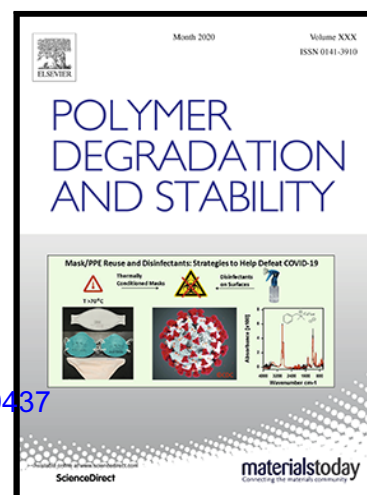# Journal Pre-proof

The effect of long-term natural aging on the iPB-1 structure and the II – I phase transformation rate

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Highlights

Natural long-term aging of iPB-1 decreased crystallinity.

Main effect of natural aging was the polymer side chain splitting off.

Spontaneous phase transformation II-I was still unfinished after 17 years.

Reduced geometric regularity of the molecule slowed II-I phase transformation.

Side chains separation led to formation of groups retarding the phase transition.

The effect of long-term natural aging on the iPB-1 structure and the II – I phase transformation rate

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ABSTRACT

The long-term natural aging of isotactic polybutene-1 samples of different molecular weight has shown that the transformation rate from the initial phase II to the stable phase I significantly decreased after natural aging, ranging from 0 to 17 years. It was found that the total crystallinity decreased with aging time and a small amount of phase II remained untransformed for at least 17 years. The transformation rate of a lower molecular weight sample, DP 0400, was higher than the PB 0110 sample, even after repeated polymer melting of aged samples and their new melt crystallization. The major phenomenon of the iPB-1 aging is the change in a ratio of methyl/methylene functional groups; possibly because of a side chain splitting that reduces the geometric regularity of the molecular chain and consecutively slows down the proceeding phase transformation.

Keywords: Isotactic polybutene - 1, phase transformation types, long-term natural aging.

INTRODUCTION

Isotactic polybutene-1 exhibits excellent physical, mechanical and chemical properties dependent on its most important polymorphic crystal forms. Isotactic polybutene-1 (iPB 1) with repeating basic unit - CH_2-$CH(C_2H_5)$- is not applied only in the pure form, but also in copolymers, blends or composites with other polymers (often polyethylene, polypropylene, ethylene propylene rubbers, and thermoplastic elastomers) in pressure piping systems [1], flexible packing [2-4], hot melt adhesives, compounding and other applications. iPB-1 can be highly filled (> 70%), so it can be used in halogen-free retardant composites or as a master batch carrier for some specific pigments [5]. Compared to other polymers, iPB-1 exhibits good mechanical properties and it is resistant to many chemicals [detergents, oils, fats, acids, bases, alcohol, ketones, aliphatic hydrocarbons and hot polar solutions, including water [6] and high temperatures. These remarkable properties are adversely affected by the slow transformation of the initial phase II to the stable phase I, which, while improving the properties it is also connected with shrinking by 4% due to the different density values of the two phases.

Isotactic polybutene-1 is one of the polymorphous polyolefines that can exist in various crystal phases [7]. A direct preparation of its most stable form I from the melt or solution is too complicated for practical applications. An unstable phase II rapidly appears after melting and cooling down and slowly (during days) transforms to the stable phase I. Another unstable phase III forms after solvent evaporation or precipitation, followed by consecutive transformation into phase I under certain conditions. Phase I structure is characterized by a twined hexagonal helix with 2*3/1 helical structure of crystal lattice parameters a = b = 1.77 nm and c = 0.65 nm, density 0.951 g/cm^3 and a melting temperature ranging from 128 to 130°C, respectively. Phase II has a tetragonal crystal lattice with crystal lattice parameters a = b = 1.542 nm and c = 2.105 nm, and helical structure 2*11/3. Its density is 0.907 g/cm^3 and its melting temperature range from 117 to 120°C [8].

In our previous studies [9-10], three existing types of II → I phase transformation processes have been described depending on the methods of formation of the transformation nuclei: P (plus – faster than standard

phase transformation), N (neutral – standard type) and M (Minus – type, characterizedby the induction period which was slowing down the transformation rate) [9]. The phase transition rate, similarly as any nucleation processes, can be affected by various factors, such as environments [10], additives [11] and physical factors (for example, deformation, temperature, and radiation, etc [12-13].

In general, the phase transformation process was well described by the Avrami equation [14]. In polymers, the phase transition usually does not occur in the whole sample; a relatively high portion (about 20 to 50%) of the untransformed (amorphous) phase can slowly proceed in the transformation. Depending on the measurement conditions, the process is described as a secondary crystallization, annealing or aging. Secondary isothermal crystallization of polymers [15] is, in principal, a continuation of the primary crystallization. It is characterized by a slow linear logarithmic density and increasing crystallinity with time. The slow crystallinity increase also indicates a further crystallization of amorphous molecular segments and/or further crystal perfection together with the rejection of non-adjustable molecular segments, short molecules and chain ends, crystal defects and non-crystallisable materials (for example, diluents, monomer residues, and heterogeneities). The crystallization is governed by a diffusion and re-orientation of the molecular sections such as chain loops, folds or entanglements. At temperatures higher than the initial crystallization temperature, the conditions of nucleation and growth may change and the process is called annealing. In cases where the structural changes with time are measured at temperatures lower than the initial crystallization temperatures, the process is called aging. To influence the process of the polymer secondary crystallization or aging means influencing the sample nucleation, particularly the growth process.

Important factors affecting the aging process of polymers are aging time, applied irradiation (solar or fluorescent light sources), presence of oxygen, ozone (O_3), applied heat, humidity, rain, and dirt in the air, etc. The resistance of polymers to chain degradation is determined both by the chemical structure of the polymer chains and the sample´s morphology. Here, the regular structures of higher density - crystalline regions, exhibit a higher resistance to diffusion of penetrating substances and irradiation. According to Allara [16], degradation of polymers by thermally induced rupture of random chain links can be regarded as unimportant at ambient temperatures. In the presence of light, degradations are sometimes accelerated if an absorbing

chromophore group (carbonyl groups, hydroperoxides, and conjugated C=C bonds) are present. Thermal and photo-oxidative degradation are the most common types of auto oxidative mechanisms, whereas the reaction is initiated by trace amount of the free radicals or atoms, which can abstract a hydrogen atom from a C-H group to produce a radical site which can react with O_2. The eventual result of auto oxidation is the formation of oxygenated functional groups in the polymer backbone (carbonyl, alcohols, ethers and hydro peroxides groups), chain scission, occasional cross linking (ether or peroxides) and emission of small molecules such as CO, CO_2, H_2O, H_2O_2 and small organic molecules. The presence of metal particles or salts often accelerates the oxidation [16]. The iPB-1 is less resistant to oxidative degradation because of a number of labile tertiary hydrogen atoms in its structure.

It is difficult to distinguish the impact of individual factors in natural aging tests, so artificial aging tests have been introduced, where the selected factors are considerably strengthened. Only few research groups have studied the aging of isotactic polybutene -1, all of which have chosen the artificial aging procedures. Kramer et al. [17] confirmed the decrease of the polymer molecular weight caused by thermo oxidative degradation. Karsson et al. [1] confirmed the results of Kramer et al. [17] and moreover noted different failure mechanisms referred to as phases I, II and III. Thermal oxidation of the amorphous phase was accompanied by the onset of phase III and led to significant increase in crystallinity and melting temperatures [1].

Singh et al. [18] mentioned that absorption of UV energy by some carbonyl groups resulted in the formation of the vinyl group. The degradation is accelerated by the reaction of singlet oxygen with vinyl groups and even saturated carbon atoms in the polymer chain to form hydroperoxides [19]. The decomposition of hydroperoxides, on exposure to light, caused the formation of macro radicals, which by disproportionation leads to degradation of the polymer chain [18]. Beníček et al. [20] confirmed that degradation caused by the UV irradiation, which significantly influenced the mobility and regularity of the macromolecules retarded the phase transformation. The existence of both alkyl and allyl radicals has been postulated [21]. According to the work of Rubin and Hubert [22], the nature of the free radicals in γ irradiated iPB-1 samples and their rate of disappearance is a function of polymer structure. They assumed the existence of radicals immobilized in the crystalline region, because radicals trapped in the amorphous phase of a polymer usually have short lifetimes

above T_g. The initial concentration of radicals was much lower in the samples of phase II than of I, probably as the result of differences in the crystalline structure between the polymorphs [22]. Bigg et al. [23] analysed the aging of iPB-1 pipes used to convey potable water and they confirmed the rapid oxidation along the interior surface of the pipes during which the carbonyl groups were formed and a significant reduction in the molecular weight [23]. Shao et al. [24] described that after hot air aging the tensile strength, elongation at break and melt flow index of iPB-1 decreased significantly, and they have suggested an aging mechanism of iPB-1. The γ -hydrogen abstraction by a backbiting peroxy radical was believed to be the key step in the eventual production of the functional groups and was labelled as the start of the termination process. This research group confirmed the positive effect of chosen antioxidants [24]. The catalyst residues accelerated the thermo-oxidative aging process [25] and metallic impurities, such as metal salts, which can act as accelerators of hydrocarbon oxidation and lower the value of the activation energy for hydroperoxide decomposition [26]. The positive effects of the photo- stabilizers were studied by Singh [27-28] and Saymal [27], similar as Chandra [29-31].

This article studies the long-term natural aging of isotactic polybutene -1 samples with respect to their crystal phase structure and mainly to the phase II → I transformation rate, because after the phase transition the density and other related commercially important material properties are improved. These factors were not studied earlier.

MATERIALS AND METHODS

Samples

The four studied highly isotactic poly(butene)-1 (iPB-1) samples were the commercial products of coordinated solution polymerization using Ziegler-Natta catalysts of LyondellBasell Industries N.V., (Netherlands) company, including the homopolymers PB 0110, PB 0300, DP 0400 and a random low butene/ethylene copolymer PB 8640. The samples PB 0110 and PB 0300 had a higher molecular weight than the sample DP

0400 (Table 1). The sample PB 0110 contained a nucleating agent of unknown composition, which was added by the producer [13]. The details of the polymerization and exact polymer were not provided.

Aging

The time of polymer sample aging was calculated from the moment of our first melting of commercially purchased polymer granules. Based on previous results [32], a standard melting procedure consisting of 5 min heating at 160°C was chosen. After first melting and cooling, samples were aged in the darkness to avoid the effect of light or UV radiation. Sample aging was performed at room temperature, ambient atmospheric pressure and air humidity in the air atmosphere (Table 3). After aging, the second melting procedure of the particular sample at standard conditions was performed (Table 4) and finally after one month of holding the same sample at room temperature in darkness, a third melting was performed (Table 5).

X-ray diffraction

Wide-angle X-ray diffraction patterns were measured using an X-pert Pro X-ray diffraction system, PANalytical, B.V. (Netherlands). The CuK_α radiation was Ni-filtered. The scans (4.5° 2θ/min) in the reflexion mode were measured in the range of 2θ, 5-30° at room temperature. The total crystallinity of the sample, X_t, was calculated from the ratio of the crystal diffraction peaks and the amorphous background areas. The fraction of phase I (X_I) was determined by comparing the crystal peak areas of first peaks belonging to form I and II, respectively [10] as illustrated in Figure 1 showing the structure of the sample PB 0110 aged 0 – 10 years.

The scans were generally taken every 24 h after the melting the sample. The values X_t and X_I given in Tables 1 to 5 were measured 30 days after melting of the particular sample. The X_{II} in previously mentioned

tables was determined immediately after sample melting. On the other hand, the values X_{t-A}, X_{I-A}, X_{II-A} stated in Table 3 were determined after long term natural aging of sample characterised the crystal structure at the same moment. The half-time of II → I phase transformation, marked as r, represents the time when the X_I during transformation equalled the percentage of the untransformed phase II (X_{II}) (Figure 2).

DSC analysis

Aged samples (Table 2) were subjected to thermal treatment as follows: samples were first heated to 160°C at the rate 10°C/min and the melting point of the phase I was obtained (T_{mI}); this was followed by subsequent cooling to 60°C at the rate 10°C/min with the obtained crystallization temperature of the phase II (T_c), and then melting for the second time while heating to 160°C at the rate 10°C/min to measure the melting temperature of the phase II (T_{mII}). For measurements using Pyris 7 (Perkin Elmer, USA) device at N_2 atmosphere, aluminium pans were filled with 10 mg of sample.

Dielectric relaxation spectroscopy (DRS)

Dielectric measurements were performed as frequency sweeps (0.1 Hz–1 kHz) at ambient temperature with an amplitude of measuring voltage equal to 1V using impedance analyser (Novocontrol Concept 50, Germany) on samples shaped as 1 mm-thick discs with 10 mm diameter.

FTIR analysis

FTIR analysis of the original aged and later thrice melted samples, PB 0110 and DP 0400 was performed on a FTIR-8201PC spectrometer (Shimadzu, Japan) connected to a AIM-8000R Infrared Microscope (Shimadzu) and Thermo Nicolet Nexus 670 FT-IR ATR (Diamond Plate) (USA). Infrared transmission spectra were recorded at ambient temperature with spectral resolution of 2.0 cm^{-1}. Each spectrum was normalized on sample film thickness. For IR analysis, typical polyethylene –CH$_2$– bending deformation bands at 1473 and 1463 cm^{-1} [32,33] and polybutene-1 –CH$_3$ wagging spectral bands at 1380.5 and 1364.6 cm^{-1} [28], were used. The intensity ratio of spectral bands at 2965 cm^{-1} (methyl groups) to 2928 cm^{-1} (methylene groups) wavelengths was used as a measure of the polymer short chain branching, representing the ratio of methyl/methylene functional groups. Additionally, the crystallinity ration was calculated according to Equation (1), where the spectral band intensity ratio at 841 to 1157 cm^{-1} was used, respectively. Polymer chain 11/3 to 3/1 helix transition was characterized by absorption bands intensity ratio at 998 cm^{-1} (short helix) to 1157 cm^{-1} (C-C stretching and CH$_3$- wagging modes which remains constant with changing crystallinity). Equation 1 is given as:

$$X_C = \frac{\left(\frac{A_{841}}{A_{1157}} - 0{,}09\right)}{0{,}38}$$ [33] (1)

RESULTS AND DISCUSSION

The effect of aging on the polymer structure

According to Biggs et al. [23], the tertiary hydrogen of the iPB-1 backbone chain is susceptible to oxidation as it is loosely bound to its associated main carbon atom. The presence of the (-CH$_2$-CH$_3$) group opposite to this hydrogen atom weakens the bond between the single exposed hydrogen and the carbon atom. Oxidation is manifested by the formation of the carbonyl groups, C=O, at the tertiary hydrogen site. The oxidation reaction

also entails breaking of the backbone chain, thus reducing the chain length. The C=O end group can be detected by infrared spectroscopy (bands at 1710 – 1730 cm^{-1}) [23]. The principle of the FTIR method is the absorption of infrared radiation transiting the sample, during which changes occur in the rotational vibrational energy states of the molecule depending on changes in the dipole moment of the molecules. This phenomenon can be used to detect molecules and their parts. Unfortunately, many IR instruments cannot focus on the top 5 -10 nm where the oxidation begins [23]. Our FTIR results confirmed only a negligible degradation in case of the samples PB 0110 (15, 14 and 6 years old) and DP 0400 (15, 14 and 6 years old) given by the presence of insignificant bands representing C=O groups.

DSC analysis used to study the temperature changes occurring during the heating / cooling proved the decrease of the melting points of phase I (T_{mI}), phase II (T_{mII}) and temperature of crystallization of phase II (T_c) with aging time, which may be connected with the shortening of the main polymer chain or splitting off of the side polymer branches (Table 2).

The differences between the aging of individual commercial homopolymers were considerable, as PB 0110 with the longest polymer chain can be characterized by a linear decrease in all measured temperatures with aging time, with T_{mI} and T_{mII} varying by 3 and 4°C, respectively, over 16 years, while crystallization temperature dropped by 7°C. The PB 0300 sample measured in this study also showed a linear decrease in the range of 0 - 8 years. A different behaviour was observed in the sample DP 0400 with the shortest polymer chain of the analysed samples, which in years 0 - 15 had a decrease in all temperatures, basically minimal, but only after 17 years where the values decreased by 4°C (T_{mI}), 3°C (T_{mII}) and in the case of T_c even by 11°C, with all measurements being repeated at least thrice. The copolymer DP 8640 changed only minimally in the range of 0 - 8 years, probably due to the presence of ethylene groups in the polymer chains. DSC scans of aged samples also showed broader peaks, indicating a decrease in crystallinity and changes in crystal shape. The decreases in melting and crystallization temperatures and the decrease in total crystallinity can be explained by changes in the segmental conformation of the polymer chains, by shortening of the macromolecules or by splitting off of the side branches.

The changes of form and sizes of crystallites, indicating detrimental effect of the segmental chain mobility on crystallinity increase accompanied with the proceeding chain degradation was confirmed by FTIR analyses. The FTIR analysis proved the linear decrease of samples' crystallinity, as well as increasing aging time as shown in Figure 3 (marks without filling). The crystallinity diminution was faster in the case of the PB 0110 sample compared to the DP 0400 sample.

From the FTIR analysis, it was found that the short chain branching decreased with increasing aging time; however, in the case of the sample PB 0110 with higher formal kinetic rate of 0.03 (1/years) the calculated formal first order kinetics half time transformation rate was about 14.6 years compared to 0.004 (1/years) for DP 0400 sample (Figure 4 – marks without filling). Short chain branching is associated with a decrease in the order of the macromolecular chain (increase in chain irregularity).

The dielectric constant of polymers is relatively a complex parameter, often represented by the relation $\varepsilon^*(\omega)$ = $\varepsilon'(\omega) - j\varepsilon''(\omega)$, with $\varepsilon''(\omega)$ as the imaginary part associated with the energy dissipation and $\varepsilon'(\omega)$ as the real part indicating the energy storage and polarization ability. At low frequencies (ω), the dielectric behaviour arises from both: 1) interfacial and space charge and 2) dipolar polarizations, where its dispersion is influenced by various factors such as method of synthesis, structural variation, chemical homogeneity, and dopants substitution, etc [34].

Figure 5a shows the variation of dielectric constant of sample PB 0110 as a function of frequency (from 10^{-1} to 10^6 Hz), measured at room temperature. All samples manifested a general linear trend. The ε' value of the non-aged sample (PB 0110, 0 years) was around ~2.5. The significant decrease of this parameter can be seen in sample PB 0110 aged 12 years (ε' ~2.1), indicatating the polymer chain shortening with increasing sample age and decrease of dipoles mobility.

In the beginning of the frequency range (Figure 5b), a decrease in $\varepsilon''(\omega)$ values can be observed, which indicates the decrease in the mobility of the main chains (an alpha relaxation). At a frequency of about 10^4 Hz, a beta relaxation was determined which could be related to the segmental motion of polymer side chains. The significant decrease of the $\varepsilon''(\omega)$ value of the sample, (PB 0110, aged 12 years) with more than one order magnitude confirmed the degradation of side chains.

The alternating current (AC) conductivity (Figure 5c) of sample PB 0110 is dependent on the frequency, and in case of the non - aged sample (PB 0110, 0 years) it was found to be about 10^{-14} S/cm. At a frequency of 100 Hz, the slope of the curve changed, which can be explained by the β-relaxation process. Significantly lower AC conductivity (10^{-16} S/cm) was found for aged samples PB 0110 with aging time of 12 years. This was due to the low mobility and the degradation of the macromolecular chain segments, and it was accompanied by the decrease of the samples crystallinity as confirmed by the FTIR analysis.

WAXS is the analysis of Bragg peaks scattered to wide angles, which are caused by sub-nanometre-sized structures [35], and this method is used to determine the phase structure, crystallinity and orientation. By WAXS analysis, the crystal structure of the samples (X_{t-A}, X_{I-A}, X_{II-A}) after aging was determined and presented in Table 3. In the case of the original material, the is the samples melted once, the total crystallinity (X_{t-A}) was higher than that of the samples melted twice or thrice (Tables 3-5), which was attributed to the longer secondary crystallisation time, that is, the conditions of the experimental settings. However, when comparing the total crystallinity of the once-melted and aged samples using WAXS, a decrease in the ordering of the system and thus the diminution or disruption of the crystallites with the increasing aging time was found (Table 3). For example, in case of the sample PB 0110, the linear decrease in total crystallinity (X_{t-A}) was 9.8% over 16 years and in the case of DP 0400 it was 12%. Samples PB 0300 and PB 8640 showed smaller absolute values of decrease in crystallinity (3.7 and 3.2%, respectively), which was due to the shorter aging time of the used samples (0 - 6 and 0 - 8 years, respectively). Phase I fraction (X_{I-A}) values showed the same decreasing trend as total crystallinity. Interestingly, even a small amount of iPB-1 unstable phase II was still present in the samples with longer aged periods of 16 or 17 years, both in samples PB 0110 (0,43%) and DP 0400 (0,28%) (Table 3). The observed data indicated that the phase transformation II → I was not yet finished even after such long period of aging (Figure 1). There no detectable amount of phase II in the copolymer sample, PB 8640 after 8 years of aging due to the resolution of the used WAXS analyser.

The natural long-term aging of iPB-1 samples resulted in a decrease in system order and only negligible oxidation documented by the insignificant presence of C = O groups. The decrease in crystallinity can be explained by changes in the polymer chain conformation and structure, further by a decrease in the

polymerization degree or by the splitting off of the side branches. Additional methods of measurement would be needed to understand in details the exact degradation mechanism.

An interesting factor is the faster degradation of the sample PB 0110 than DP 0400 sample (Figures 3 and 4), explained by a faster decrease in the crystallinity and the stereo regularity of the polymer chain. According to the results of the combustion test, sample DP 0400 was present in more inorganic residues, i.e., more metallic residues, which can accelerate chain degradation [26]. Thus, the stronger influence may be the length of the macromolecule, which is significantly longer in PB 0110, and thus the polymer chain is more likely to degrade with aging time. This suggestion contradicts the results of others, who, however, applied an artificial type of aging [20].

During the natural long-term aging of iPB -1, the chain crosslinking did not occur or was negligible, because the aged samples melted for the second and third time after analysing the effects of aging, which allowed the study of the effect of the natural aging on the II → I phase transition.

The effect of the aging on the phase transformation

In our previous analysis [32], we found a slightly accelerating effect of 101x re-melting of the same sample on the II → I phase transformation rate compared to the once-melted, non-aged samples of homopolymers PB 0110, PB 0300, and DP 0400 (2, 7, and 8 h acceleration, respectively). In the study of the effect of natural aging on the phase transformation, the following different results were obtained for samples melted two and three times, which clearly points to the effect of aging time.

Figure 2 shows a typical phase transformation coursed after 2nd melting of original and aged samples up to 17 years as characterized by the observed time dependences of X_t, X_I and X_{II}. The graphs represent the change of initial crystal phase II (X_{II}) of iPB-1 into the phase I (X_I) with time. In 14 years aged PB 0110 sample (Figure 2c), the transformation course was characterized by the initial induction period (IP = 50 h), where the phase II → I transformation was minimal, but sometimes it was completely absent. After the induction period,

the phase transformation continued faster and then changed into a slow secondary crystallization. This type of phase transformation was described as M type [9]. In all cases, the transformation after 300 h practically stopped and a small amount of the initially present phase II (1–15%) remained untransformed. Homopolymers in all studied examples proceeded according to the M type phase transformation (Table 4); the sample of the copolymer iPB-1 with ethylene changed the type of transformation from N to M, including the induction period of 3 - 10 h with aging time.

The course of phase transformation proved to be significantly slowed, as evidenced by the half-time of phase transformation (r) which significantly increased with aging time. In the case of sample PB 0110, the increase in half-time value is the most significant by 134 h for a 16-year-old sample. A comparatively old sample (17 years old) of DP 0400 with the shortest chain of the studied homopolymers, on the other hand, had an increase of only 9 h. The lower transformation rate was connected with the fact that the transformation rate was slowed down by observed induction period typical for M type. The reason for this decrease in transformation rate and presence of IP may be due to a decreased chain segmental mobility, either by addition of some foreign molecular groups or segments or by formation of new intermolecular bonds. Additionally, a significant difference may be related to the fact that the nucleating agent is added to the PB 0110 by the manufacturer to accelerate the phase transformation, which could degrade over time. Samples that aged for a shorter time (PB 0300 and PB 8640) showed similar increases of 21 and 20 h with aging for 6 and 8 years, respectively. Along with the increase in the phase transformation time was the associated growth of the induction period, with the exception of the PB 0300 sample, where a shortening of 8 h occurred for samples of 3 and 6 years old. The explanation of phenomenon of slowing phase transformation with natural aging time may be associated with reduced chain segmental mobility.

The aging time following the melting and crystallization influenced the degree of crystallinity determined 30 days after the second melting (Table 4). The longest-chain PB 0110 homopolymer showed a 12% decrease in a 16-year-old sample and DP 0400 showed 14% in a 17-year-old sample. Samples PB 0300 and copolymer PB 8640 that aged for a shorter time (6 and 8 years, respectively) also had a lower crystallinity of 7 and 6%, respectively. Phase I fraction values determined after 30 days and after 2nd melting also decreased, and it is

interesting to note that the largest proportion of X_I in the DP 0400 sample (by 11% in the 17-year sample) decreased, while a comparatively old longer chain sample (PB 0110) had a 2% decrease. Shorter aging samples PB 0300 and PB 8640 showed a smaller decrease (1%). The phase II fraction determined immediately after the second melting of the sample also showed a decrease in all monitored samples. Decreases in crystallinity and proportions of individual phases can be caused by both oxidation and increase in the irregularity of macromolecular chains. The long chain creates bends, which are regions that are more sensitive to possible chemical changes.

Another third melting of the same sample (Table 5) further influenced the segmental order. Here, the X_t and X_I determined 30 days after the third melting procedure also decreased with aging for all studied samples, while the half-time of the phase transition increased with sample age. However, it is interesting to compare the changes in phase transformation half-time values after the second and third melting. The sample, PB 0110 aged 16 years, showed a significant shortening of the phase transition, since the values of r = 194 h which it had after a further (3rd) melting and crystallization were approximately 13% lower (r = 168 h) than the same sample after the second melting. The third melting hence changed the conformation formed after the second melting by decreasing the transformation rate and increasing the transition rate again. Here, we met an interesting situation, where, after a long time aging in the polymer structure another new segmental conformation was formed, which decreased the phase transformation rate. This structure (not described) could be eliminated by a new melting, recrystallization and phase transformation. In the case of DP 0400, r values differed only slightly after the second and third melting, as was the case with the shorter aging time of PB 0300 and PB 8640 samples.

Remarkably, after the third melting, in all samples aged 0-2 years, the induction period disappeared and the type of phase transition changed from M to N. In PB 8640, this phenomenon was even observed at all aging times (0 - 8 years). The third melting removed defects that blocked the formation of nuclei. Finally, we can conclude that the structural changes characterizing the aging process of iPB-1 are connected mainly with chain segmental conformational changes.

The 3rd melting showed the influence of the change in ratio of methyl/methylene functional groups; in the case of sample PB 0110 it was present and in sample DP 0400 it was negligible (Figure 4). The 2nd melting showed both influence of the change in ratio of methyl/methylene functional groups and the unknown retarding compound on the induction period and the phase transition type, which is blocked or removed by repeated 3rd melting of the same sample. The sample PB 0110 is prone to change in ratio of methyl/methylene functional groups, but the sample DP 0400 is not. It is possible that this is due to a longer macromolecular chain or a higher amount or probably organic composition of polymerization catalysts also accelerating the aging process. Another explanation may be an organic-based phase transformation ingredient added to the sample PB 0110, or a combination of all these effects. Given by the observation that the amount of methyl functional groups is not growing, it can be assumed that if the methyl functional groups are the end groups of polymer chain, then there is no shortening of macromolecules. By the used experimental methods it was not possible to determine where and how exactly the new methylene functional group originate. The splitting off of the side chains, which could form volatile short atomic groups that are released after the melting, is probable. It can be assumed that by splitting off of the side chain, the geometric regularity of macromolecule (configuration) is violated, which leads to the deterioration of transformation nuclei, therefore leading to the slower phase transition. This effect was also observed in case of blends of isotactic polybutene-1 with atactic, geometrically irregular polypropylene [10]. The details of this supposed segmental conformation which decreases the transformation rate and the extent of transformation, is yet to be described.

Conclusion

The natural long-term aging of iPB-1 was characterized primarily by a decrease in crystallinity and even after 17 years by the presence of a detectable amount of unstable phase II. The FTIR analysis confirmed that the main effect of the iPB-1 aging was the change in ratio of methyl/methylene functional groups, which means the possible splitting off of the side chain. The reduced geometric regularity of the molecular chain resulted in

the slowing down of the spontaneous phase transformation. The presumed separation of the side chains also led to the formation of groups, further retarding the phase transformation, which can be removed by repeated melting of the sample.

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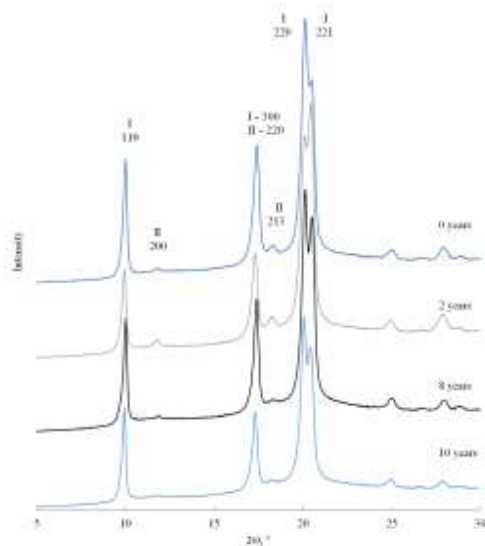
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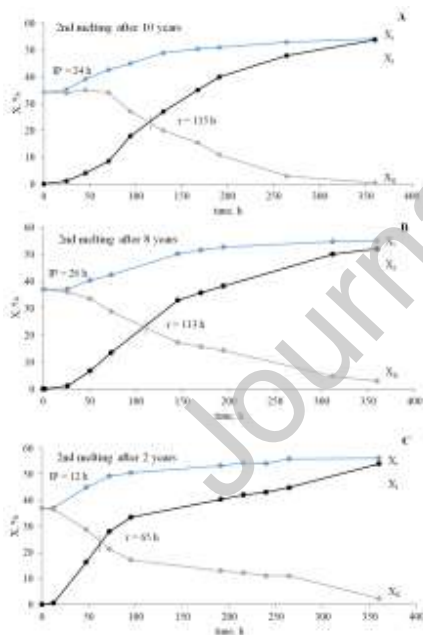
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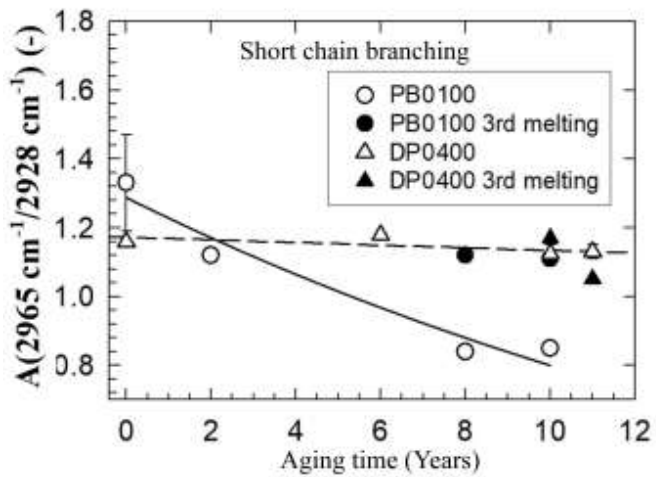
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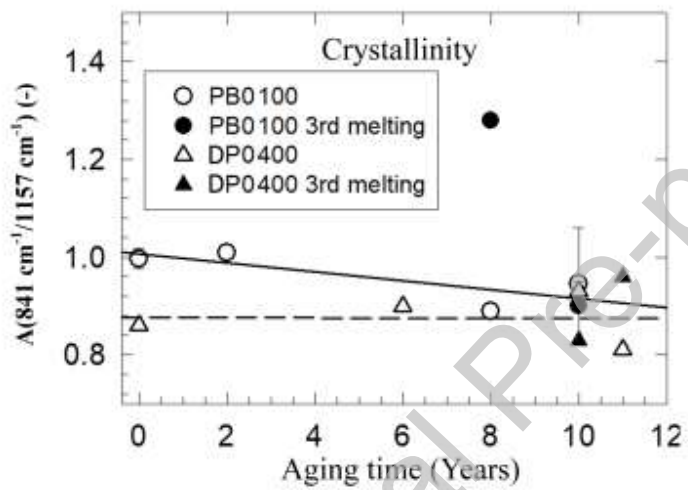
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a)
- PB 0110, 0 years
- PB 0110, 0.08 years
- PB 0110, 12 years

b)
- PB 0110, 0 years
- PB 0110, 0.08 years
- PB 0110, 12 years

c)
- PB 0110, 0 years
- PB 0110, 0.08 years
- PB 0110, 12 years
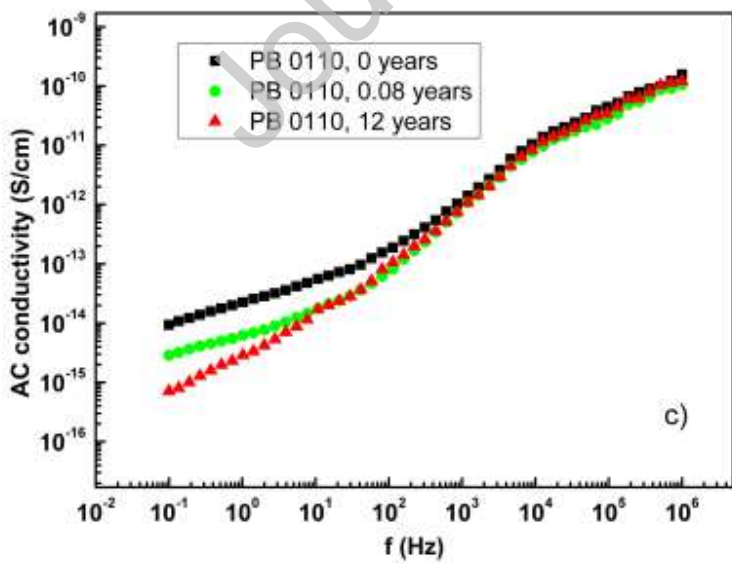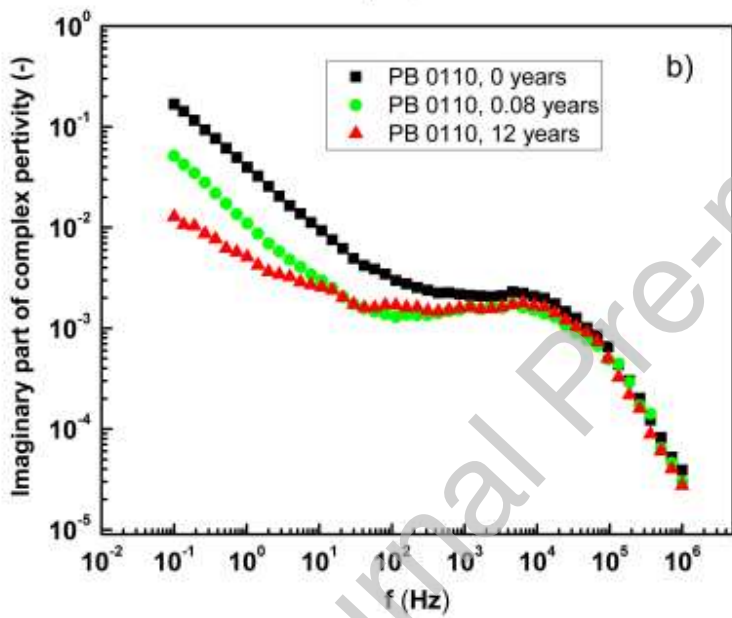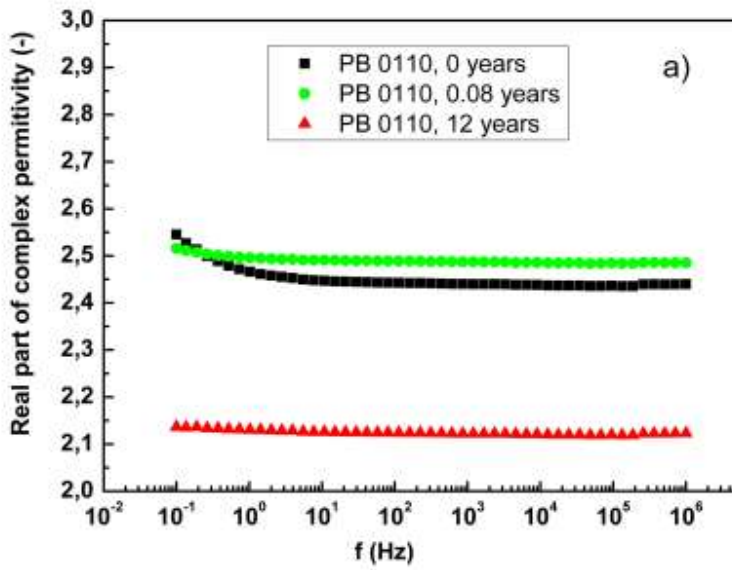
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Table 1. The available characteristics of used iPB-1 samples.

Sample labeling	Density (g/cm^3)	T_{mI} of phase 1 (°C)	MFI (g/10 min) (190°C/2.16 kg)	Molecular weight (10^{3}g/mol)	Composition	Ethylene content (m%)	Fraction of isotactic pentads (%)	R (melting 5 min at 160°C	Transformation type	IP (h)	Amorphous phase (%)	Inorganic residue (%)
PB 0110	0.914	128	0.4	711	PB-1 Homopolymer		83.1	60	M	19	58	0.00
PB 0300	0.915	127	4	347	PB-1 Homopolymer		81.7	59	M	20	54	0.00
PB 0400	0.915	126	15	293	PB-1 Homopolymer		79.5	50	M	20	54	0.02
PB 8640	0.906	113	1	470	Random low P(B/E) copolymer	0.75	87.6	20	N	x	71	

MFI test method ISO 1133-1; The test method ISO 11357-3; Density test method ISO 1183-1. Inorganic residues measured after burning at 450°C for 1 h.

Table 2. DSC results of the naturally aged samples.

Sample	Aged/years	T_{mI} (°C)	T_c (°C)	T_{mII} (°C)
	Granules [36]	**128**	**x**	**117**
PB 0110	0	128.1	73.36	116.81
	2	127.64	74.73	116.94
	3	127.32	68.53	116.77
	6	127.85	73	116.36
	14	124.92	66.76	114.05
	16	125.37	67.02	113.4
	Granules [36]	127	x	116
PB 0300	0	127.08	74.97	116.89
	3	124.33	74.74	115.93
	6	125.97	73.49	116.16
	8	124.09	71.57	116.28
	Granules [36]	126	x	114
DP 0400	0	126.61	76.47	114.79
	3	126	75.97	114.31
	6	126.75	76.06	114.56
	8	126.18	75.52	114.48
	15	125.07	65.79	113.78
	17	122.88	75.52	111.17
	Granules [36]	113	x	97
DP 8640	0	113.8	66.69	97.67
	3	112.27	67.2	97.88
	6	112.78	67.92	97.66
	8	112.03	67.4	97.7

x- Values not given by the producer.

Table 3: The results of X-ray analysis of naturally aged samples.

Sample	Aged, years	1st melting + aged		
		X_{t-A}	X_{I-A}	X_{II-A}
PB 0110	0	63	57.96	5.04
	2	62	57.66	4.34
	3	59.3	56.57	2.73
	6	61.7	59.97	1.73
	8	58	56.26	1.74
	10	55	53.35	1.65
	14	53.2	51.5	1.7
	16	54.1	53.67	0.43
DP 0400	0	67	62.98	4.02
	2	65	61.75	3.25
	3	61.9	61.65	0.25
	6	61	60.63	0.37
	8	62.9	62.52	0.38
	10	55	54.45	0.55
	11	56	55.44	0.56
	15	61.1	60.67	0.43
	17	57	56.72	0.28
PB 0300	0	62	58.28	3.72
	3	58.3	55.79	2.51
	6	60.2	57.73	2.47
PB 8640	0	55	53.35	1.65
	3	51.8	49.78	2.02
	6	54.4	53.53	0.87
	8	51.9	51.9	0

Table 4. The results of X-ray analysis of naturally aged samples - 2nd melting.

Sample	Aged, years	2nd melting + aged					Type
		X_t	X_I	X_{II}	r, h	IP, h	
PB 0110	0	62	51	40.84	60	19	M
	2	56	53.95	36.85	65	12	
	3	56.58	51.27	36.14	84	20	
	6	55.95	54.58	42.19	86	23	
	8	55	52.07	36.95	113	26	
	10	54.22	53.79	34.28	115	24	
	14	51.71	50.79	32.97	182	50	
	16	50.11	48.57	32.99	194	53	
DP 0400	0	67	62	44.38	50	20	M
	2	63.6	62.63	42.19	53	26	
	3	64.16	62.23	44.68	53	22	
	6	60.83	60.16	43.89	48	25	
	8	60.56	58.7	38.74	52	28	
	10	60	58.3	39.64	55	26	
	11	58.6	55.73	39.16	50	26	
	15	58.94	57.85	42.55	60	30	
	17	53.03	51.43	39.06	59	30	
PB 0300	0	62.8	54.56	44.07	59	20	M
	3	56.95	54.37	39.13	70	12	
	6	56.02	53.24	41.08	80	12	
PB 8640	0	51.9	45.05	28.24	20	0	N
	3	46.98	44.82	28.19	30	3	M
	6	48.96	47.34	27.4	35	10	M
	8	46.08	44.44	27.6	40	10	M

Table 5. The results of X-ray analysis of naturally aged samples - 3rd melting.

Sample	Aged, years	3rd melting					
		X_t	X_I	X_{II}	r, h	IP, h	Type
PB 0110	0	60	50	40.3	48	0	N
	2	58	51	37.58	57	0	
	3	56.81	50.43	38.73	62	24	
	6	57.79	46.53	41.3	70	24	
	8	53	43	38.49	78	24	M
	10	51	40	31.65	79	24	
	14	53.46	42.93	29.08	112	31	
	16	55.96	42.01	35.11	168	58	
DP 0400	0	63	58.43	39.1	40	0	N
	2	62	57.5	38.55	40	0	
	3	62.56	58.02	44.98	44	14	
	6	60.57	56.59	45.92	46	24	
	8	60.34	55.73	44.23	48	24	
	10	61	56.34	34.25	50	24	M
	11	60	55.42	38.59	56	24	
	15	60.13	55.54	33.96	57	48	
	17	57.89	53.47	31.31	57	48	
PB 0300	0	59.4	52.06	40.1	48	0	N
	3	57.11	50.05	39.15	68	24	M
	6	56.25	48.96	36.73	78	24	
PB 8640	0	50.53	45.52	31.01	18	0	N
	3	50.22	44.49	30.64	24	0	
	6	50.35	45.11	29.22	34	0	
	8	48.78	43.58	29.16	32	0	

Credit Author Statement

Author contributions

Kaszonyiova: Conceptualization, Validation, Resources, Data curation, Investigation, Project administration, Visualization, Writing - original draft

Rybnikar: Investigation, Supervision, Writing - review & editing

Lapcik: Data curation, Investigation, Writing - review & editing

Vilcakova: Data curation, Investigation, Writing - review & editing, Funding acquisition

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.