

AUTHOR'S SUMMARY

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1. Personal data

Name: **Czesław Ślusarczyk**

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Institute of Textile Engineering and Polymer Materials
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Current position: Adjunct

2. Education and degrees

PhD in Physics 1997 - Silesian Technical University in Gliwice
Faculty of Mathematics and Physics
Thesis: „*X-ray investigations of supermolecular structure of styrene – Co(II), Ni(II), Zn(II) acrylates*”
Promotor: Prof. Dr Andrzej Włochowicz

Master of Science: 1981 – Silesian University in Katowice
in Physics Faculty of Mathematics, Physics and Chemistry
Thesis: „*Mori formalism applied to study the angular velocity correlation function of molecules in liquids*”
Promotor: Assistant professor Edward Kluk
graduated with honors

3. Information about current employment in scientific institutions

1981 – 1994 Technical University of Lodz Branch in Bielsko-Biala
physicist, research associate

1994 – 1997 Technical University of Lodz Branch in Bielsko-Biala
senior Assistant

1997 – 2001 Technical University of Lodz Branch in Bielsko-Biala
Adjunct

od 2001 University of Bielsko-Biala
Adjunct

4. Indication of achievement underlying habilitation procedure

The scientific achievement, according to *The act on degree and academic title*, is a series of scientific publications entitled „*Crystallization in polymer systems – investigations by means of wide-angle (WAXS) and small-angle (SAXS) scattering methods*”.

4. a Bibliographic data

The scientific achievement is a series of nine scientific publications entitled „*Crystallization in polymer systems – investigations by means of wide-angle (WAXS) and small-angle (SAXS) scattering methods*”. The articles have been published in the journals of the Journal Citation Reports (JCR) database.

[H1] **Cz. Ślusarczyk:**

Structure development during isothermal crystallization of high-density polyethylene: Synchrotron small-angle X-ray scattering study

Radiation Physics and Chemistry, 2013, <http://dx.doi.org/10.1016/j.radphyschem.2013.03.038>
(IF = 1,375, my participation in the work is 100 %)

[H2] **Cz. Ślusarczyk:**

Time-resolved SAXS investigations of morphological changes in a blend of linear and branched polyethylenes during crystallization and subsequent melting

Journal of Alloys and Compounds **382** (2004) 68-74
(IF = 1,080, my participation in the work is 100 %)

[H3] K. Suchocka-Galaś, **Cz. Ślusarczyk**, A. Włochowicz:

The state of ion aggregation in ionomers based on copolymers of styrene and acrylic acid. 1. Small-angle X-ray scattering studies

European Polymer Journal **36(10)** (2000) 2167-2174
(IF = 0,745, my participation in the work is 45 %)

[H4] K. Suchocka-Galaś, **Cz. Ślusarczyk**, A. Włochowicz:

The state of ion aggregation in ionomers based on copolymers of styrene and acrylic acid obtained by copolymerization in emulsion. 2. Small-angle X-ray scattering studies

European Polymer Journal **36(10)** (2000) 2175-2184
(IF = 0,745, my participation in the work is 45 %)

[H5] **Cz. Ślusarczyk**, K. Suchocka-Galaś:

Poly(ethylene-oxide)/styrene ionomers blends: crystallization of poly(ethylene-oxide) component studied by wide-angle X-ray diffraction

Solid State Phenomena **130** (2007) 251-256 (my participation in the work is 90 %)

[H6] **Cz. Ślusarczyk**, K. Suchocka-Galaś, J. Fabia, A. Włochowicz:

Small-angle X-ray scattering study of poly(ethylene-oxide) and styrene based ionomers blends

Journal of Applied Crystallography **36** (2003) 698-701 (IF = 1,871, my participation in the work is 70 %)

- [H7] **Cz. Ślusarczyk:**
Crystallization and melting behavior of poly(ethylene oxide) and its blend with styrene based ionomer using time-resolved SAXS/WAXS experiments
 Radiation Physics and Chemistry **80** (2011) 1078-1083
 (IF = 1,149, my participation in the work is 100 %)
- [H8] J. Broda, **Cz. Ślusarczyk**, A. Włochowicz:
Influence of Heat-Stabilization on Supramolecular Structure of Colored PP Fibres
 Journal of Applied Polymer Science **73** (1999) 477 - 488.
 (IF = 0,952, my participation in the work is 40 %)
- [H9] R. Fryczkowski, **C. Ślusarczyk**, J. Fabia:
Structure and conducting properties of thermoplastic composites of polypropylene and polyaniline protonated in solid state
 Synthetic Metals **156** (2006) 310 - 317
 (IF = 1,685, my participation in the work is 30 %)

The full text of these publications are listed in Annex No. 4. The statements of co-authors of the papers, defining their participation, are presented in Annex No. 5.

In addition, the problem of referring to publications submitted to the habilitation procedure, is in the following publications outside the JCR list:

- Cz. Ślusarczyk, A. Włochowicz, K. Suchocka-Gałaś: „*Morphology of styrene-based ionomers: SAXS investigations using correlation functions*”
 Proc. SPIE (2000) 4240, 20 – 26 (DOI: 10.1117/12.401845)
- Cz. Ślusarczyk, K. Suchocka-Gałaś, J. Fabia, A. Włochowicz: „*Badania struktury nadcząsteczkowej mieszanin PEO/ionomer styrenowy*”
 Prace Naukowe Instytutu Technologii Organicznej i Tworzyw Sztucznych Politechniki Wrocławskiej Nr 52, str. 505-509. Oficyna Wydawnicza Politechniki Wrocławskiej, Wrocław 2003.
- Cz. Ślusarczyk: „*Interface distribution function from SAXS data for heat treated polyethylene*”
 Applied Crystallography, H. Morawiec, D. Stróż, Editors, World Scientific 2004

This theme was also presented at many international scientific conferences, of which the most important are:

- World Polymer Congress IUPAC MACRO 2000, Warsaw, Poland
- XII International Conference on Small-Angle Scattering SAS 2002, Venice, Italy
- European Materials Research Society Fall Meeting E-MRS 2003, Warsaw, Poland

- X International School and Symposium on Synchrotron Radiation in Natural Science (ISSRNS-10), Szklarska Poręba, Poland
- XI International School and Symposium on Synchrotron Radiation in Natural Science (ISSRNS-11), Cracow, Poland

Details of the conferences and titles of papers can be found in Annex No. 6.

4.b Description of the research objective of the aforementioned papers and the results achieved, together with a discussion of their possible use

Introduction

Crystallization is one of the major processes controlling the structure and properties of polymeric materials. This process, in addition to the thermodynamic conditions defined mainly by the temperature and the pressure, is strongly dependent on the microstructure of the polymer macromolecules. This is because the prerequisite for crystallization of a polymer is regularity of chain macromolecule structure; isotactic and syndiotactic polymers have the ability to crystallize, while atactic polymers do not have this ability. The presence of branching in the chain typically reduces the ability of a polymer to crystallize. Polymer crystallization process is characterized by:

- *A wide range of temperatures in which crystallization occurs* - the process of crystallization of polymers occurs between the glass transition temperature T_g and the equilibrium melting point T_m^o . At temperatures higher than T_m^o the thermodynamic conditions are unfavorable for the formation of crystal nuclei, while below T_g chain segment mobility is too low for their diffusion in the direction of the crystallites growth surface;
- *Low symmetry of the unit cell* - most polymers crystallize in triclinic and monoclinic systems, rarely in a hexagonal and orthorhombic ones;
- *The simultaneous occurrence of several crystallographic forms*;
- *A relatively low degree of crystallinity of the polymer (30 ÷70%)*, i.e. the fraction of the weight or volume of the crystalline phase.

In accordance with a recognized and widely used theory of crystallization of polymers, developed by Lauritzen and Hoffman¹ and based on the concept of multiple folding of macromolecules, the crystallization process is a two-stage process. In the first stage, called primary

nucleation, as a result of thermal density fluctuations or the presence of foreign substance particles in the molten polymer, a structured groupings of macromolecule fragments, which become further crystallization nuclei, are formed. In the second stage there is an increase of the crystallites which takes place by connecting segments of macromolecules to the side surfaces of primary nuclei. Single crystals of polymers may be formed by crystallization from diluted solutions, while the crystallization from concentrated solutions and from the molten state generally takes place in the form of stacks of lamellar crystals consisting of lamellae arranged in parallel, separated by amorphous layers. A single crystal lamella in such stack is a parallelepiped with transverse dimensions that are large in comparison to the thickness, which is in the range of 10 - 30 nm. Amorphous (interlamellar) area in the stack is formed by folds of chains, ends and loops of chains, chains connecting the crystalline lamellae and short side branches. In the homogeneous temperature field of polymer, lamellae stacks are formed at the same speed in all directions, leading to the formation of aggregates of lamellar crystals, called spherulites. The growth rate of spherulites, depending on temperature, is the highest at a temperature near the middle point between the glass transition temperature and the melting point. Until the mutual contact, spherulites have spherical symmetry and their radius increases linearly in time. After mutual contact and creation of borders with its neighbors, spherulites become polyhedra. Surrounding spherulite lamellae are separated with amorphous phase containing tangling, branches and those parts of chains, which were not built into the crystal as a result of different chemical structure or configuration.

The content of the crystalline phase in the polymer determines so-called degree of crystallinity. It is defined as both mass and volume degree of crystallinity. In the first case, it is a ratio of the weight of crystalline regions present in a given sample of polymer, to its total weight. In the second case, it is the sum of the volume of the crystalline areas to the total volume of the polymer. The degree of crystallinity is the parameter that determines many properties of polymer materials. This parameter has a significant impact on their mechanical, thermal, optical, electrical and chemical characteristics. With the increase in the degree of crystallinity the tensile strength, elasticity and hardness of the polymer increase. Density increases linearly, thermal stability and chemical resistance improve. What decreases is the sorption capacity of liquids and dyes. The polymer becomes less transparent, its ability to conduct electrical current deteriorates.

Despite several decades of research, knowledge of the crystallization of polymers is still incomplete. New theories and models that describe the crystallization process emerge²⁻⁵. Devel-

opment of research is driven by two factors nowadays. The first is a need for new polymeric materials related to the development of many fields of technology. In particular, interest in nanomaterials resulted in the development of research in the field of crystallization in the conditions of space constraints, where the polymer portions are reduced from micrometer to nanometer size. The second factor is the development of research methods that often allow to study the crystallization process in real time, from its early stages. The use of synchrotron radiation of a very high intensity and better position-sensitive detectors helped to expand the opportunities offered by the method of wide-angle (WAXS) and small-angle (SAXS) X-ray scattering. The development of X-ray methods is accompanied by the development of atomic force microscopy (AFM) and the introduction of high-speed scanning calorimetry.

In this context, the presented dissertation is the development of research issues related to the crystallization of polymers, which the candidate dealt with in the period after his doctorate in physics. The dissertation presents the results of research on:

- Synchrotron study of the polyethylene crystallization process in real time;
- Crystallization of poly(ethylene oxide) in the blends with styrene ionomers;
- Supermolecular structure of dyed polypropylene fibers and blends of polypropylene with protonated polyaniline.

The study of polymer crystallization process in real time, as well as complex polymer systems requires the development of the existing methods of analyzing the results of X-ray examinations and their interpretation, particularly in respect to such subtle method as small-angle X-ray scattering (SAXS). Therefore, in this study, achievements of the candidate in this field were also presented.

Synchrotron study of the polyethylene crystallization process in real time

[H1] *Structure development during isothermal crystallization of high-density polyethylene: Synchrotron small-angle X-ray scattering study.*

The linear, regular polyethylene (PE) chains crystallize in two morphologies: folded chain crystals having the orthorhombic (o) crystal structure and extended chain crystals that arise when the melt crystallizes into the hexagonal (h) phase⁶. The h-phase of PE exhibits long-range positional order of the average chain positions, but it is not a phase of well-ordered chains in which every atom has a specific place on a hexagonal lattice. Because this phase has a high degree of

disorder, its bulk density is approximately 8.5% lower than the fully ordered o-phase. The loosely packed PE chains have an enhanced chain mobility along its axis (sliding diffusion)⁷; consequently, the h-phase is often referred to as “the mobile phase”. Crystals in this “mobile” h-phase grow simultaneously in the lateral and thickness direction the resulting thicknesses successively comprising the dimensions corresponding to folded, extended and multiples of extended chains. This increase in thickness is here genuine primary growth in the thickness direction which is called “thickening growth”. This is distinct from most considered “lamellar thickenings” which usually correspond to rearrangements within already crystallized material thus corresponding to secondary crystallization. The two processes, namely “thickening growth” and “lamellar thickening”, are fundamentally different.

The h-phase is thermodynamically stable at high temperature (> 230 °C) under high pressure (> 3.2 kbar). However, the h-phase is not confined to the aforementioned h-stability regime but also arises in the o-stability regime, where the h-phase is thus metastable. This case relies on considerations of crystal size as a thermodynamic variable, namely on melting-point depression⁸, which is, in general, different for different polymorphs. It means that under specifiable conditions phase stabilities can invert with size; that is a phase which is metastable for infinite size can become the stable phase when the crystal is sufficiently small. In the case of PE it would mean that h-phase would be stable for lamellae which are sufficiently thin, even at atmospheric pressure. Evidence that under normal pressure this mechanism is possible has been theoretically predicted by Keller et al.⁹ and experimentally demonstrated by Tracz et. al.¹⁰ This investigations had a “static” character, i.e. they observed AFM images of hexagonal crystals formed after cooling a melt in contact with a surface of oriented pyrolytic graphite.

Habilitant in this study observed, for the first time in real time, the course of the crystallization from the hexagonal phase under normal pressure. In opinion of the candidate, this work is his the most important scientific achievement, because it confirms the mechanism of lamellar thickening growth predicted by Keller.

In the present study time-resolved X-ray scattering experiments were carried out on the X33 double-focusing camera of the EMBL in HASYLAB, on the storage ring DORIS of the Deutsches Elektronen Synchrotron (DESY) at a wavelength of 1.5 Å. The standard data acquisition system with two, linear-delay line detectors connected in series was used. Crystallization of high-density polyethylene (HDPE) over a wide-range of supercooling temperatures was achieved

by using a jumping hot stage consisting of two independent chambers under a nitrogen atmosphere. Each sample was first equilibrated at 200°C for 5 min in the top chamber and then quickly jumped to the bottom chamber, which was held at the chosen crystallisation temperature. During the measurements, the temperatures of the chambers as well as those of the polymer sample were individually controlled and monitored by Eurotherm controllers with a K-type thermocouple. In total, eight crystallization temperatures were investigated. The data collection time was chosen to be 6 s for samples crystallized at 40, 100, 110, 116, 118 °C, 30 s for the sample crystallized at 120°C and 120 s for samples crystallized at 122, 124 °C.

The analysis of the SAXS curves allowed the determination of time dependence of crystalline (Lc) and amorphous (La) layers thicknesses and the distribution of the long period (LP). Figure 1 summarizes the changes of the lamellar thickness during isothermal crystallisation at different temperatures.

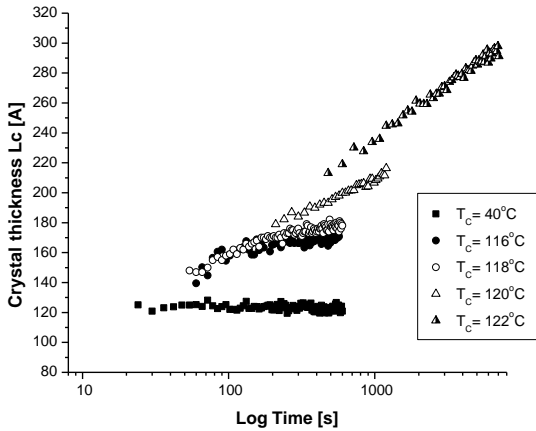


Fig. 1 Lamellar crystal thickness as a function of time during the isothermal crystallization of a high-density polyethylene.

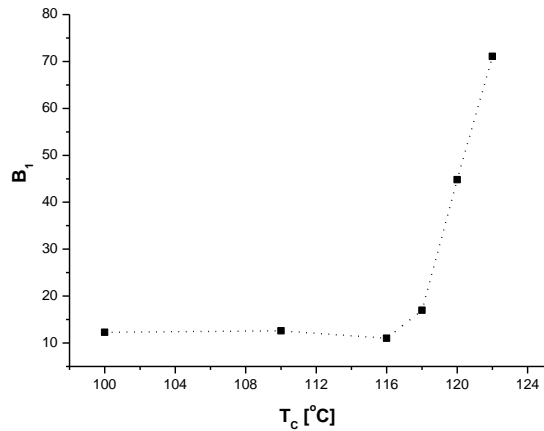


Fig. 2 The coefficient B_1 as a function of crystallization temperature T_c .

It is seen from Fig. 1 that Lc follows a logarithmic law: $L_c = B_1 \log(t) + B_2$, where B_1 and B_2 are constants. The coefficient B_1 can be used to approximate the lamellar thickening rate. The dependence of B_1 on crystallization temperature is shown in Figure 2. It is interesting to see that a very sudden increase of the B_1 value takes place at $T_c = 122$ °C. The value of the coefficient B_1 at this temperature is over four times larger than at 118 °C. This fact indicates the violent increase in the mobility of the chains along their axes (sliding diffusion) in the crystalline state. Simula-

tions of polyethylene crystallization have shown that the sliding diffusion of the chains in the growing lamella is dependent on the frictional coefficient between the chains. Because in the hexagonal phase of PE the chains are loosely packed, the friction coefficient is low, and very intense thickening during growth may occur. On the contrary, in the case of the tightly packed orthorhombic phase, the friction coefficient is assumed to be higher; hence, the sliding diffusion is low, and the thickening rate decreases. Thus, the evolution of L_C observed at $T_C = 122$ °C suggests that HDPE crystallizes by “thickening growth” in the hexagonal phase, which is metastable from the thermodynamic point of view. Time-dependent changes in the L_C of samples crystallized at 116 °C and 118 °C are different than that crystallized at 122 °C (see Fig. 1). In those cases the crystallization can be described by the “lamellar thickening” process.

The measured SAXS data were analyzed by the interface distribution functions in real space. The interface distribution function $g_1(r)$ is defined as a Fourier cosine transform of the interference function $G_1(s)$

$$g_1(r) = 16\pi^3 \int_0^{\infty} G_1(s) \cos(2\pi rs) ds \quad (1)$$

$$G_1(s) = \lim_{s \rightarrow \infty} I(s)s^4 - I(s)s^4 \quad (2)$$

where $I(s)$ is the corrected SAXS intensity ($s = 2\sin\theta/\lambda$, 2θ the scattering angle and λ , the X-ray wavelength). As seen from eq. (2), $G_1(s)$ is the difference between the higher angle asymptote of $I(s)s^4$ and the actual values of $I(s)s^4$.

Equations (1) and (2) demonstrate that $g_1(r)$ can be determined directly from the measured intensity. However, a number of corrections have to be made. The corrections were described in detail in papers [H5] and [H9]. The interface distribution function, $g_1(r)$, can easily be expressed in terms of the distributions of the crystalline and amorphous layer thicknesses. Assuming an ideal, two-phase system with a sharp phase boundary, the $g_1(r)$ is a superposition of three contributions associated with the size distributions of crystalline (L_c) and amorphous (L_a) layers and the distribution of the long period (LP). The numerous studies on crystallization of HDPE have revealed that the ensemble of lamellar stacks shows features of an inhomogeneity in the sense that the long period and lamellar crystal thickness vary from stack to stack. The approach based on the interface distribution function analysis is currently used in many SAXS studies of semi-

crystalline polymers. However, the information describing the size-distribution of the crystalline phase in this function are rarely used. In particular, such an analysis was not conducted for real-time investigations of the crystallization and melting behaviour of polymers. It seems that the analysis of the influence of the crystallization conditions on the size-distribution of lamellar crystals might provide additional information about this process. In the present paper, the interface distribution functions were deconvoluted in order to extract the statistical law governing the stacking of the lamellae during the isothermal crystallization. The relative standard deviation, σ_c/L_c , of the lamellar thickness distribution can be used as an additional parameter for analysis of this process. Figure 3 illustrates the influence of the crystallization temperature on the variations of this parameter with time.

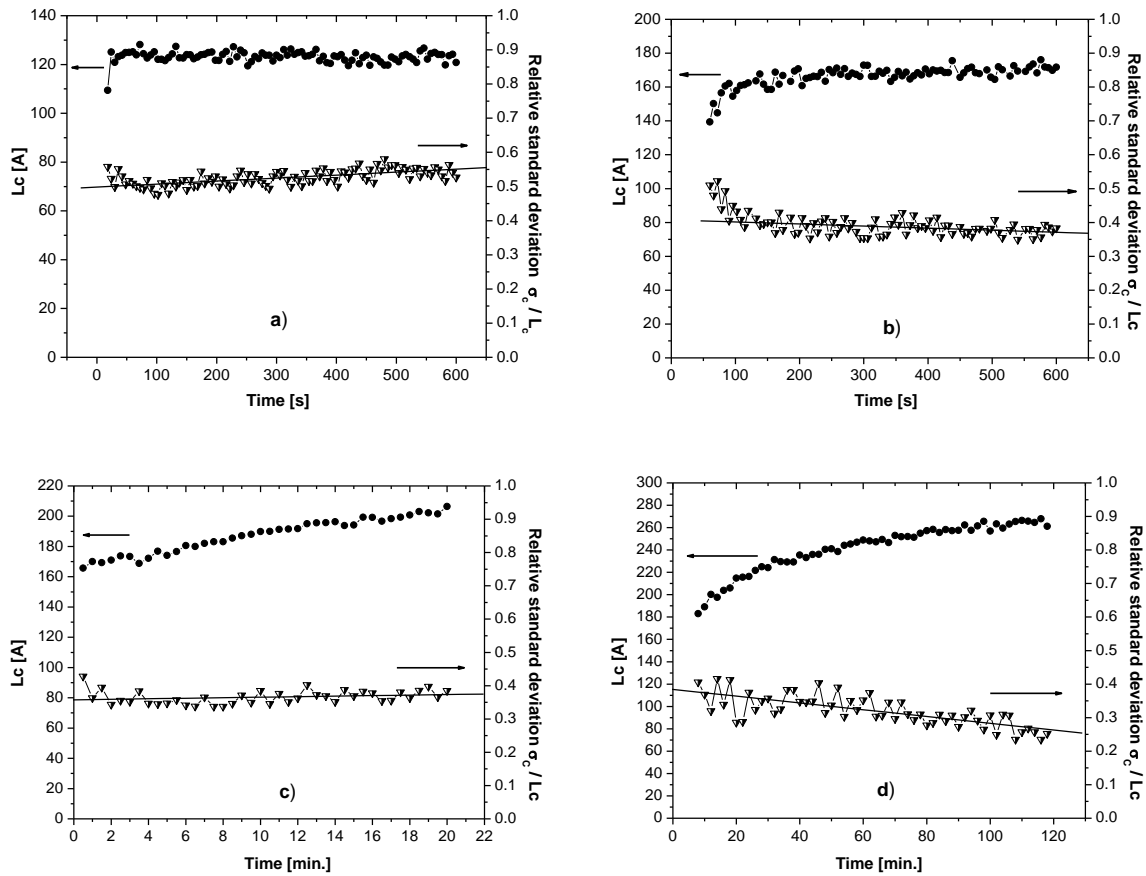


Fig. 3 Variations of L_c and the relative standard deviation with time determined from interphase distribution function for the sample isothermally crystallized at: 40 °C (a); 116 °C (b); 120 °C (c); 122 °C (d).

For the sample crystallized at 122 °C in which the crystallization proceeds via lamellar growth in the mobile h-phase, σ_c/L_c is decreasing (Fig 3d), indicating that the crystallite thickness distribu-

tion is narrowing over the course of crystallization process. During isothermal crystallization at 40 °C, when crystals formed in the orthorhombic phase without thickening, σ_C/L_c is increasing (Fig 3a), thus testifying that in this temperature the crystallization process leads to a broad distribution of crystals thicknesses.

[H2] *Time-resolved SAXS investigations of morphological changes in a blend of linear and branched polyethylenes during crystallization and subsequent melting*

The measured small-angle X-ray scattering (SAXS) data can be analyzed:

- by the interface distribution functions $g_1(r)$, which was defined and described in previous section concerning the paper [H1];
- by the correlation functions $\gamma(r)$.

Before calculations of these functions several corrections must be applied. The SAXS data should be first smoothed using spline functions in order to reduce the effect of noise. Since the experimentally accessible s range is limited, the intensity must necessarily be extrapolated to both low and high s values. The scattered intensity should be free of contributions arising from thermal electron density fluctuations within the individual phases and finite interface between the constituent phases, hence the background scattering is subtracted from experimental data.

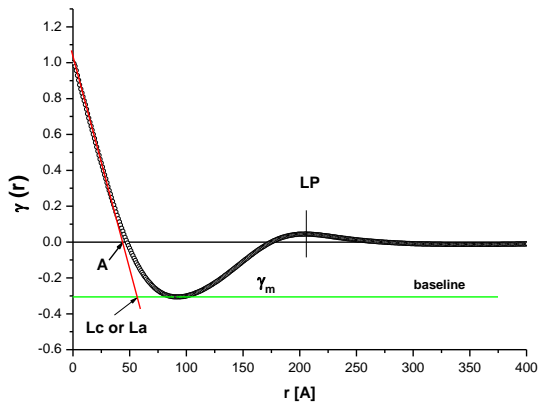


Fig. 4 One-dimensional correlation function derived from SAXS measurements.

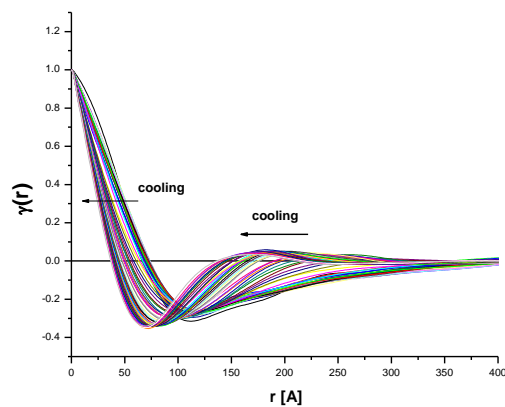


Fig. 5 Correlations functions during cooling of the (15/85)HDPE/JW1120) blend (Fig. 2 in [H2]).

Corrected intensities are so obtained and corrected data $I_C(s)$ are used in order to obtain the one-dimensional correlation function of the electron density fluctuations perpendicular to a stack of lamellar crystals:

$$\gamma(r) = \frac{\int_0^\infty I_C(s) s^2 \cos(2\pi r s) ds}{\int_0^\infty I_C(s) s^2 ds} \quad (3)$$

where “ r ” represents the distance in real space. A typical pattern for $\gamma(r)$ is shown in Figure 4.

The one-dimensional correlation function $\gamma(r)$, due to easier in comparison with the function $g_1(r)$ as its designation is often used to the analysis of the SAXS curves, in particular for synchrotron studies in which tens curves is obtained in the one time-resolved experiment. The function $\gamma(r)$, following the original contribution of Vonk¹⁵, allows for determination the values of the long period (LP), the crystalline and amorphous layer thickness (l_C and l_A respectively) and the local volume fraction crystallinity (Φ_L). Φ_L (given by the ratio of the lamellar thickness l_C , to the long period LP) can be obtained from the correlation functions in two different ways. The correlation function approach was designed for homogeneous ideal two-phase systems where a series of triangles centered at $r = 0, L_P, 2L_P, \text{etc.}$, reflect correlations within one lamella, next neighbors, second neighbors, etc. At $r = 0$, there is the formation of the so-called “self-correlation triangle”. There is also a horizontal line that passes along the bases of the rest of the triangles which is called the “baseline”. Determinations of LP, l_C , l_A , and Φ_L may be realized by locating the first minimum and maximum in the correlation function^{15,16}. The long period LP is estimated from the position of the first maximum of $\gamma(r)$ (see Fig. 4). On the other hand, the negative abscissa, γ_m , that gives place to the origin of the baseline is related to the local volume fraction crystallinity Φ_L , namely

$$\gamma_m = \frac{-\phi_L}{1-\phi_L} \quad \text{for } \Phi_L < 0.5 \quad (4)$$

$$\gamma_m = \frac{1-\phi_L}{-\phi_L} \quad \text{for } \Phi_L > 0.5$$

So, the value of the first minimum of the one-dimensional correlation function can be used to determine the Φ_L if this minimum is flat. Since, only in a such case the minimum may coincide

with the baseline. Moreover, the intersection of the linear regression to the self-correlation triangle with the baseline (Fig. 4) directly yields a value for l_C or l_A according to a value of Φ_L (it determines l_C if $\Phi_L < 0.5$). An alternative way to calculate Φ_L is the solution of the so-called quadratic expression (Q.E.):

$$A = \Phi_L(1 - \Phi_L)LP \quad (5)$$

where A equals the intersection of the linear regression to the self-correlation triangle with the abscissa ($\gamma(r) = 0$). The equation (5) yields two possible values for Φ_L . One value is lower than 0.5, the other solution is equal to $(1 - \Phi_L)$. Independent information concerning crystallinity of the sample is needed to decide which solution of Q.E. reflects the true value of a local volume fraction crystallinity. Here, in the present paper, the crystallinity values from the differential scanning calorimetry (DSC) are used as a guide. DSC measurements reveal that the lower value is the correct ones. The lamellar and amorphous layer thicknesses can then be calculated from

$$l_C = \Phi_L LP \quad l_A = (1 - \Phi_L)LP \quad (6)$$

As is apparent from Eq. (6), to determine the values of the parameters l_C and l_A is necessary to know the value of the local volume fraction crystallinity Φ_L . According to Eqs. (4) and (5) Φ_L can be obtained from the correlation functions in two different ways. Both methods have their own prerequisites and limitations. Equations (4) may be used when the correlation function has a flat minimum, while equation (5), the first maximum is clearly defined. In studies in real time the crystallization process of polymers, however, appears an issue of the proper designation of Φ_L changes, since as illustrated in Figure 5, during this process the shape of the correlation function is changed so that neither one nor the second method does not give actual values Φ_L for all curves.

In the present work, the author has developed a way to solve the problem in this case. The method is illustrated by the example of investigations of non-isothermal crystallization and melting of a blend of a high-density polyethylene (HDPE) and a homogeneous ethylene copolymer with 5.2 mol % 1-octene. A local volume crystallinity, Φ_L , was calculated by means of the minimum (CF_{\min}) of the correlation function (eq. 4) as well as from the quadratic equation (Q.E.) (eq. 5). Both methods should give identical results. However, as Figure 6 illustrates, it is fulfill only in the temperature range from 65 °C to 90 °C. At lower temperatures Φ_L obtained from CF_{\min} is

considerably lower than Φ_L calculated from Q.E. The very important condition for CF_{\min} to yield correct values for Φ_L is that it must be flat. As illustrated in Figure 5, the horizontal plateau of $CF(r)$ at lower temperatures gradually disappears causing that the CF_{\min} gives incorrect Φ_L -values in that temperature region. Therefore the results based on Q.E. are correct. For temperatures greater than 90 °C similar dependence can be observed (i.e. Φ_L from CF_{\min} is lower than Φ_L calculated from Q.E) but in this case the interpretation is different. In this temperature region the first side maximum in $CF(r)$ is very broad and hence it is very difficult to determine LP accurately. Hence, the use of Q.E. is not appropriate and more accurate Φ_L -values were calculated based on CF_{\min} . At these temperatures correct values of the long period LP were calculated using Q.E. with the Φ_L values obtained from CF_{\min} . Thus, the evolution of the Φ_L in the whole temperature range during cooling must be composed from results of both methods. Figure 7 illustrates the final course both for cooling and heating scans. Because the thickness of crystalline and amorphous layers (l_C and l_A) are calculated from the product of LP with Φ_L or $(1 - \Phi_L)$, respectively, according to equation (6), the correct determination of Φ_L is very crucial.

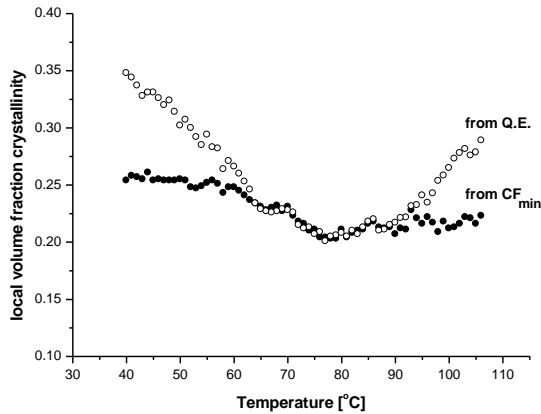


Fig. 6 Local volume fraction crystallinity Φ_L obtained by means of two methods.

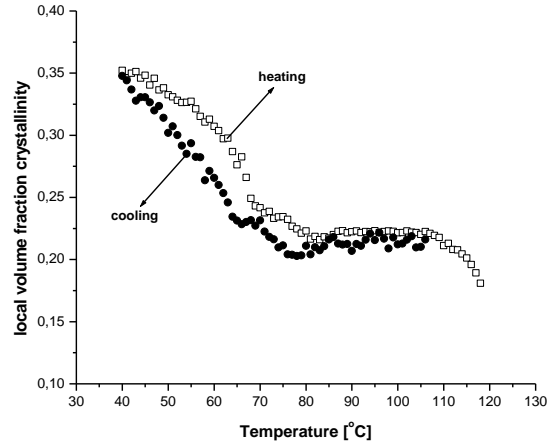


Fig. 7 Real evolution of Φ_L during cooling and heating of the investigated blend.

The correct determination of Φ_L in whole temperature range during cooling and heating of the investigated blend allowed to observe real changes of the crystalline layers thickness l_C . It was found that non-isothermal crystallization of the investigated blend leads to a bimodal distribution of lamellar thicknesses within the blend due to an extensive separation of its components according to their ethylene sequence length (see Fig. 6 in the paper H2). The evolution of l_C dur-

ing cooling scan can be interpreted according to the nucleation theory¹ under which, the thickness of a crystalline lamella is inversely proportional to the undercooling (i.e. the difference between the equilibrium melting temperature T_m and a crystallization temperature T_C). During slow cooling, at the initial stage of crystallization, only thick crystals can be formed. These crystals arise as a result of crystallization of a relatively long ethylene sequences which mainly belong to the HDPE, the minority fraction of the investigated blend. The copolymer ethylene sequences that have the critical length for nucleation at that temperature are also involved, but in general the copolymer sequences are shorter and crystallize separately at lower temperatures into thinner crystals. A chain microstructure of the ethylene-1-octene copolymer can be imagine as a linear one divided into crystallizable sequences by hexyl branches. Sequences lengths are mainly dictated by the distribution of branches, because they are excluded from the polyethylene crystal during crystallization process. During subsequent heating such bimodal population melts in the reversed sequence of their formation. The thinnest crystals melt first, yielding an increase l_C value at temperatures where the thinner lamellae (copolymer) have melted and the thicker (HDPE) lamellae are still undamaged (see Fig. 6 in the paper H2).

Crystallization of poly(ethylene oxide) in the blends with styrene ionomers

Blends of the polymers, one component of which is a crystallizable polymer and the other an amorphous polymer, are the subject of numerous studies due to their interesting properties caused by their diverse morphology. Crystallization of one of the components of the mixture involves separation of the other component. Depending on the miscibility of the components, amorphous polymer may reside in interlamellar, interfibrillar or interspherulitic areas¹⁷. Furthermore, blends of this type may exhibit different types of morphology simultaneously, which significantly affects their utility properties. Among semicrystalline polymer/amorphous polymer blends, relatively little research concerns blends with ionomers. Ionomers are copolymers in which the functional groups are readily ionized. The presence of such groups strengthens the intermolecular interactions that may become a dominant factor impacting the amorphous component separation and crystallization process of the other component of the blend.

Poly(ethylene oxide) (PEO) is a polymer from the polyethers group with the general formula $H - O - [CH_2 - CH_2 - O]_n - H$. Thanks to identical dimension of the structural unit and water molecule, it is soluble in water over a wide concentration range. It is a flexible polymer

with a waxy consistency, with a glass transition temperature of $T_g = -59\text{ }^\circ\text{C}$ and a melting point in the range $66 - 70\text{ }^\circ\text{C}$. PEO is used in the textile, paper (paper coat) industry, as an emulsifier and thickener in paints and as a flocculant for dewatering suspensions. Due to its non-toxicity and biocompatibility is used in the cosmetic and pharmaceutical industries. PEO is a non-polar polymer, however, the presence of ether groups in its chain makes it capable of hydrogen bonding and solvation of various inorganic salts. For these reasons, it is now widely applied as a matrix for solid polymer electrolytes used for the production of batteries. A disadvantage of PEO in this context is its high crystallinity (70 - 90 %), which is the greatest barrier to the transport of ions and typically results in poor ionic conductivity. Mixing PEO with amorphous polymer is a convenient method of lowering its crystallinity, hence the works H3, H4, H5, H6, H7, present test results of supermolecular structure of blends of polyethylene oxide (PEO) and a styrene-acrylic acid (S-AA) copolymer neutralized with Cs^+ , Na^+ , Li^+ and K^+ cations. Scientific issues related to the study of these blends were initiated by the candidate, who invited to cooperation dr Kazimiera Suchocka-Galaś (PhD) from the Department of Chemistry, University of Nicolaus Copernicus - a research unit of a great reputation and experience in the synthesis of ionomers. Using a wide-angle (WAXS) and small-angle (SAXS) X-ray scattering, differential scanning calorimetry (DSC) and scanning electron microscopy (SEM), supermolecular structure was evaluated depending on the composition of the blend, the content of ionic groups in the ionomer and the type of cation neutralizing these groups. In particular, these works focused on the following issues:

- Examining the status of aggregation of ionic groups in ionomers, depending on the temperature, ionic group content and the kind of the neutralizing cation;
- Establishing the degree of miscibility of PEO with styrene ionomer;
- Evaluating the impact of styrene ionomer content on the degree of crystallinity and sizes of PEO crystallites;
- Examining the degree of separation of mixture components and the location of the amorphous component in it;
- Using synchrotron radiation, the impact of styrene ionomer on the process non-isothermal crystallization of PEO was studied in a real-time.

[H3] *The state of ion aggregation in ionomers based on copolymers of styrene and acrylic acid. 1. Small-angle X-ray scattering studies*

[H4] *The state of ion aggregation in ionomers based on copolymers of styrene and acrylic acid obtained by copolymerization in emulsion. 2. Small-angle X-ray scattering studies*

The studies of supermolecular structure of ionomers conducted for many years demonstrated the existence of isolated anion/cation pairs and two types of aggregates called multiplets and clusters in ionomers. The multiplets, whose sizes range from 3 Å to 20 Å are a cluster of several ion pairs closely linked together. As Eisenberg¹⁸ has shown, only up to 8 ion pairs can form multiplets, due to steric constraints. Multiplets do not contain hydrocarbon structural units, but are surrounded by them. Under certain conditions multiplets combine into larger domains whose clusters called, whose sizes range from 50 Å to 200 Å. Within the clusters multiplets are not in direct contact with each other but are separated by hydrocarbon segments¹⁸. Ionomer in which the clusters are present is a polymer system with separated phases, differing in electron density. Clusters are the ionic phase, and hydrocarbon segments - non-ionic phase. Despite much research, issues of spatial distribution of multiplets in the polymer matrix, the inner structure of clusters and the conditions in which they are formed remain unresolved. In ionomers there is no long range ordering, and the ion aggregate sizes are small, so these problems are difficult to solve. The majority of the data on the supermolecular structure of ionomers is derived from research carried out using X-ray methods, in particular the wide-angle (WAXS) and small-angle (SAXS) X-ray scattering. Depending on the concentration of ionic groups and their degree of neutralization, in the diffractograms of ionomers a broad maximum in the range of small angles of diffraction, i.e. from $2\theta \approx 1^\circ$ to $2\theta \approx 7^\circ$ is present. This maximum, called an "ionomer peak," indicates the aggregation of ionic groups.

In articles [H3] and [H4] results of the SAXS studies of ionomers based on styrene – acrylic acid copolymers neutralized by alkali metal cations have been reported. The ionomers have been obtained by two copolymerization methods, namely in bulk and in emulsion. Details concerning copolymerization procedures are described in the articles. The formation of ionic aggregates as a function of the content of ionic groups, the nature of the alkali metal and temperature have been studied.

The dominant feature of the SAXS patterns of ionomers, containing less than 10 mol% of caesium acrylate (ACs) is the appearance of the scattering maxima characteristic of ionomers which are usually taken as evidence for ionic aggregation. For ionomers containing more than 10

mol% of ACs, a second maximum appears on SAXS patterns. These patterns also show a significant upturn in the small angular range, which may be caused by an inhomogeneous distribution of isolated ionic groups in the material. Assuming that an ionomer is a dilute system of ionic aggregates dispersed in a polystyrene matrix, the interference maxima may be connected with the internal structure of aggregates and from angular position of these maxima the sizes of aggregates can be calculated.

The appearance of two maxima on the scattering patterns is connected with two types of ionic aggregates. The first interference maximum have been attributed to larger aggregate clusters, which is confirmed by the calculated sizes of these clusters of 6,0 – 13 nm. The second maximum have been attributed to smaller aggregate multiplets of 2,0 nm diameter. The performed studies indicate that the state of ion aggregation in ionomers is dependent not only on the concentration but also on the type of introduced alkali metal. For ionomers containing lithium and potassium ions only one scattering maximum appears on the SAXS patterns. The maximum indicates that in that cases only smaller aggregate multiplets are formed. The sizes of these multiplets are dependent on the type of the alkali metal introduced.

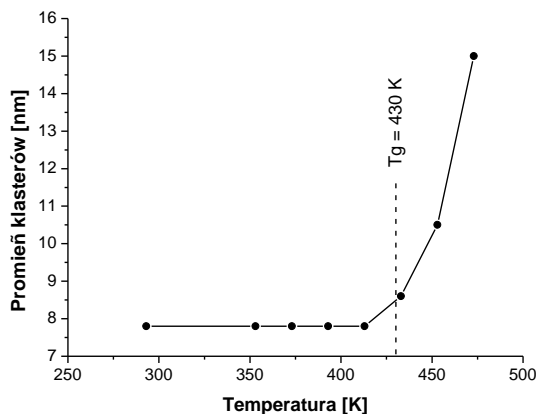


Fig. 8 The influence of the temperature on the cluster radii for the ionomer sample containing 14,1 %mol of ACs.

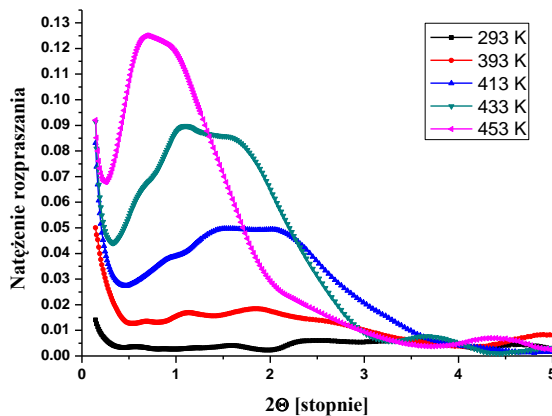


Fig. 9 The influence of the temperature on SAXS patterns of the ionomer sample containing 3,7 mol% of ALi.

Interesting results were achieved according to studies of aggregation of ionic groups on the temperature. For all ionomers containing ACs groups, the increase of the temperature causes the increase of the sizes of clusters at the expenses of diminution of the number and sizes of multiplets. This effect called “the clustering effect”, which is to connect to the multiplets in clusters

and/or increased size of existing clusters, takes place at temperatures higher than the glass temperature T_g of ionomers (see Fig. 8). The explanation of the clustering effect may be attributed to the increased mobility of the polymer at temperatures higher than T_g . In this case, the electrostatic interactions between ionic groups dominate and the increased chain mobility allows for the growing of ionic aggregates.

Particularly interesting effect was observed in the paper [H4] for the ionomer containing a 3,7 mol% of lithium acrylate (ALi). At room temperature for this ionomer, there is no scattering maximum on the SAXS patterns, but as the temperature is raised above 393 K there appears a broad interference maximum which indicates that clusters are formed, with the sizes of 5,0 nm. As the temperature is further raised, this maximum is moved to lower angles, and the sizes of these aggregates increase (see Fig. 9).

The clustering effect is strongly dependent on both the type of alkali metal cations and the copolymerization method. For ionomers synthesized in bulk, containing lithium and potassium cations, this effect does not occur. For the same ionomers synthesized in emulsion clustering effect occurs, even for low concentrations (3.7 mol%) of ionic groups.

[H5] *Poly(ethylene-oxide)/styrene ionomers blends: crystallization of poly(ethylene-oxide) component studied by wide-angle X-ray diffraction*

In the present paper the morphology of crystalline phase of blends of poly(ethylene-oxide) (PEO) and styrene-acrylic acid (S-AA) copolymers neutralized with sodium ions (Na^+) have been

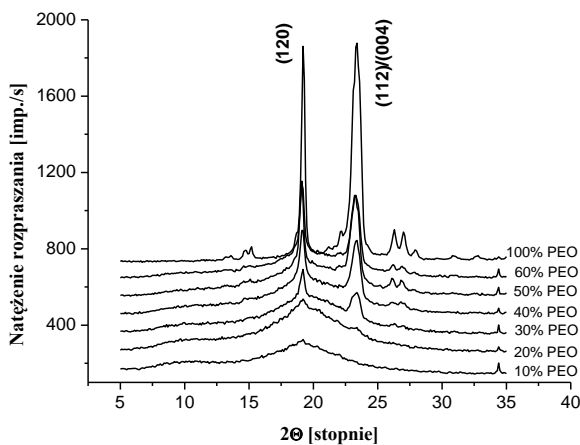


Fig. 10 WAXS curves for pure PEO and blends containing various content of the ionomer neutralized by 6,4 %mol ANa.

investigated. Details concerning the blends preparation are described in the paper. In this study, the effects of blend composition and the content of ionic groups in amorphous ionomers on the degree of crystallinity and the crystallite sizes of PEO have been investigated. These microstructural parameters have been obtained by means of wide-angle X-ray scattering (WAXS) method and compared with corresponding values for a neat PEO

A comparison of the WAXS curves of blends with that of pure PEO homopolymer is shown in Figure 10. Two major peaks with the highest intensities are observed at $2\theta = 19.1^\circ$ and 23.4° , assigned to the reflections from (120) and (112)/(004) crystallographic planes of the monoclinic unit cell, respectively. It is clear that the angular positions of these major peaks are almost identical. This suggests that the unit-cell dimensions of PEO are not significantly modified by blending with ionomers. The (120) plane is parallel to the molecular axis while (112)/(004) plane is more orthogonal to the molecular chain direction. In order to determine the degree of crystallinity WAXS curves were deconvoluted into crystalline and amorphous scattering components using the profile fitting program WaxsFit^{19,20}. Each peak was modeled using a Gaussian-Cauchy peak shape. The crystallinity index was calculated as a ratio of the area under crystalline peaks to the total area of the scattering curve. It was found that the degree of crystallinity of PEO in the blends decreases distinctly with increasing S-ANa(6.4) content. The crystallinity of PEO also decreases with increasing ANa content; the depression of the crystallinity index in this case is, however, much less pronounced. The degree of crystallinity measured by WAXS method for all samples corresponds quite well to the values of this parameter obtained from differential scanning calorimetry (DSC) measurements (see the paper [H6]). Moreover, DSC measurements revealed the decrease of the melting temperature, T_m , of PEO from $66,8^\circ\text{C}$ for a neat PEO to $59,8^\circ\text{C}$ for the blend containing 20% of PEO. Both the decrease in the degree of crystallinity and value of T_m is typical indicating partial miscibility of the components of the semicrystalline/amorphous polymers blend²¹. Revealed partial miscibility conditions indicate strong interaction between the components of the mixtures tested.

To evaluate the variations of crystallite sizes of PEO, the Scherrer equation has been used. The crystallite sizes have been calculated in the direction perpendicular to the (120) planes as well as perpendicular to the (112)/(004) planes. It was found that in both directions the crystallite sizes are almost independent of ionic groups content in the amorphous component of the blends but they decrease with increasing S-ANa(6.4) content. The decrease of crystallite sizes upon blending, in comparison to the values for pure PEO, confirms the strong interactions between the components of the investigated blends. PEO is a polymer which contains ether oxygens that are capable of forming hydrogen bonds and coordinating with alkali metal ions. Such interactions were observed in the mixtures of sodium poly(α -L-glutamate) (PGNa) and PEO²². It was found that the PEO crystallite blocks were anchored to the PGNa helical core via sodium ion – dipole

interactions. This could be the case of the investigated system. The interactions between the components of blends can significantly change the crystallization conditions of PEO, especially for the blends containing small amounts of PEO. It results in crystallization of PEO within hard-confined environment. Hence, the smallest crystallite sizes for these samples have been observed for the blend containing 10% of PEO.

[H6] *Small- angle X-ray scattering study of poly(ethylene-oxide) and styrene based ionomers blends*

Partial miscibility of poly(ethylene oxide) (PEO) with styrene based ionomers raises the question of the location of the amorphous diluent (i.e. ionomer) in the PEO matrix. In a miscible crystalline/amorphous blend crystallization is accompanied with the segregation of amorphous diluent. Depending on the distance of segregation, various types of morphology are created. The diluent molecules can reside in interlamellar, interfibrillar or interspherulitic regions¹⁷. Moreover, a blend system does not have to display only one type of morphology. Different types of microstructures may coexist, leading to multiple locations for the amorphous diluent, which in turn lead to different material properties. To resolve the matter in the case of the tested blends in the paper [H6] SAXS method was used. The SAXS curves of the investigated blends exhibit a distinct maximum, which is connected with the lamellar structure of PEO. The value of the angular position at which the intensity maximum is located increases with increasing ionomer content, implying that the long period, L , is reduced upon blending. Moreover, it has been observed that the lamellar layer thickness l_C substantially decrease while the amorphous layer thickness l_A increases slightly with increasing the ionomer content (see Fig. 11). However, the composition variations of parameters in Figure 11 cannot identify directly the presence of the interlamellar segregation, because the observed increase in l_A , characteristic for the interlamellar separation, is accompanied by a decrease in the long period. In case of this type of separation, the values of the long period should also increase with the ionomer content in the blend.

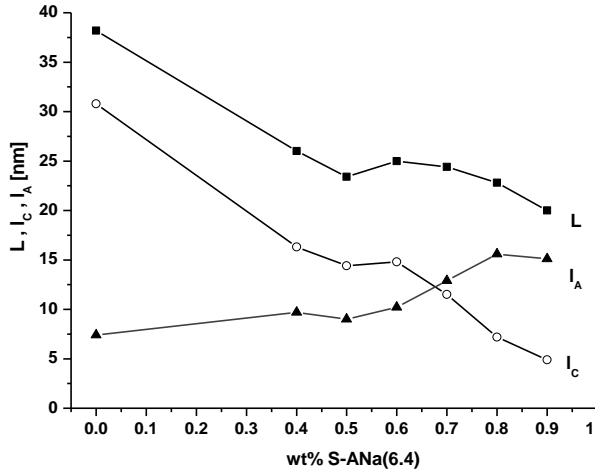


Fig. 11 Variations of long period (L), crystal thickness (l_C), and amorphous layer thickness (l_A) with the content of the ionomer having 6,4 mol% of ANa.

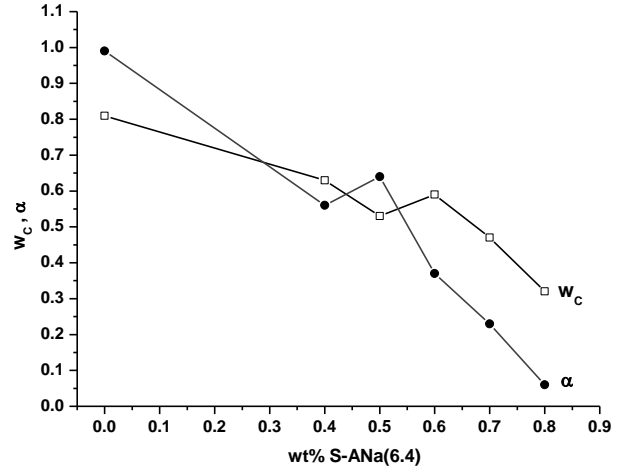


Fig. 12 Variations of the linear crystallinity (w_C) and the volume fraction of lamellar stacks (α) with the content of the ionomer having 6,4 mol% of ANa.

Analysis of the linear crystallinity coefficient, w_C , and the coefficient α describing the volume fraction of the lamellar stacks allowed only deal with the issue localization of the ionomer in the blend. The linear crystallinity, w_C , defined by Eq. (6), is related to the volume crystallinity, x_C by $x_C = \alpha w_C$. If the whole volume is filled with lamellar stacks, $\alpha = 1$ and $w_C = x_C$; if the sample is not homogeneously filled with the lamellar stacks, $\alpha < 1$ and $w_C > x_C$. For the sample of a neat PEO, $\alpha \approx 1$ (see Fig. 12) and in the case of the interlamellar segregation its value should not be changed, depending on the composition of the blends. However, research has shown that the value of this coefficient decreases rapidly with increasing ionomer content in the blend (see Fig. 12). This means that this component of the blend is not included in the areas between the crystalline lamellae, and locates out the stacks of lamellae. Thus, the use of the SAXS method revealed that in the investigated blends of poly (ethylene oxide) with styrene ionomers, the interfibrillar separation of amorphous component exists. In the paper [H6] has also been shown that the extent of the interfibrillar segregation of the ionomer component is rather independent on ionic groups content.

[H7] *Crystallization and melting behavior of poly(ethylene oxide) and its blend with styrene based ionomer using time-resolved SAXS/WAXS experiments*

The use of synchrotron radiation of high intensity enabled us to study a real-time of microstructure development and crystallization of neat PEO and its 50/50 blend with ionomer containing 6.4 mol% of sodium acrylate (S-ANa(6.4)). Simultaneous SAXS and WAXS measurements were carried out in HASYLAB – DESY synchrotron facility. During the experiments the specimens were first heated to 150 °C to erase their thermal history. After 20 min, there were cooled to 0 °C and subsequently heated after 10 min to 150 °C at a rate of 10 °C/min. Diffraction patterns were recorded every 6 s, corresponding to a resolution of one pattern per 1 °C.

Analysis of the WAXS curves has been shown that the crystal sizes perpendicular to the (120) and (112)/(004) planes of PEO in the blend are almost independent of temperature and are smaller when compared to those of pure PEO sample. The smaller values of crystallite sizes upon blending, in comparison to the values for pure PEO, confirms the results obtained in the aforementioned paper [H5]. SAXS data have been analyzed by means of correlation functions, which allowed for determination the values of the long period (LP) and the crystalline and amorphous layer thicknesses (l_C and l_A respectively). It has been found that the long period LP is independent of temperature and amorphous layer thickness l_A substantially decreases with increasing temperature, both for pure PEO and for PEO in the blend. In contrast, the lamellar crystal thickness l_C increases with temperature. Interpretation of changes in the thickness of crystalline lamellae has been based on the kinetic theory of crystallization¹. According to the theory, the crystal thickness of polymers is determined kinetically, and gives the observed dependence of lamellar thickness l_C on supercooling $\Delta T = T_m^0 - T$ (T_m^0 is the equilibrium melting temperature, T is the crystallization temperature) by the following equation (l_C shows a single linear dependence on inverse supercooling, $1/\Delta T$): $l_C = A/\Delta T + \delta l$, where $A = (2\sigma_e T_m^0)/\Delta h_f$ and δl are constants. Here, σ_e is the fold surface free energy per unit area of polymer crystals and Δh_f the heat of fusion per unit volume of the crystal phase. Figure 13 shows lamellar crystal thickness l_C as a function of the inverse supercooling, $1/\Delta T$, (T_m^0 is 342.2 K for PEO, as given by van Krevelen²³). The $1/\Delta T$ dependence of l_C demonstrates a single linearity over the whole temperature range investigated, which is in accordance with the nucleation theory. The growth mechanisms described by the nucleation theory seems to be working in the crystallization process of pure PEO.

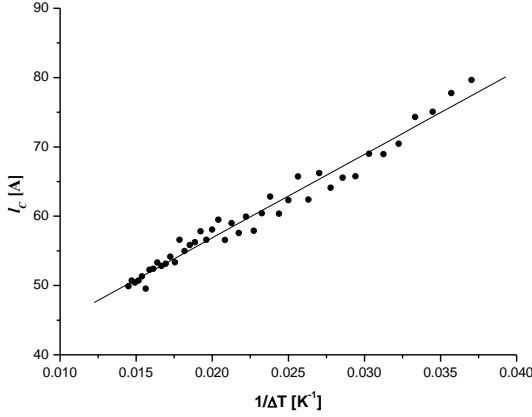


Fig. 13 Lamellar crystal thickness l_C as a function of the inverse supercooling $1/\Delta T$ for neat PEO.

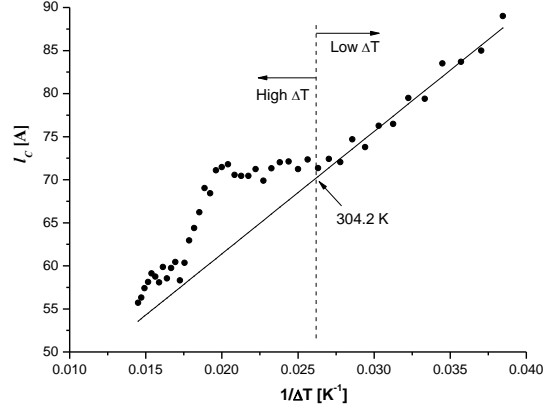


Fig. 14 Lamellar crystal thickness l_C as a function of the inverse supercooling $1/\Delta T$ for the blend PEO/ionomer, containing 6,4 %mol of ANa

The extrapolation to $1/\Delta T$ dependence to zero by the straight line in Fig. 13 gives the values of δl to be $32.2 \pm 0.8 \text{ \AA}$. The slope gives the value of A to be $(1.20 \pm 0.03) \times 10^3 \text{ \AA}$; σ_e is estimated as $(4.22 \pm 0.12) \times 10^{-2} \text{ Jm}^{-2}$, using the values $\Delta h_f = 2.4 \times 10^8 \text{ J/m}^3$ and T_m^0 given by van Krevelen²³. The obtained value of σ_e is in very good agreement with the value $4.3 \times 10^{-2} \text{ Jm}^{-2}$ given for PEO by van Krevelen, what again confirms the conclusion that the crystallization process of neat PEO obeys the nucleation theory.

Figure 14 shows the lamellar crystal thickness l_C plotted against $1/\Delta T$. The dependence deviates from a single linearity. The linear relationship between l_C and $1/\Delta T$ can be observed only in the low ΔT range. It indicates that the crystallization process of PEO in the blend (i.e. in the presence of interactions with the amorphous component of the blend) follows the nucleation theory only in the narrow ΔT range. The extrapolation of the straight line in Fig. 14 gives the value of δl to be $33.3 \pm 2.5 \text{ \AA}$. The slope gives the value of A to be $(1.42 \pm 0.08) \times 10^3 \text{ \AA}$; σ_e is estimated as $(4.98 \pm 0.28) \times 10^{-2} \text{ Jm}^{-2}$ and is about 16 % greater in comparison to the value for pure PEO sample. According to relations mentioned above, it is clear that the lamellar crystal thickness l_C is not only dependent on degree of supercooling ΔT but is also dependent on the values of the surface free energy of chain folding σ_e . The l_C is proportional to the surface free energy of chain folding. As a result the l_C depends on the competition between σ_e and ΔT . The surface free energy of chain folding is proportional to the concentration of a nucleating agent²⁴. The nuclei can be formed homogeneously by means of statistical fluctuations in the molten phase, or heterogene-

ously when it is induced by the presence of heterogeneities. The small aggregates of ionic groups (multiplets) which are present in the styrene ionomer, i.e. in the amorphous component of the investigated blend, may play a role of such heterogeneities. Multiplets produce the physical cross links and cause that amorphous component of the blend forms a network in which the second component (PEO) crystallizes. The interaction between the PEO chains and the ionomer network causes an abnormality in the inverse supercooling dependence of l_C , observed in Fig. 14. From these observations one can conclude that the crystallization process of PEO in the blend is much more complex in comparison with those of neat PEO. Because the crystallization of PEO causes the separation of blend components, deviation from linearity observed in the temperature range 10 - 30 ° C can be interpreted as a manifestation of this process. The research presented in the paper [H6] has shown, where the amorphous component of the blend is located after phase separation. Synchrotron research suggested, in turn, at what point the crystallization of PEO following separation of the components of the blend.

Supramolecular structure of dyed polypropylene fibers and blends of polypropylene with protonated polyaniline

[H8] *Influence of Heat-Stabilization on Supramolecular Structure of Colored PP Fibres.*

Fibers formed from isotactic polypropylene (PP) are commonly used and are currently the third textile material in the world as far as production volume is concerned. Starting from the first fiber produced to this day, their supramolecular structure has been the subject of many studies. As a result of these studies, a significant variation of the structure under the influence of changes in the conditions of fiber formation and further processing (thermal stabilization, stretching) were found. The significant differences in supramolecular structure of polypropylene fibers are the result of strong tendencies of polypropylene to create different polymorphs. Polypropylene macromolecules, forming a right- or left-handed helix, may be arranged in various ways relative to each other to form mesophase paracrystalline structure and three crystalline polymorphs: the monoclinic α -form, hexagonal β -form and triclinic γ -variant. Each of these structures is formed as a result of crystallization under certain conditions.

The polypropylene fibers, due to their water-repellent properties, can not be dyed using traditional bath methods. These fibers are dyed in mass, during the forming process, with the use of pigments. Pigments, mixed with the molten polypropylene are present in the volume of solidi-

forming fiber and affect the crystallization process, and thus the structure of the fiber at different levels of the hierarchical structure. No studies on the impact of pigments on the process of forming polypropylene fibers, in particular, the issue of their location in the fiber material, were carried out at the time of publication of the present paper. Also, there was no information on the effect of thermal stabilization on the supermolecular structure of such fibers.

In the present paper the investigations have been carried out for colorless PP fibers and fibers colored with following pigments: a phthalocyanine Blue pigment B, a quinacridone pigment EchtRot E3B and an azo pigment HF4B. The chemical formulas of used pigments are presented in the paper. Fibers were extruded from the melt with a temperature of 250 °C to the air temperature of 20 °C by means of a Brabender extruder. The pigments were mixed with a polymer granulate immediately before forming fibers in the amount of 0.5 % to the polymer mass. Fibers were spun with a take-up velocity of 1350 m/min. and submitted to the heat-treatment in a “not tensed” state for 3 min. in hot air with temperatures of 120, 130, 140, 150, and 160 °C.

The wide-angle X-ray scattering (WAXS) investigations revealed that for all colorless fibers and colored with Blue pigment B and an azo pigment HF4B, the structure of PP, created during the fiber formation, includes well-formed α -crystals. The degree of crystallinity for all not stabilized as well as stabilized fibers had the same value of 0.47 – 0.51. Similar values of crystallinity were received irrespective of pigment content. For stabilized fibers, the degree of crystallinity increased with the increase of stabilization temperature to 140 °C. For fibers stabilized in higher temperatures of 150 and 160 °C, the degree of crystallinity did not increase and was the same with the value for fibers stabilized in temperature 140 °C. Irrespective of added pigment, for all stabilized and colored fibers, values of the degree of crystallinity were about 10 % higher compared to colorless fibers. For fibers colored with a quinacridone pigment EchtRot E3B, peak (300) from the β -form of PP has been seen on the WAXS pattern, together with characteristic α -form peaks. Pigment EchtRot E3B is a very effective nucleating agent of the β -form. By proper selection of pigment concentration and crystallization parameters, the content of the β -form can be very high and the Turner-Jones²⁵ coefficient K-value may reach 0.6 – 0.8. A much lower content of the β -crystal (K = 0.06) observed for fibers colored with EchtRot E3B has been caused by the following two factors: high temperature of extruded polymer melt and orientation. The tested fibers were formed from the melt with high temperature of 250 °C, with a high take-up velocity of 1350 m/min. When the temperature of melted polymer increases, the content of the β -form

decreases. When the melt temperature exceeds 260 °C, then the β -crystal does not develop in spite of a great content of nucleator²⁷. In fiber-forming conditions, the solidifying polymer melt is submitted to strong orientation. Under the orientation polymer, crystallization occurs much faster on row nuclei. In these conditions, the nucleation influence of pigments is very limited.

SAXS curves for investigated fibers exhibited a distinct maximum, which was connected with the lamellar structure of PP. The use of the correlation function calculated from the SAXS curve enabled a more accurate characterization of the lamellar structure. Results obtained revealed that for colorless fibers, heat-stabilization caused small changes in the values of a long period and other structural parameters. The changes of these parameters for colored fibers were more distinct. For these fibers the highest value of the long period and lamellar crystal thicknesses were achieved after stabilization in the temperature of 120 °C.

[H9] *Structure and conducting properties of thermoplastic composites of polypropylene and polyaniline protonated in solid stat*

X-ray scattering at small angles is subject to the existence in the test sample of electron density inhomogeneities, which, in the case of polymers, are caused firstly by the existence of areas with a various degree of macromolecules ordering, i.e. crystalline and amorphous areas, and secondly by the presence of various substances which improve their mechanical, thermal, sorptive, etc. properties. The theory of small-angle X-ray scattering (SAXS) has been developed for the so-called two-phase systems consisting of two kinds of areas with different electron densities. For such systems, SAXS method allows, inter alia, to assess the shape of the radiation scattering particles, to determine their size, weight and surface area. In the case of polydisperse systems, it is possible to determine particle size distribution. For lamellar systems, typical for polymers, as discussed in the previous sections of this summary of professional accomplishments, the long period of such structure, the thickness of crystalline lamellae and amorphous layers, their volumes and the thickness of the transition layer between the crystalline and amorphous regions can be established. Ever new, often multiple-component, polymeric materials are being created, and therefore, in terms of electron density heterogeneity, they are no longer two phase systems and become multiphase. In SAXS examination of such systems many new effects can be observed, interpretation of which goes beyond the classical theory of two-phase systems.

An example of a multiphase system is a mixture of polypropylene (PP) and protonated polyaniline (PANI) studied in the discussed paper. Details of the mixture components, its composition and method of obtaining it is described in the paper. Blend without the addition of compatibilizer and with lauryl gallate (LG) as compatibilizer was investigated. PP and PANI are poorly miscible without the addition of compatibilizer. The SAXS curves of such blends interference

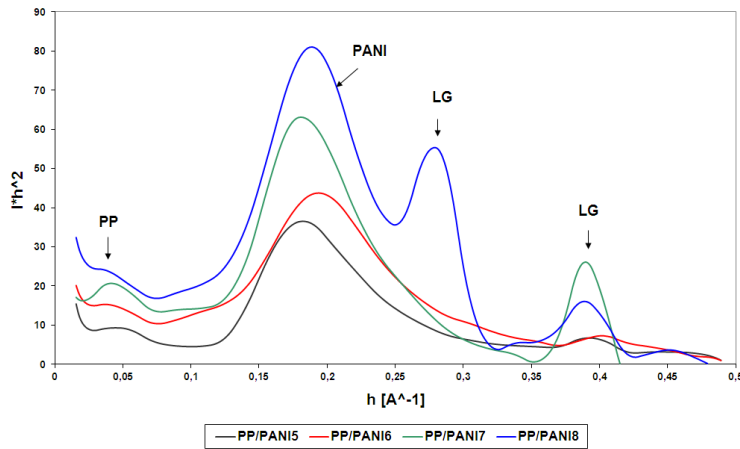


Fig. 15 SAXS curves for PP/PANI blends compatibilized by lauryl gallate (LG).

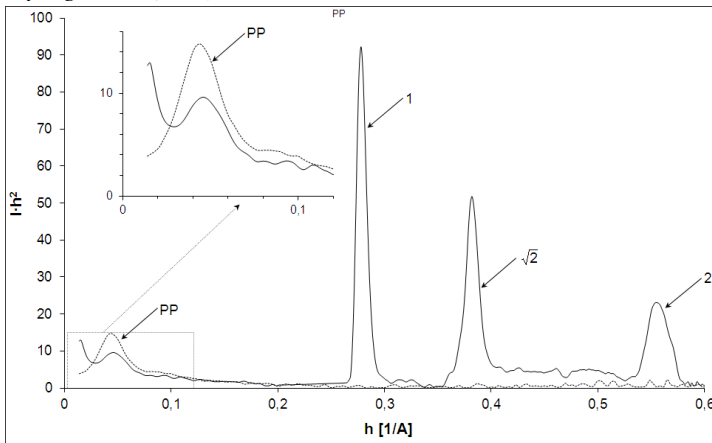


Fig. 16 SAXS curves for pure polypropylene (PP) and polypropylene with 20 %wt. of LG.

effects due solely to the lamellar structure of PP are observed. There is no scattering of PANI due to the large size of domains of the component, exceeding the resolution of the camera used for SAXS studies. The use of compatibilizer significantly improves the miscibility of the mixture components and reduces the size of PANI domains. An example of SAXS curve for a mixture of PP/PANI with the addition of LG compatibilizer is presented in Fig. 15. On the curve, in addition to the peak corresponding to the lamellar structure of PP, there are several other interference effects, the origin of which is associated with the other components of the studied system. To identify the cause of the observed peaks, we examined a

sample of PP containing 20 wt% of LG. On the SAXS curve of this sample (Fig. 16), in addition to PP scattering, a sequence of three peaks was observed. As for pure PP these peaks are not observed, their origin is attributed to the presence of LG. The ratio of angular positions of the peaks in Fig. 16 is $1 : \sqrt{2} : 2$, which indicates that the LG domains are arranged in a PP matrix, forming a simple cubic network. The angular positions of the first two peak series correspond to the posi-

tions of similar peaks shown in Fig. 15 for a PP/PANI blend, which means that also in this blend LG domains are more or less arranged in a cubic network. The remaining, broad peak in Fig. 15, representing the values of the scattering vector $h \approx 0.2$, is attributable to PANI domains scattering. Because of its far position in the SAXS curve, this peak should be attributed to the interference within the PANI domains. Assuming a spherical shape of these domains, the maximum position allows to estimate their size at approx. 3.2 nm.

The use of WAXS and SAXS methods in this paper was aimed at studying the correlation of parameters describing the supermolecular structure of the tested blends with their electrical conductivity. On the basis of WAXS studies, it was found that a mixture having the smallest PP crystallite sizes showed the largest coefficient of conductivity. Perhaps the presence of small-size crystallites promotes the formation of conduction paths by PANI.

Summary

In a series of publications entitled „*Crystallization in polymer systems – investigations by means of wide-angle (WAXS) and small-angle (SAXS) scattering methods*” the results of the studies on the crystallization process of linear polymers is presented. Crystallization of high-density polyethylene, poly(ethylene oxide) and polypropylene has been investigated by means of diffraction method of X-rays using synchrotron radiation. Topics of research is very timely and is one of the main issues in modern physics of polymers. Following results has been achieved in these publications:

- The time evolution of the lamellar thickness confirms the significance of the mobile hexagonal phase in polyethylene crystallization, which proceeds by the thickening-growth mechanism at crystallization temperature 122 °C. This is distinct from the lamellar-thickening mechanism observed for samples crystallized at lower temperatures (116 °C and 118 °C).
- Performance of the impact the crystallization temperature on the distribution of the thickness of crystalline lamellae during their formation has been evaluated.
- The method for the analysis of the correlation functions in order to obtain the real course of the changes in the linear crystallinity has been developed.
- The developed method has been used to investigations of a bimodal distribution of lamellar thicknesses in the blend of two polyethylenes with different ethylene sequence length.

- The formation of ionic aggregates as a function of the content of ionic groups and the nature of the alkali metal neutralized styrene-based ionomers has been determined. Especially, the clustering effect at elevated temperatures has been observed.
- The influence of the ionomer content on the degree of crystallinity and the sizes of PEO crystallites in PEO/styrene based ionomers has been estimated.
- The degree of separation of the components and the localization of ionomers in the blends of PEO and styrene based ionomers has been evaluated.
- On the basis of synchrotron radiation measurements in a real-time, specified temperature range in which the separation of the blend components succeed has been defined.
- The effect of the supermolecular structure of the multiphase PP/PANI/LG system on its electrical conductivity has been estimated.

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5. Overview of other scientific and research achievements

5. a Graduate traineeships in foreign research institutions

During my scientific activity I have stayed in number of research centers of world reputation in the field of polymer structures studies, which use in these studies X-ray diffraction methods:

Belgia	Uniwersytet Leuven, 1990, 1 week
Francja	Laboratorie Leon Brillouin, 1993, 1 week
Brazylia	National Synchrotron Light Laboratory, 1996, 1 week
Austria	Montanuniversität Leoben, 2000, 1 week
Belgia	Uniwersytet Leuven, 2001, 2 months
Belgia	Uniwersytet Leuven, 2003, 1 week

5. b Awards resulting from academic research

1999 – Bronze Cross of Merit, Polish President

2001 – Individual Award of the Rector of University of Bielsko-Biala

2005 – Individual Award of the Rector of University of Bielsko-Biala

2007 – Individual Award of the Rector of University of Bielsko-Biala

2008 – Individual Award of the Rector of University of Bielsko-Biala

2009 – Individual Award of the Rector of University of Bielsko-Biala

5. c Activity as a reviewer

I reviewed scientific articles for the following scientific journals (from the List of Philadelphia):

Polymer – 1 manuscript

Langmuir – 1 manuscript

Radiation Physics and Chemistry – 1 manuscript

Plasma Chemistry and Plasma Processing – 1 manuscript

Fibres and Textiles In Eastern Europe – 3 manuscripts

Moreover, I reviewed 1 scientific project for *The Czech Science Foundation*.

5. d Participation in research projects

After obtaining the doctoral degree I took (or take) part in the implementation of 3 international and 13 national research projects

International research projects:

1) Flemish-Polish bilateral international scientific project BIL 99/23, sponsored by the Ministry of The Flemish Community, „*Morphology-properties relations in homogeneous copolymers of ethene and 1-alkenes. Modulating polymer properties by chain microstructure and thermally induced superstructures*” – date of realization: 01. 01. 2000 - 31.12.2002

2) Project BIOCELSOL „*Biotechnological process for manufacturing cellulosic products with added value*”, sponsored by European Union, 6th Framework Programmes for Research – date of realization: 01. 04. 2004 – 31. 03. 2007

3) Project MEMSTENT „*Absorbable polymeric surgical systems with shape memory*”, No. POIG.01.03.01-00-123/08-03, sponsored by European Union, Innovative Economy Programme – date of realization: 01. 04. 2009 – 30. 09. 2013

National research projects:

1) Grant No. 3 T09B 071 11, Polish Committee for Scientific Research, „ *Properties of electrically conductive fibers formed from derivatives of polyaniline*” – the contractor – date of realization: 01.08.1996 – 31.12.1998

2) Grant No. 3 T09B 082 11, Polish Committee for Scientific Research, „ *Structure and properties of mixtures of liquid crystal oligomers with PE and PP*” – the contractor – date of realization : 01.09.1996 – 28.02.1999

3) Grant No. 3 T09B10212, Polish Committee for Scientific Research, „ *Effect of thermal stabilization for supermolecular structure and selected properties of polypropylene fibers*” – the contractor , date of realization: 01. 01. 1997 – 30. 06. 1998

4) Grant No. 7 T08E 035 13, Polish Committee for Scientific Research, „ *Identification of fibers thermally metamorphosed*” – the main contractor 1 – date of realization: 01.07.1997 – 31.12.1999

5) Grant No. 7 T08E 034 14, Polish Committee for Scientific Research, „ *The study on biomineralization mechanism taking into account the effect of colloidal silica and heavy metals on wool fiber under varying conditions of pH*” – the contractor , date of realization: 01. 03. 1998 – 31. 01. 2001

6) Grant No. 7 T08E 04716, Polish Committee for Scientific Research, „ *Physical dimensions narrowing and generalized in the study of the structure and morphology of the polymer in the solid state*”, the main contractor 2, date of realization: 01. 03. 1999 – 28. 02. 2002,

- 7) Grant No. 7 T08E 009 17, Polish Committee for Scientific Research, „*Investigations of supermolecular structure of bacterial cellulose*” – the contractor, date of realization: 01. 08. 1999 – 31. 03. 2002
- 8) Grant No. 7 T08E 069 18, Polish Committee for Scientific Research, „*The structure of polypropylene fibers formed with the addition of nucleating agents*” – the main contractor 2, date of realization: 01. 01. 2000 - 30.06.2002
- 9) Grant No. 7 T08E 070 18, Polish Committee for Scientific Research, „*Research on supermolecular structure and mechanical properties of the polisiloksanouretane films*” – the main contractor 2, date of realization: 01. 01. 2000 - 31.12. 2002
- 10) Grant No. 7 T08E 048 21, Polish Committee for Scientific Research, „*The binding of modern colors (based on the non-toxic derivatives of benzidine) with natural fibers*” – the main contractor 3, date of realization: 01. 09. 2001 – 31. 12. 2002
- 11) Grant No. 7 T08E 027 20, Polish Committee for Scientific Research, „*Morphology and properties of the homogeneous copolymers of ethylene and 1-alkenes*” – the main contractor 2, date of realization: 01. 04. 2001 - 30. 09. 2003
- 12) Grant No. 4 T08E 082 25, Polish Committee for Scientific Research, „*Alginate fibers for medical purposes*”- the contractor, date of realization: 01. 11. 2003 – 30. 09. 2006
- 13) Projekt badawczy zamawiany Polish Committee for Scientific Research, „*Nanostructure of nanocomposites fiber obtained from molecular complexes*” – the contractor, date of realization: 10. 12. 2003 – 30. 09. 2006

5. e Publications

Total number of scientific articles: **74 (59 after doctorate)**,

Number of articles from Journal Citation Reports database: **41 (36 after doctorate)**.

The chapter in the monograph entitled “*Ionomers. Structure, Properties and Applications*”, Nicolaus Copernicus University Press, 2010

Number of citations: **195**

Number of citations without self-citations: **167**

This includes two articles having 16 citations and one articles with 12 citation.

Hirsch index: **h = 7**

Total impact factor: **31,291**

State according to ISI Web of Science database on the 24th July, 2013

List of publications after obtaining the doctoral degree is contained in Annex No. 6.

5. f Participation in scientific conferences

Organization of conferences:

For 25 years, the Institute of Textile Engineering and Polymer Materials regularly organizes conferences under the name *International Conference on X-Ray Investigations of Polymer Structure XIPS*. In these conferences take part dozens of scientists from many countries of the world. I was a member of the organizing committee of five such conferences, which take place in the 1998, 2001, 2004, 2007 and 2010 years. Now, I am a member of the organizing committee of the next such conference, which will be held in Zakopane, Poland, 9 – 12 December 2013.

Papers presented orally:

- *Small-angle X-ray scattering (SAXS) investigations of the ionic groups aggregation in styrene-based ionomers.* XLI Scientific Meeting of the Polish Chemical Society, Wrocław, September 14-18, 1998
- *Supramolecular structure of bacterial cellulose.* Annual Meeting of the Material Sciences Committee of the Polish Academy of Sciences, Bielsko-Biala, 2001
- *Time-resolved SAXS study of crystallization and melting behaviour of high density polyethylene.* XLIV Crystallographic Conversatorium, Wrocław, June 27-28, 2002
- *Time-resolved SAXS studies of structure development in polyethylene during isothermal crystallization.* Workshop on Polymer Crystallization, Leuven, Belgium, March 13-14, 2003

In addition, I have participated in 25 international and 12 national conferences after obtaining the doctoral degree. List of papers presented is included in Annex No. 6.

6. The research work

6.a Period prior to obtaining the degree of doctor

Immediately after obtaining a master's degree at the Faculty of Mathematics, Physics and Chemistry at the University of Silesia in Katowice in 1981 (MA thesis entitled: "*Application of Mori formalism to study the angular velocity correlation function of molecules in liquids,*" written under the supervision of doc. dr hab. Edward Kluk, PhD), I was employed at the Institute of Textiles, a Branch of the Technical University of Łódź in Bielsko-Biala in the X-ray laboratory

of the Institute. In the same organizational unit, transformed later into the Institute of Textile Engineering and Polymer Materials of the University of Bielsko-Biala, led by prof. zw. dr hab. inż. Andrzej Włochowicz (PhD, Eng), followed by prof. ATH dr hab. Jarosław Janicki (PhD, Prof. of the University of Bielsko-Biala), I have been working throughout my professional career, promoted to the position of physicist, X-ray laboratory manager, senior assistant and adjunct. Within the organizational structure of the Institute, I work for the Department of Physics and Structural Investigations led by prof. ATH dr hab. inż. Stanisław Rabiej (PhD, Eng, Prof. of the University of Bielsko-Biala). From September 1981 to September 1982, I served in military, which was obligatory for university graduates.

After completing the military service and returning to work at the Institute, I was involved in research, conducted in the X-ray diffractometry laboratory, mainly related to the issues of evaluation of polymers and fibers structure at the level of the primitive cell and supermolecular structure. During this period, under the supervision of prof. Włochowicz, together with Jarosław Janicki and Stanisław Rabiej (currently professors of the University of Bielsko-Biala), later also with dr. Ryszard Kwiatkowski, we began to apply the small-angle X-ray scattering (SAXS) method to the study of polymers. The first measurements using this technique were made with the Rigaku slit collimation camera. Courtesy of Prof. Vonk from the Catholic University of Leuven (Belgium), we received a computer program for analysis of the SAXS curves, which allowed to carry out research at a level on a par with other research centers in the world.

The first study using SAXS method in which I was involved, investigated the porosity of the carbon fibers and the effect of dyes on supermolecular structure of polypropylene and polyamide fibers dyed in mass. The findings have been published in *Acta Polymerica and Die Angewandte Chemie Makromolekulare*.

SAXS method is particularly useful in the study the morphology of the copolymers in which the individual blocks, due to their incompatibility, are separated and aggregated into sphere-, cylinder- or lamella-shaped domains. Depending on the structure of copolymer macromolecule, its composition, temperature and many other factors, the domains are spatially organized to form macro-network the type of which (cubic, hexagonal, lamellar, Gyroid) can be studied using SAXS method. In my scientific work, I conducted research on multiblock styrene-bisphenol-A-carbonate copolymers and star styrene-butadiene epoxy block copolymers, . For the first type of copolymers, it was found that the content of 0.34 and 0.47 parts by weight of bi-

sphenol A carbonate formed macro-network domains of cubic type centering on the walls. For the content of 0.767 parts by weight of the carbonate, its domains form a lamellar network. Also, the distances between the domains were established. In the SAXS studies of star copolymer it was found that prior to epoxidation of butadiene blocks the separation of the blocks led to the lamellar structure. As the degree of epoxidation of butadiene in copolymer increased, the structure was disappearing, becoming more homogeneous, the separation of the copolymer components disappeared. The obtained results were published in *Die Angewandte Makromolekulare Chemie* and *Colloid and Polymer Science*.

I also conducted my first research on the process of polymers crystallization. I examined the process of polyethylene (PE) crystallization in a mixture of poly(methyl methacrylate) (PMMA) in the conditions in which the PE chain macromolecules formed an interpenetrating network with PMMA chains. The research results were published in *Journal de Physique IV*. Furthermore, I studied the impact of crystallization temperature on polymorphism and supramolecular structure of polyamide 6.10.

In 1987, I met for the first time with ionomers, i.e. polymers whose properties depend on ionic interactions occurring in certain micro-regions of the polymers (in ionic aggregates: multiplets and clusters). Understanding the relationship between chemical structure, morphology and physical properties of ionomers contributes to the growing popularity and entirely new applications of this interesting and highly promising group of polymers. For these reasons, ionomer morphology studies have become one of my main research interests. The first studies in this field focused on copolymers of styrene with zinc acrylate, obtained by dr Adam Gronowski (PhD), working at that time at the Department of Chemistry, Nicolaus Copernicus University in Toruń. Using both WAXS and SAXS methods, as well as infrared spectroscopy, I examined the state of aggregation of the ionic groups, I established the sizes of multiplets and the dependence of the sizes of the ionic component content. The research results were published in the prestigious *Polymer* journal. Later, I conducted a study on the impact of temperature on the state of aggregation in these ionomers and ionomers containing nickel and cobalt acrylates. The results served as a basis of my doctoral thesis entitled "*Studies of supermolecular styrene - acrylate ionomers Co (II), Ni (II), Zn (II) using X-ray methods,*" written under the supervision of prof. Andrzej Włochowicz (PhD, Prof.). I obtained supervisor's research grant for completion of the disserta-

tion. The dissertation was defended at the Faculty of Mathematics and Physics of Silesian University of Technology in Gliwice on 15 January 1997.

Before obtaining a doctoral degree, I also studied another interesting ionomer type which was a copolymer of ethylene terephthalate and sulfo-terephthalic acid, neutralized with potassium cations (K^+). Unlike the researched styrene ionomers, this type of ionomer comprises a polymeric matrix which can crystallize. Therefore, I conducted an extensive study the impact of the ionic component content and temperature on the crystallization and melting process of poly(ethylene terephthalate). The results were published in the *Journal of Macromolecular Science - Physics*. This work was positively reviewed by one of the leading authorities in the field of polymers crystallization Prof. Phillip H. Geil of University of Illinois, author of "*Polymer Single Crystals*" monograph.

The team in the works of which I participated, led by prof. Andrzej Włochowicz (PhD, Prof.), in 1993 received the 1st Level Award of the Minister of Education for its achievements in the use of X-ray methods in the study of polymers and fibers.

In 1994, I contributed significantly to the preparation of an application to the SEZAM (SESAME) program of the Foundation for Polish Science, which passed the competition procedure and received funding. The program financed the purchase of a state-of-the-art MBraun SWAX diffractometer (Austria), equipped with a modified Kratky camera recording X-rays using linear position-sensitive counters.

Before obtaining a doctoral degree, I participated in over twenty international and national scientific conferences. The most valuable for the further development of my research was the participation in "*International Conference on Small-Angle Scattering, SAS,*" which dealt with the applications of small-angle scattering of: light (SALS), X-ray (SAXS) and neutrons (SANS). Before the dissertation, I took part in three of these conferences: SAS'90 in Leuven (Belgium), SAS'93 in Saclay (France) and SAS'96 Campinas (Brazil).

6.b Period after obtaining the degree of doctor

After the dissertation, I continued to develop my interest in ionomers, and specifically I began studying the mixtures of poly(ethylene oxide) with styrene ionomers neutralized with cations of lithium, cesium, potassium and sodium. I convinced dr Kazimiera Suchocka-Gall (PhD) from the Department of Chemistry of Nicolaus Copernicus University in Toruń to cooperate in

the synthesis and preparation of ionomer blends of different composition. I continued the work steadily for many years, and the results have become an important part of my postdoctoral thesis and are discussed in section 4b of this summary of professional accomplishments.

Preparation of polymer blends, studying their properties, including the supermolecular structure, is an important issue in the works of the Institute where I work, so I have dealt with it in my research activities for many years. This issues are still valid, present in the field of interest of many research centers in the world, however, difficult due to the fact that the polymer blends are multi-phase systems, for which the results of X-ray diffraction techniques, if necessary to know the structure of the blends, are often difficult to interpret. In my work I investigated the structure of supramolecular mixtures of polypropylene and polyamide 6, i.e. two semi-crystalline polymers. I have studied the mixtures of polypropylene and maleate esters, and a mixture of polypropylene and the protonated polyaniline, very interesting from the point of view of morphology and potential applications. The research results of the latter mixture were included in my postdoctoral thesis and discussed in section 4b of this summary of professional accomplishments. The studies of mixtures of polypropylene (PP) and low density polyethylene (LDPE) with ethylene-propylene-diene (EPDM) rubber, conducted in collaboration with professors Ludomir Ślusarski and Dariusz Beliński of the Technical University of Łódź resulted in interesting findings. The difference in the crystallization of LDPE and PP in the rubber matrix, caused mainly by the phenomenon of co-crystallization of EPDM propylene mers into PP crystallites was observed. For LDPE/EPDM mixtures, the co-crystallization phenomenon has not occurred.

In the years 2000 - 2002, I took part in the Polish-Flemish research project *"Morphology-properties relations in homogeneous copolymers of ethene and 1-alkenes. Modulating polymer properties by chain microstructure and thermally induced superstructures"*. In the frameworks of the project, I participated in a two-months scientific internship program at the Laboratory of Macromolecular and Structural Chemistry, Catholic University of Leuven (Belgium), headed by Prof. Harry Reynaers. I was then assigned to study the crystallization and melting processes of high density polyethylene (HDPE) and its mixtures with homogeneous ethylene - 1-octene. Synchrotron X-ray studies were carried out in HASYLAB-DESY research facility in Hamburg. I consider the participation in these surveys and the results I have achieved to be one of the most important in my academic career, therefore I included them in the presented postdoctoral thesis and discussed in section 4b of this summary of professional accomplishments.

An interesting subject, undertaken in collaboration with dr Maria Dębowska (PhD) from the Institute of Experimental Physics, University of Wrocław, was the issue of correlation of test results obtained for polymers using positron annihilation lifetime spectroscopy (PALS) and SAXS method. The basis of the comparison of these methods is that both allow to identify areas of different electron densities. Positron thermalized in matter may annihilate from the free state or state associated with the electron - positronium. Positronium can exist in two states of spin: para-(p-Ps), wherein the positron and electron spins are antiparallel and ortho-(o-Ps) with parallel spins. The lifetime of the positron in the p-Ps is 125 ps, it annihilates with its electron, regardless of its environment. o-Ps lives much longer, so its presence is evident by the appearance of components larger than 0.5 ns in the positron lifetime spectra. Generally, this time is lower than 142 ns because of the positron annihilation into o-Ps by "*pick-off*" reaction, that is, electron annihilation with a foreign electron in the environment. Positronium is not formed in materials with high electron density such as metals or semiconductors. However, it may be formed in porous materials such as polymers and in amorphous areas, where so-called free volume occurs, due to packing of the polymer macromolecules that is lower than in crystalline regions. Positron lifetime spectrum thus comprises three main components: one coming from positron annihilation in the free state, one coming from the annihilation of p-Ps and one derived from positron annihilation in the "*pick-off*" process of o-Ps in free volume. Analysis of the latter component (often denoted as τ_3) is used in polymer studies using PALS technique. Comparison of this method and the SAXS method was conducted for a number of samples of polypropylene (PP) and polyamide 6 (PA6), specially prepared to account for different morphologies. For PP, for which the degree of crystallinity varied in the range of 0.41 - 0.53, and the thickness of the crystalline lamellae in the range of 4.2 - 12.3 nm, a decrease in the value of τ_3 component and its intensity value I_3 was observed with increasing of crystallinity and thickness of lamellae, which should be associated with the decrease of the amorphous areas in which o-Ps is formed. In the studies of PA6, impact of polymorphism of the crystallographic forms of the polymer on the PALS spectrum was further observed. For a sample with a high content of γ crystal form, τ_3 component value and its intensity was much higher than in a sample containing a small proportion of this variety. These observations should be associated with lower density of γ variation as compared to α PA6. In PA6 studies, the correlation between changes in the value of the τ_3 component and thickness of the bound-

ary between amorphous and crystalline regions of the polymer, established using SAXS method, was observed.

As I mentioned at the beginning of discussing my research career, I have worked in the research unit derived from the Institute of Textiles and therefore throughout the whole period of my work I was involved in research of fibers, both artificial and natural, using WAXS and SAXS methods. This summary paper is not meant to present in detail this range of my work. Allow me only to note that after the dissertation I conducted, among others. studies of a new generation of supermolecular structure of polypropylene fibers produced from mixtures of amorphous polyester and elastomers, as well as the impact of dyes and flame retardants on the structure. I initiated many of these studies, for example, studies of the impact of layered aluminosilicates (montmorillonite) on crystallization of polymer matrix in the nanocomposite polypropylene and polyamide fibers.

Among my research of natural fibers, I think the results of wool fiber studies using SAXS method are the most significant. The fiber material is keratin, fiber-forming protein, which adopts three types of conformation: helical, rectal and globular. In the wool fiber volume there are ordered areas - microfibrils, consisting of polypeptide chains of helical and rectal conformation and disordered areas - a matrix made up of chains of a globular conformation. SAXS diffractogram of keratin contains equatorial reflections corresponding to distances of 8.2 nm, 3.9 nm, 2.7 nm and meridional reflections of 6.6 nm, 4.2 nm and 2.8 nm. Equatorial reflections describe the distribution of microfibrils in the matrix and the organization of protofibrils in microfibrils, and the meridional reflections represent periodic changes in the electron density along the axis of the fiber. Registration of small-angle reflections of keratin is very difficult due to the small difference in electron density between microfibrils and the matrix, hence the SAXS method is rarely used in such studies. Thanks to the careful sample preparation and skillful use of the research functions on the equipment used, all reflections described above were recorded. This allowed investigating the impact of orthosilicic acid on the yellowing of wool fibers and changes in their structure under the influence of azo dyes. The results of these studies were presented at the most important wool industry event, 10th International Wool Textile Research Conference, November 26 - December 1, 2000 in Aachen and published in the *Textile Research Journal*.

In the years 2004 - 2007, I participated in the BIOCELSOL project: "*Biotechnological Process for manufacturing cellulosic products with added value,*" realized under the FP6 of the

