Effect of Crystal Morphology and Crystallinity on the Mechanical α- and β-Relaxation Processes of Short-Chain Branched Polyethylene

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Received March 30, 2004; Revised Manuscript Received November 5, 2004

ABSTRACT: The temperature and the Gibbs free energy of activation of the α-relaxation in ethylene-1-octene and ethylene-1-hexene copolymers drop with decreasing crystal size which is triggered by increasing concentration of short-chain branches and/or increasing cooling rate during melt crystallization, respectively. The activation enthalpy and entropy, unexpectedly, increase with decreasing crystal size, obtained by increasing the cooling rate at constant branch concentration. Both effects can be explained by hindrance of the intracrystalline translational mobility and the restricted segment exchange between the crystalline and amorphous phases, caused by branch points accumulated at the crystal surface. The significant drop of the activation enthalpy and the temperature of β-relaxation with increasing branch-concentration point to decreasing restriction of cooperative segmental mobility by crystals. The restriction is reduced as result of decreasing crystallinity or increased crystal perfection, respectively. Thus, the distribution of the local branch concentration controls the molecular mobility of short-chain branched polyethylene expressed both in the α- and β-relaxation.

1. Introduction

The Mechanical α- and β-Relaxation Processes. The α-relaxation process can be described by the well-accepted rotation−translation−twist−tension (RT−TT) model.[1] The RT−TT model considers the α-relaxation as a result of the formation and propagation of dynamic conformational defects in crystals, and of the connected change of the local equilibrium at the crystal surface. The defects develop by a localized smooth twist of the molecule by 180° along the chain axis which includes about 12 methylene units regardless of the crystal thickness. The twisted methylene sequence and accordingly axial chain length shorten by half a lattice constant $c_0/2$, which in the case of orthorhombic polyethylene is 0.127 nm. Thus, due to the shortening by $c_0/2$ and a turn by 180°, the CH_2 groups located on the ends of the mismatch remain in the crystal register together with the neighbored molecules within the crystal.[1] The formation and propagation of the mismatch requires an activation energy which depends on the crystal thickness. The RT−TT model enables the prediction of motion of molecular segments between the amorphous and crystalline phase at the crystal surface.[1,2] The complete propagation of the twist-defect between the crystal boundaries causes chain-sliding diffusion by $c_0/2$. The net effect of the combined shortening of the axial chain length by twist formation and chain-sliding diffusion is a change of the local conformation of the molecule at the crystal−amorphous interface, including the rearrangement of tight and loose folds, cilia, or intercrystalline links and, therefore, a change of the local mechanical modulus.[2,3] In particular the change of the local structure of the crystal−amorphous interface is assigned to the α-relaxation process since it requires an additional deformation of the amorphous phase.[2,3] The concept is supported by evaluation of the anisotropy of the α-relaxation in oriented polyethylene which allowed to assign the relaxation to simple interlamellar shear.[4] A further indirect indication that the mechanical manifestation of the α-process is caused by the deformation of the amorphous phase is the experimentally established dependence of the relaxation strength on the crystallinity.[2]

The segment exchange at the crystal−amorphous interface as well as 180° flip motions in crystals of linear high-density polyethylene (HDPE)[5−7] and of a particular short-chain-branched polyethylene[8] were recently investigated by two-dimensional ^{13}C NMR.[5−7] The activation energy for 180° chain flip of 122 ± 22 kJ/mol agrees well with data based on dielectric[9,10] and mechanical[2,10,11] measurements. On the contrary, the most-probable relaxation time increases from 10^{-6} to 2×10^{-3} and to 1.5 s, if detected by NMR, dielectric, and mechanical analysis, respectively.[2,3,6,7] The same tendency was observed for the width of the relaxation-time distribution. The increase of the relaxation time is caused by the increase of the number of translation steps and therefore increased *cooperativity* of molecular motion, which is required for detection of the chain-sliding diffusion in mechanical analysis, or detection of dipole orientation in dielectric analysis of polyethylene functionalized with polar groups.

The α-relaxation seems to be largely affected by the crystallinity and by the crystal morphology. The investigation of the α-relaxation of a broad spectrum of polyethylenes and ethylene-vinyl acetate copolymers revealed a linear decrease of the temperature of the mechanical loss peak with increasing reciprocal of the crystal thickness.[12] Similar observations were found in metallocene-catalyzed HDPE of different molecular weight and in ethylene-1-hexene copolymers with a 1-hexene content between 0 and 3.5 mol %.[13] Summarizing the effect of structural parameters on the α-relaxation, as can consistently be explained by the RT−TT model, by the soliton model,[1,14] and by atomistic simulation,[15] it can be concluded that the activation energy ΔE_α (or more precisely activation enthalpy; see section 4), the characteristic temperature T_α, and the relaxation time τ_α increase strongly with increasing

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10.1021/ma0493776 CCC: $30.25

crystal thickness up to about 10 nm. If the crystal thickness exceeds about 10 nm, i.e., if the crystal thickness is much larger than the length of the twist defect (about 1.5 nm), then ΔE_α becomes constant, and the further increase of T_α and τ_α is insignificant. Data obtained on extended-chain crystals in *n*-paraffins, however, do not fit the same linear relation between the α-relaxation temperature and inverse crystal thickness, which is valid for folded-chain crystals in polymers.[12] This points to a different mechanism of the α-relaxation in extended-chain and folded-chain crystals.

The β-relaxation is assigned to the cooperative segmental mobility of disordered chains,[2,3,10,12] and connected to the glass transition.[16] The mobility of noncrystalline segments is strongly controlled by the crystal morphology and the degree of crystallinity in semicrystalline polymers. In high-density polyethylene, the β-relaxation is completely suppressed by the restriction of the mobility of the amorphous phase due to the present crystals.[2–4,9,10,17] In the case of branched polyethylene of medium or low crystallinity, in contrast, the β-relaxation is clearly detectable.

Investigation of the Relaxation Processes of Homogeneous Ethylene-1-Alkene Copolymers. After the commercial establishment of the homogeneous ethylene-1-alkene copolymers in 1993, a large number of investigations on the dynamic-mechanical behavior have been carried out to study these new materials.[13,18–24] The motivation can be seen in the broad spectrum of available phase structures and crystal morphologies for fundamental studies as well as the need for general characterization for practical purposes. The physical structure of these copolymers and therefore the properties are adjustable in a wide range by the variation of the 1-alkene concentration. The enthalpy-based crystallinity can vary between zero and almost 90%.[25] The melting and crystallization processes are controlled by the concentration and the distribution of short-chain branches (SCB). The longest ethylene sequences crystallize and melt at the highest temperature, and often the melting and crystallization processes are extended down to the glass transition temperature.[26–29] The melting temperature is a measure of the thermodynamic stability of crystals, which includes the size and surface energies, respectively, and the internal order. Thus, it is possible to obtain by crystallization at high temperatures, i.e., in the vicinity of the melting point, typical chain-folded lamellae whereas at low temperatures bundlelike crystals or fringed micelles are formed.[18–20] The lamellar crystals dominate in copolymers of low and medium 1-alkene concentration, however, the ratio of two crystal types will change in favor of fringed micelles, and the primary crystallization temperature will be lowered with increasing 1-alkene concentration. Furthermore, the crystal morphology is adjustable within certain limits by the conditions of melt crystallization.[30] It is proven that large supercooling, as can be achieved by quenching, results in smaller crystals with an increased specific surface area.[31] The homogeneous copolymers of ethylene and 1-alkenes offer therefore an unique opportunity for systematic analysis of both the effect of crystal size/perfection/specific surface area and the effect of crystallinity on the relaxation processes of polyethylene. In the present study, we investigated samples with the crystallinity ranging from about 15 to 75%, with a corresponding transition of the crystal morphology from fringed micelles to folded-chain lamellae. By variation of the crystallization history including annealing, we obtained preparations of similar crystallinity but different crystal size and perfection.

Previous studies of the relaxation processes of ethylene-1-alkene copolymers often employed only a single frequency and a relatively large heating rate for analysis.[13,18–24] The data allowed one to extract the temperature of relaxational transitions by the maximum of mechanical loss peak but not the evaluation of the activation enthalpy as is possible by the multifrequency analysis performed in the present work. The dynamic-mechanical behavior of ethylene-1-octene copolymers was comprehensively investigated as a function of the composition and the crystallization history by Hiltner, Baer, and co-workers.[19,20] It was found that the characteristic temperatures of the α- and β-relaxation processes in slowly crystallized specimens decrease with increasing 1-octene content, which was changed between 0 and 12.3 mol %. Furthermore, the intensity of the β-relaxation increases and that of the α-relaxation decreases with increasing 1-octene content due to the decrease of the crystallinity. In the sample with 12.3 mol % of 1-octene, the α-relaxation is even completely absent. The effect of the crystallization history was evaluated on a single copolymer with 2.8 mol % of 1-octene, and it was concluded that a poorly ordered fold surface, as determined by transmission electron microscopy and atomic force microscopy,[19,20] causes a decrease of intensity and a shift of the α-relaxation to lower temperature.

The present study is an extension of former research on linear[1–4,9–11] and branched polyethylene,[12,13,17–24] gaining new and quantitative insight about the influence of the crystal morphology on the mechanical relaxation processes. The data of dynamic-mechanical analysis (DMA) were collected as a function of temperature and frequency permitting the determination of the activation parameters of the α- and β-relaxation processes in dependence on the controlled crystal morphology.

2. Experimental Section

2.1. Instrumentation. Dynamic-Mechanical Analysis (DMA). DMA measurements were performed in tensile mode using a Mark III measuring head (Rheometric Scientific). The cross section of the samples and the distance between the clamps were 0.5 × 5 mm^2 and 15 mm, respectively. The samples were loaded with a prestress of about 80 kPa, and subsequently the strain was modulated with an amplitude of 0.03% at frequencies between 0.215 and 63 Hz. The temperature was changed continuously at a heating rate of 0.5 K/min. In the case of the evaluation of the effect of annealing of quenched preparations a single frequency of 1 Hz and a heating rate of 2 K/min were used.

Differential Scanning Calorimetry (DSC). Samples were investigated with a DSC 7 (Perkin-Elmer) equipped with the liquid nitrogen accessory for controlled cooling. The sample-furnace temperature was calibrated by the onset temperature of melting of indium, tin, and zinc on heating at a rate of 20 K/min. The instrument was additionally calibrated for operation at low temperatures using first-order transitions of cyclopentane and adamantane ($C_{10}H_{16}$) as done by Sarge et al.[32] The initial heat-flow rate calibration was done using the heat of fusion of indium. The sample mass was about 10 mg. Heat-flow-rate raw data were corrected for the instrumental asymmetry, and converted into apparent heat capacity data, using sapphire as standard as recommended by Wunderlich.[33] The measured apparent heat capacity in conjunction with theoretical values of heat capacity for crystalline and amorphous polyethylene, taken from the advanced thermal analysis

Table 1. Molecular and Physical Parameters of the Used Copolymers

type	content on 1-alkene, mol %	short-chain branches per 1000 C	mass-average molecular mass[c] $\bar{M}_w$, kg/mol	polydispersity[c] $\bar{M}_w/\bar{M}_n$	melting temp[d] T_m, K	density[e] ρ, kg/m^3	sample type
	0	0	357	3.5	409	954	sc
						939	q
1-hexene	3[a]	15	122	2.6	392	921	sc
						914	q
1-octene	4.6[b]	23	49	1.8	382	914	sc
						913	q
1-hexene	6[a]	30	111	2.2	371	901	sc
						899	q
1-octene	6.6[b]	33	53	2.2	374	904	sc
						901	q
1-hexene	8[a]	40			363	895	q
1-octene	10.1[b]	50	61	1.8	355	883	sc
						883	q
1-octene	14.3[b]	71	70	1.8	341	874	sc
						876	q

[a] Estimated by Fourier transform infrared spectroscopy. [b] Manufacturer information. [c] Determined by high-temperature GPC (gel permeation chromatography). [d] Peak temperature in DSC melting endotherm. [e] By density-gradient column, obtained on slowly cooled (sc) and quenched (q) samples.

Table 2. Effect of Comonomer Content and Thermal History on Structural Parameters of Ethylene−1-Octene Copolymers

1-octene content, mol %	cooling rate from melt, K/min	crystallinity		unit cell parameters		long period L, nm	crystal thickness L_c, nm	average ethylene sequence length $\langle L_{EC} \rangle$, nm
		χ_c^{ρ} (density), %	χ_c^{WAXS} (WAXS), %	**a**$_0$, nm	**b**$_0$, nm			
0	−1	68	75	0.743	0.496	26.5	21.9	
	quenched	58	64	0.746	0.496	17.0	11.2	
4.6	−1	42	44	0.748	0.499	19.2	8.5	5.4
	−4	41	44	0.749	0.499	18.4	8.1	
	−10	40	42	0.749	0.499	17.6	7.4	
	−40	40	41	0.750	0.499	17.1	7.0	
	quenched	36	35	0.752	0.501	13.8	4.8	
6.6	−1	33	35	0.750	0.499			3.8
	−40	33	35	0.750	0.500			
	quenched	31	28	0.752	0.502			
10.1	−1	19		0.756	0.502			2.5
14.3	−1	13		0.757	0.503	16.5	2.1	1.8
	−4	13				16.2	2.1	
	−10	13				15.9	2.0	
	−40	13				15.8	2.0	
	quenched	14				14.1	2.0	

system (ATHAS) were utilized for calculation of an enthalpy-based crystallinity on the basis of the two-phase model as described by Mathot.[26]

Small-Angle and Wide-Angle X-ray Diffraction (SAXS and WAXS). Small-angle data were collected with a two-dimensional CCD detector (Mar) at the Beamline A2 in Hasylab at the Deutsches Elektronensynchrotron Hamburg (DESY). The wavelength of the X-ray beam was 0.15 nm and the sample-to-detector distance 1.78 m. WAXS of differently crystallized copolymers was recorded in transmission mode with a scintillation counter on a diffractometer URD 63 (Seifert-FPM), using Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm).

Density. The density of the samples was determined by a density gradient column (Ray-Ran) at 296 K using a water/2-propanol mixture.

Atomic Force Microscopy (AFM). AFM micrographs were taken with the NanoScope IIIa microscope (Digital Instruments) using a standard silicon cantilever, operated with medium force in tapping mode. Samples were prepared by melt crystallization at different cooling rates in the presence of a mica substrate.

2.2. Materials and Sample Characterization. Materials. The materials used in this study are linear polyethylene HDPE (Dow Plastics), homogeneous ethylene-1-octene copolymers EOC (DuPont Dow Elastomers), and homogeneous ethylene-1-hexene copolymers EHC (Exxon Mobil Chemical) with the molecular characteristics shown in Table 1. The EOCs and EHCs were synthesized by means of single-site catalysts by the INSITE and EXXPOL technology, respectively. Table 1 includes additionally the melting temperatures and the densities at room temperature (296 K), with the latter being dependent on the crystallization history. Specimens of 500 μm thickness were prepared by compression-molding, using cooling rates of 1, 4, 10, and 40 K/min and by quenching in cold water. Subsequently, the samples were stored at least 2 weeks at room temperature before analysis.

Sample Characterization. Table 2 contains structural parameters of the used samples which are essential for the complete analysis of the mechanical relaxation behavior. The crystallinity was determined by density data and by WAXS. The density-based crystallinity χ_c^{ρ} was calculated using 1.00 and 0.85 g/cm^3 as densities of the crystalline and amorphous structures, respectively. The WAXS raw data were collected between 12° and 28° 2θ, background-corrected and fitted by three Gaussian functions, representing the amorphous halo, and the 110 and 200 orthorhombic reflections. The intensity of the amorphous halo and two crystalline reflections were weighted according[34] and served for calculation of the WAXS-crystallinity χ_c^{WAXS}. Hence, the density- and WAXS-based crystallinities, given in Table 2, are based on a two-phase model. In particular in the case of the samples with high comonomer concentration the two-phase model is questionable and does not allow a reliable evaluation of the crystallinity. Evidence for a distinct three-phase structure in samples of low crystallinity was gained by nuclear magnetic resonance (NMR) spectroscopy,[35] by WAXS,[35,36] and by infrared spectroscopy.[37] In general, the crystallinity decreases with increasing concen-

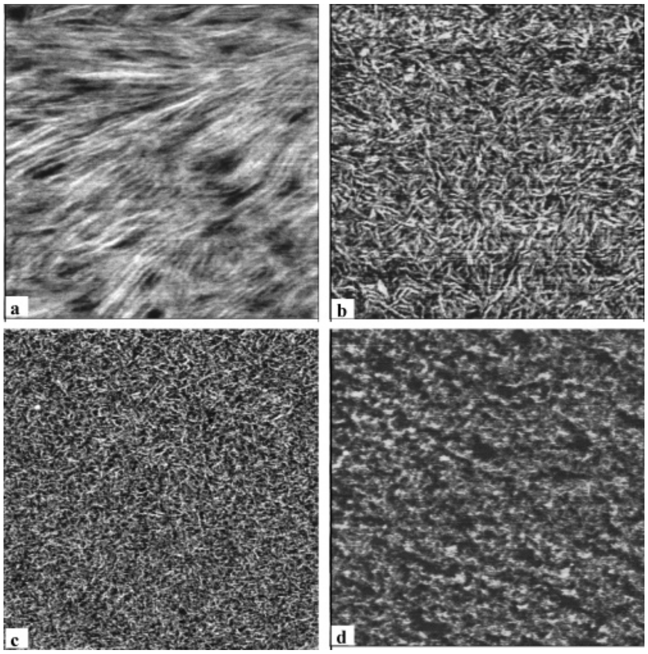

Figure 1. AFM phase images of slowly cooled (a, c) and quenched (b, d) poly(ethylene-*co*-1-octene) with 4.6 (a, b) and 10.1 (c, d) mol % 1-octene. The scanned area is $1.5 \times 1.5\ \mu\mathrm{m}^2$.

tration on 1-octene, and with increasing cooling rate during melt crystallization. An exception is the poly(ethylene-*co*-1-octene) with 14.3 mol % which shows a higher crystallinity in the quenched state rather than after slow cooling, consistent with investigations of Peeters et al.[38] The decrease of the crystallinity is furthermore accompanied by an increase of the unit cell parameters in cross-chain direction, a_0 and b_0, which is due to an increasing imperfection of crystals in samples of high concentration on 1-octene or after fast cooling. The Lorentz-uncorrected values of long period L was estimated from the SAXS peaks, and served together with the volume WAXS crystallinity for calculation of the crystal thickness L_c on the basis of the two-phase model as performed for example by Nitta et al.[13] The average crystal thickness at room temperature decreases from about 8.5 nm in slowly cooled EOC with 4.6 mol % to 4.8 nm after quenching. The copolymers with 14.3 mol % exhibit a crystal thickness of about 2 nm, almost independent of the thermal history. Table 2 finally includes the average ethylene sequence length which is controlled by the SCB concentration.Figure 1 shows AFM phase images of slowly cooled (a and c) and quenched (b and d) poly(ethylene-*co*-1-octene) with an 1-octene content of 4.6 (a and b) and 10.1 (c and d) mol %, respectively. In the case of slowly cooled samples with medium 1-octene content, well organized and laterally extended lamellae can be seen clearly. The quenched specimen of the same composition, in contrast, exhibits exclusively lamellae which are not organized within stacks and which are considerably shorter. While the slowly cooled copolymers of high 1-octene content show still very fine and random oriented lamellae for quenched preparations the discrete lamellae already cannot be observed. Thus, the ascertained trends concerning the change of the crystal morphology as a function of the cooling rate during nonisothermal melt crystallization for the copolymers of higher concentration on 1-octene are similar to recent investigations of several authors.[18−20,28] Additionally, it should be pointed to the transition of the lamellar crystal morphology at low concentration on 1-octene to increasingly disordered lamellae/fringed micelles at high 1-octene content in accordance with the results of mentioned works.[18−20,26−28]

3. Results

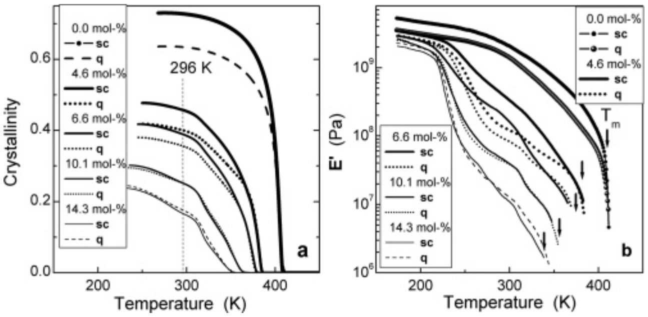

Figure 2. Effect of the comonomer content and of the thermal history on the temperature dependencies of the enthalpy-based crystallinity (a) and of the storage modulus E' (b) at 1 Hz for HDPE and EOC. Slowly cooled (at -1 K/min) and quenched samples are marked as sc and q, respectively.

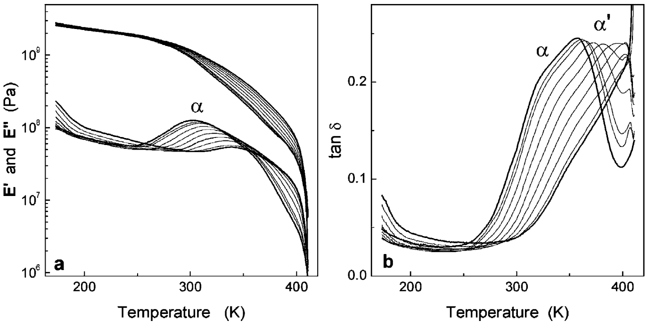

Figure 3. Temperature dependence of the storage and loss modulus E' and E'' (a) and of the loss tangent tan δ (b) for quenched HDPE at frequencies of 0.215, 0.351, 0.464, 1.0, 2.15, 4.64, 10.0, 21.5, 46.4, and 63.0 Hz. The curves shift toward higher temperature with increasing frequency.

Figure 2 shows the crystallinity (a) and the storage modulus E' (b) of slowly cooled and quenched HDPE and EOC of different 1-octene content as a function of temperature. The crystallinity decreases with increasing temperature and with increasing 1-octene content according to the ethylene sequences length distribution, as is established by former studies.[26,28,30] There is observed a tight correlation between the crystallinity and the storage modulus in the temperature range from glass transition to melting point for all samples. Simultaneously the steplike decrease of the storage modulus E' with increasing temperature in the temperature range of the glass transition is large in particular in the case of the low-crystalline copolymers, i.e., for copolymers with high comonomer content. A further, more diffuse and substantially smaller steplike change is observed in the temperature range of the α-process.

With increasing cooling rate during melt crystallization a decrease of the storage modulus E' is seen, whereas for the copolymers with medium SCB concentration larger values of E' were registered. The effect of the thermal history on the crystallinity and the corresponding change of the storage modulus E' is rather small at higher SCB concentration.In Figure 3, the isochronous temperature dependences of the loss modulus E'' and the loss tangent tan δ for HDPE are presented which show that the β-process is suppressed in the analyzed frequency range. The α-relaxation in HDPE causes an intense peak in the curve of loss modulus vs temperature $E''(T)$, and it appears as shoulders in the temperature dependence of the loss tangent tan $\delta(T)$, respectively, independent of the thermal history.Quenched HDPE shows an additional α′-relaxation (see Figure 3) with the characteristic temperature $T_{\alpha'|1\mathrm{Hz}} = 374$ K at the frequency of 1 Hz and the activation enthalpy $\Delta H_{\alpha'} = 101$ kJ/mol. The

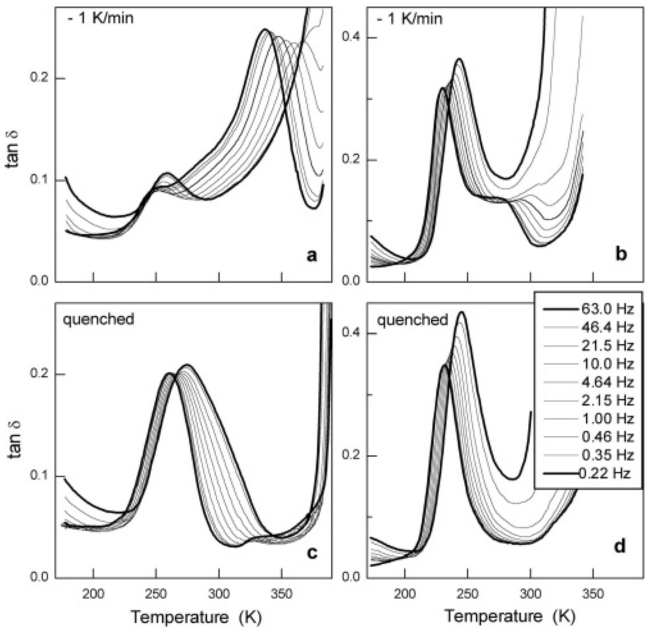

Figure 4. Effect of thermal history and of frequency on the loss tangent tan δ as a function of temperature for EOC with 1-octene content of 4.6 mol % (a, c) and 14.3 mol % (b, d). The cooling rates of the samples from the melt and the used frequencies are indicated in the legends.

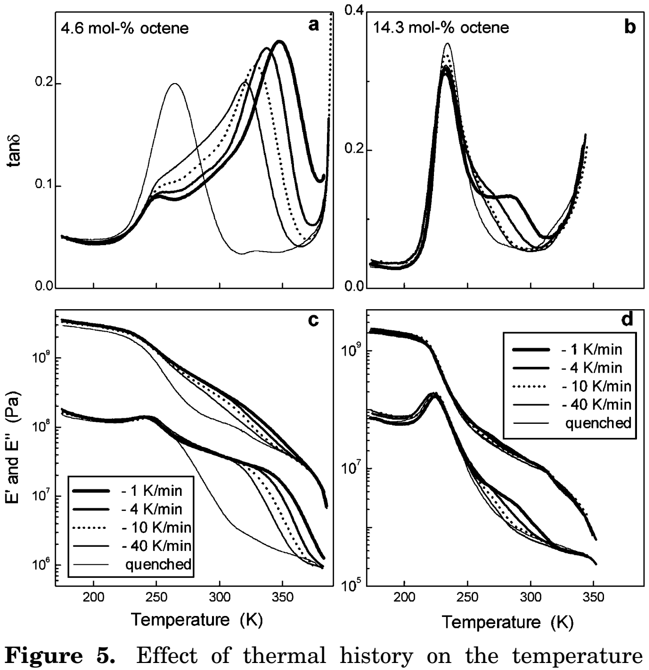

Figure 5. Effect of thermal history on the temperature dependence of the loss tangent tan δ (a, b) and of storage E' and loss modulus E'' (c, d) at a frequency of 1 Hz for ethylene-1-octene copolymers with 4.6 (a, c) and 14.3 mol % (b, d) of 1-octene.

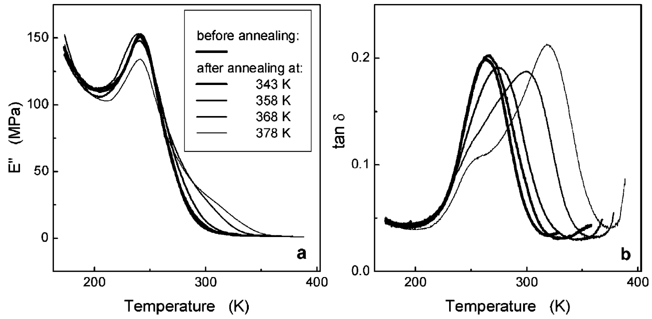

Figure 6. Temperature dependence of the 1-Hz loss modulus E'' (a) and loss factor tan δ (b) for a quenched EOC with 1-octene content of 4.6 mol % before and after annealing for 1 min at various temperatures (see legend). The heating rate was 2 K/min.

molecular origin of α′-relaxation has not yet been convincingly clarified up to now.

Contrary to the quenched branch-free HDPE, the α-relaxation in *all* quenched ethylene-1-alkene copolymers was completely suppressed independent of the type and the content of comonomer, as shown in Figures 4 and 5. This effect is caused by the presence of SCB into the copolymers.

In contrast to recently published results of Minick et al.,[18] Bensason et al.,[19] and Chen et al.,[20] in the present investigation the α-relaxation was observed also in EOC with higher SCB concentration (14.3 mol % 1-octene) if the samples were slowly cooled from the melt. The α-relaxation appears in this case as shoulder at the β-peak in the tan $\delta(T)$ curves. The shift of the shoulder to higher temperatures with increasing frequency (Figure 4b) is evidence of the relaxation nature of the transition. For quantitative estimation of the characteristic temperature of the α-process, the contribution of the superimposed β-relaxation was subtracted.

In general, the increase of the cooling rate during melt crystallization results in a reduction of the temperature and intensity of the peaks and/or shoulders of $E''(T)$ and tan $\delta(T)$ caused by the α-relaxation as well as in a decrease of α-relaxation strength, i.e., the change of $E'(T)$ generated due to α-process (see Figures 4 and 5). This applies both to medium and high SCB concentration. The β-relaxation strength and the intensity of the β-peaks, in contrast, increase with increasing cooling rate during the crystallization of copolymers. The temperature and intensities of the α-peaks measured at constant frequency decrease regular with increasing SCB concentration or cooling rate during the crystallization, respectively. The intensity of the β-peak increases with increasing cooling rate from the melt at a medium content of 1-hexene/1-octene of $\lesssim$6 mol %. A distinct increase is seen for the quenched samples. Unexpectedly, the temperature of the β-peak increases with increasing cooling rate during crystallization at constant SCB concentration (see Figures 4a,c and 5a,c). However, for the copolymers with high SCB concentration, the temperature of the β-peak remains practically unchanged at constant measuring frequency, and the intensity of β-peak increases only weakly with increasing cooling rate during crystallization (see Figures 4b,d and 5b,d).

It should be noted that the α- and β-relaxations in EOC are shifted to lower temperatures with increasing SCB concentration, in accord with studies of the authors.[19−24] The intensities of the α- and β-peaks show at the same time a decrease and an increase, respectively. This behavior was observed in the entire investigated frequency range. The shift of the α-peak of HDPE and of the α- and β-peaks of EOC toward higher temperature with increasing frequency (see Figures 3 and 4) is evidence for the relaxation nature of α- and β-processes in HDPE and EOC.Figure 6 illustrates the influence of the temperature of short-term annealing on the mechanical relaxation behavior of the quenched EOC samples with medium SCB concentration. The annealing was carried out for 1 min during the DMA measurements at successive increasing temperature.

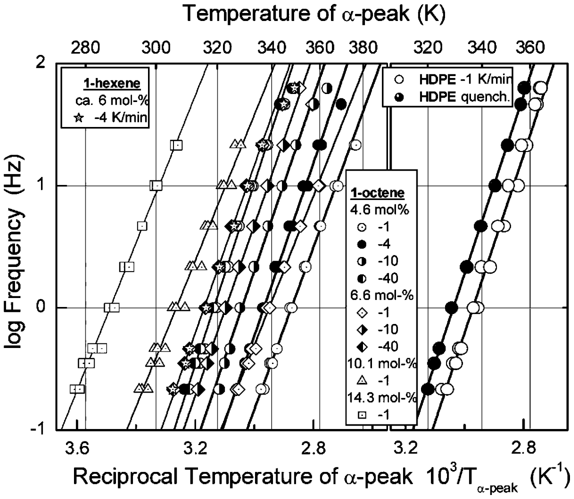

Figure 7. Arrhenius plots of HDPE and ethylene-1-alkene copolymers with different comonomer content and thermal history in the temperature range of the α-relaxation based on loss tangent peaks ($T_{\alpha-\mathrm{peak}}$). The composition and the cooling rates of specimens from the melt are given in the legends.

Originally, the temperature dependences of E'' and tan δ show only one β-peak, which is typical for all quenched copolymer samples. An increase of the temperature and weak broadening of the existing β-peak is only observed at an annealing temperature of 358 K. A further increase of the annealing temperature leads to the development of a separate α-peak. The temperature and intensity of the α-relaxation become considerably larger with increasing annealing temperature. The temperature and intensity of the β-relaxation, in contrast, decrease with increasing annealing temperature. The tan $\delta(T)$ and $E''(T)$ dependencies are similar to those of the slowly cooled preparations of identical comonomer content after annealing at high temperature. Thus, the described behavior points to distinct crystal perfection due to annealing or recrystallization near the ultimate melting point T_m in quenched EOC samples. The Arrhenius plots shown in Figure 7 are based on the temperatures of the α-peak which were determined from isochronous tan $\delta(T)$ curves at different frequencies (Figures 3 and 4). The data were analyzed using the following equation of the absolute rate theory:[39]

$$\ln(\pi f) = \ln(k_B T_\alpha/h) + \Delta S_\alpha/R - \Delta H_\alpha/(RT_\alpha) \quad (1)$$

with

$$\Delta G_\alpha = \Delta H_\alpha - T_\alpha \Delta S_\alpha \quad (2)$$

ΔG_α is the Gibbs free energy of activation, ΔH_α is the activation enthalpy, ΔS_α is the activation entropy, and T_α is the characteristic temperature of the α-relaxation at the frequency f. k_B, h, and R are the Boltzmann constant, the Planck constant and the gas constant, respectively.

From the slope and the position of the Arrhenius plots ΔH_α was determined, which occasionally is termed as activation energy, and the characteristic temperature of the α-relaxation $T_{\alpha|1\mathrm{Hz}}$ at a frequency of 1 Hz, respectively. The ΔS_α and ΔG_α values were computed using eqs 1 and 2 for f = 1 Hz and $T = T_{\alpha|1\mathrm{Hz}}$. In a similar way, the data evaluation was done for the β-relaxation. The results determined for the α-relaxation are summarized in Table 3. The comparison of the data collected in Tables 2 and 3 shows that the characteristic temperature of α-relaxation, as expected according to theory,[1] is reduced with decreasing crystal thickness as a result of both the cooling rate during crystallization and the SCB concentration. ΔG_α values changes in qualitatively similar way, although, the determined changes are not large. In the comparison to this fact, the increase of the ΔH_α and ΔS_α values with increasing cooling rate during crystallization and at a constant SCB concentration is especially remarkable (see Table 3). It should to be emphasized that the EHC samples exhibit qualitatively the same trend although the presented results are based with priority on the investigation of EOC.

Table 3. Effect of Comonomer Content and Thermal History on Relaxation Parameters and Crystallinity of Ethylene-1-Alkene Copolymers

sample						
1-alkene type[a] content, mol %	cooling rate from the melt, K/min	$T_{\alpha\|1\mathrm{Hz}}$, K	ΔH_α, kJ/mol	ΔS_α, J/(K·mol)	ΔG_α, kJ/mol	χ_c^{Dens}, %
0	−1	337	139	177	80	68.3
	quenched	329	140	189	78	58.5
O 4.6	−1	348	127	128	82	41.9
	−4	337	135	164	80	40.9
	−10	329	136	177	78	40.7
	−40	319	142	209	75	40.1
H ca. 6	−4	316	129	173	75	31.3
O 6.6	−1	339	117	109	80	33.3
	−10	323	132	173	76	32.8
	−40	315	131	180	74	31.3
O 10.1	−1	306	114	137	72	18.8
O 14.3	−1	287	115	166	67	12.9

[a] Key: **O** = 1-octene; **H** = 1-hexene.

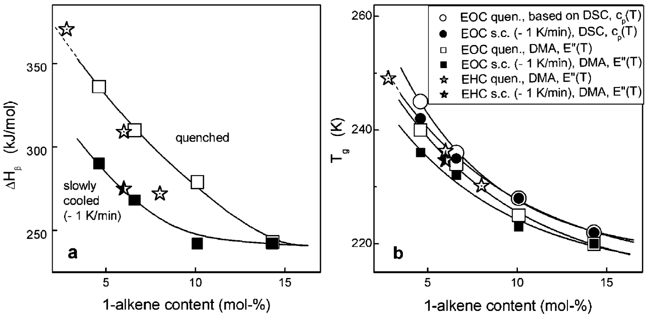

Figure 8. Effect of the comonomer content and the thermal history on the apparent activation enthalpy ΔH_β of cooperative segmental mobility based on E'' (a), and on the glass transition temperature T_g (b).

Since preceding investigations[13,19−24] were usually carried out at a single frequency of 1 Hz, the influence of the thermal history and the SCB concentration on the apparent activation enthalpy ΔH_β and on the characteristic temperature of the β-relaxation T_β of ethylene-1-alkene copolymers were examined in the present work for the first time. The determined notably large ΔH_β values permit an unambiguous assignment of the β-relaxation to the cooperative segmental mobility. The glass transition temperature T_g was determined both as a characteristic temperature of the β-relaxation $T_{\beta|0.1\ \mathrm{Hz}}$ at a frequency of 0.1 Hz ($T_{\beta|0.1\mathrm{Hz}} \equiv T_g$) and as a peak temperature from the first derivative of the thermal capacity vs temperature, dc_p/dT, in the range of the glass transition. T_g and ΔH_β values decrease considerable with increasing SCB concentration (Figure 8). Figure 8 shows that the observed dependencies are unique for all types of copolymer (EOC or EHC).

Simultaneously the slowly crystallized medium 1-alkene content show unexpectedly lower T_g and ΔH_β values than the quenched samples of the same composition. It should be noted that the slowly cooled samples possess a somewhat higher crystallinity than the quenched samples (see Table 2 and Figure 2a). The T_g and ΔH_β differences between slowly cooled and quenched copolymers decrease with increasing comonomer content and approach zero at a 1-octene content of 14.3 mol %. Thus, the thermal history has practically no influence on the β-relaxation and therefore on the T_g and ΔH_β values of the ethylene-1-alkene copolymers with high comonomer content and accordingly with lower crystallinity.

4. Discussion

Dynamic-Mechanical Relaxation Spectra of Ethylene-1-Alkene Copolymers. It is usually assumed that the SCB are not incorporated into the crystal lattice,[18−20,26−28] which is certainly correct if the crystallization occurs at low cooling rates, i.e., at moderate supercooling. In this connection, it should be noted that the average values of the crystallite thickness, L_c, for quenched samples agree best with the average ethylene sequence length $\langle L_{ES}\rangle$ (see Table 2). This supports the assumption that the SCB are excluded from the lattice during the crystallization. The assumption agrees also with the reduction of the crystallinity and the crystal size which is observed by the increasing SCB concentration and/or by the increasing cooling rate from the melt. Because of the rejection of branches during the crystallization the local SCB concentration within the amorphous regions increase with increasing crystallinity at constant average SCB concentration. The consequence for the amorphous phase would be the increase of the free volume and the dilution of the cooperativity of segmental mobility in the amorphous regions. In other words, this effect leads to size reduction of cooperatively rearranging regions and to an increase of the effective chain flexibility, i.e., to the decrease of the apparent activation enthalpy of the β-relaxation and the glass transition temperature, respectively. Such a behavior was experimentally confirmed (Figure 8). Moreover, the proposed explanation agrees also well with the increase of ΔH_β and T_g differences between quenched and slowly cooled preparations at decreasing SCB concentration and increasing crystallinity. On the other hand, the crystal perfection and the decrease of the restriction of the amorphous phase caused by the crystals can also be responsible for the effects mentioned above and which are due to the decrease of the *specific* crystal surface. The disadvantage of the above-described assumption about the branch rejection from crystals is the inability to explain the suppression of the α-relaxation in branched polyethylenes at rapid crystallization and/or high SCB concentration.

By rapid cooling or quenching of the samples, the primary crystallization occurs at larger supercooling and accordingly with larger rates. Therefore, it cannot completely be excluded that individual SCBs are inserted into the crystallites. The inserted SCB blocks the 180° flip mobility of folded chains, which is the basis of α-relaxation and the connected chain-sliding diffusion. The concentration of such defects in crystals should be increased with increasing SCB concentration and increasing crystallization rate. The hypothesis about the inclusion of the SCBs into the crystallites agrees with the above-mentioned increase of the crystal lattice constants a_0 and b_0, i.e., with the increase of the distance between the neighboring chains with increasing cooling rate during crystallization and/or SCB concentration. However, for sterical reasons it is difficult to imagine that a SCB can be incorporated into the crystal lattice.

The experimental results represented in the previous section should be obviously explained by the strong influence of the local SCB concentration in the crystalline interface on the mechanical relaxation behavior of the ethylene-1-alkene copolymers. The described relaxation behavior can be better explained if it is assumed that the installation of SCB occurs only on the fold surface of the crystallites. It is obvious that the chain which contains a SCB on the fold surface cannot participate in the translation mobility. The slide of an appropriate section of the molecular chain through the crystal is then blocked even if the rotation component of the molecule mobility still remains. The crystallization rate increases rapidly and the diffusion rate of the molecule chains decreases drastically with increasing cooling rate. Therefore, for kinetic reasons the SCBs can be frozen at the crystal surface. If the SCB cannot generally be incorporated into the crystal, that should entail the appearance and thereafter the increase of gradients of SCB concentration in the crystalline interface, which are directed into the crystal. Thus, the local SCB concentration on the crystal surface and therefore the number of blocked crystal stems grow with increasing cooling rate. In addition, the subsequent development of the mechanical α-process in the amorphous phase is also hindered due to SCB, which are aggregated in the crystal−amorphous interface. Under extreme conditions of quenching the branch points predominate on the both sides of fold surfaces of the crystals, and the mechanical α-process is therefore completely suppressed.

The need for consideration of the crystal−amorphous interface as separated fraction by the development of physical models for semicrystalline polymers was shown first by Menczel and Wunderlich.[40] As the subsequent development of this idea the concepts of rigid and mobile amorphous fractions were introduced.[41] Thus, in terms of a three-fractions model, the rigid amorphous fraction in branched polyethylenes is responsible for blocking the molecular α-mobility and in particular chain-sliding diffusion in structures with poor crystals. It should be noted here that we attempt not to generalize this statement for other polymers including a linear polyethylene.

α-Relaxation. The qualitative model which is presented above allows a noncontradictory discussion of the characteristics of the dynamic-mechanical relaxation behavior of ethylene-1-alkene copolymers. Slow crystallization and low supercooling lead to the development of perfect crystals and therefore to a clear appearance of the α-relaxation both in short-chain branched ethylene copolymers and in branch-free HDPE. Crystals containing a high local concentration of SCB at the fold-surface are formed at high cooling rates and high average SCB concentrations. Therefore, the molecular α-mobility in such crystals is constrained. In this connection, the α-relaxation is suppressed in quenched ethylene-1-alkene copolymers while the intensity of the α-relaxation in branch-free HDPE remains nearly unchanged compared to slowly cooled preparations.

The RT−TT model[1] predicts the reduction of the temperature and the activation energy of the α-relaxation with decreasing lamella thickness. For the examined ethylene-1-alkene copolymers, only a qualitative agreement with this prediction was observed for both the temperature and the Gibbs free energy of activation of the α-relaxation. The relationship between the temperature and activation energy of the α-relaxation, respectively, and the lamellar thickness is predicted for defect-free crystals. The restrictions caused by the accumulation of defects at the crystal−amorphous interface are therefore not considered.

Apart from the formation and propagation of twist mismatch the segment-exchange of the molecule between the amorphous and crystalline phase is also necessary for the mechanical activity of the α-relaxation.[3,4,10,17] This is connected with the overcoming of an additional energy barrier. The activation enthalpy is associated with the height of the potential barrier between two equilibrium states. Both characteristics (ΔH_α and ΔS_α) increase with increasing cooling rate during melt crystallization at constant SCB concentration (see Table 3), although, the lamellar thickness (see Table 2) and characteristic temperature T_α decrease at the same time. Obviously, the change of ΔH_α mirrors the increase of the potential barrier for segment exchange between the amorphous and crystalline phases.

Activation entropy of α-relaxation reflects apparently a change of state in those molecular chains, which participate in molecular α-mobility inside the crystallites and in further transfer of this mobility through the crystalline interface and the amorphous phase. Within the framework of this assumption the increasing activation entropy and, correspondingly, the decreasing initial entropy of the relaxing chains with increasing local SCB concentration on the crystalline interface is explained by the restriction of the mobility of these chains caused by SCB. The great values of activation entropy of α-relaxation (low values of the initial entropy of the relaxing chains) in linear polyethylene are obviously explained by the strong restriction of chain mobility in the amorphous phase of linear polyethylene (e.g., “tie” molecules).

Heating of EOC samples with a 1-octene content of 4.6 mol % to temperatures above 360 K results in the perfection of less-organized and thin crystals by melting and recrystallization. During annealing and following slow cooling, the new crystals are formed with an interface containing a substantially smaller amount of SCB. The higher the annealing temperature, the larger is the average crystal thickness of the new population and correspondingly the higher is the temperature of the α-relaxation (see Figure 6).

***β*-Relaxation.** The restriction of cooperative segmental mobility is reduced with increasing SCB concentration as it is shown by the decrease of apparent activation enthalpy of the β-relaxation ΔH_β and of glass transition temperature T_g (Figure 8). This effect is primarily explained by the decrease of total crystal surface connected with the decrease of crystallinity. Furthermore, the loosening of amorphous phase due to short-chain branches and the connected reduction of the size of cooperatively rearranging regions contribute obviously to the decrease of ΔH_β and T_g. The decrease of apparent activation enthalpy of the β-relaxation ΔH_β and of glass transition temperature T_g with decreasing cooling rate during crystallization at constant SCB concentration is due to the influence of several factors:[42] (1) decrease of restriction of the cooperative segmental mobility generated by crystals, caused both by a reduction of specific crystal surface as a result of growth of average crystal size and by a some “decoupling” of amorphous phase and crystals with a better ordered surface (in accordance with the distinct appearance of α-process only in slowly cooled samples); (2) the additional loosening of the amorphous phase in slowly cooled samples, caused by complete rejection of branches from the crystals and more uniform distribution of rejected branches in the amorphous phase compared to rapid crystallized samples.

The perfection and area of the crystal surface become less important due to the decrease of the crystallinity and the replacement of more perfect lamellar crystals by disordered lamellae/fringed micelles with increasing SCB concentration.

5. Conclusions

On the basis of a comparative experimental investigation of the dynamic mechanical relaxation of ethylene-1-alkene copolymers with controlled crystal morphology a model is proposed in order to qualitatively explain the effect of SCB concentration and thermal history on the α- and β-processes of molecular mobility. A complete rejection of SCB from the core of crystals independent from crystallization conditions and an increasing accumulation of SCB on and near the fold surface in lamellar crystals with increasing cooling rate during crystallization and/or with increasing SCB concentration are suggested. The results of the investigation allow one to draw the following conclusions:

In contrast to quenched HDPE the α-relaxation in quenched ethylene-1-alkene copolymers in a wide range of composition is completely suppressed. This phenomenon is due to a kinetically forced installation of SCB on the fold surface of lamellar crystals during rapid crystallization. The trapped SCBs block the translation motion of crystal stems.

The temperature and intensity of the α-relaxation increase distinctly with decreasing SCB concentration and/or cooling rate during crystallization as well as with increasing annealing temperature, caused by an increase of the lamella thickness. This behavior agrees qualitatively with theoretical predictions. The enthalpy and entropy of activation of the α-relaxation, in contrast, increase noticeable with increasing cooling rate during crystallization at constant average SCB concentration. These changes mirror the increasing hindrance of molecular segment exchange due to the increasing locale concentration of branch points.

The β-relaxation is attributed to the cooperative segmental mobility which is justified by extraordinary large values of the apparent activation enthalpy and relaxation strength. The reduction of the restriction of amorphous phase with increasing SCB concentration is caused by a decrease of the total crystal surface connected with reduction of the crystallinity and leads to a decrease of glass transition temperature, and apparent activation enthalpy of β-relaxation.

The decrease of the glass transition temperature as well as apparent activation enthalpy of the β-relaxation in slowly cooled ethylene-1-alkene copolymers in comparison to quenched samples of same composition is due to a reduced specific crystal surface and therefore reduced restriction of the amorphous phase. The effect is drastically reduced with increasing SCB concentration due to the decreased crystallinity.

Acknowledgment. The authors gratefully acknowledge financial support by Deutsche Forschungsgemeinschaft (DFG). EOC samples were kindly provided by Omya GmbH (Germany). Thanks are due to Dr. C. Gabriel (Friedrich Alexander University Erlangen-Nürnberg, Germany) and Dr. R. Adhikari (Martin Luther University Halle-Wittenberg, Germany) for the molecular characterization and for assistance in preparation of AFM micrographs, respectively. Special thanks go to Dr. S. Funari (HASYLAB, DESY, Hamburg, Germany) and Priv.-Doz. Dr. N. Stribeck (University of Hamburg, Germany) for assistance in performing of SAXS experiments.

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MA0493776