Journal of Thermal Analysis and Calorimetry, Vol. 73 (2003) 59–70

TEMPERATURE-RESOLVED DERIVATIVE FTIR
Melting and formation of mesomorphic poly(ethylene)

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(Received November 21, 2002; in revised form May 12, 2003)

Abstract

The fine-structure of the 720/730 cm^{-1} doublet of FTIR spectra has been evaluated by derivative spectroscopy as function of temperature on low-density poly(ethylene-co-1-octene). The pseudo-hexagonal mesophase in poly(ethylene), obtained at atmospheric pressure, is a non-equilibrium phase which develops preferred in presence of short-chain branches. An increasing concentration of short-chain branches slows down the ethylene-sequence selection process which is required for the formation of largely branch/defect-free orthorhombic crystals. Non-isothermal melt-crystallization at sufficiently high rate of temperature-change favors the development of metastable mesomorphic domains which likely form by entrapment of branches. It is proven that the mesophase transforms to the orthorhombic structure exclusively via the liquid phase.

Keywords: crystallization and melting, poly(ethylene), temperature-resolved Fourier-transform infrared spectroscopy (FTIR)

Introduction

Structure of poly(ethylene-co-1-octene)

Differential scanning calorimetry (DSC) on inter- and intramolecular homogenous poly(ethylene-co-1-octene) provides quantitative evidence for a broad spectrum of melting temperatures on heating, which is due to the existence of crystals of different stability/size. The formation of crystals of different thermodynamic stability is caused by selection of ethylene sequences of proper length for crystallization as function of temperature. The maximum ethylene sequence length is controlled by the concentration on 1-octene, and determines the maximum crystallization temperature, i.e., the onset of crystallization on cooling. Shorter ethylene-sequences crystallize at lower temperature, and are part of smaller/thinner crystals [1–3]. Equilibrium, i.e., full exclusion of hexyl-branches, can only be achieved if the diffusion-controlled process of selection of ethylene sequences of a length, which is pre-determined by the

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
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crystallization temperature, can be terminated under the respective conditions of the crystallization process. Non-equilibrium crystals, i.e., disordered crystals which contain branches, are easily obtained if melt-crystallization is forced at high rate of cooling [4, 5], or if the crystallization temperature is sufficiently low, even at lowest rate of cooling [2, 6]. The increase of the molar concentration on 1-octene is furthermore connected to a regressive-exponential decrease of the crystallinity [7–9], and by a gradual changeover of the crystal morphology from lamellae to fringed micelles [10].

The phase diagram of (unconstrained) poly(ethylene) predicts for atmospheric pressure and for temperatures less than 414 K the orthorhombic crystal structure as the most stable phase [11, 12]. In fact, the orthorhombic structure is only observed in slowly crystallized preparations, or in copolymers with low content on 1-octene. Wide-angle X-ray scattering (WAXS) clearly proofed the existence of non-orthorhombic, i.e., less stable crystals, in copolymers with relatively high concentration on 1-octene, independent of the conditions of crystallization, or in samples which were crystallized at fast cooling. The non-orthorhombic structure was identified to have a pseudo-hexagonal symmetry by X-ray fiber analysis, i.e., the molecules are aligned parallel, and there is only two-dimensional order in cross-chain direction [13]. The suggested arrangement of chains within a triclinic unit cell [5] was not confirmed. Further indications for the formation of crystalline domains with non-orthorhombic symmetry were gained by Fourier-transform infrared spectroscopy (FTIR), by analysis of the fine structure of the methylene rocking mode [14].

Despite unambiguous evidence for the existence of pseudo-hexagonal crystals there is still a lack of knowledge about the thermodynamic stability of these non-equilibrium but metastable crystals. In this paper we apply temperature-resolved FTIR in order to follow for the first time the melting process of the different, simultaneously occurring polymorphs in poly(ethylene-co-1-octene) separately. Measurements were performed as function of the concentration on 1-octene and as function of the history of crystallization, which allow to draw conclusions about the kinetics and the sequence of the various stages of the crystallization process.

Application of FTIR for analysis of the local structure of poly(ethylene)

The structure of a single poly(ethylene)-molecule can be described by the sequence and concentration of *trans*- and *gauche*-conformations. The equilibrium *gauche*-concentration is about 40% in the melt, and was proven to be less than 1% in the orthorhombic crystalline structure well-below the melting temperature by analysis of the temperature-dependence of the 1300 cm^{-1} CH$_2$-wagging/twisting mode in alkanes of different lengths, i.e., the chains in orthorhombic crystals exhibit an all-*trans* conformation [15–17]. Furthermore it was shown that the *gauche*-concentration in hexagonal crystals is about twice or triple the *gauche*-concentration in orthorhombic crystals [16], despite the three-dimensionally ordered hexagonal/rotator phase of alkanes [18] is of different thermodynamic stability than the two-dimensionally ordered high-pressure hexagonal phase in poly(ethylene) [19]. The increased concentration of *gauche*-conformations in disordered hexagonal crystals causes an increase of the average intermolecular distance, and a shortening of the average repeating distance along the chain which is evidenced by WAXS [20].

FTIR was applied to follow the isothermal melt-crystallization process of high-density poly(ethylene) (HDPE) and linear low-density poly(ethylene) (LLDPE) [21]. The experimental data revealed evidence that the crystallization from the melt into the stable orthorhombic structure occurs via formation of disordered short *trans* sequences, detected at 1368 cm^{-1}, which grow to longer and regular *trans* sequences, detected at 728 cm^{-1}. The data did not permit an assignment of the disordered *trans* sequences, which are predominantly evident at the early stage of the crystallization, to the disordered high-pressure hexagonal phase. Time-resolved small-angle X-ray scattering (SAXS) was applied later on in order to confirm the FTIR results and lead to the conclusion that at first disordered *trans* segments are formed by increased density-fluctuations in the melt, which secondly transform by conformational ordering to rather small domains with a regular zigzag-all-*trans*-conformation. Finally the small domains merge to typical lamellae [22]. The idea of this multi-step process was confirmed for the case of syndiotactic polystyrene [23] and was proposed as a general route of polymer crystallization [24].

The effect of variation the condition of melt-crystallization on the local structure of poly(ethylene) was investigated by analysis the fine-structure of the CH_2 rocking mode [25]. The rather broad rocking band of the melt is centered at about 721 cm^{-1}, and splits into a doublet at frequencies of 731 and 721 cm^{-1} in presence of orthorhombic crystals due to the specific arrangement of chains within the unit cell. The position and width of the bands are approximations and vary slightly with temperature and degree of long range order [26–28] and the intensity or total absorbance, respectively, is related to the crystallinity [29, 30]. The spectrum of poly(ethylene) single crystal mats was compared with the spectrum of quenched specimens by calculation of the difference spectrum [25]. The quenched preparation revealed an additional band at 716 cm^{-1} which was assigned to a localized monoclinic structure at grain boundaries in the interior of regular folded-chain crystals, similar as was suggested earlier based on analysis of mechanically deformed samples [31], or to a local arrangement of chains in stacking faults [32].

In the present study we provide evidence that the metastable disordered pseudo-hexagonal structure is stabilized by the specific kinetics of the branch-controlled crystallization process in ethylene copolymers. The paper includes an estimation of the temperature-dependence of the concentration on orthorhombic and disordered hexagonal structure, and is considered as continuation of the initial work about the phase structure and crystal structure in poly(ethylene-co-1-octene) [13]. The estimation of the temperature-dependence of the concentration of the different crystalline phases by FTIR relies on the reliable separation of the strongly overlapping bands. As an effective alternative to profile fitting [21] and calculation of difference spectra [26] we employed derivative spectroscopy [33–35] since no further information/assumptions, i.e., starting parameters for the fitting procedure are needed, and since the concentration dependence of the absorbance of the specific mode, according to the Beer-Lambert-law [36], is maintained in the higher derivatives of the spectra.

Experimental section

Materials

In the present study commercial inter- and intramolecular homogeneous copolymers of ethylene and 1-octene (DOW) were investigated as function of the concentration on 1-octene and as function of the thermal history. The concentration on 1-octene was determined by FTIR and was varied from 19 to 38 wt% [35, 37]. The density of the copolymers at ambient temperature covered therefore the range from 0.902 to 0.870 g cm^{-3}, which corresponds to crystallinities of about 40 to 15%, respectively.

Compression-molded films of 200 μm thickness were prepared by quenching in a mixture of dry-ice and ethanol and subsequent annealing at ambient temperature for several days until equilibrium was reached [38]. The effect of the condition of crystallization was evaluated on samples which were melt-crystallized at cooling rates of 1, 4, 10, 40 K min^{-1}, and by quenching in cooled water, followed by annealing at ambient temperature. Furthermore, films of 500 μm thickness were prepared in order to check independence of experimental data on instrumental effects.

Instrumentation

Measurements were performed on a Fourier-transform infrared spectrometer S2000 (Perkin Elmer) in reflection mode, using a golden gate single reflection ATR (attenuated total reflection) system (Specac) and a heated diamond top-plate, attached to a 3000 series temperature controller. The spectral and digital resolution were set to 2 and 0.5 cm^{-1}, respectively. The rate of temperature-change was 1 or 5 K min^{-1}, respectively, on heating, and 1 K min^{-1} on cooling.

Results and discussion

Structure as function of branch concentration

Figure 1 shows as an example the absorbance, A, of quenched poly(ethylene-co-1-octene) of density 0.870 g cm^{-3} in the rocking region as function of the wavenumber, ν, (a), the second derivative of the absorbance *vs.* wavenumber, $d^2A/d\nu^2$, as function of ν, (b), and the magnitude of $d^2A/d\nu^2$ at $\nu = 717$ cm^{-1} and $\nu = 719.5$ cm^{-1}, $|d^2A/d\nu^2|_{717}$ and $|d^2A/d\nu^2|_{719.5}$, as function of temperature, T, (c), obtained on continuous heating from 298 to 373 K at a heating rate of 1 K min^{-1}. The original data $A(\nu)$ were not smoothed before double-derivation, as is often required due to noisy data. Furthermore, the broad and almost negligible second derivative of the melt-spectrum was subtracted in order to enhance the contribution from ordered domains. Thus, the peaks in Fig. 1b are solely due to ordered domains. It can clearly be recognized that both $|d^2A/d\nu^2|_{719.5}$

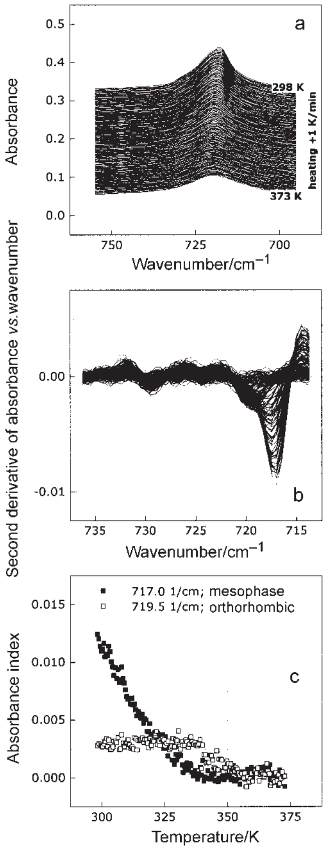

Fig. 1 Absorbance, A, as function of wavenumber, ν, and as function of temperature (a), second derivative of the A *vs.* ν, $d^2A/d\nu^2$ as function of ν (b), and magnitude of $d^2A/d\nu^2$ at $\nu = 717$ and $\nu = 719.5$ cm^{-1} as function of T (c). The data were obtained on quenched poly(ethylene-co-1-octene) of density 0.870 g cm^{-1}, on continuous heating from 298 to 373 K at a rate of 1 K min^{-1}

and $|d^2A/d\nu^2|_{730}$, which are due to orthorhombic structure, are considerably less intense than $|d^2A/d\nu^2|_{717}$, which is due to non-orthorhombic domains, in the following denoted as (pseudo-hexagonal) mesophase. $|d^2A/d\nu^2|_{719.5}$ and $|d^2A/d\nu^2|_{717}$ are plotted as open and closed squares in Fig. 1c after subtraction of a linear baseline which was constructed between the satellite peaks [33]. The particular method of data reduction seems rather simple, however, we proved that the results are largely independent on the calculation scheme. Alternatively we fitted the baseline-corrected second-derivative spectra using Gaussian functions and defined the absorbance index by the area of the bands at 719.5 and 717 cm^{-1}. In a third approach the original melt-spectrum was subtracted from the spectra measured below the final melting temperature before the calculation of the second derivative and fitting. Neither of the two alternative calculation schemes resulted in a different course of the absorbance index *vs.* temperature, which provides confidence for further interpretation. The bottom graph of Fig. 1 unambiguously reveals that in quenched poly(ethylene-co-1-octene) of 0.870 g cm^{-3} density the major part of the total crystal population exists as pseudo-hexagonal mesomorphic structure. The orthorhombic phase can be detected by FTIR, in contrast to the analysis by WAXS, which does not permit such a clear assignment of scattering intensity to the various phases in isotropic samples. The mesophase obviously immediately starts to melt on heating, whereas the concentration of orthorhombic crystals remains almost constant before decreasing in a narrow temperature-interval at the end of the melting process.

Figure 2a-d shows in the left column d^2A/dν^2 (ν), and in the right column the absorbance index as function of T for quenched poly(ethylene-co-1-octene) of density 0.870 (a), 0.885 (b), 0.896 (c), and 0.902 g cm^{-3} (d). The sample thickness was

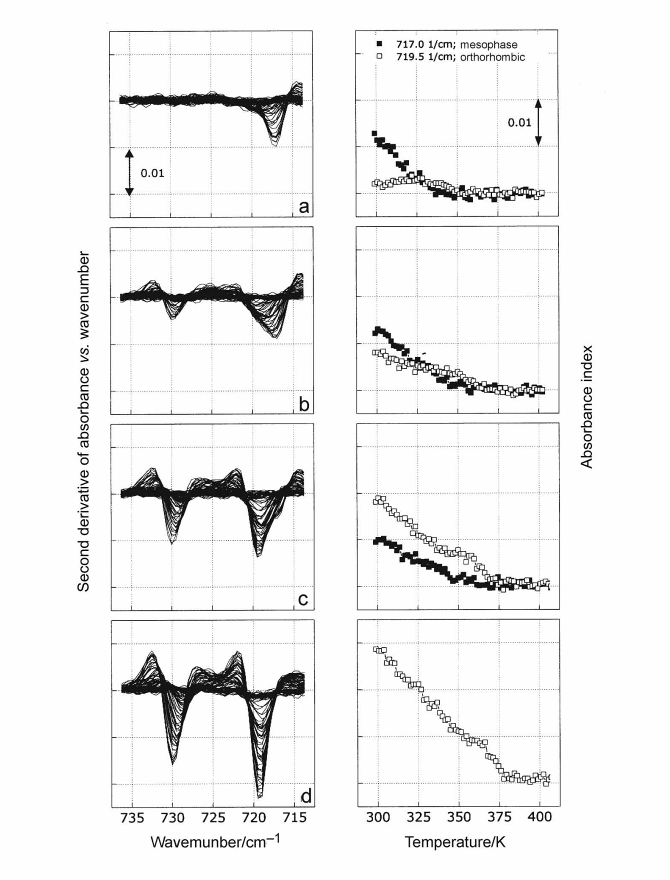

Fig. 2 Second derivative of the absorbance *vs.* ν, d^2A/dν^2, as function of ν (left), and absorbance index as function of T (right) of quenched poly(ethylene-co-1-octene) of density 0.870 (a), 0.885 (b), 0.896 (c), and 0.902 g cm^{-3} (d)

500 μm, and the heating rate was 5 K min^{-1}. Obviously there is no effect of the sample thickness and the heating rate on the result as can be concluded from the comparison of Figs 1b, c and 2a. Note furthermore that scaling is identical in all plots of Fig. 2. Figure 3 shows the sum of the absorbance indices, $|d^2A/d\nu^2|_{719.5} + |d^2A/d\nu^2|_{717}$ [= total absorbance index], as function of the macroscopic density of the samples. The closed squares were calculated from the data of Fig. 2, and the open square is taken from the data of Fig. 1c. The linearity between the total absorbance index and the macroscopic density of the samples confirms the correctness of the FTIR-data reduction via derivative spectroscopy, and justifies the quantitative evaluation of the ratio between mesomorphic and orthorhombic structure.

The experimental data of Fig. 2 display the trivial information of (a) an increasing total absorbance/crystallinity with increasing macroscopic density at 298 K (see also Fig. 3), and (b) a shift of the completion of melting toward higher temperature if the density increases, which both are discussed in detail by recent research [39] and are not subject of the present research. The novel information of the experiment which is shown by data of Figure 2 is the determination of the fraction of pseudo-hexagonal mesomorphic structure compared to the total ordered structure, (a) as function of the branch concentration and (b), for a given sample, as function of temperature. The higher the density/crystallinity of the copolymer the smaller is the relative amount of mesophase with respect to the orthorhombic structure. The sample with a density of 0.902 g cm^{-3} obviously consists only of orthorhombic structure, beside the amorphous phase which is not evident in the baseline-subtracted derivative spectra. Initially we expected that the mesophase forms independent on the copolymer composition if the temperature is sufficiently low; i.e., that the formation is triggered by the crystallization temperature/critical size of nuclei. The argument would be straightforward because in all of the shown samples a similar crystal morphology may be expected at a given crystallization temperature if the ethylene-sequence length selection process works perfectly. The fraction of mesomorphic crystals on the total crystal population, in contrast, decreases with increasing total

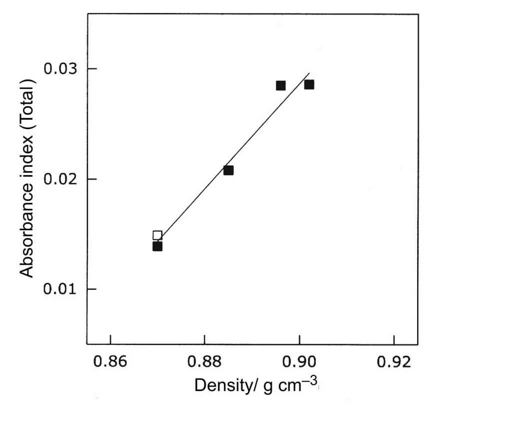

Fig. 3 Total absorbance index of poly(ethylene-co-1-octene), $|d^2A/d\nu^2|_{719.5} + |d^2A/d\nu^2|_{717}$, as function of macroscopic density

crystallinity and, intersects zero at a total density of about 0.906. The kinetics of the formation of orthorhombic structure, if compared at a fixed reference temperature, is depending on the copolymer composition, and is accelerated in samples of lower branch content (sample of 0.902 g cm^{-3}; Fig. 2d). The conclusion is supported by the consistently increasing slope [d $|d^2A/d\nu^2|_{719.5}$ / dT] (T), which reflects the enhanced formation of orthorhombic domains at low temperature with decreasing branch concentration. Vice versa the slope [d $|d^2A/d\nu^2|_{717}$ / dT] (T) decreases with decreasing branch content which indicates the preferred formation in low-crystalline copolymer preparations.

Structure as function of condition of crystallization

Figure 4 is a plot of the absorbance index of poly(ethylene-co-1-octene) of 0.870 g cm^{-3} density as function of temperature, obtained on heating at 1 K min^{-1}. Samples were prepared by melt-crystallization at cooling rates of 1 (a), 4 (b), 10 (c), and 40 (d) K min^{-1}, and by quenching (e). The data permit to evaluate the effect of the condition of melt-crystallization on the phase structure, i.e., the ratio between orthorhombic and mesomorphic domains. Samples of higher density were not investigated as function of the condition of melt-crystallization since the fraction of mesomorphic structure decreases with increasing density (Fig. 2), and since there is no qualitative change of the crystallization behavior with respect to the ratio between orthorhombic and mesomorphic

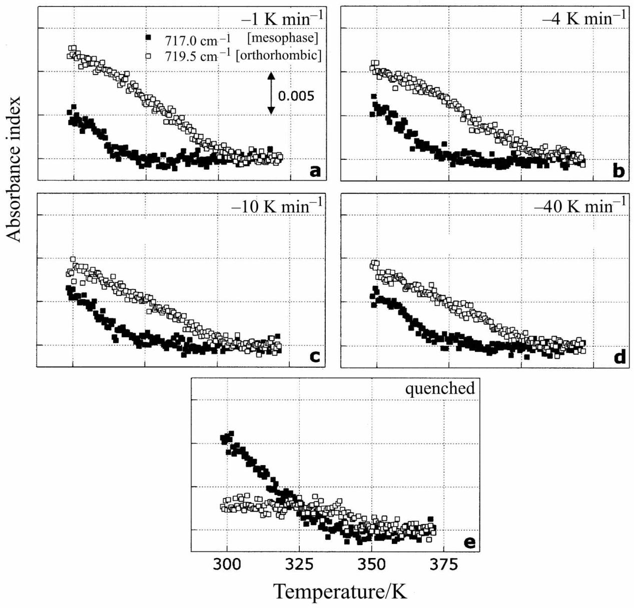

Fig. 4 Absorbance index of poly(ethylene-co-1-octene) of 0.870 g cm^{-3} density as function of temperature, obtained on heating at 1 K min^{-1}. Samples were prepared by melt-crystallization at a cooling rate of 1 (a), 4 (b), 10 (c), and 40 (d) K min^{-1}, and by quenching (e)

domains. The data of Fig. 4 reveal an increasing amount of mesomorphic, pseudohexagonal domains on expense of orthorhombic structure at 298 K with increasing rate of cooling on prior melt-crystallization. The fraction of mesomorphic domains on the total population of ordered domains is about 0.3 after melt-crystallization at 1 K min^{-1}, and increases to almost 0.8 after quenching. The orthorhombic structure is dominant up to a cooling rate of 40 K min^{-1} (Fig. 4a-d) in contrast to quenching (Fig. 4e) where the mesophase prevails. The result is in excellent correspondence with earlier reported WAXS data, which however, did not provide such clear evidence for the existence of the mesomorphic structure in isotropic samples as in case of FTIR [5, 14, 40]. Since melting of the mesomorphic domains is completed at lower temperature than melting of orthorhombic crystals, independent of the rate of cooling, we assume that the latter structure forms first on cooling. Furthermore, the completion of melting of mesomorphic domains is shifted to higher temperature on increasing rate of cooling on prior crystallization. In case of crystallization at 1 K min^{-1} is the melting process of the mesophase completed at about 325 K whereas completion of melting is retarded to about 340 K when the sample was crystallized on quenching. The mesomorphic structure develops on cooling at increasingly higher temperature on expense of the orthorhombic structure if the cooling rate is increased. An increasing cooling rate results therefore in an increase of the total free enthalpy of the sample since the specific heat of formation of mesomorphic crystals is lower than the specific heat of formation of orthorhombic crystals. The statement, however, only is true if the total amount of disordered structure remains constant which is at present not evidenced. The data of Fig. 4 provide clear evidence that the formation of mesomorphic crystals in the investigated ethylene-1-octene copolymers is controlled by the condition of crystallization.

However, it is not clear whether the melt transforms always, i.e., also at low cooling rate, first into mesomorphic and subsequently into orthorhombic structure, or, which seems more likely, only into mesomorphic structure when defects are entrapped by accident on fast cooling and non-perfect sequence-length selection, respectively. Isothermal (primary) crystallization experiments and analysis of the rocking mode provided no evidence that the formation of orthorhombic crystals process occurs via the mesophase.

The notion of direct formation of orthorhombic crystals from the melt without formation of mesomorphic crystals as an intermediate stage of the crystallization process is strengthened by the data of Fig. 5. The quenched poly(ethylene-co-1-octene) of density 0.870 g cm^{-3}, which contains as major crystalline phase the pseudo-hexagonal structure, was heated at 1 K min^{-1} to a pre-defined maximum temperature of 313, 318, 323, 328, and 333 K, as indicated in the plots of the left column. Thus, the left column of Fig 5. is a repetition of the experiment of Fig. 1, interrupted at the various annealing temperatures, and serves additionally for visualization of the reproducibility of experimental data. Subsequently the samples were cooled (middle column), and immediately heated into the melt (right column). The mesophase of the quenched preparation melts partially on first heating, whereas the orthorhombic structure seems not or only slightly to change in amount. With increasing maximum temperature we observe on subsequent cooling an increasing amount of orthorhombic structure on expense of mesophase. Obviously, the for-

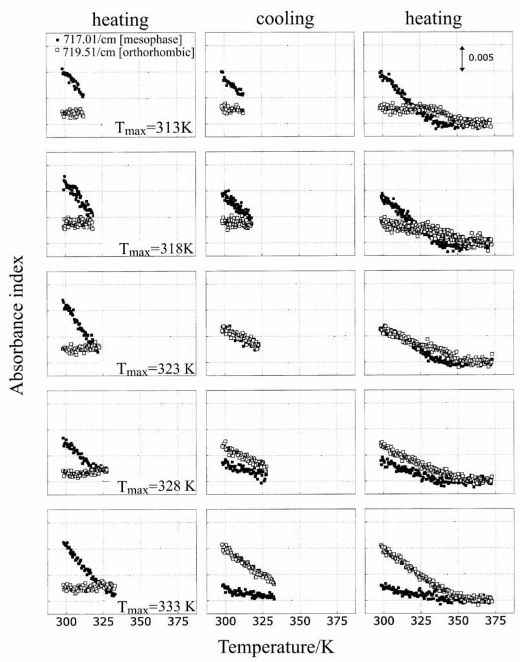

Fig. 5 Absorbance index of quenched poly(ethylene-co-1-octene) of density 0.870 g cm^{-3} as function of temperature on heating up to a pre-defined maximum temperature (left column), followed by cooling (middle column) and immediate subsequent heating (right column). The rate of temperature-change was 1 K min^{-1} in all experiments

merly on quenching within the mesophase crystallized material can recrystallize via the melt into orthorhombic structure if the cooling rate is sufficiently low. In fact, the mesophase does not transform at constant temperature into orthorhombic structure but only after melting. The data of the right column show that at 298 K any ratio between mesophase and orthorhombic phase can be generated with the specific knowledge of phase transition behavior in low-crystalline copolymers.

Conclusions

The data of the present study are in accord to earlier investigations about the structure and the phase transformation behavior of low crystalline poly(ethylene) using calorimetry and X-ray scattering. WAXS revealed a clear and well-separated interference maximum at about 4.5 Å due to the existence of non-orthorhombic pseudo-hexagonal structure. The present investigation using FTIR predicts the relative amount of the pseudo-hexagonal structure as function of the chemical composition, and as function of the thermal history. Strikingly new is the evaluation of the thermal stability of the pseudo-hexagonal crystals in direct comparison to that of orthorhombic crystals. The formation of the pseudo-hexagonal phase in homogenous ethylene-1-octene copolymers at ambient pressure is controlled by the kinetics of the transition from the isotropic melt to the stable orthorhombic structure. We suggest that the formation of the non-equilibrium mesophase is caused by entrapped short-chain branches as result of an inadequate and non-perfect branch-exclusion process on cooling. The imperfection of the ethylene-sequence selection process naturally increases with increasing rate of cooling, and increasing branch content. Annealing at constant temperature does not result in transformation of mesomorphic domains, which developed at elevated and identical temperature, into orthorhombic crystals since the structure is arrested by the continued cooling process and the incorporated branches, respectively. There were found no indications of a direct transformation of mesomorphic crystals into orthorhombic crystals, *i.e.*, the pseudo-hexagonal crystals in low crystalline polyethylene, which are stabilized by branches, are of different nature/stability as the disordered *trans* phase obtained in the early stage of the crystallization process of standard polyethylene.

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