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Mechanical α-Process in Polyethylene[†]

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Introduction. Although the origin and the underlying mechanisms of the mechanical α-process in polyethylene have been extensively studied,[1−8] there is still no general agreement about the microscopic origin. Two points are mainly discussed: first, whether there are two α-processes (α_I and α_{II} in the order of increasing temperature) as often seen in measurements using dynamic mechanical analysis (DMA)[5,7−15] or whether there is only one high-temperature process as observed in nuclear magnetic resonance (NMR)[16−27] and dielectric spectroscopy measurements;[1] second, even if the existence of the two α-processes is accepted, there is no agreement as to whether they are both due to processes in the crystalline phase or whether one of them is linked to the amorphous phase. On one hand, many authors believe that the α_I-process is due to the interlamellar amorphous phase because the β-process often is not seen in the DMA data of high-density polyethylene (HDPE);[28] it is thought that the α_I-process coincides with the β-process, which is shifted to high temperatures because of the constraints imposed by the high entanglement density in the amorphous phase after crystallization. On the other hand, pioneering work of Takayanagi has led to an assignment of the α_I-process to an intralamellar slip process of mosaic blocks.[8] This process can be identified with the block slip process postulated by Strobl et al.[29,30] Different from the α_I-process, there is agreement about the assignment of the α_{II}-process: it is believed that the α_{II}-process is due to the diffusion-like motion of polymer segments in the crystals.[3,4,7,8]

In this report, we present a comparative study on the dynamic mechanical properties of three selected polyethylene samples with similar crystallinity, melting behavior, and long period but with different molecular weight distributions, branch content, and branch length to clarify the existence of the two α-processes and to clarify the assignment of the α_I- and α_{II}-processes. Our results support the original assignment of Takayanagi that the α_I-process is due to the intralamellar block grain boundary slip process and the α_{II}-process is due to the diffusion-like motion of chain segments in the crystallites.

Experimental Section. Polyethylene samples used in this work were provided by Basell Polyolefine GmbH. Samples were prepared by compression-molding the pellets into sheets with a thickness of about 2 mm at 190 °C for 5 min. Crystallization occurred during cooling in the press to room temperature at a rate of 15 K/min. Some key parameters for the three samples are summarized in Table 1. It can be concluded that the three samples used in this study show similar properties with respect to melting behavior, crystallinity, long period, and lamellar thickness, though they differ with respect to their branch content and the different molar mass fraction. They thus provide a suitable set of samples for comparative studies of their DMA behavior.

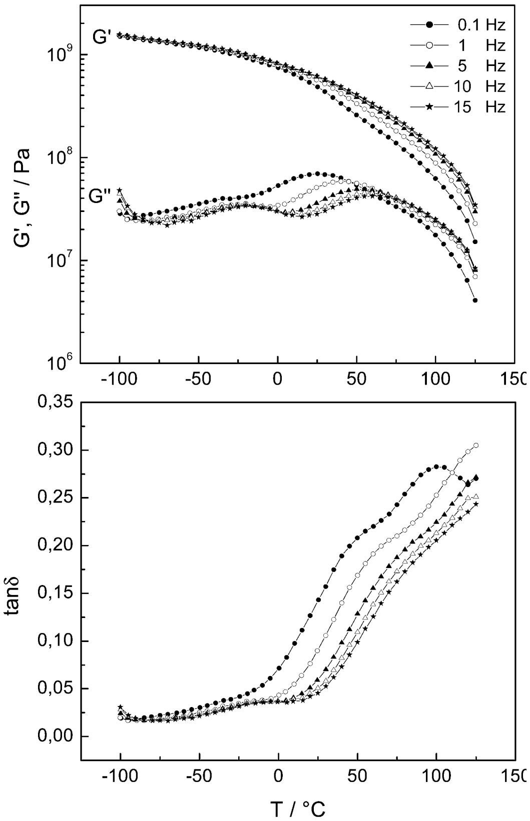

Figure 1. PE3: Temperature dependence of the storage (G') and loss modulus (G'') (top) and the loss factor (tan δ) (bottom) at different frequencies.

DMA measurements were preformed in a Rheometrics RDA II instrument in torsional mode. Samples (with a dimension of 2 × 10 × 40 mm) were heated from −100 to 125 °C with isothermal steps of 5 K and a waiting time of 180 s. Frequency scans, from 0.1 to 15 Hz, were carried out at the different temperatures. The strain used in the measurements was 0.2%.

Results and Discussion. As an example, Figure 1 shows typical DMA results for sample PE3. In the curves of G'', at least three thermally activated process can be readily distinguished. They are the γ-process characterized by an upward curvature of G'' for temperatures lower than about −80 °C, the β-process indicated by the peak in the range from −60 to 10 °C, and the α-process demonstrated by the peak located between 20 and 75 °C, depending on the frequency. The peak position of the γ-process is known to be in the vicinity of −120 °C,[5] which lies out of the range of our measurements. The β-process is generally assigned to cooperative processes in the interlamellar amorphous phase. It is often called the dynamic mechanical glass transition.[31] It is thus clear that the high temperature α-process must be related to the crystalline phase. A closer look at the G'' curves in the temperature range of the α-process provides two interesting results. First, the shape of the peaks is asymmetric; this effect

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[†] Dedicated to the memory of Prof. Bingzheng Jiang.

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Table 1. Basic Characterizations of the Three Samples

sample name	$M_w \times 10^5$	M_w/M_n	MWD	branch type	branch content 1/1000C	melting point[a] (°C)	crystallinity[a] (%)	long period[b] (nm)
PE1	3.9	22	unimodal	C_4H_9-	2	134	64	23
PE2	3.3	38	bimodal	C_2H_5-	3.7	134	67	23
PE3	4.4	44	bimodal	C_4H_9-	3.1	135	66	26

[a] Deduced from differential scanning calorimetry (DSC) measurements, for crystallinity calculation, an ideal value of heat of fusion of 100% crystallinity $\Delta H_{id} = 293$ J/g was used. [b] Deduced from small-angle X-ray scattering (SAXS) measurements.

becomes more pronounced for the data taken at 0.1 Hz where an additional shoulder becomes visible. Second, the magnitude of the α-process —as seen in G''— decreases with increasing temperature, indicating a temperature-dependent change in the structural mechanisms that are responsible for the α-relaxation. This effect can also be found in the curves of G' where the storage modulus drops dramatically when the temperature is raised from 0 to 100 °C. It is to be noted that the crystallinity of the sample exhibits only minor changes in this temperature range. The observation of the multiple relaxation feature at high temperatures is also confirmed in the plots of tan δ as a function of temperature (Figure 1). Although curves taken at frequencies larger than 1 Hz do not present two peaks, the multiplicity of the α-process is obvious because the relaxation corresponding to the peak in G'' appears as a shoulder in tan δ located a few kelvin above that of the peak position in G''. Moreover, when the frequency is low enough, i.e., in our case 0.1 Hz, one finds clear evidence for two peaks. It is thus clear that the lack of the second peak at high frequencies is due to the melting of the crystals prior to the full activation of the α_{II}-process. By separating the α-process into α_I and α_{II}, Takayanagi[8] had pointed out this remarkable feature and showed that the relaxation magnitude for α_{II} remains constant at different temperatures. He also showed that the high-temperature relaxation behavior of a PE single crystal mat is thermorheologically simple. It appears that the α_I-process in PE is a feature of the melt-crystallized polyethylene. Indeed, crystallization of a polymer from the melt often yields a blocky substructure of crystalline lamellae, which can be directly viewed by using atomic force microscopy (AFM).[30,32] The origin of this blockiness of lamellae has been considered as an intrinsic property of the melt crystallization of polymers.[30] The assignment of the α_I-process in PE to the intralamellar block grain boundary slip process indicates that this relaxation process could be also an intrinsic property of the melt-crystallized polymers. To examine this, Men and Strobl[29] carried out DMA measurements on syndiotactic polypropylene, a polymer in which the chains in the crystalline phase are fixed (i.e., no sliding diffusion in the crystals),[33] and found the respective high-temperature relaxation process which then was assigned to block slip phenomena. Support of this view can also be found in a series of reports on the tensile recovery properties of semicrystalline polymers where a critical strain behavior is always found.[34−37] It has been concluded that during stretching the force is transmitted first by the crystalline network because the semicrystalline polymer systems can be viewed as two interpenetrating networks built up by the amorphous entanglement phase and the crystalline phase.[36−39] This explains the drop in G' and G'' with temperature because the viscous friction between the blocks becomes weaker at high temperatures, which reduces the ability of the crystalline network to sustain external forces.

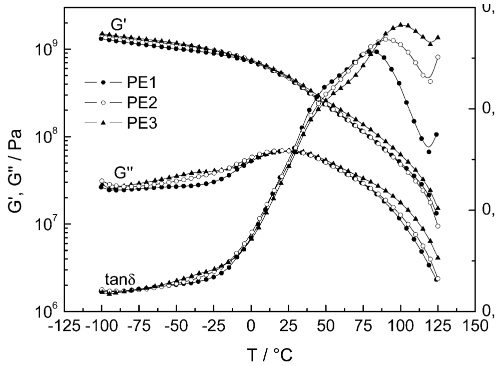

Figure 2. Comparison of PE1, PE2, and PE3: temperature dependence of the storage (G'), loss modulus (G''), and the loss factor (tan δ) at 0.1 Hz.

To further confirm the argument discussed above, we compare the DMA results for the three samples in Figure 2. Here, experimental results carried out at 0.1 Hz are shown. For all samples, two α peaks are distinguishable in the curves of tan δ. Interestingly, the position of the α_I peak is nearly the same for all samples whereas the position of the α_{II} peak varies greatly. This becomes even clearer if the curves of G'' are taken into consideration. In the curves of G'', all samples show identical relaxation magnitude and nearly identical peak position for the α-relaxation. This result agrees with the assumption of the block slip nature of the α_I-relaxation because all samples show similar crystallinity and lamellar thickness and thus a similar amount of the inner block slip interface. The large variation in the peak position of the α_{II}-relaxation in tan δ first of all excludes the correlation of this peak to the peak in G''. It, however, corresponds to the well-accepted mechanism of longitudinal chain diffusion inside crystals. The occurrence of this diffusion process is determined to a great extent by the surrounding environment of the crystals because in the DMA measurements the polymer segment diffusion-like motions in crystallites are accomplished by the motions of the chains connecting the crystalline and amorphous phases. Tightly backfolded chains at the surface of the crystals cannot transmit forces between the crystalline and the amorphous phases. It has been reported that the diffusion of the chains in the crystalline phase becomes slower when the cross-link density in the amorphous phase is increased.[17] In our case, the shift of the α_{II}-peak in tan δ is caused by increasing of the branch content and the branch length, both bringing additional constraints to the diffusion process.

The activation energy of the α_I-process was calculated on the basis of the peak temperatures of G'' at different frequencies. Figure 3 shows the corresponding Arrhenius plots for the three samples. At same frequencies, the difference in the peak temperature among different samples is less than 5 K as can also be seen in Figure 2 (G'' curves). For all samples the Arrhenius plots yield a similar apparent activation energy of about

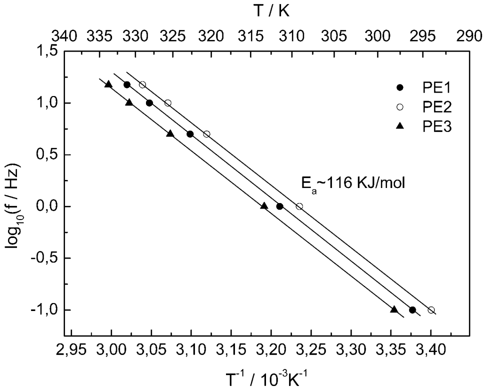

Figure 3. Arrhenius plots yield similar activation energy for the three samples. Data obtained from the peak position in G''. The solid lines are linear fits of the experimental data.

116 kJ/mol. This value is similar to that of the chain diffusion-like motions in the crystalline phase (α_{II}-process) as obtained by NMR[16] or dielectric measurements.[1] Unlike in the case of α_{II}-process, we consider the activation energy of the α_I-process an apparent one because the structure of the sample; i.e., the coupling of the blocks undergoes large variations when the temperature is changed. Therefore, the block slip based α_I-process in fact is not of the Arrhenius type (for details see ref 29). This is also evidenced by reports of some very high activation energies of the α-process in PE where experimental data were fitted within different temperature intervals in an Arrhenius plot.[12,14]

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