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Rheological Properties of a Partially Molten Polypropylene Random Copolymer during Annealing

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ABSTRACT: Semicrystalline polymers exhibit a broad melting transition. This effect is due to the lamellar thickness distribution in the materials. The melting temperature $T_m(l)$ of a given lamella increases with its thickness l. When heating to a temperature T_a in the melting range, the crystalline lamellae with $T_m(l) < T_a$ melt. This process is accompanied by the thickening of the nonmolten lamellae which suck in molten polymer chains. We used a polypropylene random copolymer as a convenient material to investigate rheological and structural aspects of this reorganizational process. The temperature and time dependence of the dynamic moduli G' and G'' in oscillatory shear flow and for the first time of the transient uniaxial elongational viscosity were measured during the reorganization of the partially molten material. Data from differential scanning calorimetry (DSC) runs on the annealed samples are correlated with the respective data from the rheological experiments. With increasing amount of crystalline material the shear viscosity function increases at small shear rates. At the same time marked strain hardening shows up in uniaxial elongation. The rheological phenomena observed during annealing at temperatures in the melting range are interpreted by assuming a network of nonmolten, growing lamellae which are connected by tie chains.

1. Introduction

Semicrystalline polymers, such as polyethylene, polypropylene, and polyamide, exhibit a broad melting range of up to 100 K and more. This effect is due to the distribution of the thickness of the crystalline lamellae. The melting temperature $T_m(l)$ of a given lamella increases with its thickness l; see ref 1. When a semicrystalline polymer is heated to a temperature T_a ($T_0 < T_a < T_m$) and kept at T_a for a given time interval τ, the thin lamellae with a thickness up to $l < l_a$ melt. T_0 and T_m are the melting temperatures of the thinnest and the thickest lamellae, respectively. In Figure 1 a typical heat-flow curve from differential scanning calorimetry (DSC) is shown together with sketches of lamellae of different thickness which melt at the respective temperatures.

It is a well-known fact that during the process of melting substantial reorganization of the polymeric chains may occur on the mesoscopic level, thus leading to a recrystallization of the already molten polymer chains into yet nonmolten lamellae: Numerous authors investigated the annealing of semicrystalline polymers at temperatures close to, but below, the ultimate melting point defined by the thickest lamellae present in the respective material.[2] Being annealed at T_a, the molten material exerts micro-Brownian motion. Driven by thermodynamic forces, chains from the amorphous (molten) regions are partially "sucked in" by nonmolten lamellae via diffusional processes; the nonmolten lamellae grow thicker. For two recent studies the reader is referred to refs 3 and 4.

The reorganization just described can be monitored indirectly by DSC as follows. The sample is annealed for a given time τ at T_a and then quenched to room temperature where the diffusional processes are essentially stopped. Now the material is heated at a constant heating rate into the melt. A typical heat-flow curve which is taken in such a run is shown in Figure 2. The first endothermic peak corresponds to the melting of material which was molten at T_a and which crystallized during (and after) quenching. The high-temperature peak is assigned to the melting of lamellae which underwent a thickening process during annealing at T_a. The fact that thickening did occur can be derived from the shift of the peak temperature toward higher temperature, as compared to the peak in Figure 1. Since the time scale of the heating is short compared to the annealing time τ at T_a, further reorganization during the DSC heating is negligible.

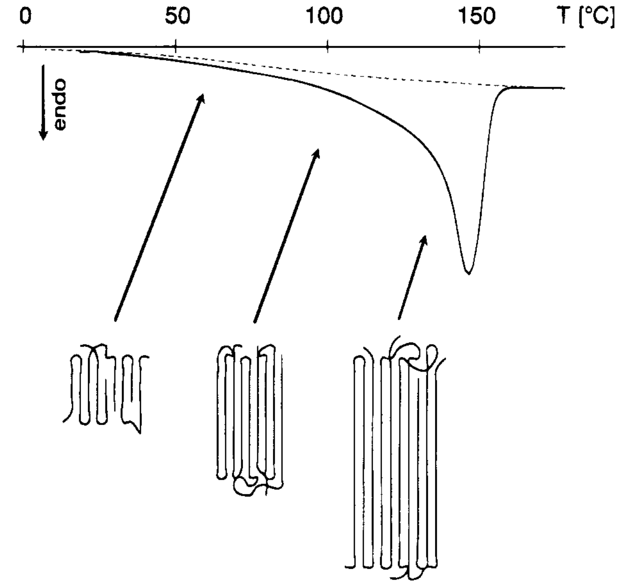

Figure 1. Heat-flow curve covering the melting transition of polypropylene. The width of the transition is due to the lamellar thickness distribution. As schematically shown, the respective melting temperature rises with the lamellar thickness.

In general, thermoplastic polymers are processed at a temperature where they are completely molten. The rheological behavior of the melt is determined by the molecular weight and the shape of the molecular weight distribution alone. The relation between shear flow properties and molecular parameters has been extensively studied and obeys well-known rules. These can

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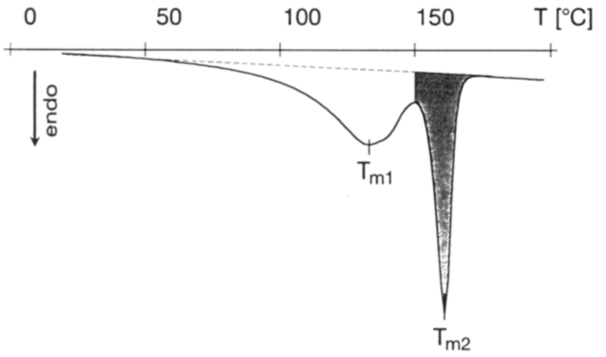

Figure 2. DSC heat-flow curve taken on a polypropylene sample which was annealed for 18 h in the melting range (at 156 °C in the rheometer) and subsequently quenched.

Table 1. Properties of the Polypropylene Random Copolymer Used in This Study

M_w	3.02×10^5
M_n	6.8×10^4
C_2 (% by wt)	2.3
mm triads (%)	95.4
mmmm pentads (%)	94.3
crystallinity (%)	42

be applied to optimize products for processes which are governed by shear deformation. In elongational flow, the data and the knowledge of the relation between molecular parameters and flow behavior are much more scarce. However, it is qualitatively understood that for this type of deformation the molecular weight distribution is less important than the structure of the polymer chain. Long-chain branched polymers are known to exhibit pronounced strain hardening and an increased elongational viscosity function. Recently, the flow behavior of linear conventional polypropylene was contrasted to branched samples.[5,6]

Interestingly, few efforts have been spent on the examination of the rheological behavior of partially molten polymers during reorganization of lamellae. One reason for this abstinence might be the experimental difficulties connected with the respective rheological measurements. A narrow temperature range and an extremely pronounced temperature dependence of the time scale for the reorganization process demand careful performance of the experiments and sophisticated temperature calibration of the instruments. It must be mentioned that rheology is used to examine the crystallization of polymers upon cooling from the melt.[7-9]

To the best of our knowledge, we present for the first time rheological measurements in shear and elongational flow geometry on semicrystalline isotactic random polypropylene under varying annealing conditions. The rheological results are compared with data from DSC. Preliminary calculations to relate shear and elongational flow data are shown.

2. Experimental Section

2.1. Measurements. The dynamic moduli G' and G'' as a function of frequency ω were measured by means of a Rheometrics dynamic spectrometer (RDS2) and an Instron rotational rheometer (Type 3250). Both instruments were equipped with cone-and-plate geometry (cone angle 2.2°, cone diameter 25 mm and cone angle 7.5°, cone diameter 40 mm, respectively). The strain amplitude was kept constant at $\hat{\gamma} = 0.05$ for all measurements with the Instron rheometer and at $\hat{\gamma} = 0.2$ for the Rheometrics instrument. Temperatures were varied between 154 and 175 °C. The complex viscosity $|\eta^*|$ was calculated from the moduli as follows:

$$|\eta^*| = \frac{1}{\omega}(G'^2 + G''^2)^{1/2} \tag{1}$$

Uniaxial elongational flow experiments were carried out with a rheometer constructed in our laboratory.[10] In this instrument cylindrical samples are stretched vertically in a silicon oil bath which is used both as a thermostat and as an eliminator of gravitational effects. Samples of an initial length L_0 of about 25 mm can be stretched to a final length L of approximately 500 mm. This corresponds to a maximum Hencky strain $\epsilon = \ln(L/L_0)$ of 3. The measurements were carried out at a constant strain rate

$$\dot{\epsilon} = \frac{1}{L}\frac{\mathrm{d}L}{\mathrm{d}t} \tag{2}$$

of 5×10^{-2} s^{-1}. From the measured tensile stress $\sigma(t)$ the transient elongational viscosity

$$\mu^+(t) = \sigma(t)/\dot{\epsilon} \tag{3}$$

was calculated. The elongational experiments were performed in a temperature range from 154 to 160 °C.

In order to guarantee an adjustment of the temperature between different rheometers, all instruments were calibrated with the same thermometer. Thermoelements were calibrated with this standard and then used to measure the temperature inside the samples in the case of the rotational rheometers. For the oil bath rheometer temperature was checked along the pathline of the filament.

The heat-flow curves were measured with a DuPont 912+990 differential thermal analyzer. The instrument was calibrated using mercury and tin for temperature and indium for enthalpy. Typical sample weights were 6−7 mg. Heating rates were chosen to be 20 K/min. The melting enthalpies ΔH were determined by integrating the area between the heat-flow curve and a tangent to the curve from room temperature to the melt region; cf. Figures 1 and 2. In addition, we determined the enthalpy ΔH_2 corresponding to the high-temperature peak as indicated by a shaded area in Figure 2. The temperatures T_{m1} and T_{m2} of the peaks were defined as shown in Figure 2.

2.2. Sample and Sample Preparation. The material used in this study was a statistical copolymer of isotactic polypropylene with ethylene. It was polymerized in a continuously running vertically stirred gas-phase reactor[11] using a silica-supported Ziegler catalyst system. Propylene and ethylene feed rates were adjusted to yield a copolymer with an ethylene content of 2.3% by weight. Triethylaluminum was used as cocatalyst and a dialkyldimethoxysilane as stereomodifier. The catalyst was prepared according to ref 12. The relevant product data are summarized in Table 1.

For the measurements in the rotational rheometers samples from the granules were molded into small disks fitting to the geometry of the rheometers. This procedure was carried out at a temperature of 190 °C, i.e., in the melt. Annealing of the samples was performed directly in the rheometer. For the elongational experiments the material was extruded at 190 °C by means of a modified melt indexer into a fluid bath of matched density. The extrudates were subsequently annealed in the oil bath of the rheometer. Pieces of length of about 25 mm and diameter of about 6 mm were then cut from the extrudates and prepared for the elongational rheometer by gluing aluminum clamps to both ends of the rods. As studied in ref 6, the absorption of oil in the sample has no influence on its rheological behavior.

3. Results

3.1. Shear Flow Data. Figure 3 shows the results of a series of oscillatory measurements with the Rheometrics dynamic spectrometer at a temperature of 154 °C, i.e., at a temperature where the material was partially molten. The cold sample was loaded into the rheometer, which was heated to 154 °C before use. The measurement was started 9 min later. The experiments

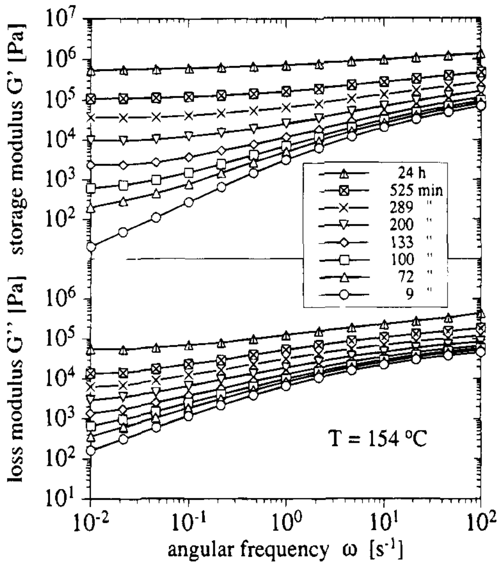

Figure 3. Storage modulus G' (top) and loss modulus G'' (bottom) versus angular frequency ω at a temperature of 154 °C. The frequency sweeps (from high to low frequency) were repeated with the same sample over a time period of 24 h.

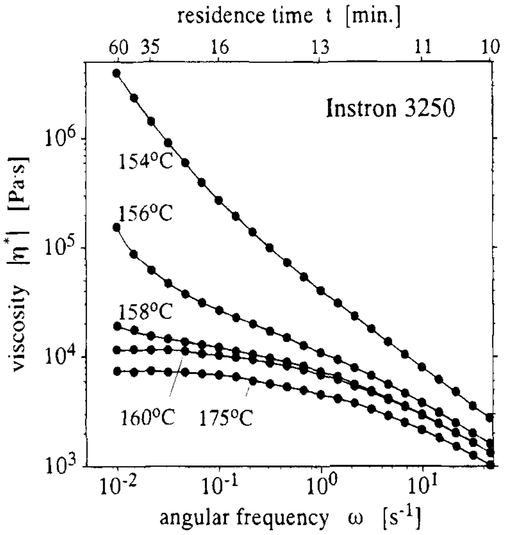

Figure 4. Viscosity functions measured for different temperatures. For each experiment a fresh sample was used. Frequency sweeps were conducted from high to low frequency. The time for a sweep amounts to 60 min. The time scale is indicated by the upper x-axis.

were performed with decreasing angular frequency from 10^2 to 10^{-2} s^{-1}. The total time for one sweep amounts to 20 min. The first sweep results in dynamic moduli which decrease with falling frequency. The flow regime in which the loss modulus G'' and the storage modulus G' are proportional to ω and ω^2, respectively, is not reached. With increasing residence time, both the storage and the loss moduli level out. The change of the slope is more pronounced for G' than for G''. This measuring sequence was performed over a time period of 24 h. The thermal stability of the sample was checked at 175 °C before. At an angular frequency of 10^{-2} s^{-1} a decrease of $|\eta^*|$ of less than 10% was found within 24 h.

Complex viscosities $|\eta^*|$ measured with the Instron rheometer at different temperatures are shown in Figure 4. For each test a fresh sample was used. Again the sweeps started with the highest frequency 9 min after loading the sample into the rheometer. With decreasing frequency the residence time of the specimen increases as denoted by the upper x-axis of Figure 4. The number of data points was chosen such that a sweep lasts 60 min in total. For temperatures larger than 160 °C viscosity functions with zero shear rate viscosity are obtained. At a temperature of 158 °C a weak viscosity increase is found with decreasing angular frequency. Further reduction of the temperature results in viscosity functions which steeply rise at small frequency. Figure 5 depicts the viscosity evaluated at an angular frequency of 10^{-2} s^{-1} as a function of temperature. This graph comprises data from a greater number of experiments than shown in Figure 4. The data points are mean values from at least three measurements. The error bars of the viscosity denote the reproducibility of the experiments. In the Instron rheometer the temperature in the sample could be controlled within ±0.5 °C. Above 160 °C the data represent the zero shear rate viscosity. The temperature dependence follows the well-known Arrhenius law with an activation energy E_0 = 45 kJ/mol. At lower temperature, an abrupt viscosity increase of more than 2 orders of magnitude within 4 °C is found.

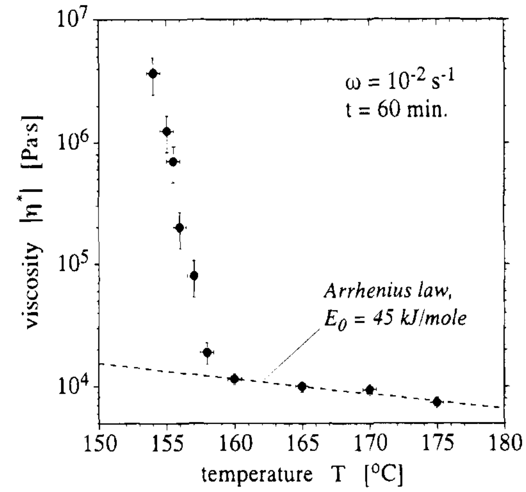

Figure 5. Temperature dependence of the viscosity evaluated at $\omega = 10^{-2}$ s^{-1} and an annealing time of 10 min. The dashed line corresponds to an Arrhenius law with an activation energy of 45 kJ/mol.

The result of a DSC measurement on a sample prepared for the rotational rheometer is shown in Figure 6a. There is a wide melting region with a maximum at 145 °C. Toward higher temperatures the melting region is sharply limited. Figure 6b shows DSC heat-flow curves for samples which were removed from the rheometer immediately after the end of measurements of the type shown in Figure 4. At 160 °C, i.e., in the melt, there is no difference in the behavior of the sample before the experiment. At 156 °C, i.e., at a temperature where the material is not yet completely molten, a second melting maximum shows up. With decreasing temperature the second melting peak is growing and the melt enthalpy of this component exceeds the one of the lower peak. The arrows in Figure 6 indicate the temperature at which the rheological experiments were carried out. Figure 7 shows the dependence of ΔH_2 on annealing time when annealing the material at 156 °C in the rheometer with continuous measurements at $\omega = 10^{-2}$ s^{-1}. The data indicate a logarithmic dependence of ΔH_2 on annealing time, $\Delta H_2 \propto \log(\tau)$. Since the total enthalpy ΔH remains essentially constant throughout the annealing time (ΔH = 100 J/g), it is evident that ΔH_2 must saturate after some time. Thus, the given

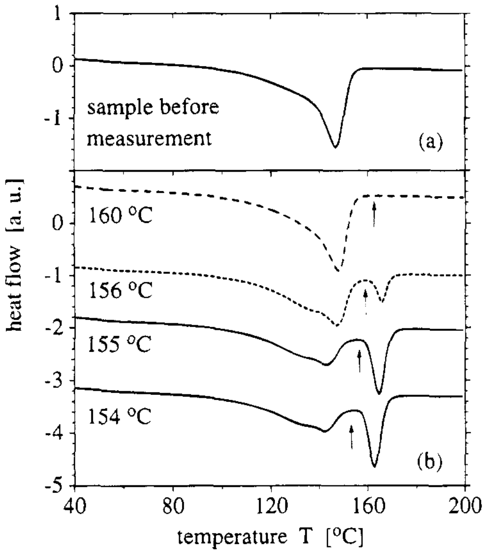

Figure 6. DSC heat-flow curves for a sample (a) as prepared for the rotational rheometer and (b) after the end of a frequency sweep of the type shown in Figure 4. The arrows indicate the temperature of the measurement.

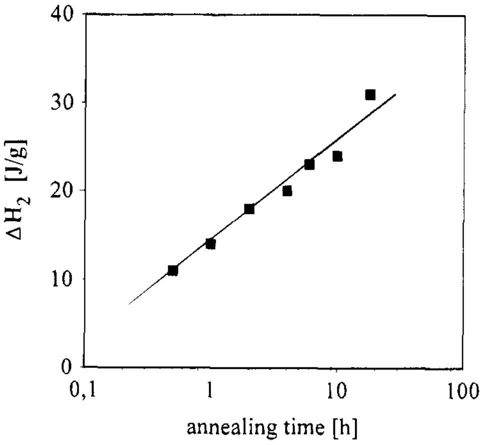

Figure 7. Dependence of the melting enthalpy of the high-temperature peak (shaded area in Figure 2) on the annealing time. Annealing was performed in the rheometer at 156 °C.

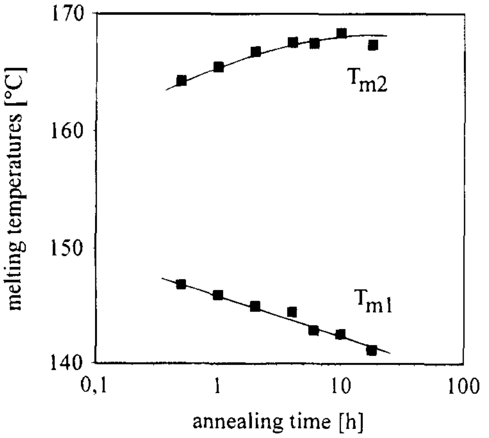

Figure 8. Dependence of the peak temperatures T_{m1} and T_{m2} on annealing time. Annealing was performed in the rheometer at 156 °C.

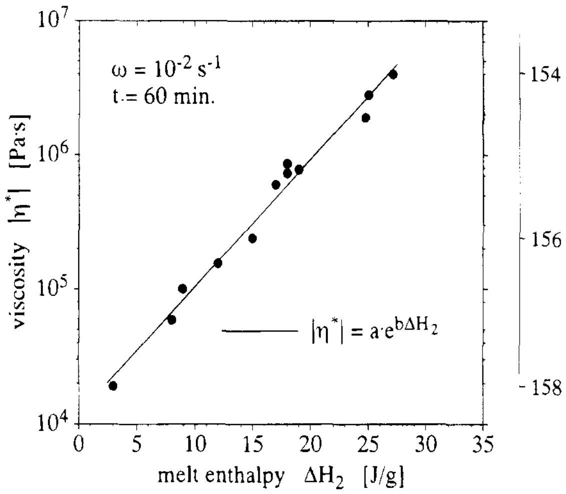

Figure 9. Viscosity $|\eta^*|$ versus melt enthalpy measured for samples removed from the rheometer after a frequency sweep from 10^2 to 10^{-2} s^{-1} which lasts 60 min.

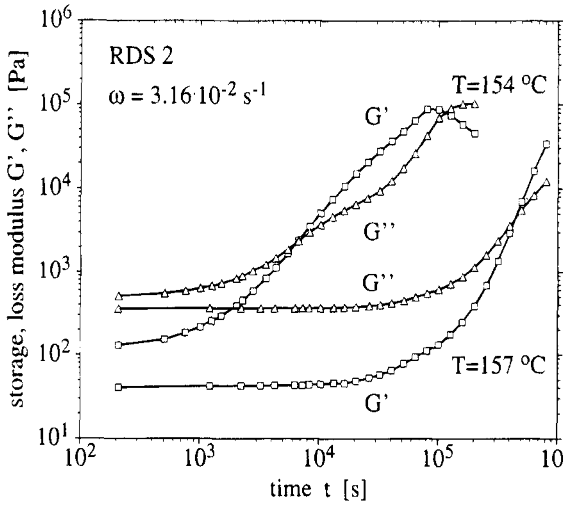

Figure 10. Storage modulus G' and loss modulus G'' as a function of time measured at a frequency of 3.16×10^{-2} s^{-1} and a strain amplitude of $\hat{\gamma} = 0.2$. At 154 °C the increase of the moduli occurs much faster than that at 157 °C.

logarithmic dependence can be valid only in a limited time interval. The dependence of the peak temperatures on annealing time when annealing at 156 °C is depicted in Figure 8. T_{m2} increases with prolonged annealing because of two effects. First, molten material recrystallizes into the nonmolten crystallites. Second, these crystallites increase in perfection and size. T_{m1} decreases upon annealing since a decreasing amount of molten chains is left for crystallization and since the crystallization of lamellae is impeded by the constrained chains. A detailed presentation of DSC and X-ray measurements on annealed polypropylene is in preparation.[13]

A plot of ΔH_2 versus viscosity $|\eta^*|$ taken at $\omega = 10^{-2}$ s^{-1} is shown in Figure 9. Again, this presentation contains more data points than shown in Figure 4. The dependence of the viscosity $|\eta^*|$ on ΔH_2 can be described by the relation

$$|\eta^*| = a \exp[b\Delta H_2] \qquad (4)$$

with $a = 1.2 \times 10^4$ Pa·s and $b = 0.22$ g/J.

Measuring the moduli G' and G'' continuously as a function of time for a given angular frequency of 3.16 × 10^{-2} s^{-1}, one obtains data as shown in Figure 10. This experiment was performed with the Rheometrics dynamic spectrometer. At a temperature of 154 °C notable increase of the moduli occurs within a 10^3 s residence time. At 8 × 10^3 s storage modulus G' and loss modulus G'' have a crossover. A second crossover is found at

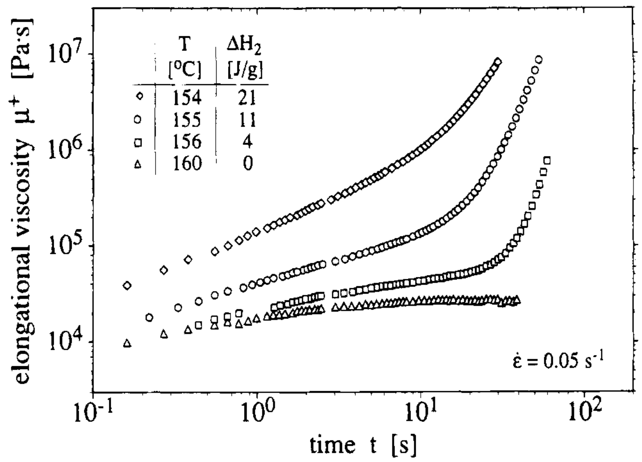

Figure 11. Transient elongational viscosity of samples annealed for 60 min at different temperatures. The melting entropies ΔH_2 measured by DSC after the experiment are listed in the inset.

about 10^5 s. The changes occur on a much longer time scale at a temperature of 157 °C. Within 10^4 s no change of the moduli is observed and the first crossover is shifted to approximately 4×10^5 s.

3.2. Elongational Viscosity. Transient elongational viscosities μ^+ measured at a strain rate $\dot{\epsilon} = 0.5$ s^{-1} and for temperatures between 154 and 160 °C are shown in Figure 11. The samples were annealed in the oil bath for 60 min before the experiment. Annealing and elongation were performed at the same temperature. At 160 °C the transient elongational viscosity does only weakly depend on the strain and reaches a nearly steady state at a time larger than 10 s. The same experiment performed at a temperature of 156 °C results in a transient elongational viscosity with notable strain hardening at a total strain larger than $\epsilon \approx 1$. Further lowering the temperature leads to an increase of the slope of μ^+ as a function of time. Strain hardening is still obtained, but it is less pronounced. Similar to the procedure for the shear experiments, the samples were studied by DSC after the experiment. The corresponding values of ΔH_2 are shown in the inset of Figure 11.

4. Discussion

The present study demonstrates that annealing of random polypropylene close to the upper end of the melting range can be performed in a rotational rheometer with simultaneous measurement of the dynamic moduli. It was confirmed that under such conditions a second melting peak at higher temperature is obtained in the DSC heat-flow curves. The experimental method of small-amplitude oscillatory shear flow probes the sample quasi at rest. The kinetics of the formation of the second melting peak depends sensitively on temperature as demonstrated in Figure 10. The temperature range is so narrow that the quality of the temperature control of the rheometers limits the reproducibility of the measurements. Since the formation of the high-temperature peak is a dynamic process with a time scale similar to the time scale of the shear flow experiments, the measured data have to be regarded as transient data. The experiments shown in Figure 4 are an example for this complication.

Viewed on a linear time scale, the reorganization of lamellae, i.e., the growth of their thickness, slows down for two reasons. First, mobile chain segments in the amorphous phase, which are attached by both their ends to crystalline lamellae, are sucked in until the gain in free energy of crystallization via lamellar thickening is balanced locally due to the loss of entropy by the shortening of the segments in the amorphous region.[14] Second, the reorganization of individual chain segments in the amorphous regions is hindered by entanglements. Local reorganization stops when two chains cannot disentangle on the time scale of the experiment.

During annealing at T_a one expects that the non-molten lamellae act in some way like dispersed crystalline fillers. Correspondingly, the shear flow behavior turns into one of a filled polymer melt. This is characterized by an increase of the viscosity with decreasing shear rate as shown in Figure 4. In Figure 9 the melt enthalpy ΔH_2 of the second melting peak is plotted as a function of the viscosity $|\eta^*|$. Since the zero shear rate plateau vanishes with decreasing temperature, an angular frequency of $\omega = 10^{-2}$ s^{-1} for the determination of $|\eta^*|$ was chosen. As a consequence, the relation (4) is of empirical quality and might not be suited to establish a model for the correlation of ΔH_2 and the volume fraction of the filler.

In contrast to conventional fillers, the crystallites are coupled to the molten phase by the chains which emanate from the crystallites. If the crystalline fraction is not too low and if the chains are not too short, there is a considerable amount of tie chains which connect different lamellae. Thus, during the annealing process at T_a one expects that the rheological behavior is influenced because of two effects. First, the volume fraction of filler material, i.e., the crystalline lamellae, increases with time. Second, the network of lamellae which are connected by tie chains becomes stiffer because of the sucking-in of chains into the lamellae.

These considerations are compatible with the evolution of the moduli G' and G'' as a function of time (Figure 10). Starting from a lower level than the loss modulus G'', the storage modulus G' increases much more rapidly than the loss modulus G'' until a crossover of the moduli occurs. This time dependence corresponds to the formation of filler particles. Whether they are coupled by a weak network from tie chains cannot be deduced from these data. In a later stage the storage modulus G' of the melt decreases again and a second crossover occurs as shown in Figure 10 for $T = 154$ °C. This corresponds to a reduction of the elasticity of the material response due to the increase of the volume fraction of the crystalline lamellae. This evolution of the moduli is similar to the one reported by Lin et al.[15] Their experiments are somewhat different in that they observe recrystallization of an elastomeric polypropylene from a supercooled state. In contrast, our study reveals the thickening of crystalline lamellae upon annealing of partially molten material.

As depicted in Figure 11, the transient elongational viscosity strongly depends on the annealing conditions. The completely molten material ($T = 160$ °C) shows an elongational behavior which is well-known from conventional polypropylene. The partially molten samples behave differently: First, the slope of μ^+ versus time gets steeper with decreasing temperature, e.g., increasing ΔH_2. Second, an additional strong hardening is found at a strain $\epsilon \geq 1$.

In order to explain these phenomena and to relate shear and elongational flow properties, relaxation time spectra from the dynamic measurements as shown in Figure 4 were calculated with the IRIS program.[16]

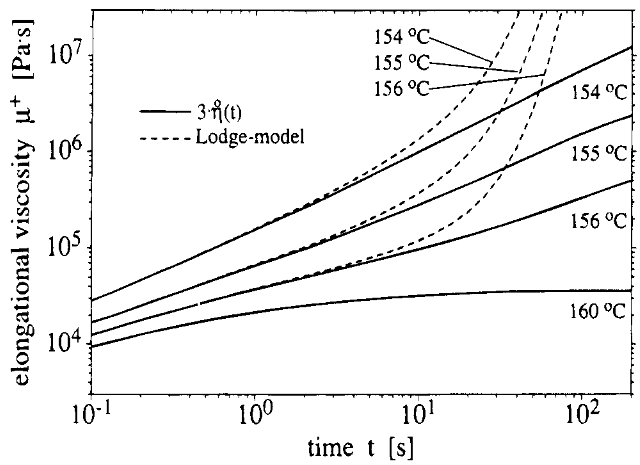

Figure 12. Linear viscoelastic stressing viscosity $3\mathring{\eta}(t)$ (full lines) and transient elongational viscosities calculated with the Lodge model (dashed lines) based on the relaxation time spectra deduced from dynamic measurements at similar annealing conditions.

From a technical point of view this procedure is easy to perform. However, it has to be kept in mind that the result of the dynamic measurements has transient character. Moreover, the flow regime is not reached, which results in a truncation of the spectra at long relaxation times. This effect gets stronger with decreasing temperature. Nevertheless, the corresponding relaxation times λ_i and relaxation strengths g_i were used to calculate the linear viscoelastic stressing viscosities $\mathring{\eta}(t)$ at the different temperatures according to

$$\mathring{\eta}(t) = \sum g_i \lambda_i (1 - \exp(-t/\lambda_i)) \qquad (5)$$

For homogeneous polymer melts the 3-fold value of $\mathring{\eta}(t)$ is equal to the transient elongational viscosity $\mu^+(t)$ at least up to a Hencky strain ϵ of 1. In our case a direct comparison of the elongational flow data with the calculated stressing viscosity is not given, since, apart from the restrictions with respect to the relaxation time spectra, it cannot be guaranteed that the annealing conditions in the different rheometers are identical.

The results of calculations of $3\mathring{\eta}(t)$ for different temperatures are shown in Figure 12 as full lines. Qualitatively, the increase of the slope of the transient elongational viscosity is described by this approach. The strain hardening at $\epsilon \geq 1$, however, is not predicted by this calculation. This problem is well-known for weakly long-chain branched polymers, which in contrast to linear polymers exhibit pronounced strain hardening. The influence of branches in polypropylene was studied by Phillips et al.[5] and Hingmann and Marczinke.[6] Using the Lodge model,[17] which was successfully used to describe the strain hardening in branched polypropylene, the dashed lines in Figure 12 are obtained. The shape of these curves is very similar to our experimental results in Figure 11. This finding strongly supports the existence of a network of tie chains between crystalline lamellae as suggested above.

In summary, this study presents rheological data of random polypropylene in a partially molten state during reorganization of molten material into crystalline lamellae in shear and for the first time in elongational flow. It has to be emphasized that crystallization of partially molten material has an outstanding influence on the flow behavior in both shear and elongation. It could be revealed that during reorganization of amorphous chain segments into existing lamellae a filled polymer melt with a network of tie chains is formed. The parameters which control the kinetics, the temperature dependence, and the strength of the reorganization process, however, are not yet fully understood. Moreover, the influence of deformation on the observed phenomena is the subject of future investigations.

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