). Simultaneously, the step shifts inside the polymeric matrix, the fronts of the graft PMAA collide in the fiber core and the latter is gradually filled with graft PMAA. Simultaneously the fiber diameter noticeably increases (by more than 30%).

Thus it follows that upon grafting polymerization of MAA onto PCA two processes proceed simultaneously: Increasing concentration of PMAA in the surface layer followed by increasing diameter of the fiber and penetration of graft PMAA inside the fiber.

The study of the kinetics of the PMAA concentration changes along the sections of the samples made it possible to quantitatively separate them. The kinetics of penetration (intergrowth) of the graft layer inside PCA characterizing the rate of the grafting concentration front shift towards the sample center is given in Figure 3 (curve 2). The kinetics of the changes in the PMAA concentration in the graft layer is shown in the figure for comparison (curve 1). This comparison shows that the degree of grafting on the surface layer of the modified fiber increases much faster than the rate of accumulation of the amount of the graft PMAA inside the matrix depth. In other words, the rate of grafting in the surface-modified layers is higher than in the phase of nongraft PCA.

The process of grafting polymerization of PMAA is followed by substantial structural transformations in the fiber as a whole. As seen from Figure 4, at low degrees of grafting, that is, at $\omega < 9\%$, separate structural-morphological formations appear on the

surface of the PCA fiber. The size of these formations considerably exceeds the size of paracrystalline layers and the PCA crystallites (the structure of the latter is seen in microphotographs in the form of paracrystalline layers situated perpendicular to the direction of the axis of the fiber orientation). Upon further increase in the grafting degree ($\omega > 30\%$) the graft PMAA forms phase inclusions and solid layers. It is most obviously seen in microphotographs of cross sections of graft PCA-PMAA copolymers with $\omega > 50\%$ after their etching by HFIP (Fig. 5).

As seen from microphotographs of cross sections of modified fibers (Fig. 6), penetration of the graft polymer inside the polymeric matrix takes place in interfibrillar space. It appears to result in destruction of the fibrillar structure of PCA and formation of the heterogeneous system at high degrees of grafting: extracted paracrystalline PCA layers-*g*-PMAA.

Figure 7 shows a microphotograph of phase structure of the PCA-PMAA mixtures obtained from mutual solvent. It should be noted that the observed character of the phase arrangement of the mixture seems to be due to crystallization of polymeric components which occurs after removal of the solvent. However, according to the data on X-ray structural analysis, the PMAA crystalline structure is absent in the graft PCA-PMAA systems. As seen from Figure 7, the PCA-PMAA system is thermodynamically incompatible. Following this, we sup-

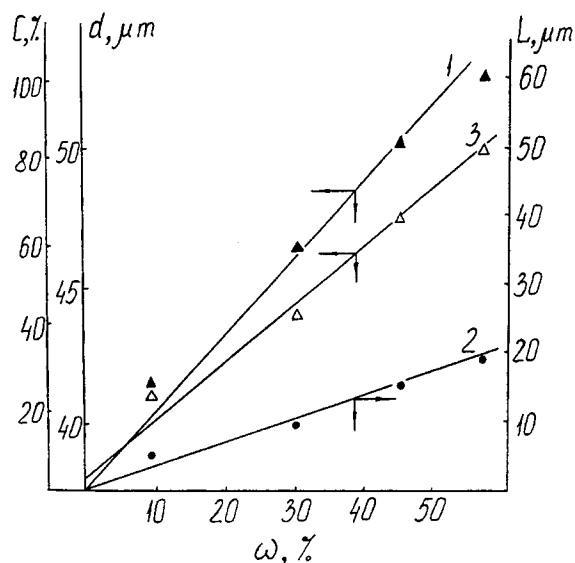


Figure 3 Kinetics of the changes in sizes of the concentration profile of PMAA towards the sample center and in the graft layer depending on the degree of grafting: (1) the highest of the concentration profile; (2) the shift of the concentration profile towards the sample center (L); (3) the change in the fiber diameter (d).

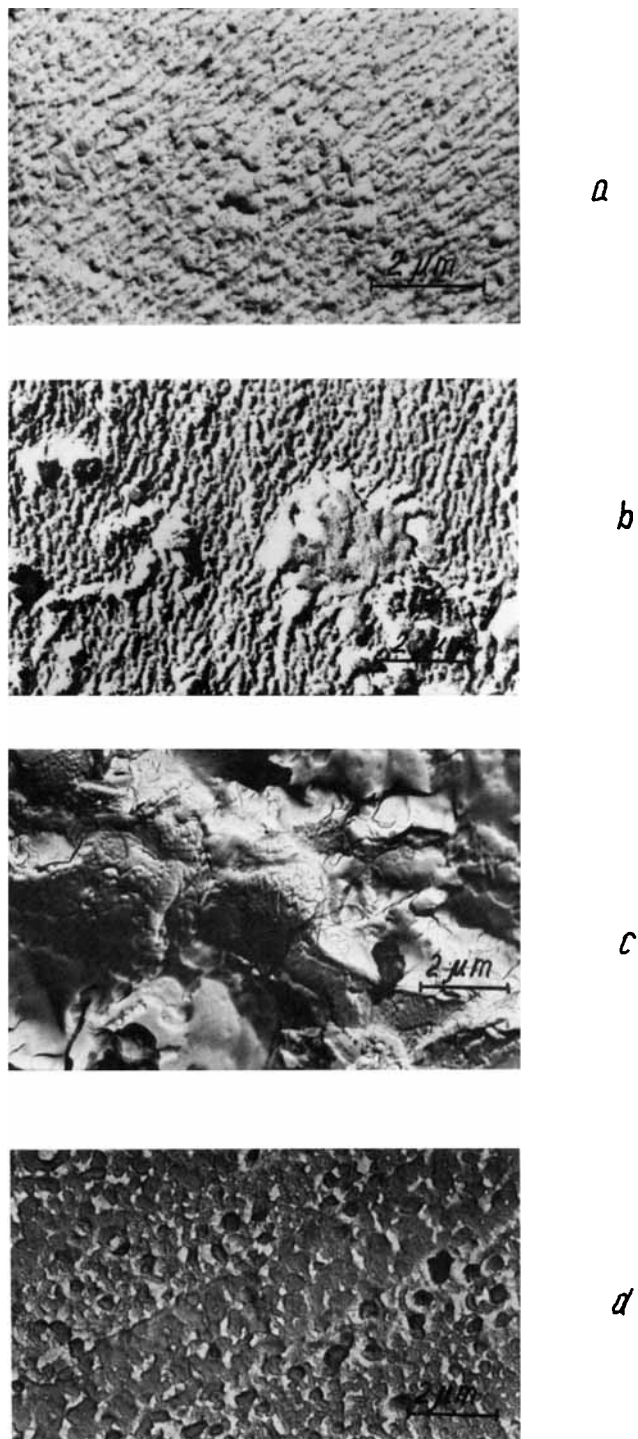


Figure 4 Microphotographs of the PCA fiber surface modified by PMAA grafting. ω : (a) 0%; (b) 4.9%; (c) 28%; (d) 57.2%.

pose that, with increasing degree of grafting, the PCA-PMAA system passes through all phase transformations typical for this type of binary systems, all these transformation being realized within the range of the concentration profile. Comparison

of this profile with the phase structure shows (see Fig. 5) that in the region of the profile corresponding to 90% PMAA, which is realized in the surface layers, the segregated PMAA chains represent the continuous phase and spherical particles of PCA are

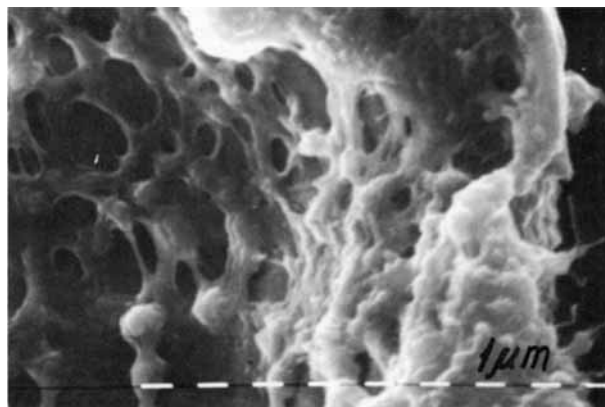


Figure 5 Microphotographs of the cross section of the PCA graft fiber etched by HFIP. $\omega = 57.2\%$.

inclusions. As the movement along the concentration profile proceeds towards the fiber core, the sizes of the PCA inclusions increase to 1–3 μm , their concentration increases, and at $\omega = 70\%$ PMAA (it is marked with an arrow on the concentration profile) the process of phase transformation takes place. PCA becomes a continuous phase and PMAA becomes inclusions.

The results given above enable us to express some assumption about the mechanism of grafting polymerization of PMAA on PCA. At the initial stage, the process of grafting polymerization proceeds predominantly in the near-surface layer of the PCA fibers since it is less oriented than the surface layer.¹² As is known, the thickness of this layer reaches 1–3 μm . As the degree of grafting increases (more than 30%), the process proceeds in such a way that the rate of accumulation of the graft PMAA on the fibers surface is two times more than the rate of the diffusion front towards the fiber center. Such character



Figure 6 Microphotographs of the cross section of the PCA graft fiber. $\omega = 30.7\%$.



Figure 7 Microphotographs of the films of the PCA-PMAA polymeric mixtures (PCA : PMAA = 80 : 20, mass %).

of the process is due to two factors: First, the constants of the growth rate exceed the constants of the rate of the growing graft chain rapture due to restriction to diffusion mobility of the graft chain and decreasing probability of its rapture according to the recombination mechanism¹³; second, the monomer has a higher diffusion rate in the sample surface layers and, consequently, a higher local concentration of the monomer near the active centers. When the near-surface layer contains a considerable amount of PMAA, the diffusion of the growing chain is hampered probably because of increasing density of the graft layer. It creates such conditions when the growing chains readily penetrate along the interfibrillar space to nongraft parts of PCA in the fiber center. Probably, in this case the chain is transferred from the growing radical to the PCA macromolecule to form new active centers, initiating the grafting polymerization, and thus the front of the graft layer of PMAA shifts towards the fiber center.

Diffusion character of the process of grafting polymerization illustrates the correlation of the MAA diffusion coefficients calculated according to the kinetics of PCA swallowing in aqueous solutions of MAA, sorption of MAA vapors, and concentration profiles. The results are given in Table I.

The data on weighted average molecular masses (M_w) of the PMAA graft chains are found to be a convincing evidence of the above assumption about the character and mechanism of structural transformations of the PCA matrix as the grafting polymerization of MAA proceeds. It was found that the process of grafting polymerization is followed by a considerable elongation of the graft chains which seems to promote the phase transformations in the PCA-PMAA system. Thus at low degrees of grafting

Table I Value of the Diffusion Coefficients of Methacrylic Acid, D_{MAA} , in PCA Fibers

Method of D_{MAA} Calculation with Respect to	D_{MAA} (cm^2/s)
Kinetic curves of the MAA vapor sorption	7.77×10^{-12}
Kinetic curves of swallowing in aqueous solutions of MAA	4.94×10^{-10}
Rate of the concentration profile movement	5.17×10^{-10}

($\omega \sim 7\%$), \bar{M}_w is equal to 72,000, with increasing to 30% \bar{M}_w increases to 404,000, and at $\omega \sim 50\%$ the molecular mass reaches $\sim 800,000$. We can also expect the distribution of the molecular masses to be uneven along the sample cross section. High molecular masses appear to be realized in the near-surface layers, which are characterized by elevated local concentration of the monomer and where the reaction of the chain transfer onto PCA is hampered. It is probably due to the fact that the sizes of the PMAA phase particles in the regions near the sample surface exceed the sizes of the particles inside the fiber. We assume that the constant growth of the molecular mass in the near-surface layers should promote the additional phase decay in the dispersed medium.

The character of the transformations which the PCA matrix undergoes was studied in more detail by the method of X-ray structural analysis. As seen from Figure 8, the initial PCA fiber has a highly disordered hexagonal structure of the γ -shape. The X-ray photograph shows one wide maximum at the diffraction angle $2\theta = 21.5^\circ$ ($d = 4.12 \text{ \AA}$), the degree of crystallinity is equal to 40%. The comparison with the diffractograms of graft PCA-PMAA copolymers shows that, as the amount of the graft PMAA increases, the degree of crystallinity substantially decreases (in all the cases the degree of crystallinity was correlated with the mass share of PCA). However, it should be noted that the dependence of the degree of crystallinity on the degree of grafting has its maximum at low values of ω . It should be also noted that the study of the effect of the sorbed MAA on the PCA fibers structure has shown that the treatment of PCA by aqueous solutions of the monomer contributes to both further perfection of the PCA crystalline structure and orientation of the crystals in the fibers. Thus it follows that it is possible to suggest that the extreme dependence of the degree of crystallinity on ω results from two com-

peting processes: secondary crystallization of PCA under the action of the plastisizing effect of the medium and destruction of the PCA crystalline structure by the graft chains of PMAA. As ω increases, the sizes of crystallites increase too. This increase proceeds stepwise at low degrees of grafting, and, as the amount of the graft polymer increases, the size of the crystallites increases gradually. The growth of the crystallites sizes at low ω seems to be also due to the processes of secondary crystallization under the action of the reaction medium.

Thus the comparison of the data on the crystallinity degree decrease and simultaneous increase of the crystallites sizes due to the increasing amount of the graft PMAA shows that, first, the grafting process proceeds not only in amorphous regions but also in crystalline ones; second, grafting "eats up" first of all small and less imperfect crystallites and,

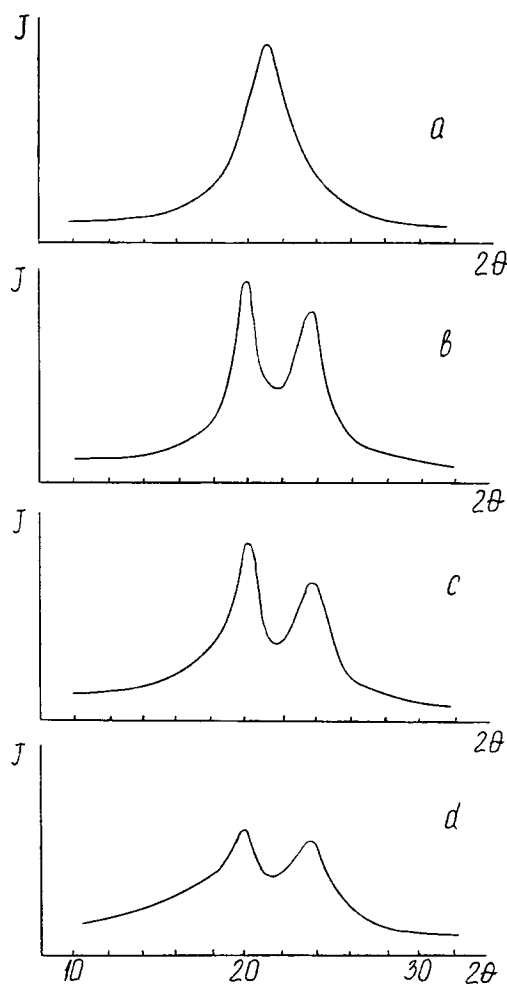


Figure 8 Diffractograms at ordinary angles of the initial PCA fibers (a) and PCA with graft PMAA (b, c, d). ω : (b) 7.8%; (c) 31.1%; (d) 51%.

as a result, the diffraction picture exhibits "growth" of the crystallites sizes.

Thus it follows that the process of chemically initiated liquid-phase grafting polymerization of MAA on PCA is followed by substantial structural transformations of the polymeric matrix. Under the given conditions of grafting, the concentration profile is of diffusion character; as the degree of grafting increases, the penetration of PMAA inside the fiber takes place and is followed by filling the interfibrillar spaces. The concentration of PMAA in the near-surface layers of the fiber also increases.

REFERENCES

1. P. L. Nayak, *J. Macromol. Sci. Rev. Macrom. Chem.*, **C17**, 267 (1979).
2. M. I. Khalil, S. H. Abdel-Fattah, and A. Kantouch, *J. Appl. Polym. Sci.*, **19**, 2699 (1975).
3. E. E. Magat, I. K. Miller, D. Tanner, and J. Zimmerman, *J. Polym. Sci. Polym. Symp.*, 615 (1963).
4. S. Takigami, M. Nakamura, and Y. Nakamura, *Polymer*, **25**, 963 (1984).
5. H. A. J. Battaerd and G. W. Tragear, *Graft Copolymers*, Wiley-Interscience, New York, 1967.
6. K. Kaji, *J. Appl. Polym. Sci.*, **32**, 4405 (1986).
7. G. Bogoeva-Gatseva, N. Yu. Pimonenko, F. A. Fazlyev, and G. A. Gabrielyan, *Vysokomolek. Soed.*, **A30**, 922 (1988).
8. G. Bogoeva-Gatseva, G. A. Gabrielyan, and L. S. Gal'braikh, *Vysokomol. Soed.*, **A29**, 406 (1987).
9. E. V. Alekseevskii, R. K. Golts, and A. P. Musakin, *Kachestvennyi Analiz (Qualitative Analysis)*, Goskhimizdat, Leningrad, 1955.
10. J. I. Goldstein, *Practical Scanning Electron Microscopy*, Plenum, New York and London, 1975.
11. A. Ya. Malkin and A. E. Chalikh, *Diffusion and Viscosity of Polymers. Measurement Methods*. Khimia, Moscow, 1979 (in Russian).
12. K. E. Perepyelkin, *Structure and Properties of Fibers*. Khimia, Moscow, 1985 (in Russian).
13. A. K. Andrianov, A. V. Olenin, and V. P. Zubov, *Vysokomol. Soed.*, **A25**, 1987 (1983).

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