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Communications to the Editor

Formation of Entanglements in Initially Disentangled Polymer Melts

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Chain dynamics in polymer melts is a complex process. Using the concept of chain reptation introduced by de Gennes,[1] Doi and Edwards[2] developed a theory to describe the experimental rheology of monodisperse entangled polymer melts. The model reduces the intricate problem of topological constraints to the notion of a virtual tube. The tube provides a pathway for the chain dynamics, and its diameter is defined from the constraints on the test chain by its neighbors. The constrained chain dynamics give rise to a characteristic time (τ_d) for a chain to diffuse one tube length. A salient feature of the theory is that it requires very few parameters: the tube diameter, a (or equivalently the molecular weight between topological constraints, M_e, or the plateau modulus, G_N^0), and the monomeric friction coefficient, $\zeta_0(T)$ (or equivalently $\tau_e(T)$, the characteristic relaxation time for a segment between two entanglements).

The average molecular weight between entanglements, $\langle M_e \rangle$, is inversely proportional to the entanglement density. This is related to the elastic modulus in the rubbery plateau region, G_N^0, according to

$$G_N^0 = g_N \rho RT / \langle M_e \rangle \qquad (1)$$

where g_N is a numerical factor (1 or 4/5 depending upon convention), ρ the density, R the gas constant, and T the absolute temperature.

From these basic concepts it appears that the plateau modulus is an intrinsic property as it arises from the elastic response of the entangled polymer melt. It is therefore independent of the total number of entanglements per chain, which increases as molar mass.

On cooling from the melt, many polymers tend to crystallize. Depending on the molar mass and crystallization conditions, entanglements are confined to the amorphous regions, whereas the crystalline regions are void of them. Thus, in the solid state of a semicrystalline polymer the distribution of entanglements can be highly heterogeneous. Usually this heterogeneous distribution is lost on melting, which causes an immediate entropy gain, and the entanglements are again uniformly distributed along the chain. So far studies have only been performed on such entangled melts.

Table 1.

	M_w [kg mol^{-1}]^a	M_w/M_n^{a}	η_0 [Pa·s]	buildup time (s)	longest relaxation time (s)
A	90	1.4	1.3×10^4	120	16
B	380	2.6	6.0×10^5	200	450
C	800	1.8	2.9×10^6	600	1200
D	1400	3.6	1.6×10^7	4000	8700
E	3600	2.8	3.4×10^8	54000	140000

[a] Molecular weight and molecular weight distribution are determined from gel permeation chromatography.

By controlling polymer synthesis, ultimately it is possible to obtain disentangled crystals, i.e., a single chain forming a single crystal, where chains are fully separated from each other.[3] Several attempts have been made to obtain disentangled melt either via controlled synthesis[4,5] or via enhanced chain mobility along the *c*-axis in the hexagonal phase of linear polyethylene.[6−9] Upon melting of these disentangled crystals, chains will tend to entangle to reach the maximum entropy thermodynamic equilibrium state, where the entanglements are homogeneously distributed and their density is constant. In this Communication we report a series of measurements highlighting the formation of entanglements of an initially disentangled melt for a range of molar masses, therefore probing the thermodynamically nonequilibrium melt state.

To obtain the desired disentangled crystals, we used a simple concept. The active sites of the catalyst are separated to an extent that growing chains do not meet each other.[5] Further, the polymerization temperature is kept lower than the crystallization temperature. Thus, the growing chain crystallizes immediately. To meet the requirements for a single chain forming a single crystal, homogeneous complexes were used, which are single site in nature and hence display uniform activity and produce linear polymers with a narrow molecular weight distribution[5,10] A series of linear polyethylene samples summarized in Table 1 have been synthesized using this concept. To follow the entanglements formation in the melt, buildup of the plateau modulus with time is investigated via oscillatory shear rheometry (in the linear viscoelastic regime).

To investigate the entanglement density of the materials listed in Table 1, as polymerized (disentangled) powders are first compressed, and the resulting disks are heated fast (∼30 °C/min) to 180 °C in an ARES rheometer. A constant strain of 0.5% at a fixed frequency of 10 or 100 rad/s is applied next. The frequency is chosen to be in the plateau region of the fully entangled material. The change in the modulus is followed as a function of time.

As the disentangled crystals are rapidly heated above the melting point (∼30 °C/min), chains will immediately adopt a

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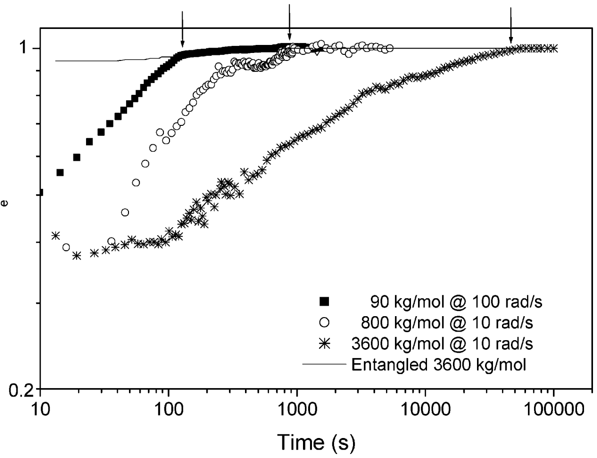

Figure 1. Buildup of modulus in disentangled polymer melts with time. Samples compressed at 50 °C and 200 bar for 1 h, having diameter of 8 mm and thickness 1 mm, were heated at 30 °C/min to 180 °C in the rheometer. A constant strain of 0.5% was applied at a fixed frequency of 10 or 100 rad/s. In the figure, the measured plateau modulus (G') is normalized by the equilibrium plateau modulus (G_N) at the measurement frequency. Arrows in the figure correspond to the buildup time where $G'/G_N = 0.98$. For comparison, the corresponding evolution for an entangled melt is also shown. Thermal equilibrium is reached after 200 s.

random coil conformation through the well-known “chain explosion” process.[11,12] Immediately thereafter, the chains are essentially disentangled because entanglements formation unavoidably takes time. Indeed, a lower plateau modulus is observed. This most probably reflects the low entanglement density according to eq 1 (which, we assume, will at least *qualitatively* hold in this nonequilibrium situation). With time, as chains tend to mix, entanglements formation should take place and should be reflected by an increase in modulus. Figure 1 summarizes a series of experiments showing a buildup of modulus as a function of time for different molar masses. This strongly suggests the occurrence of entanglements in the initially disentangled melt. During the modulus buildup phase, the melt is in a thermodynamically unstable state where equilibrium rheological concepts cannot be applied. Ultimately, as the modulus reaches its asymptotic value, the chains reach to the equilibrium state where the tube is present and classical reptation takes place. It is to be noted that when a *fully entangled* crystalline sample of the same molar mass and molar mass distribution is melted under the same conditions, no such buildup of modulus is observed (see Figure 1). The time required for modulus buildup increases with the molar mass.

From Figure 1, the buildup time (at 180 °C) can be approximately determined.[13] Arrows in Figure 1 illustrate the time required for the modulus to reach the asymptotic equilibrium value of the fully entangled melt. The buildup time vs average molar mass is plotted in Figure 2. It is important to note that the time required for the stabilization of temperature within the rheometer is nearly 200 s. For molar masses with buildup time larger than the stabilization time for the temperature, the buildup time appears to scale as molar mass to the third power. This will be discussed at the end of the paper. The sample with the molar mass 90 000 g/mol falls off the curve but has to be discounted as the stabilization time for the temperature is shorter than the time required for buildup of the modulus.

Ultimately, the initially disentangled chains become a fully entangled thermodynamically stable melt. Frequency sweep measurements have been performed on the fully entangled samples listed in Table 1. Figure 3 shows the corresponding dynamic viscosity vs angular frequency for different molar masses. Unfilled symbols at low frequencies are determined by stress-relaxation experiments, which cover the very low frequencies inaccessible to the dynamic experiments.[16] Extrapolation of the plateau to zero frequency yields the zero shear viscosity (η_0). The excellent overlap between the two types of measurements guarantees the accuracy of the extrapolated zero shear viscosity values.

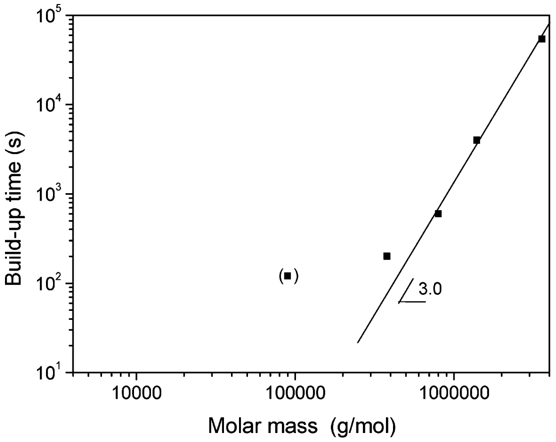

Figure 2. Data point represent buildup time obtained from the Figure 1 for a range of molar masses. When the buildup time is comparable with the time required to reach thermal equilibrium (<200 s), the data cannot be trusted.

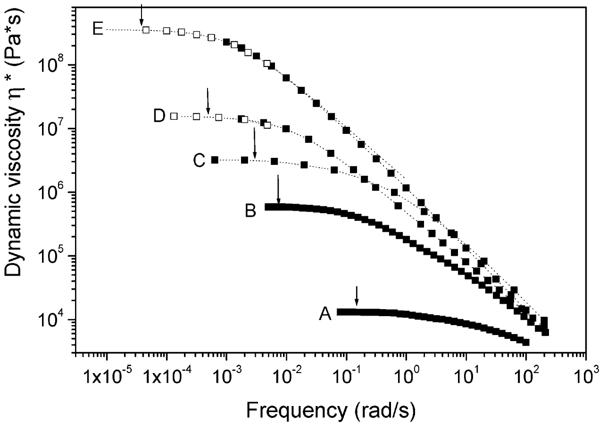

Figure 3. Dynamic viscosity as a function of frequency for fully entangled polymer melts of different molar masses. Unfilled symbols in the figure represent data points obtained from stress-relaxation experiments.

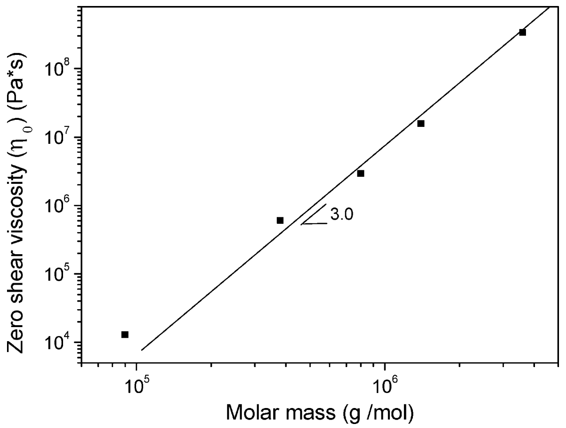

Figure 4. Zero-shear viscosity vs molar mass. The data points for different molar masses are obtained by the extrapolation of the dynamic viscosity in Figure 3 to zero frequency. A slope of 3.0 is observed.

Figure 4 shows the zero shear viscosity vs molar mass curve. The viscosity follows a pure reptation scaling (molar mass to

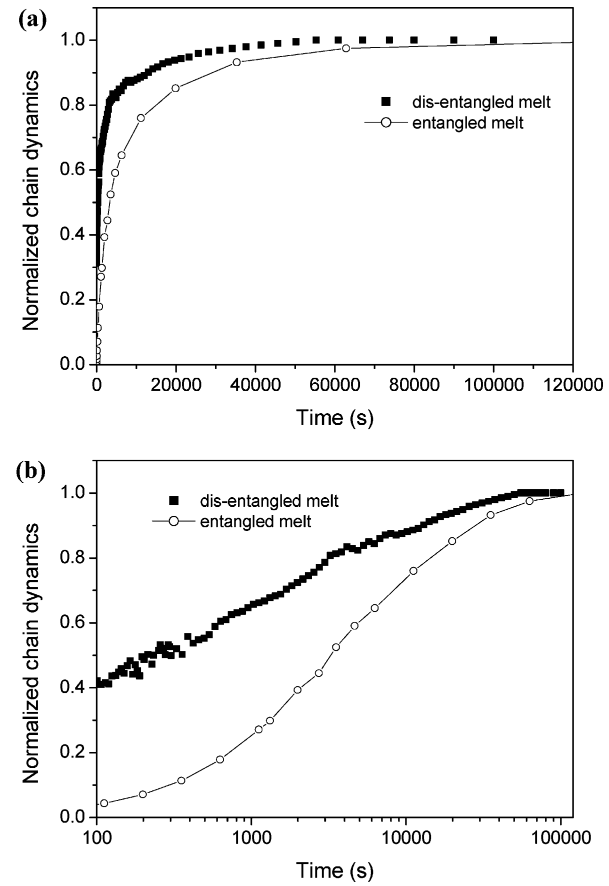

Figure 5. Chain dynamics of the disentangled and entangled melt state for a polymer of molar mass 3.6 × 10^6 g/mol at 180 °C. Chain dynamics of the disentangled melt state is represented as the normalized plateau modulus during the buildup phase ($G'(10\ \mathrm{rad/s})/G_N^0$) (filled symbols). Chain dynamics of the entangled melt is obtained from a stress-relaxation experiment as the relaxed fraction ($1 - (G(t)/G_N^0)$) (open symbols). The applied stress is 2% inside the linear viscous-elastic regime. The plateau modulus is a measure for the entanglement density; therefore, it follows the entanglements formation. Whereas the stress relaxation is a measure for the relaxation of entanglements. The chain dynamics involved in both process are essentially the same. In both cases chain movement (reptation) is required to build up entanglements or to release stress. In **(a)** the data are plotted on a linear scale and in **(b)** on a semilog scale.

the power 3.0) and disagrees with the more usual 3.4 exponent.[14] The latter is classically ascribed to the influence of chain contour length fluctuations. However, our observation is in agreement with recent tube-based models,[15] which predict a crossover from the 3.4 to a 3.0 exponent (hence pure reptation) for chains with more than about 200 entanglements. For polyethylene, the molar mass between entanglements is 1200 g/mol.[17] The crossover to pure reptation is therefore expected around 240 000 g/mol, compatible with our findings.

Figure 2 shows that the time required for the formation of entanglements scales as the third power of molar mass. To gain more insight into the mechanism of entanglements formation, we now compare modulus buildup of a disentangled sample with stress relaxation of the same fully entangled melt. The unfilled symbols in Figure 5 represent the relaxed fraction as a function of time ($= 1 - G(t)/G_N^0$) obtained for a molar mass of 3.6 million g/mol (sample E in Table 1). The filled symbols in Figure 5 represent the modulus buildup of the initially disentangled melt for the same molar mass. Both curves are representative of chain dynamics in the initially disentangled and fully entangled environments. This comparison is made, since in both cases chain motion is required to buildup entanglements or to release stress.

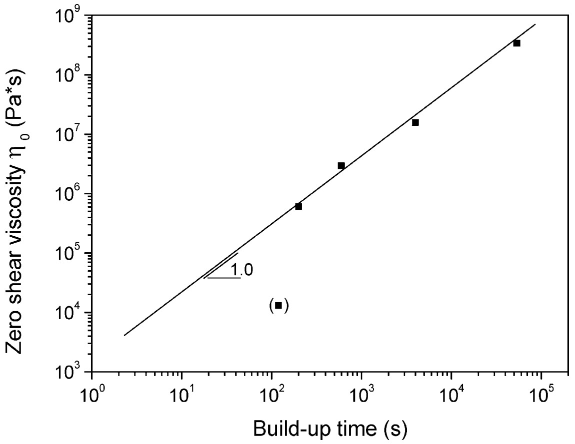

Figure 6. Correlation between chain dynamics of entangled and disentangled samples, represented by the zero-shear viscosity and the modulus buildup time, respectively, for the samples listed in Table 1. The figure shows a linear relationship.

At all times, the modulus buildup is faster than the stress-relaxation curve, highlighting faster chain dynamics. The two curves only merge at very long times of the order of 100 000 s. Since 200 s is required for stabilization of the rheometer, it is not possible to comment on the very early stages of modulus buildup.

From Figure 5, it is evident that the initial chain dynamics of the disentangled sample are much faster than the dynamics of the corresponding entangled melt. This difference can be attributed to the lesser amount of physical restrictions present in the disentangled melt state compared to the entangled melt. On the other hand, the convergence of the two curves at long times suggests that chain dynamics of the initially disentangled melt later on become dominated by chain reptation. To confirm this suggestion, the zero shear viscosity of different fully entangled samples (Figure 3) has been compared with the modulus buildup time (Figure 2). This is shown in Figure 6. A linear correlation is observed. From here can be concluded that the modulus buildup time of the disentangled samples scales as the reptation time of the corresponding fully entangled system. This is in fact reasonable. Whereas the initial stages of entanglement formation are fast and probably follow a different scaling, the later stages have to occur at the approximate rate of fully entangled melt reptation. In a forthcoming paper, with the help of solid-state NMR, detailed mechanisms involved in the entanglements formation of the disentangled melt at the initial stages will be elucidated. The entanglements formation in a disentangled polymer melt demonstrated in this paper should hold for all disentangled polymer melts.

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