Stable Critical Gels of a Crystallizing Copolymer of Ethene and 1-Butene

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ABSTRACT: Crystallization of molten polymers involves a liquid–solid transition. In its first stage, the solidification process may be viewed as a physical gelation, which can be monitored with small-amplitude oscillatory shear experiments. A threshold crystallinity, $X_{\text{cr}}$, is required for the sample to reach the critical gel state (gel point). Samples of a metallocene random copolymer of ethene and 11 mol % 1-butene were quenched from the melt to a crystallization temperature $T_X$ and then held at that temperature for isothermal crystallization. The objective was to find the highest value of $T_X$ at which the polymer would crystallize only to the threshold crystallinity $X_{\text{cr}}$ and no further. The result would be a stable critical gel at a temperature $T_X = T_{\text{cr}}$. We start at large degrees of supercooling where the critical gel is only a transient state which is passed through as the sample solidifies to greater degrees of crystallinity. The gel time increases with temperature, obeying a power law, and can be extrapolated to infinity at 68.8 °C. The crystallinity at the gel point is about $X_{\text{cr}} = 1\%$, almost independent of $T$. The rheological experiments are inherently difficult since the characteristic transition behavior, where tan $\delta$ is independent of frequency, occurs only in the terminal frequency region which is at very low frequencies for the sample of this study.

Introduction

Crystallizing polymers are known to show typical gelation behavior when undergoing a liquid–solid transition (physical gelation). The gel point (GP) in a solidifying system is defined by the appearance of sample spanning connectivity. In chemical gelation, small molecules connect by covalent bonds into larger clusters; the GP is established when the first molecular cluster has grown to infinite size, i.e., to the size of the sample. Physical gelation results from the growth of long-lived, thermoreversible aggregates which interconnect directly or indirectly. The physical gelation in crystallizing polymers shows many similarities with chemically cross-linking polymers. In the case of the chemical gelation of a two-component system, for instance, the stoichiometric ratio of cross-linker and precursor determines the phase state of the material after completion of reaction. There exist a lower and an upper stoichiometric ratio, $r_L$ and $r_U$, which define the range of composition in which gelation can occur. Off-balanced reaction mixtures, $r < r_L$ or $r_U < r$, would not develop sufficient connectivity to establish a sample spanning, three-dimensional molecular network structure. $r_L$ and $r_U$ are threshold values of composition which, at complete conversion of chemical cross-linking, generate a stable critical gel. The question arises whether a threshold value exists in thermoreversible gelation. Crystallizing conditions are sought which lead to a threshold crystallinity $X_{\text{cr}}$ for a stable critical gel.

Rheologically, chemical gels and physical gels at the GP express themselves with the same universal relaxation pattern. The critical gel is characterized by a self-similar relaxation modulus.

\[ G = S_c t^{-n_c} \text{ for } t > \lambda_0 \]  

\[ S_c \] 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 dynamics). Therefore, we can use the rheological experiment to detect the gel point in crystallizing samples.

In comparison to polymers, small molecules differ considerably in their crystallization behavior. Crystallization of a one-component, low molar mass system causes a solid, crystalline phase to separate from a liquid, amorphous phase. Only at one specific temperature, the melting point, do both phases coexist; at other temperatures the sample is either totally crystalline or completely amorphous. For polymers, on the other hand, crystallization and melting can occur in a broad temperature range although polymers can be identified from their transitions determined by DSC or by other means. At a given crystallization temperature only lamellae of a minimum thickness can form, since the crystalline fraction never reaches unity. The sample always contains noticeable amounts of amorphous material, and it never reaches the equilibrium melting temperature of the infinite crystal.

Crystallization and melting of polymers are not simple processes; they include several states. For polyethylene the crystallization process may be viewed as two consecutive main steps: (1) the formation of lamellae growing radially from a nucleus and (2) the filling of these structures with tangential lamellae. In many cases these structures are spherulites.

For sufficiently high degrees of supercooling, i.e., at a sufficiently low crystallization temperature, the final degree of crystallinity is independent of temperature.

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within experimental errors. At higher temperatures it
decreases with rising temperature, and above the equi-
librium melting temperature, it is zero; i.e., the material
is in the melt state. For random copolymers of a
crystallizing and a noncrystallizing monomer this curve
becomes very flat because of the sequence length
distribution. At a given temperature a minimum
thickness of the lamella is required for stability: Un-
interrupted sequences of the crystallizable monomers
must be longer than this length to be eligible for
crystallization. Since the minimum stable lamella thick-
ness increases with temperature, the crystallizable
fraction of the copolymer becomes smaller and smaller,
causing the flat crystallinity versus temperature curve.

At the gel point, the local structures are interconnected
by a supermolecular structure, which is not
understood in great detail. But if one considers the
possibilities how connectivity can be achieved, three
ways come to mind: (i) immediate contact between
structural units, (ii) a network of bridging molecules
which have segments in neighboring crystalline phases
(the tie molecules should be more or less in their
equilibrium configuration as long as no external stress
is applied), or (iii) impingement of amorphous chains,
immobilized by their attachment to segments within a
crystalline structure, with similarly immobilized chains
from adjacent structures. Case i is realized for com-
 pounds of low molar mass, whereas polymers seem to
pass the macroscopic liquid–solid transition at an
earlier stage of structure development. The gel point
occurs at so low a crystallinity (ca. 1–2 wt %) that a
solidification according to case i is most unlikely. The
model system for case i would be a suspension of hard
spheres solidifying as the volume fraction of the spheres
is raised. Solidification of a system of hard spheres by
gradual removal of free volume between spheres is well-
known. An experimental example is the suspension of
sterically stabilized latex particles. For connectivity
according to case i the critical gel should be hard and
brittle, but semicrystalline polymers of low crystallinity,
even beyond the gel point, show a rubberlike behavior,
so it is unlikely that they have structure of type (i). Case
ii corresponds to network formation during chemical
cross-linking, whereas case iii may be compared to a
system of swollen spherical microgels in a solvent, the
apparent diffusion coefficients of which diverge when
the sphere volume reaches the dose freezing point. Crystallizing from the melt state, case iii occurs earlier
than case ii since the structures should be closer
together to enable bridging. The rheological properties
of the critical gel may provide insight into the question
of when the gel point is reached. Case ii should result
in an elastic rubber, which can only be stretched to a
certain amount, whereas case iii should give a sample
with a yield stress, which can be elongated infinitely.
To date it is unknown exactly at which structural state
the macroscopic solidification occurs.

In this study, the terms “solid” and “liquid” always
refer to a macroscopic length scale; the rheometer
observes the properties of the overall system, which is
solid only after the aforementioned crystal structures
are interconnected across the entire sample. This is
analogous to Flory’s definition of infinite cluster size at
the gel point. For other experiments or considerations,
the length scale of interest might be smaller, and then
the terms “liquid” and “solid” might be used with a
meaning different from the one in this paper. On an
intermediate scale the crystal structures can be consid-
ered solid, even if they consist mostly of amorphous
polymer, and the phase surrounding the structures can
be considered liquid. A microscopic observer, e.g., a
small tracer molecule, would only see the crystal phase
of the lamellae as solid and everything else as liquid,
neglecting the phenomena at the interface. DSC would
also detect a crystal fraction, however, without realizing
macroscopic connectivity or lack thereof.

Knowledge of the slightly crystalline state near the
gel point is of direct practical importance for polymer
processing. An example is vacuum molding which is
purposely performed near the gel point where the
polymer sheets need to be stiff enough to be self-
supporting in the earlier phase of the process but soft
enough to deform under relatively small stress during
molding.

For an investigation of this crystallization-induced
critical gel state, it is important that the crystallization
reaches the gel point at a steady state so that the
structure of the polymer at the gel point is stable and
can be investigated. The threshold crystallinity \( X_{c \infty} \)
and the semicrystalline structure will depend on tempera-
ture history (path dependence) and other processing
parameters (pressure, nucleation aids and other addi-
tives, strain). A major difficulty for this experimental
study is the critical retardation of the crystallization
process near the gel point. In principle, there are two
ways to reach a stable critical gel state, either by cooling
from the melt state (supercooling) or by heating from
the solid state (partial melting). This study focuses on
the first possibility, i.e., cooling of a completely molten
polymer to a temperature \( T_{X} \) which is below its equi-
librium melting temperature, \( T_{m} \), and then observing
the changing rheological properties during equilibriation
at \( T_{X} \). We search for the temperature \( T_{X} = T_{c \infty} \) at which
the polymer has just enough crystallinity to reach its
gel point.

The objective of this paper is to determine whether
\( T_{c \infty} \) exists and, if so, how it can be approached and what
the rheological properties in the stable critical gel state
are. It should be much easier to find a temperature
where an intermediate degree of crystallinity is realized
for a copolymer than for a homopolymer. Early mea-
surements of Flory et al. 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. A copolymer of
ethylen and 1-butene was chosen for the present
measurements, having a much lower melting temper-
ated than pure PE. DSC will be used to determine
the crystallinity as a function of the crystallization
conditions. Small-amplitude oscillatory shear experi-
ments will monitor the gelation process, especially the
distance of the sample from its gel point.

**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 with a small amount of nucleating agent by
Exxon without purification.

**Methods. a. DSC.** Thermal analysis experiments were
performed under 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.
Figure 1. Temperature schedule for the measurements. The sample is preheated at \( T_0 \) for a certain time \( t_0 \) and then rapidly cooled to the crystallization temperature \( T_X \). In the case of the DSC experiments samples are held at \( T_X \) for some time \( t_c \). The heat of fusion \( \Delta H_m \) is determined by heating the crystallized sample at 10 K/min. The oscillatory shear measurements are carried out continuously at \( T_X \).

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

\[
G'(\omega) = S_* \Gamma (1 - n_c) \cos \left( \frac{\eta c \pi}{2} \right) \omega^{n_c} \quad \text{for} \quad \omega < \omega_0 = 1/b_0 (2)
\]

\[
G''(\omega) = S_* \Gamma (1 - n_c) \sin \left( \frac{\eta c \pi}{2} \right) \omega^{n_c} (3)
\]

\[
\tan \delta = \frac{G''}{G'} = \tan \frac{\eta c \pi}{2} = f(\omega) (4)
\]

\( G' \) and \( G'' \) are the storage and loss moduli, \( \delta \) is the loss angle, \( \omega \) is the angular frequency, and \( \Gamma \) is the gamma function. Frequency independence of \( \delta \) enables the detection of the gel point. Mechanical spectroscopy at a range of frequencies (frequency sweep) yields a constant \( \delta \) for a critical gel at sufficiently low frequencies.

Small-amplitude oscillatory shear (SAOS) was performed in a RMD-800 of Rheometric Scientific Inc., equipped with parallel plates (diameter 25 mm). The instrument is controlled by Rhois software. After preheating and then cooling to the crystallization temperature \( T_X \) (about 6 min), isothermal SAOS was used to monitor the evolution of loss and storage modulus, \( G'' \) and \( G' \), at a sequence of frequencies between 0.004 and 10 rad/s. The choice of frequency range was limited by the fact that the time for one frequency sweep has to be short compared to the gel time.\(^\text{l} \) Each data point takes at least one cycle, resulting in very long experimental times for the low frequencies. Therefore, the lowest frequencies could only be used for samples with very long gelation times, i.e., for slow crystallization at high temperatures. The strain amplitude was \( \gamma_s = 0.03 \), and in some cases \( \gamma_s = 0.05 \). There was no noticeable difference in the results, so strain and shear rate are assumed to be small enough not to influence the crystallization process.

Results

DSC. In the temperature protocol of Figure 1, the sample was kept at a preheating temperature \( T_0 \) for a certain time \( t_0 \) to remove influences of thermal history as much as possible; then it was quenched at 320 K/min to a given crystallization temperature \( T_X \) and kept there for the time \( t_c \). In a subsequent DSC heating scan (10 K/min), the heat of fusion \( \Delta H_m \) was determined together with the nominal melting temperature \( T_m \) as defined by the peak maximum.

The actual choice of \( T_0 \) was not obvious, since a plot of \( T_m \) versus \( T_X \) did not allow any extrapolation to an equilibrium melting temperature. To overcome this problem, we suggest choosing \( T_0 \) high enough so that the heat of fusion, as measured according to Figure 1, becomes independent of temperature history.\(^\text{25} \) For a typical parameter choice (\( t_0 = 5 \) min, \( T_X = 58 \) °C, and \( t_c = 30 \) min) in the most sensitive region of our sample, we varied the preheating temperature \( T_0 \). The heat of fusion \( \Delta H_m \) decreases with increasing \( T_0 \) in the temperature range below 120 °C; above this temperature \( \Delta H_m \) is constant. On the basis of this observation, the preheating conditions were set at \( T_0 = 130 \) °C and \( t_0 = 5 \) min for all following measurements.

DSC heating scans are shown in Figure 2. The melting process starts almost immediately upon heating; the difference between \( T_X \) and the peak onset is only 2–5 K, increasing slightly with \( t_c \). The value of heat flow at the peak maximum and the peak area increase with \( t_X \) and decrease with \( T_X \). The peak maximum shifts to higher temperatures with longer annealing times and higher crystallization temperatures. In all cases melting ends at 80 °C. At low \( T_X \) and short \( t_X \), a shoulder— or even a second peak—can be seen on the high-temperature side of the DSC-diagram (cf. Figure 2a).
Rheology.
The temperature schedule for the oscillatory shear experiments was chosen identical to that of the DSC experiments, except for the fact that the cooling from $T_0$ to the crystallization temperature $T_X$ takes longer, about 6 min. Frequency sweeps were carried out continuously during crystallization at $T_X$.

Figures 3 and 4 show the evolution of $\tan\delta$ and of the moduli. In a plot of $\tan\delta$ versus $\omega$, the data for the different sweeps overlap. To avoid overlapping in the graphical representation, curves were shifted horizontally by a factor SF so that the curve for one frequency sweep begins where that of the preceding sweep has ended.

Interpretation
DSC. Multiple melting behavior,26,27 as expressed in a shoulder or second peak at higher temperatures, also shown in Figure 2a, has been reported for various polymers such as isotactic polypropylene (ref 28, Figure 5a), propylene–ethylene copolymers (ref 29, Figure 4b), and poly(butylene terephthalate) (ref 30, Figure 2).

Multiple melting can be caused by melting of the most unstable crystals and recrystallization at higher temperatures, hence resulting in crystals with a higher melting temperature. The shape of the DSC melting curve is then explained as the superposition of two melting peaks and a negative recrystallization peak in between. An alternative explanation of the double DSC peaks might be polymorphism. However, the second peak or shoulder becomes less pronounced at higher heating rates (see Figure 5), which suggests that recrystallization is its most likely cause. X-ray investigations are very difficult for this sample because of its low crystallinity, even at room temperature. One finds a broad peak of the amorphous melt and, superimposed, some very small peaks caused by the crystalline regions. In addition to the peaks of the orthorhombic phase, a peak at lower scattering angle is found which can be attributed to a monoclinic phase. This implies that the cause for multiple peaks could also be polymorphism.

Since it is the goal of this study to find the temperature $T_X = T_{cg\rightarrow\infty}$ at which the critical gel state is stable, the experimental temperature was purposely limited to values where the crystallinity remains very small. Unfortunately, this results in very slow crystallization rates. As can be seen in Figure 6, the heat of fusion never reaches a steady value even at 1300 min, roughly
1 day. Assuming that no butene units are included in the crystalline phase,22 i.e., the crystalline phase is pure PE, one may assume that the heat of fusion of the crystal is about the same as that for the homopolymer. The value of the polyethylene crystal can be found in the literature31 and is 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.

In the experimental time and temperature range, no plateau of $\Delta H_m(t_X)$ was reached. The crystallinity increases almost linearly with the logarithm of $t_X$. Only at 50 °C (see Figure 6) can a slight negative deviation from the straight line be seen. This slowing down of the crystal growth indicates the approach of a plateau.

The “melting” temperature $T_m$ at the maximum of the melting peak increases with $t_X$ (Figure 7) and $T_X$, but it does not reach a plateau value. It increases with $t_X$ over the whole time range and runs almost parallel with $T_X$ being about 10 K higher at the long annealing times. This makes it impossible to apply the classical extrapolation to determine the equilibrium melting temperature according to Hoffman–Weeks32 or others.33,34

**Rheology.** The frequency independence of tan δ gives access to the determination of the gel point. For the case of a crystallizing polymer tan δ($\omega$) should exhibit a negative slope as long as the polymer is in the melt state. At the gel point tan δ is independent of $\omega$, at least at low frequencies. Therefore, a plateau should result, as shown schematically in Figure 8. At further solidification the polymer behaves like a solid; the slope of tan δ($\omega$) is expected to be positive for small $\omega$. The evolution of tan δ (Figure 3) with time shows that no clearly frequency-independent loss angle was observed. At first the slope is negative in the whole frequency range; later it becomes positive at low frequencies, resulting in a shoulder or a maximum. The reason is that the measurement is not carried out in the terminal zone as can be deduced from Figure 4. The slope of G’ is less than two and that of G” less than one. The required low frequencies cannot be realized since than the measuring time would be too long as compared to the gel time. Fortunately, near the threshold temperature, $T_g$, the gel times become very long, and low-frequency experiments are possible. However, the required low frequencies could not be used since the scattering in the rheological data becomes dominating at frequencies lower than 0.004 s$^{-1}$, and no reliable determination of the gel point is possible.

Because of these inherent problems, the method to determine the gel time has to be slightly modified. A shoulder or a maximum in tan δ($\omega$) at low frequencies means that the slope is zero; i.e., tan δ is independent of $\omega$, at least at one point. Therefore, the gel point is assumed to have occurred at some point during the first frequency sweep to exhibit a shoulder or a maximum in tan δ($\omega$). The gel time is estimated as the time when the first data point of this frequency sweep was taken. The error in the gel time is at least the measuring time for one frequency sweep. The estimated gel time might be longer than the actual gel time, since a flat tan δ($\omega$) might have occurred earlier at frequencies below the experimental range, but the determined value cannot be shorter than the actual gel time.

The two rheological parameters of the critical gels, the gel stiffness $S_c$ and the relaxation exponent $n_c$ as defined in eqs 2–4, are strongly dependent on $T_X$ (Figures 9 and 10). The values for $S_c$ and $n_c$ were determined at the frequency of the first maximum in tan δ($\omega$). With increasing $T_X$ (less supercooling), the critical gels become softer as expressed in a low $S_c$ value and a high $n_c$ value. $S_c$ decreases exponentially with $T_X$, and $n_c$ increases linearly with $T_X$. This is similar for polypropylene.35,36 The gel times increase more than...
exponentially with $T_X$ as can be seen in Figure 11.

**Discussion**

A power law can describe the dependence of the gel time on the crystallization temperature

$$t_{gel} = A \left( \frac{T_{cg}^\infty - T_X}{T_{cg}^\infty} \right)^{-\alpha}$$

(5)

where $(T_{cg}^\infty - T_X)/T_{cg}^\infty$ is the relative distance from the stable gel point and $\alpha$ is the critical exponent. Fitting of the data gives parameter values $A = 3.87 \times 10^{-6}$ s, $T_{cg}^\infty = 342.0$ K, and $\alpha = 6.46$. This function is shown in Figure 11 as solid line together with the experimental points. The validity of eq 5 is better seen in Figure 12 where $t_{gel}^{-1/\alpha}$ is shown as a function of $T_X$ yielding a straight line.

We define the threshold temperature $T_{cg}^\infty$ by the value of $T_X$ at which $t_{gel}$ diverges to infinity. The intersection with the abscissa at $T_{cg}^\infty$ marks the point where the crystallization time becomes infinite; i.e., the material requires infinite time to reach the gel point. At these conditions, the solidification reaches the gel point but does not proceed beyond. Furthermore, reaching the gel point at infinite times means the state of the critical gel is stable at $T_X = T_{cg}^\infty$.

Figure 11 can be read in similar ways as a phase diagram. Below the solid line, indicating the liquid—solid transition, i.e., at high temperatures and short crystallization times, the system is liquid; above the line, at low temperatures and long crystallization times, the polymer is solid. At $T_{cg}^\infty$ the curve diverges; for temperatures higher than $T_{cg}^\infty$, the polymer is a liquid independent of equilibration time.

It should be noted that $T_{cg}^\infty$ is not the equilibrium melting point. There is finite crystallinity $X_{cg}^\infty$ in the polymer, just enough to reach the gel point. The line in Figure 6 gives the heat of fusion at the gel point. It is almost constant at approximately 3 J/g, which corresponds to $X_{cg} = 0.01$, i.e., 1% crystallinity. This is a much lower value than for polypropylene.35 The reason for this low crystallinity of the critical gel might be the unusual crystallization path. Samples look clear, even at 10% crystallinity, far beyond the gel point. No large spherulites are formed. The crystalline domains remain very small so that visible light is not markedly scattered. This observation is consistent with the fact that the as-received samples contain a nucleation agent, which promotes growth of many very small crystallites.

**Conclusions**

The frequency independence of the loss angle at the gel point can be used to define the material state of the critical gel. The critical gel is a transient state for the crystallizing polymer. It is reached at longer and longer gel times as the crystallization temperature $T_X$ is increased to $T_{cg}^\infty$. The critical gel state, at which the polymer develops sample spanning connectivity for the first time, depends on thermal history; i.e., it is path dependent. However, DSC scans for various critical gels (with $T_X$ near $T_{cg}^\infty$) are quite similar. The threshold crystallinity is about 1%, but the melting temperature increases with increasing $T_X$ (as expected). At $T_{cg}^\infty$ the gel point is reached when the crystallization process is completely finished. Here, the critical gel state is not transient but it is stable. In the case of the crystallizing polymer of this study, a stable critical gel state could not be reached for finite experimental time. The threshold temperature of the stable critical gel was determined by extrapolation to find the temperature $T_{cg}^\infty$ where $t_{gel}$ becomes infinite.

The physical gelation caused by crystallization seems very similar to the chemical gelation by cross-linking.
Crystalline structures connect into a sample spanning network instead of chemical cross-links. Previous studies on the solidification behavior of crystallizing polypropylene showed that the reaction time in the latter case (chemical cross-linking) corresponds to the crystallization temperature where the sample behaves as a stable gel. For the physical gelation this happens at \( T_{cg} \).

At \( T = T_{cg} \), the polymer should exactly reach the threshold crystallinity \( X_{cg}^- \) at infinite time; the stable critical gel is realized. At \( T < T_{cg}^- \), the final crystallinity is higher than \( X_{cg}^- \), and the gel time becomes finite; the sample is a solid after sufficient crystallization time \( (t_x > t_{gel}) \). For \( T > T_{cg}^- \), the crystallinity is too low for a sample spanning connectivity (gel point). If \( T \) is above the equilibrium melting temperature, the sample does not crystallize at all; it is in the melt state.

Furthermore, it should be possible to determine the temperature where the sample behaves as a stable critical gel starting from the solid side by partial melting. The problem here is the much more complex temperature history. The cooling process from the melt, the storage conditions, and finally the heating conditions can influence the solidification behavior. Also, the effect of melting and recrystallization has to be taken into account. Future studies will elucidate this approach from the low-temperature side.

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