Comparative Analysis of Structure and Temperature Behaviour of Two Copolyamides - Regular KEVLAR and Statistical ARMOS

Andrei A. Levchenko*, Evgueni M. Antipov, Nikolaj A. Plate'

A.V. Topchiev Institute of Petrochemical Synthesis of Russian Academy of Sciences, Leninsky prospect, 29, 117912, Moscow B-17, Russia

Manfred Stamm*

Max Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

SUMMURY: In the present investigation X-ray diffraction techniques, DSC and dynamic mechanical relaxation (DMR) methods have been employed to compare the structure and thermal behaviour of Kevlar ("DuPont", USA) and Armos (Russia) fibers. Our recent studies have indicated that the non-crystalline phase of copolyesters always contains LC smectic structure in addition to some part of the nematic LC mesophase. It turned out that the copolyamides also possess this interesting feature. Moreover, on heating of a semicrystalline copolyester always the second order phase transition from the crystalline state to condis mesophase has been observed, whereas in the case of copolyamides such a transition has the «virtual» character. As was established by other authors both polymers under study reveal the moisture content. The changes in wide angle X-ray scattering of copolyamides under heat treatment were interpreted in terms of desorption of bound water and structural rearrangement in the plane perpendicular to the chain axis involving of the hydrogen bonding between neighboring macromolecules.

Introduction

Kevlar aramid fibers based on poly(p-phenylene terephthalamide) were developed and commercialized by Du Pont Co in 1972[1)]. These fibers were presented as an ultra-high modulus and ultra-high strength material possessing the high flame resistance and thermal stability. Armos is a copolyamide, consisting of para-substituted phenylene and benzimidazole, and exhibiting comparable mechanical properties to those of Kevlar fibers.

Many of functional properties, particularly tensile properties, of such systems like aramide fibers can be related to the fiber structure[1)]. The most important structural parameters that effect fiber properties are the polymer chain conformation and rigidity, the intermolecular hydrogen bonding, crystalline orientation, and crystallinity.

The presence of hydrogen bonding in aramid fibers has an essential effect on chain reorientation during heat treatment giving rise to the improvement of orientation of macromolecules and development of crystallinity in the material[1,2)]. The equilibrium

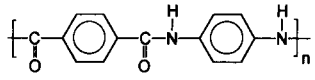
 CCC 1022-1360/99/$ 17.50+.50/0

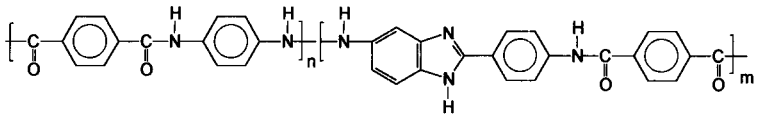
moisture (water) content or moisture regain of a fiber is also an important physical property[2]. This is related to the ionically bound water.

The present study provides information not only on the structure and temperature behaviour of two copolyamides - regular Kevlar and statistical Armos, but also on the mechanism of desorption of water from these materials during heating.

Materials and methods

Objectives of this investigation were fibers based on poly(p-phenylene terephthalamide) (Aramid Kevlar fiber) and poly(p-phenylene-benzimidazole-terephthalamide-co-p-phenylene terephthalamide) (Armos fiber). The chemical structures of both polymers under study are shown below:





X-ray diffraction studies were performed with a standard θ–θ diffractometer Siemens D 500T (CuK_α, λ = 0.154 nm). The temperature was varied from 20 to 300 °C. WAXS and SAXS patterns were registered by the 2D-detector equipped to the 18 kW Rigaku X-ray generator with a rotating anode (copper radiation). Measurements were carried out at ambient and elevated temperatures.

Thermal properties of the samples were studied with Mettler TA 4000 differential calorimeter within a temperature range extending from 20 to 350 °C at a heating or cooling rate 20 °C/min. All DSC measurements were carried out with CPE's fibers kept with the free ends (nonisometric conditions).

Dynamic viscoelastic characteristic of materials (dynamic Young's modulus E' and mechanical loss tangent tg δ) as a function of temperature were studied by examining low-frequency acoustic properties of the fibers with resonance techniques that use vibrations of vertically suspended fiber.

Results and discussion

The Fig. 1 presents the results of TGA for Armos fibers. As is seen from this figure, the copolymer under study did not undergo intensive decomposition until 470 - 500°C in a nitrogen atmosphere. It is comparable with Kevlar fibers that do not indicate a decomposition temperature above 460 °C[1)]. Moreover, the inflection of the TGA trace is well pronounced in the range of 70-140 °C indicating 3 % weight loss of a sample. The inflection point of this process is located at 120 °C. This can be associated with desorption of the bound water from the sample under heat treatment. This observation is consistent with literature data[1-3)] for regular Kevlar[2,3)] and copolymers[1)] based on poly(p-phenylene terephthalamide).

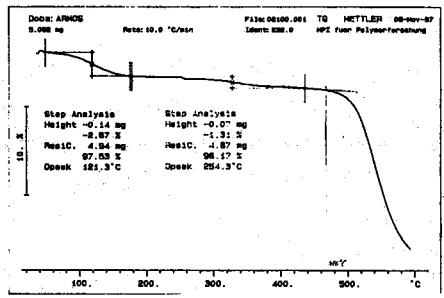


Fig. 1: TGA data for Armos.

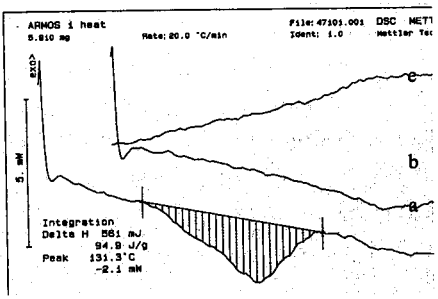


Fig 2: DSC traces for Armos on first (a), second (b) heatings and cooling (c).

DSC traces for ARMOS fibers are given in Fig. 2. On the first heating of the sample the very broad endothermic peak ranging from 0 to 200 °C can be seen in Fig. 2a. The maximum is located at 120 °C. This process takes place in the same temperature range like a process of weight loss registered by TGA measurement (Fig. 1). Such a thermodynamic transition is irreversible; hence, there is no indication of this peak in the cooling and second heating thermograms. On the other hand, the another thermal process, extended from 200 to 350 °C, can be clearly

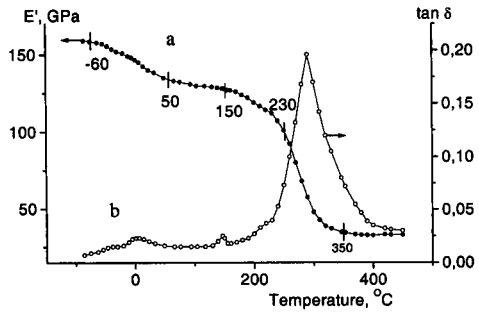


Fig. 3: Temperature dependences of the modulus E' (a) and mechanical tangent loss tg δ (b) for Armos

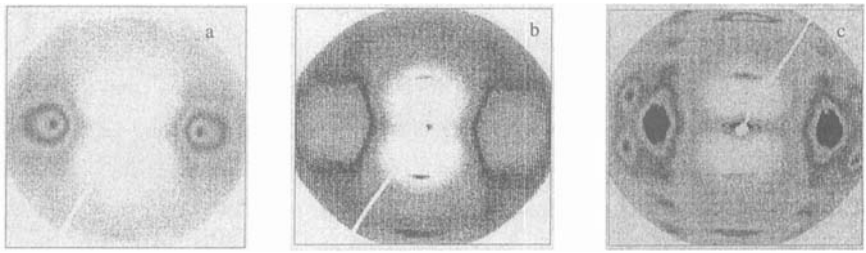


Fig. 4 : X-ray diffraction patterns of as-spun Armos (a), Kevlar (c) and annealed Armos (b) fibers.

seen on the cooling and second heating DSC traces (Fig. 2b, c). It is likely that this process corresponds to the glass transition. But the temperature of glass transition can not be determined from an inflection point even approximately due to the complicated shape of DSC curves.

The results of DSC measurements were in a good agreement with those obtained by dynamic mechanical analysis (Fig. 3). A sharp drop in the modulus E' and an intensive tangent loss tg δ peak coincide with relaxation transition registered in the DSC thermograms. According to our previous investigations[4,5], we believe that the temperature of defreezing of the local mobility of the most thermostable comonomer unit in copolyamide macromolecules, namely, benzimidazole group, corresponds to the glass transition temperature of 280 °C. Moreover, it has been shown[5] that such a feature is the universal one of all thermotropic LC CPEs and copolyamides. The first and the second peaks are related to the defreezing of the terephthalic acid and diamine units in the temperature ranges of 60-50 and 150-230 °C, respectively.

The X-ray pattern for as-received Armos fibers exhibited a high degree of orientation of macromolecules is shown in Fig. 4a. Hence, equatorial diffraction spots, centered at a

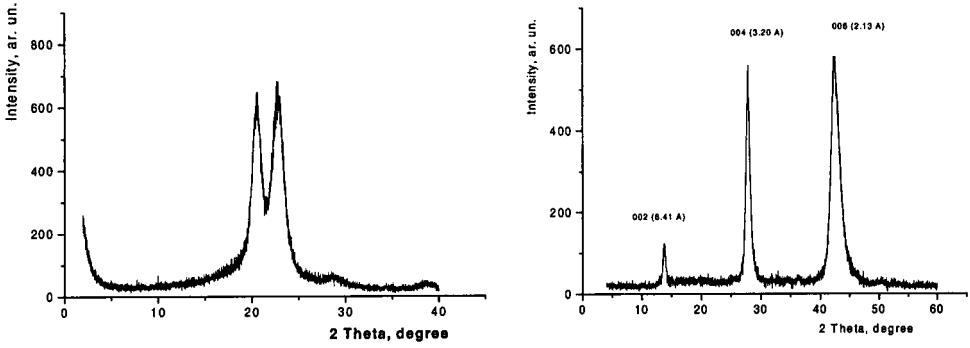


Fig. 5: Equatorial and meridional X-ray diffraction scans of Kevlar.

spacing of 0,434 nm, were clearly seen. In contrast to the regular Kevlar (Fig. 4c), the X-ray patterns for as-spun (Fig. 4a) and even annealed (Fig. 4b) Armos fibers do not indicate any Bragg reflections in their quadrants due to principally non-crystalline structure of the material.

With accordance to several authors[1,7], the X-ray pattern of Kevlar fibers almost does not show amorphous halo, indicating high-degree of crystallinity (Fig.5a, b). In contrast to Kevlar, an equatorial diffraction scattering of Armos (Fig. 6a) consists only of a broad asymmetric peak with a pseudoamorphous profile indicating an absence of three-dimensional order in the plane perpendicular to the chain axis in the copolymer. The character of the meridional scattering for Armos (Fig. 7) fibers is similar to that of Kevlar, but differentiated from equatorial scattering by the fact that there are three intensive Bragg peaks with a complicated profile on the meridian. The analysis of profiles of meridional reflections also indicates that copolyamide contains LC smectic structure in addition to some part of the nematic LC mesophase[4-6]. The «crystallite» size along the chain axis derived from the integral breadth of the second peak for Armos is ~ 20 nm, comparable to that of Kevlar fibers of ~ 25 nm.

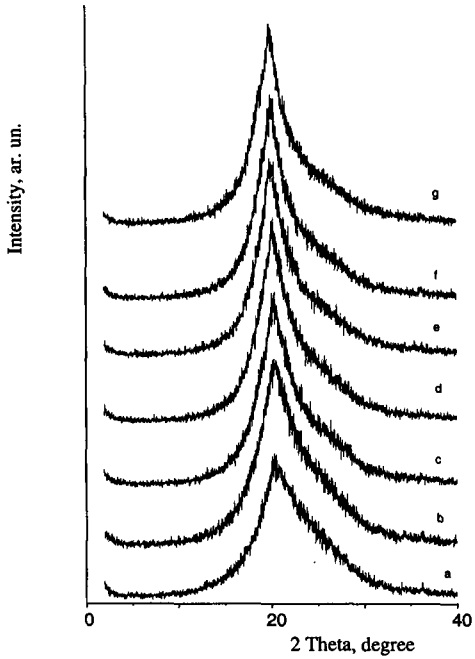


Fig. 6.: Equatorial X-ray diffraction scans of Armos fibers at elevated temperatures (a – 25, b - 100, c- 150, d - 200, e - 250, f - 270 and g – 300 °C)

In order to explain an existence of the register along the chain axis, resulting in sharp Bragg peaks in meridian pattern, and its absence in the perpendicular plane in copolyesters Antipov[6] et.al. proposed the model of periodic smectic type and

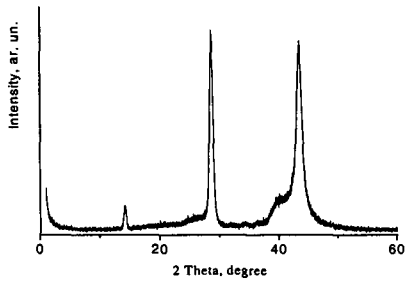


Fig. 7.: Meridional X-ray diffraction scan of Armos

aperiodic smectic type structures depending on the ratio of the lengths of comonomer components. In other words, a typical periodic mesophase is formed in a case of structural units of equal lengths giving rise to appearance of the periodic maxima on the meridian and in the case of different lengths vice versa. Both two models are a development of non-periodic layers model proposed by Windle et.al. to explain the existence of crystalline order in thermotropic LC copolyesters[8].

The Fig. 6 presents the equatorial scans for Armos recorded at different temperatures. As can be seen from these data the intensity of the equatorial peak markedly increases with a temperature increase that is probably to be associated to the improvement of existing structure or development of crystallization. Meanwhile, the increase of the intensity for the first maximum on the meridian, taking place in the same temperature range of 25-120 °C, is observed. This effect can be clearly seen in Fig. 8, presenting temperature dependences of intensity of three reflections on the meridian. The analysis of both literature and obtained data suggests that desorbsion of bound water takes place in this temperature range. It is also believed that this behaviour is caused by structure rearrangement in the plane perpendicular to the macromolecular axis and formation of hydrogen bonds between neighboring macromolecules.

There was no significant distinction of changes in the intensity distribution of X-ray scattering of Kevlar fibers. But it was absolutely unexpected that two main equatorial peaks indexed as (110) and (200) of pseudo-orthorhombic lattice[7] of Kevlar fibers tend to come closer during heating as given in Fig. 9. If the polymer does not undergo any decomposition up to 1000 °C, the second order phase transition from the crystalline state to condis mesophase would be observed.

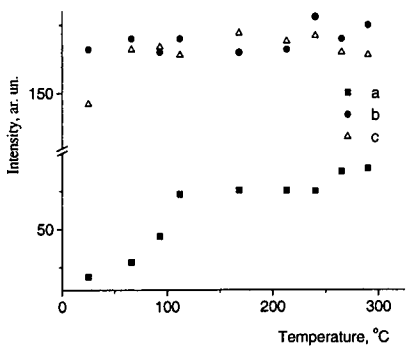


Fig. 8: Temperature dependences of the intensities of meridional maxima of Armos fibers.

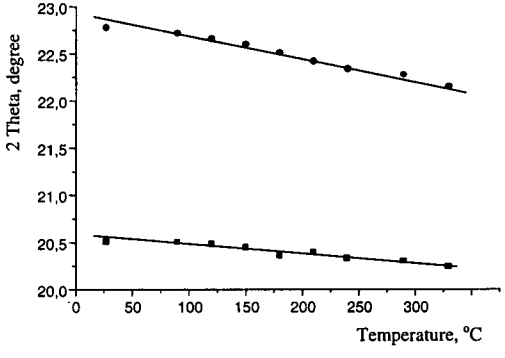


Fig. 9: Temperature dependences of the equatorial angular positions of Kevlar fibers.

Conclusions

As one could expect in contrast to regular Kevlar, as-spun fibers of statistical Armos does not indicate any crystallinity. But it is unexpected, that the non-crystalline phase of copolyamides contain LC smectic structure in addition to some part of the nematic LC mesophase. The results for Armos are compared with axial "crystalline" sizes determined for Kevlar.

It has been found also that the heating of Armos fibers results in desorption of bound water and structural rearrangement in the plane perpendicular to the chain axis, accompanied by formation of hydrogen bonds between neighboring macromolecules.

In addition it has been shown that the temperature of defreezing of the local mobility of the most thermostable comonomer unit in Armos macromolecules, namely, benzimidazole group, corresponds to rather high glass transition temperature of 280 °C, as revealed by DSC and DMR.

Acknowledgements

Financial support by Deutsche Forschungs Gemeinschaft and Russian Foundation for Basic Research (grant No 99-03-04003) as well as the Foundation of Russian Academy of Sciences for Young Scientists (grant No 40) is gratefully acknowledged.

References

1. H. H. Yang, Aromatic High-Strength Fibers, John Wiley & Sons, New York, (1989)
2. M. Fukuda and Kawai, *Polym. Sci. B: Polym. Phys.*, V. 35, p.p.1423-1432, (1997).
3. R.G. Garza, C.O. Pruneda and R.J. Morgan, Bound Water in Kevlar 49 Fibers, ACS Meeting, New York, (1981).
4. E. M. Antipov, I. A. Volegova, Yu. K. Godovsky, S. Ye. Kudryavtseva, D. O. Zhukov, *Russian Polymer Science*, V. A 39, No 11, p.p. 1791-1804, (1997).
5. E. M. Antipov, A. A. Levchenko, M. Stamm, E. W. Fischer, P. J. Lemstra , submitted to *Acta Polymerica* (1999).
6. E. M. Antipov, S. D. Artamonova, I. A. Volegova, Yu. K. Godovsky, M. Stamm, E. W. Fischer. Chapter 17 in the book "Liquid Crystalline Polymer Systems. Technological Advances", edited by Prof(s) A. I. Isaev, T. Kyu, and S. Z. D. Cheng, ACS, Washington, DC, p.p. 259-303, (1996).
7. Hanna S., Romo-Uribe A., Windle A.H., *Nature*, V. 366, p.546, (1993).
8. Northolt M.G. *Eur.Polym. J.*, No 9, p. 799, (1974).