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# Stable Critical Gels of a Copolymer of Ethene and 1-Butene Achieved by Partial Melting and Recrystallization

Roland H. Horst\* and H. Henning Winter

Department of Chemical Engineering and Department of Polymer Science & Engineering,  
University of Massachusetts, Amherst, Massachusetts 01003

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**ABSTRACT:** The transition from solid to liquid during the melting of a semicrystalline polymer can be viewed as reverse gelation since the physical gel point (state of liquid-to-solid transition) is approached from the solid side. In this study we explore routes of stopping the melting process at the gel point and stabilizing the semicrystalline structure at sufficiently low crystallinity. Such material at the gel point is called a "critical gel". By approaching the gel point from the solid state, we are indeed able to form a stable critical gel. Under the applied conditions, slowly heating (0.2 K/min) from room temperature to the annealing temperature, the stable critical gel was found at 71 °C. One purpose of making stable critical gels is to measure its structure and properties. The critical gel was found to be relatively soft, having a surprisingly high relaxation exponent. The crystallinity at the gel point is below 1 wt %. Crystalline regions whose nature is mostly unknown achieve connectivity between molecules.

## Introduction

Crystallizing polymers are known to show typical behavior of physical gelation when undergoing a liquid–solid transition (gel point).<sup>1–3</sup> In extension of Flory's definition of the chemical gel point,<sup>4</sup> the gel point (GP) in a crystallizing polymer may be defined by the appearance of sample spanning connectivity. The transition through the gel point occurs either during melting of a crystallized polymer or during crystallization of a liquid, molten polymer. At the transition state where the material is neither a liquid nor a solid, the material is called a "critical gel". Rheologically, *chemical* critical gels and *physical* critical gels express themselves with the same universal relaxation pattern: The slow dynamics of the critical gel is characterized by a self-similar relaxation modulus<sup>5–9</sup>

$$G = S_c t^{-n_c} \quad \text{for } t > \lambda_0 \quad (1)$$

$S_c$  is the gel stiffness,  $n_c$  is the critical relaxation exponent, and  $\lambda_0$  is the relaxation time denoting the crossover to some faster dynamics (entanglements, segmental). Therefore, we can use the rheological experiment to detect the gel point, including that of crystallizing samples.

In the preceding paper,<sup>10</sup> we explored the existence of stable critical gels for crystallizing polymers; i.e., the equilibrated polymer is exactly at the gel point. A completely molten material (LLDPE) was quenched to an experimental temperature,  $T_X$ , for crystallization. Time-resolved rheometry was used to detect the gel point and, thus, to measure the gel time,  $t_{\text{gel}}$ , which is the time needed to bring the material to the gel point. A high value of  $T_X$  results in a low final crystallinity and a slow crystallization process.

$t_{\text{gel}}$  grows in a power of  $T_X$ , and it diverges at  $T_{\text{cg}}^\infty$ , where it would need infinite experimental time before the stable critical gel is formed. However, this divergence of the gel time provides a convenient definition of the stable gel point. The stable critical gel could not

be achieved by crystallization from the melt; we deduced its existence from an extrapolation. The crystallization temperature, at which the stable critical would exist, was estimated as  $T_{\text{cg}}^\infty = 69$  °C. The preceding paper<sup>10</sup> contains a detailed discussion of the characteristics of the critical gel state in the case of the physical gel in crystallizing polymers.

In this study we investigate the possibility of reaching the gel point from the solid side by partial melting.<sup>11,12</sup> Instead of completely melting the polymer at high temperatures and then crystallizing it at  $T_X$ , the polymer is first crystallized at low temperatures where the crystallization is very fast and crystallinity reaches high levels. Then the sample is heated to  $T_X$ , thereby partially melting the crystal domains and decreasing the crystallinity. Since the melting processes are much faster than the crystallization processes, it should be possible to realize a stable critical gel. A similar study<sup>13</sup> on the behavior of a partially molten polypropylene copolymer can be found in the literature. The authors did not focus on the transition itself but on the rheological behavior of near-critical gels, especially under elongational flow.

It is much easier to find a temperature where an intermediate degree of crystallinity is realized for a copolymer than for a homopolymer. A copolymer of ethylene and 1-butene was chosen for the present measurements, having a broad melting range and a much lower melting temperature than pure polyethylene.<sup>14</sup> Measurements by Flory and co-workers<sup>15</sup> showed that polymethylene containing randomly distributed ethyl side groups shows a very flat crystallinity versus temperature curve,  $X(T)$ . This is caused by the fact that the branched units are excluded from the crystalline phase.<sup>16–18</sup> DSC will be used to determine the crystallinity as a function of the crystallization conditions. Small-amplitude oscillatory shear experiments will monitor the gelation process.

In this article a specific terminology is used to describe the phenomena of gelation. The reader might not be accustomed with these terms, and it seems necessary to give definitions:

\* Corresponding author. E-mail horst@mail.pse.umass.edu.

**Gel:** A material that is firm in consistency, although containing much liquid, like softened gelatin. Its storage and loss moduli are very low for a solid material.

**Chemical Gel:** The connectivity is achieved by chemical bonds, like in the chemical cross-linking of curing resins. Chemical gels are cross-linked networks of polymers swollen with liquid.<sup>19,20</sup>

**Physical Gel:** The connectivity is achieved by physical bonds. The most well-known example is the thermo-reversible gelatin-gel, which is solidified by the formation of helices. This gel concept may be applied to crystallizing polymers at low crystallinity. In this case the macromolecular network is held together by crystalline regions, and it is "swollen" by amorphous molecules (liquid) which are not attached to the crystals.

**Gel Point:** Polymeric materials often show a gradual liquidification or solidification. The transition point from one state of aggregation to the other is called the gel point.

**Gel Time:** The time needed to reach the gel point.

**Critical Gel:** A material exactly in the state of the liquid–solid transition. It is neither a solid nor a liquid.

**Transient Critical Gel:** In most cases, the critical gel exists only for one moment during the solidification or liquidification; e.g., cooling a semicrystalline polymer from the melt leads to solidification of the initially liquid sample. The liquid–solid transition, the critical gel, is passed, and the polymer forms a gel as the crystallization proceeds. The critical gel is only a transient state.

**Stable Critical Gel:** Under certain conditions, the equilibrated sample stays a critical gel. For semicrystalline polymers, this means that the temperature is adjusted so that the crystallinity in the equilibrated material is exactly that needed to bring the material to the liquid–solid transition. For chemical cross-linking, a fine adjustment of the stoichiometric ratio of the reactants yields a stable critical gel.

## Experimental Section

**Sample.** A statistical copolymer of ethylene and 1-butene, metallocene synthesized, containing 11 mol % of 1-butene was chosen because of its low crystallinity and its broad melting transition, caused by the sequence length distribution. It was used as supplied by Exxon without purification. GPC with polyethylene calibration gives  $M_n = 39\,500$ ,  $M_w = 72\,800$ , and  $M_w/M_n = 1.84$ . The temperature to reach the threshold crystallinity corresponding to the stable gel point was estimated previously<sup>10</sup> as about  $T_X = 69\,^{\circ}\text{C}$ .

**Methods. a. DSC** Thermal analysis experiments were performed under a nitrogen atmosphere in a Perkin-Elmer calorimeter DSC 7 with water-bath cooling. The instrument was calibrated with high-purity standards of indium and tin.

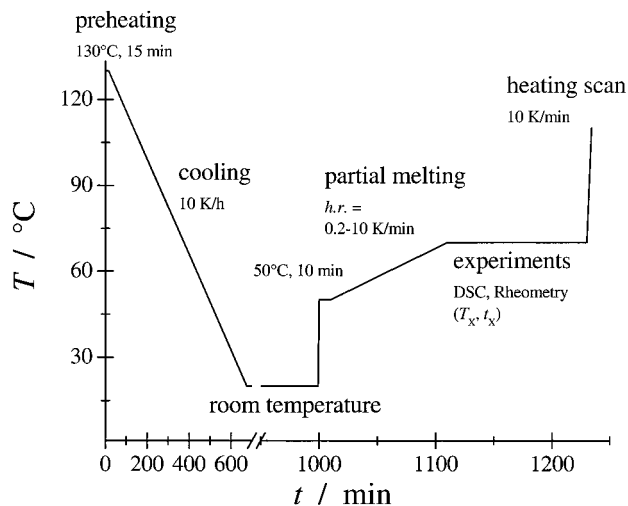
**b. Rheology.** Because stress relaxation experiments require long measuring times, they are not applicable to materials which are changing with time. In this case, the relaxation modulus is better determined in oscillatory shear. Eq 1 can be translated into the frequency domain to give

$$G'(\omega) = S_c \Gamma(1 - n_c) \cos\left(\frac{n_c \pi}{2}\right) \omega^{n_c} \quad \text{for } \omega < \omega_0 = 1/\lambda_0 \quad (2)$$

$$G''(\omega) = S_c \Gamma(1 - n_c) \sin\left(\frac{n_c \pi}{2}\right) \omega^{n_c} \quad (3)$$

$$\tan \delta = \frac{G''}{G'} = \tan \frac{n_c \pi}{2} \neq f(\omega) \quad (4)$$

$G'$  and  $G''$  are the storage and loss moduli,  $\delta$  is the loss angle,  $\omega$  is the angular frequency, and  $\Gamma$  is the gamma function.



**Figure 1.** Temperature protocol for DSC and mechanical spectroscopy. The sample is preheated at  $130\,^{\circ}\text{C}$  for 5 min and then slowly ( $10\,\text{K/h}$ ) cooled to the room temperature where it is stored for several days. At the beginning of the actual measurement, the sample is equilibrated at  $50\,^{\circ}\text{C}$  and then, with various heating rates (hr), brought to the experimental temperature  $T_X$ . In the case of the DSC experiments samples are held at  $T_X$  for some time  $t_X$ . The heat of fusion  $\Delta H_m$  is determined by heating the sample at  $10\,\text{K/min}$ . The oscillatory shear measurements are carried out continuously at  $T_X$ .

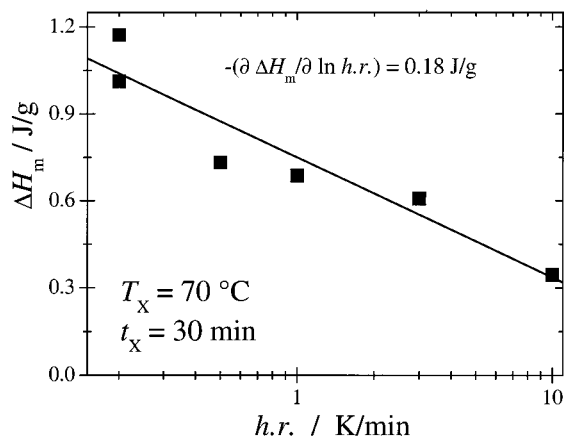
Frequency independence of  $\delta$  (eq 4) enables the detection of the gel point. Mechanical spectroscopy over a range of frequencies (frequency sweep) yields a constant  $\delta$  for a critical gel at sufficiently low frequencies. Equations 2–4 can be used for any material to calculate a gel stiffness  $S_c$  and a relaxation exponent  $n_c$ , but only in the case of a critical gel are these two quantities independent of  $\omega$ .

Small-amplitude oscillatory shear (SAOS) was performed in a RMS-800 of Rheometric Scientific Inc., equipped with parallel plates (diameter 25 mm), with Rhios software controlling the instrument. After heating the sample to the crystallization temperature, the sample was held at constant temperature  $T_X$  to monitor the evolution of loss and storage modulus,  $G''$  and  $G'$ , at a sequence of frequencies between 0.01 and  $10\,\text{rad/s}$ . The strain amplitude was  $\gamma_a = 0.03$ .

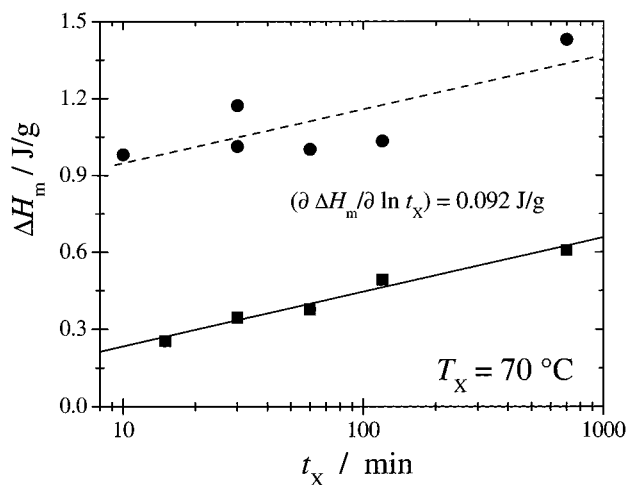
## Results

**DSC: Melting and Recrystallization.** The crystallization conditions are known to influence the morphology of the material. Therefore, a defined temperature history was chosen (Figure 1). The sample was first kept at a preheating temperature of  $130\,^{\circ}\text{C}$  for 15 min to remove influences of previous thermal history.<sup>10</sup> Then, it was cooled to room temperature at a low cooling rate of  $10\,\text{K/h}$ . At this temperature it was stored for several days until the actual measurement was performed. The actual experiment began by heating the sample to  $50\,^{\circ}\text{C}$  and equilibrating it for at least 10 min. Then it was brought to the experimental temperature  $T_X = 70\,^{\circ}\text{C}$  with various heating rates (hr) and kept at  $T_X$  for the time  $t_X$ . A subsequent DSC heating scan ( $10\,\text{K/min}$ ) yields the heat of fusion  $\Delta H_m$  together with the nominal melting temperature  $T_m$  as defined by the position of the peak maximum of  $\Delta H_m(T)$ . The experimental temperature was varied, but data are only shown for  $T_X = 70\,^{\circ}\text{C}$  since it is close to the temperature of the stable critical gel as will be shown below.

The heating rate applied to reach  $T_X$  has a large influence on the crystallinity. The melting peak (heat of fusion,  $\Delta H_m$ ) decreases markedly as the heating rate is.  $\Delta H_m$  increases little when crystallizing for longer



**Figure 2.** Heat of fusion  $\Delta H_m$ , measured in a DSC heating scan at 10 K/min, as a function of the heating rate (hr) (during approach of  $T_x$ ) for constant values of  $T_x$  and  $t_x$ .

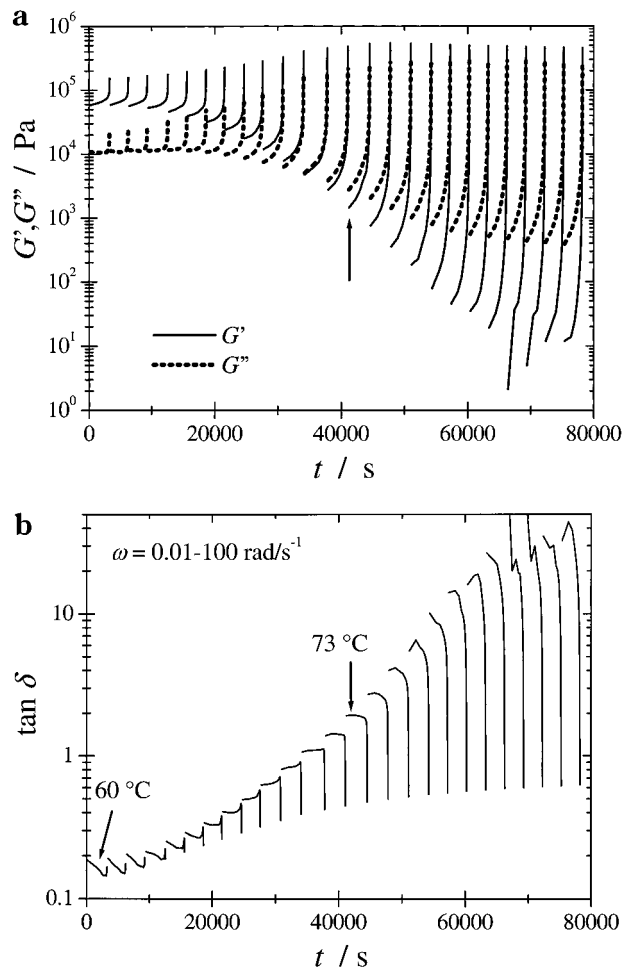


**Figure 3.** Heat of fusion  $\Delta H_m$  as a function of the experimental time for constant  $T_x$  and two different heating rates of 0.2 (●) and 10 K/min (■). The solid line is a linear fit to the data for 10 K/min; the dashed line has the same slope.

times  $t_x$ . The hr dependence (slope in Figure 2) is much more pronounced than the  $t_x$  dependence (slope in Figure 3). The same DSC experiments show that the DSC melting peak temperature,  $T_m$ , increases linearly with  $\ln$  hr from 75.1 to 75.8 °C and linearly with  $\ln t_x$  from 74.5 to 77.0 °C for hr = 0.2 K/min and from 75.2 to 77.7 °C for hr = 10 K/min. For the following rheological experiments we chose a slow heating rate of 0.2 K/min.

Since butene units are excluded from the crystalline phase,<sup>16,17</sup> the crystalline phase can be assumed to be pure PE. Its heat of fusion of the crystal is about the same as that for the PE homopolymer. The value of the polyethylene crystal can be found in the literature<sup>21</sup> and is  $\Delta H_{PE} = 295.8$  J/g. Under the above assumptions, dividing the measured heat of fusion by 295.8 J/g gives a reasonable value for the crystallinity  $X$  of the sample. At  $T_x = 70$  °C and hr = 0.2 K/min the sample reaches a crystallinity of approximately 0.5 wt % after 1 day. At that time, the sample has not yet reached a steady state, but  $\Delta H_m$  as a function of  $t_x$  seems to level off.

**Mechanical Spectroscopy during Changes in Crystallinity.** At first, temperature–frequency sweeps were carried out to check the behavior of the sample on slow heating. Each line in Figure 4 represents a frequency sweep requiring approximately 53 min. Since

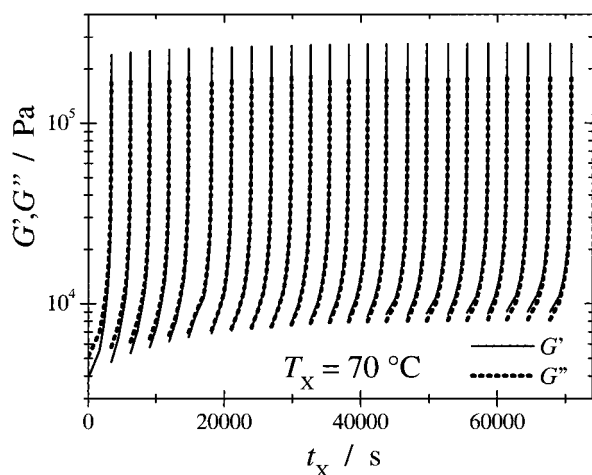


**Figure 4.** Consecutive temperature–frequency sweep; the temperature is raised by 1 K from one frequency sweep to the next. Part a shows the evolution of the storage ( $G'$ ) and loss modulus ( $G''$ ) and part b that of the loss tangent  $\tan \delta$ . At 73 °C the initial slope of  $\tan \delta$  is zero, indicating a critical gel.

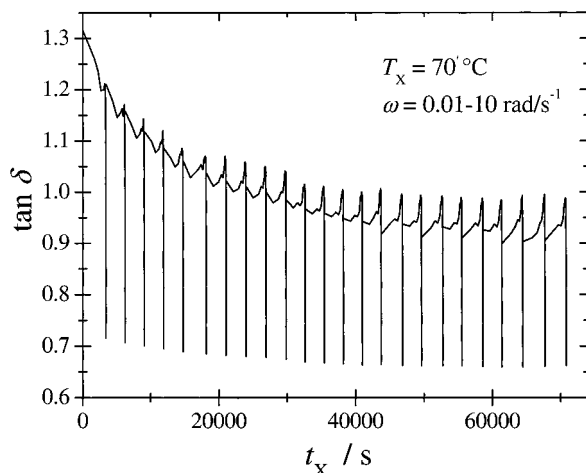
the frequencies were varied from low to high values, the initial part of the lines shows the behavior at low frequencies. The temperature was raised by 1 K after each frequency sweep. The moduli decay gradually for these experimental conditions (Figure 4a). The softening does not occur at a single point, but it is a smooth transition over a broad temperature interval. Figure 4b shows the change in the  $\tan \delta(\omega)$  curve. The first frequency sweeps at low temperatures exhibit a maximum; i.e., the slope of  $\tan \delta(\omega)$  is positive at low frequencies. This increase of  $\tan \delta$  with  $\omega$  is typical for solids. The last sweeps at the high temperatures have a negative slope at all frequencies, the typical dependence for liquids. At 73 °C the maximum has just disappeared, and the low-frequency part of the curve is horizontal; i.e., the first points of the frequency sweep give a constant  $\tan \delta$ . This independence of  $\delta$  on  $\omega$  signifies a critical gel. The gel point is passed at this temperature for the above-mentioned conditions.

To study the time dependence of melting and recrystallization, the same temperature schedule was applied for rheology as for the DSC measurements. The heating rate from 50 °C to  $T_x$  was 0.2 K/min for all rheological measurements discussed below. As an example, the evolution of the moduli and of the loss angle is shown in Figures 5 and 6 for  $T_x = 70$  °C. Each curve represents one frequency sweep  $\tan \delta(t_x, \omega_i)$ , the lower frequencies  $\omega_i$  being measured first. The moduli increase with  $t_x$ ;





**Figure 5.** Evolution of the storage ( $G'$ ) and loss modulus ( $G''$ ). Each single curve represents a frequency sweep starting with the low frequencies ( $\omega = 0.01$  rad/s) and ending at the highest frequency ( $\omega = 10$  rad/s).

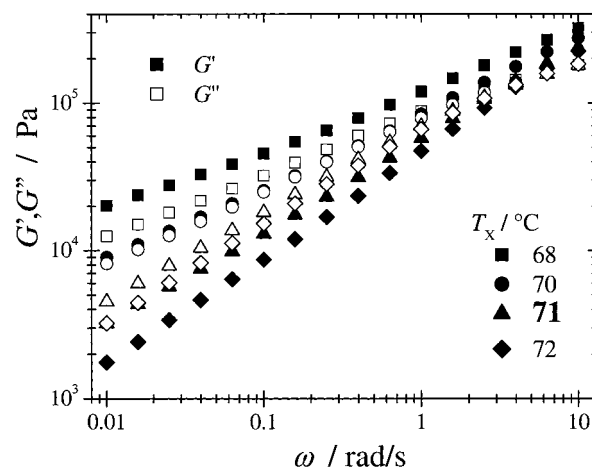


**Figure 6.** The loss tangent as a function of time  $t$  for  $T_x = 70$  °C.

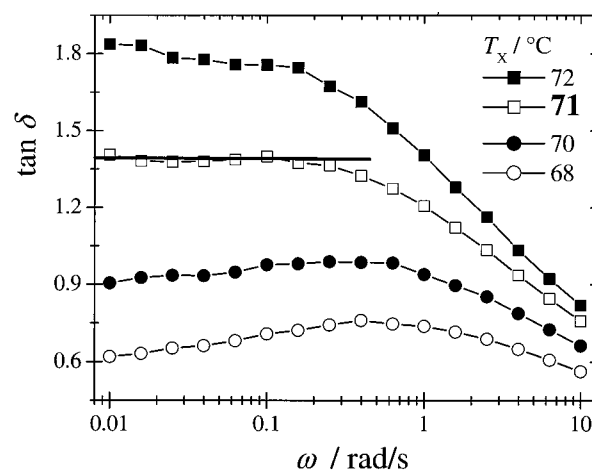
after 15 h they seem to have reached a steady value. The sign of the slopes of  $\tan \delta(t_x, \omega_i)$  and  $\tan \delta(\omega)$  are identical; we can use a flat  $\tan \delta(t_x, \omega_i)$  for detecting the instant of the liquid–solid transition. It should be noted that no simple relation exists between the values of  $(\partial \tan \delta(t_x, \omega_i) / \partial t_x)$  and  $(\partial \tan \delta(\omega) / \partial \omega)$ , since experiments at low  $\omega$  require much more time than those at high  $\omega$ . However, this does not cause a problem if a short-cut method is used for detecting the gel point, since one only needs to know where  $(\partial \tan \delta(t_x, \omega_i) / \partial \omega)$  becomes zero.

At the beginning of the actual gelation experiment, when the sample temperature has just reached  $T_x$ , the sample is mostly molten and behaves as a liquid (negative slope at low frequencies). Later, at sufficiently large annealing time  $t_x$ , a pronounced maximum in  $\tan \delta(t_x, \omega_i)$  is visible which indicates solidlike behavior (positive slope at low frequencies). The sample undergoes a liquid-to-solid transition; the gel point is passed through during this annealing process. These observations of melting into a liquid followed by solidification correlate with the DSC results, which show that crystallinity reaches a minimum at the end of the heating step and then increases during annealing at  $T_x$ .

The main focus of this study is not the time dependence, but the attempt to produce a critical gel in the steady state. The continuous frequency sweeps were



**Figure 7.** Steady-state values of the storage ( $G'$ ) and loss modulus ( $G''$ ) as a function of  $\omega$  for various  $T_x$  given in the graph.



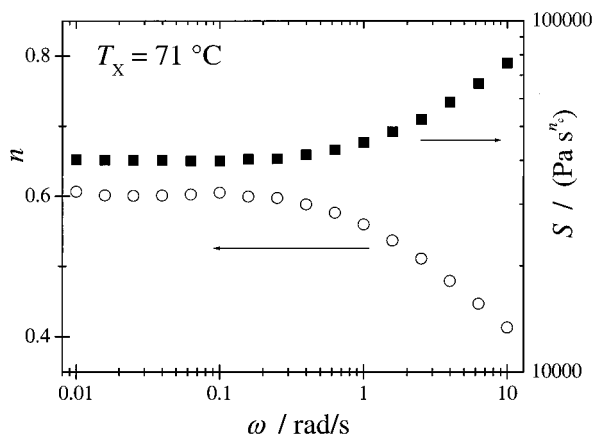
**Figure 8.** Steady-state values of  $\tan \delta$  as a function of  $\omega$  for various  $T_x$  given in the graph. At  $T_x = 71$  °C the sample is at the gel point.

performed at different temperatures  $T_x$  until the rheological properties did not change with time—at least within the duration of our experiments—and the steady state was reached. The results shown in Figures 7 and 8 represent values for these long experimental times (several days). Figures 7 shows the moduli and Figure 8  $\tan \delta$  as a function of  $\omega$ . At 71 °C  $\tan \delta(\omega)$  is a horizontal line at low  $\omega$ , i.e., the loss angle is independent of the frequency, and the sample behaves as a critical gel.

## Discussion

No structural information is available at these low crystallinity levels. However, we assume that the rheological behavior is an expression of melting and recrystallization in the sample. This will be speculated on in the following.

The polyethylene crystal possesses a high mobility provided by the  $\alpha$ -process,<sup>22</sup> which enables a rapid adaptation of lamellar thickness according to temperature.<sup>23,24</sup> Thicker lamellae are associated with higher melting temperatures.<sup>25</sup> On heating above its characteristic temperature, any given lamella has two options. Either the lamella melts into an amorphous state or it increases its thickness. Such thickening requires time and cannot occur at high heating rates; the lamella will preferably melt. This can be avoided by slowly heating



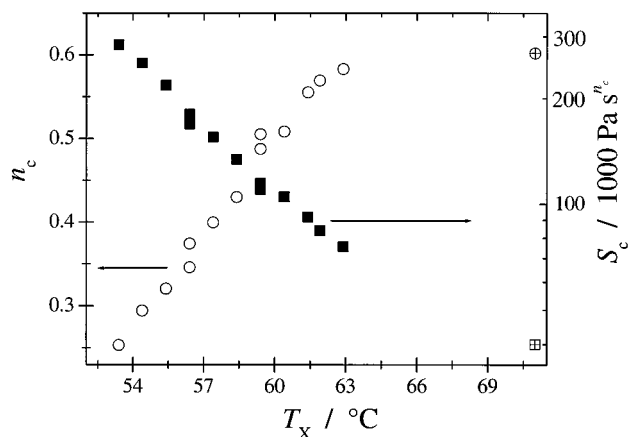
**Figure 9.** Steady-state values of relaxation exponent  $n$  and gel stiffness  $S$  as a function of  $\omega$  for the stable critical gel at  $T_X = 71$  °C. The plateau at low  $\omega$  gives the values for the stable critical gel,  $S_c$  and  $n_c$ .

to  $T_X$ . In our first trials to reach the gel point from the low-temperature side, we heated the sample much too fast. This caused an almost complete melting and resulted in kinetics of (re)crystallization which were not markedly faster than in the case of the undercooled melt (of the preceding study<sup>10</sup>). The slow crystallization dynamics prevented us from achieving the stable critical gel within a reasonable time. By lowering the heating rate, however, larger fractions of the lamellae have sufficient time to grow and to reach the minimum thickness required for stability at the raised temperature  $T_X$ . Keeping the temperature constant allows some of the molten material to recrystallize. The absolute value of the slope in Figure 3,  $(\partial \Delta H_m / \partial \ln t_X)$ , describing the recrystallization, is smaller than the dependence in Figure 2,  $-(\partial \Delta H_m / \partial \ln \text{hr})$ , related to the thickening.

One can take advantage of the fast thickness growth by slowly heating to the desired temperature. Some of the crystallinity will be retained to nucleate the recrystallization processes. In this way it is possible to achieve a stable critical gel at  $T_X = 71$  °C in a reasonably short time.

In the preceding paper,<sup>10</sup> the temperature at which the stable critical gel should occur was determined to be about 69 °C by extrapolation. The slow kinetics in the case of undercooling allowed only measurements up to 62.5 °C. The discrepancy to  $T_X = 71$  °C might be caused by experimental errors, the extrapolation by 7 K, or a different structure of the critical gel. For example, the nucleation mechanism depends on the temperature, and so the number density of crystalline structures is different for undercooling and partial melting.<sup>11</sup>

The rheological properties of the equilibrated sample at  $T_X = 71$  °C are exactly the expected properties for a polymer at its gel point. Figure 9 shows the stiffness  $S$  and the relaxation exponent  $n$  as a function of angular frequency; the slow dynamics do not depend on the frequency over a wide range of  $\omega$ , for  $\omega < 0.25$  rad s<sup>-1</sup>. The huge extension of the power law region (Figures 7 and 8) at the gel point is very surprising and a clear statement of the critical gel. The transient critical gels achieved by undercooling<sup>10</sup> never showed such clear evidence, indicating structural differences. The rheological parameter values of the critical gel, the low-frequency limits of  $S$  and  $n$  (eq 1), are  $S_c = 40\,000$  Pa s<sup>0.60</sup> and  $n_c = 0.60$ .



**Figure 10.** Critical relaxation exponent  $n_c$  and gel stiffness  $S_c$  as a function of  $T_X$  for the transient critical gels made by undercooling (open circles,  $n_c$ ; full squares,  $S_c$ ) and the stable critical gel (partial melting, symbols with cross within).

The values of  $S_c$  and  $n_c$  can be compared to those for the transient critical gels,<sup>10</sup> shown in Figure 10. The crystallization at the temperature of the stable critical gel is so slow that transient critical gels as one point in the crystallization process of an undercooled melt could only be realized at much lower temperatures. Therefore, there are no data points between 63 and 71 °C. The values of the stable critical gel might be positioned on the same smooth curve through the data for the transient critical gels, but the broad temperature interval makes this difficult to prove conclusively. The only conclusion we can draw is that there is no indication of path dependence for the properties of the critical gel, although this path dependence cannot be excluded, since the solidification is caused by crystallization, which is known to be path dependent. A path dependence could, for example, be caused by a different nuclei density in the case of partial melting as compared to undercooling.

## Conclusions

Making use of the faster kinetics of crystal thickening and recrystallization, we accomplished a stable critical gel at steady-state conditions in a (practically) equilibrated sample. For polyethylenes, partial melting and recrystallization is the preferred way to reach their physical critical gel state.

The critical gel state is not achieved by just melting a fraction of the crystals. Mechanical spectroscopy shows that the melting went beyond the gel point into the liquid state. It is through recrystallization that the sample returns to the gel point, and the stable critical gel state is attained.

The time-resolved rheometry method of Figure 8 has been effective for finding the gel point. Since in this case the critical gel is stable, we could test the result of the short-cut method with more extensive mechanical spectroscopy and confirm the findings.

The stable critical gel state is softer than the transient critical gels (at lower  $T_X$ ) which might be due to thicker lamellae and higher network functionality. This needs to be explored further. However, it will be difficult to characterize the crystal structure because of the very low crystallinity, which does not reach detection level for most physical methods.

In future studies, the stable critical gel state will be reproduced in other model polyolefin samples for further rheological testing.

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