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Thermoreversible gelation of polyethylene/decalin mixtures by self-nucleated crystallization

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The critical gelation concentration of polyethylene gels formed in decalin by self-nucleation was studied as a function of the gelation temperature, the polymer dissolution temperature, and the time at the dissolution temperature. A comparison was also made with gels formed after cooling from a high temperature. The morphology of the various gels was examined to elucidate the gelation behavior. Self-nucleation of crystalline polymers in solution produces efficient gels that have a low critical gelation concentration and are relatively stronger at higher polymer concentrations than gels produced otherwise. The efficiency arises from the structural unit being a single lamella (but not necessarily a single polymer crystal) and by neighboring lamellae tending to rotate in solution to approach coplanarity, which allows an extensive attachment area between the lamellae. In addition, the lamellae in the gels appeared to all have the same size, and the critical gelation concentration was found to be relatively independent of the lamellar size. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyethylene; gelation/crystallization; self-nucleation)

INTRODUCTION

Thermoreversible gels can be formed from solutions of polyethylene and other highly crystalline polymers by cooling, and such gels drew renewed interest after Smith and coworkers[1,2] developed ultra-high modulus polyethylene fibers by gel spinning. When prepared under quiescent conditions from homogeneous solutions, the gels form by the interlinking of spherulites or other multilamellar structures[2-11].

A measure of the efficiency of gelation is the critical gelation concentration. This is the minimum polymer concentration under given conditions that will form a gel. The lower the critical gel concentration, the more developed and stronger the gel is when formed at higher concentrations. By the use of self-nucleated crystallization, in which the previous crystallinity is incompletely melted or dissolved before cooling for recrystallization, Blundell *et al.*[12-14] observed the gelation of polyethylene in solutions of relatively low concentration (0.5–1.0%). Although self-nucleation has been widely used to prepare polymer single crystals, it seems to have been little used for preparing gels or for studying gelation, though it was applied recently to the toughening of brittle epoxy resins with poly(butylene terephthalate)[15,16]. The formation of strong gels at low polymer concentrations is also important for the preparation of ultrahigh modulus fibers by gel spinning[17] and of microporous membranes by thermally induced phase separation[18].

The purpose of this report is to describe the experimental parameters involved in the gelation of polyethylene from decalin by self-nucleated crystallization.

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EXPERIMENTAL

The polyethylene used in this study was a commercial high density polyethylene (Marlex EHM 6007, Phillips 66 Company). It had a nominal density of 0.964 g/cm^3 and a weight average molar mass (M_w) of 125 000 g/mol. The polydispersity index (M_w/M_n) was 8.9, and it was used without fractionation. Decalin (decahydronaphthalene, 99%, a mixture of *cis* and *trans* isomers) (Aldrich) was used as the solvent; 1000 ppm of octadecyl-3,5-bis-(1,1-dimethylethyl)-4-hydroxybenzene propanoate (Irganox 1076, Ciba-Geigy), an antioxidant, was added to the solvent to prevent degradation of the polyethylene during preparation of the gels.

In the first step of preparing specimens, polymer and solvent in various concentrations were placed in 10-mm-inner-diameter glass tubes. The filled tubes were purged with nitrogen and evacuated to remove oxygen before sealing. After sealing, the tubes were heated in a convection oven at 150°C to form clear solutions and then cooled in water at 20°C to form a dispersion of polymer crystals. Tubes containing these dispersions of crystals were the starting point for each of the following experiments.

For self-nucleated gelation, the above dispersions of crystals were heated for specific lengths of time in either an oil or water bath (depending on whether the temperature was above 98°C or not) at dissolution temperatures (T_s) that were in the vicinity of or just above the clearing temperature, T_{cl}. (For polymer concentrations of 0.6–1.0%, $T_{cl} = 91°C$.) Specimens were then cooled by plunging them into water baths at various gelation temperatures, from 20° to 70°C, and held for 30 min. For 'normal' gelation, the dispersions of crystals were heated in a convection oven for 10 min at the dissolution temperature of 140°C. Specimens

were then cooled by plunging into water baths at various gelation (crystallization) temperatures (T_c), from 20° to 70°C, and held there for 30 min. Before ascertaining whether or not a gel had formed, the tubes were then placed in a water bath at 20°C for an additional 30 min.

To determine the relationship between the critical gelation concentration (C^*_g) and the dissolution temperature, a similar procedure was used. The crystal dispersions were heated to and maintained for specific times at various dissolution temperatures ($T_s = 91–140°C$) and then cooled to 20°C and held for 30 min. Three specific times were used: 5 min, 10 min, and 30 min.

To test for gelation, the tube containing the specimen was turned upside down. The specimens were considered to be gelled if the contents at the bottom of the tube did not flow down the wall. The critical gelation concentration for a given treatment was the minimum polymer concentration at which a gel formed.

The morphologies of the dried gels were examined using scanning electron microscopy (SEM) (Hitachi S-800 SEM). For this, 5% polyethylene in decalin was used because the gels with lower polymer concentration were too weak to maintain their integrities during washing and drying. The clearing temperature (T_{cl}) of 5% polyethylene in decalin was 94°C, rather than 91°C, as for 0.6–1.0% polymer concentrations. To prepare the SEM specimens, the decalin in the wet gels was exchanged for cyclohexane, and then the cyclohexane was removed by freeze drying under vacuum at 0°C for 48 h. To obtain a structure undisturbed by the above preparation, the dried gels were cleaved to expose the structure inside, and these surfaces were coated with Au–Pd metal prior to SEM observation. The SEM acceleration voltage was lowered to 2 kV to minimize electron beam damage of specimens, but slight curling of the edges of the lamellae still occurred during the slow scanning of the electron beam to obtain micrographs.

RESULTS

The critical gelation concentrations (C^*_g) for polyethylene in decalin were determined as a function of three variables: the gelation temperature (T_c), the dissolution temperature (T_s), and the dissolution time (t_s).

The effect of gelation temperature (T_c) on the critical gelation concentration (C^*_g) for constant dissolution temperature and time is shown in *Figure 1*. The dissolution temperature was 92°C or 1°C above the clearing temperature for these concentrations, and the dissolution time was 10 min. The critical gelation concentration was about 0.8 wt%, and it changed little with change in gelation temperature. (The slight decrease in critical concentration with increasing gelation temperature may have arisen from a higher degree of crystallinity at higher gelation temperatures.)

Also shown in *Figure 1*, for comparison, are the critical gelation concentrations for 'normal' gelation, in which the polyethylene was fully melted and dissolved at 140°C before cooling to the gelation temperatures shown. The critical gelation concentrations for these specimens are much higher than for those cooled from 92°C at all gelation temperatures. In addition, the critical gelation concentration is seen to decrease significantly with the decrease of the gelation or crystallization temperature, T_c, which is a result noted also by Domszy *et al.*[4] Though each specimen was rapidly cooled to its gelation temperature by plunging into a water bath at that temperature, some of
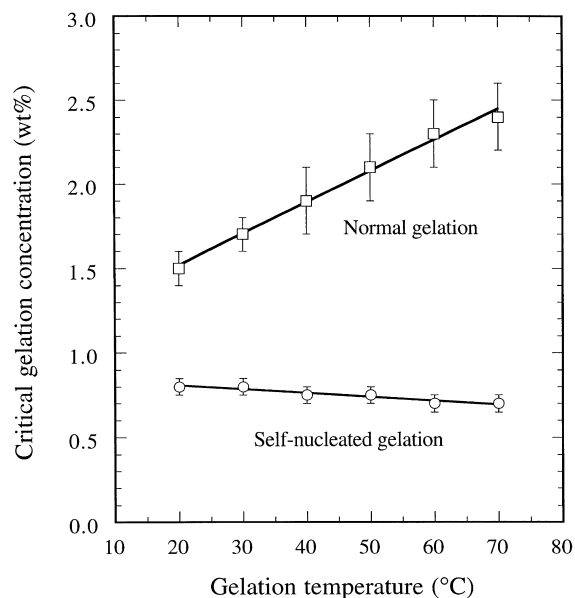

Figure 1 Effect of gelation (or crystallization) temperature (T_c) on the critical gelation concentration (C^*_g) for self-nucleated gelation (dissolution temperature (T_s), 92°C) of polyethylene/decalin mixtures. Also shown is the effect of T_c on C^*_g for normal gelation ($T_s = 140°C$)
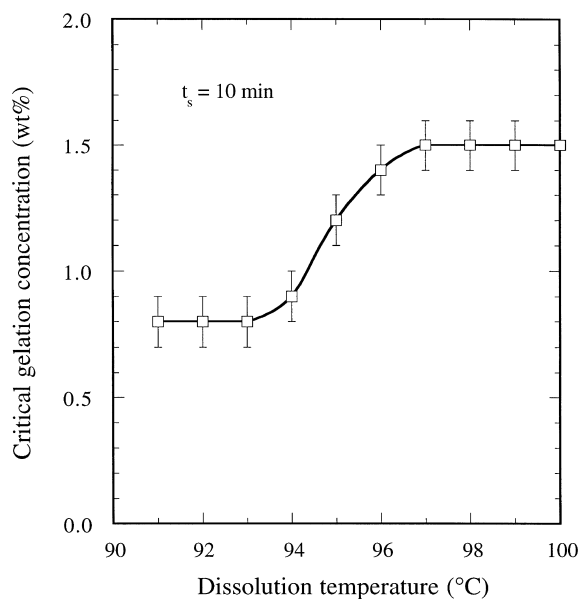
Figure 2 Effect of dissolution temperature (T_s) on the critical gelation concentration (C^*_g) of polyethylene in decalin. Dissolution time (t_s) was 10 min and gelation temperature (T_c) was 20°C for all specimens. The clearing temperature (T_{cl}) for 0.6–1.0% polyethylene was 91°C

the lower-temperature-gelling specimens may have crystallized before reaching the bath temperature, because these specimens turned white within seconds of being immersed in the bath. Crystallization at the bath temperature was more certain for the higher-temperature-gelling specimens because these specimens turned white only after some minutes of being immersed in the bath.

The effect of dissolution temperature (T_s) on the critical gelation concentration (C^*_g) for constant dissolution time (t_s) and gelation temperature (T_c) is shown in *Figure 2*. The dissolution time was 10 min and the gelation temperature was 20°C. The critical gelation concentration decreased from about 1.5% to about 0.8% when the temperature at
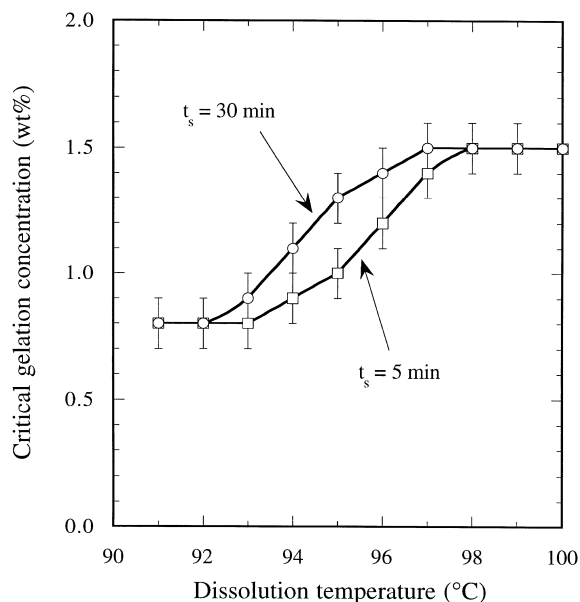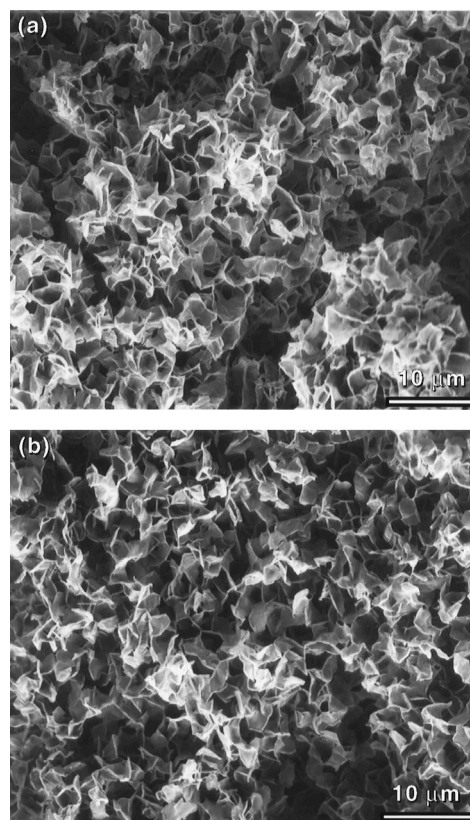
Figure 3 Effect of dissolution time (t_s) on the critical gelation concentration (C^*_g) of polyethylene in decalin. The two dissolution times were 5 and 30 min; the gelation temperature (T_c) was 20°C for all specimens. The clearing temperature (T_{cl}) for 0.6–1.0% polyethylene was 91°C

Figure 4 Scanning electron micrographs of dried gels formed by self-nucleated gelation of 5% polyethylene in decalin. Dissolution temperature (T_s) was 95°C; gelation temperatures (T_c) were (**a**) 70°C and (**b**) 20°C. The clearing temperature (T_{cl}) for 5.0% polyethylene was 94°C. Gels were freeze dried at 0°C after exchanging decalin with cyclohexane

which the dispersion of polyethylene crystals in decalin was held for 10 min was changed from 97°C to 93°C. For all temperatures above 97°C (including 140°C), the critical gelation concentration remained unchanged, at about 1.5%, and for the range 91–93°C, the critical concentration remained at about 0.8%. (Although gels can be formed when the dispersion of crystals was heated to temperatures below the clearing temperature, these gels tend to lack strength and were not studied.)

The effect of dissolution time (t_s) on the critical gelation concentration (C^*_g) for various dissolution temperatures and a constant gelation temperature of 20°C is shown in *Figure 3*. The two curves shown are for the dissolution times of 5 and 30 min. The curve in *Figure 2*, for the dissolution time of 10 min, fits between the two in *Figure 3*. As with the dissolution time of 10 min, the critical gelation concentration decreased from about 1.5% to about 0.8%. Though the two times, 5 min and 30 min, differ by a factor of six, the shift in the critical gelation concentration curve along the temperature axis is at most two degrees.

The morphologies of dried self-nucleated gels formed at the gelation temperatures of 70°C and 20°C from 5% polyethylene in decalin are shown in *Figure 4*. Both shrank about 10% in each dimension on drying. At a polyethylene concentration of 5%, the clearing temperature in decalin was about 94°C. To maintain comparability with the gels in *Figure 1*, a dissolution temperature 1°C above that, or 95°C, was used for the gels in *Figure 4*. The diameters of the lamellae are 2–3 μm in both of the gels in *Figure 4*. Both gels exhibit a continuous network with much edge-to-edge joining of the single-lamellar units, which is the mode of lamellar linking previously seen by Blundell *et al.*[12–14] with polymer concentrations much smaller than 5%. There was little effect of gelation temperature. The occasional strings that can be seen in these micrographs probably occurred during cleavage of these specimens, and they suggest good interlinking of the structures.

When the dissolution temperature of the 5% dispersion was 94°C (=T_{cl}), the diameter of single-lamellar units in the
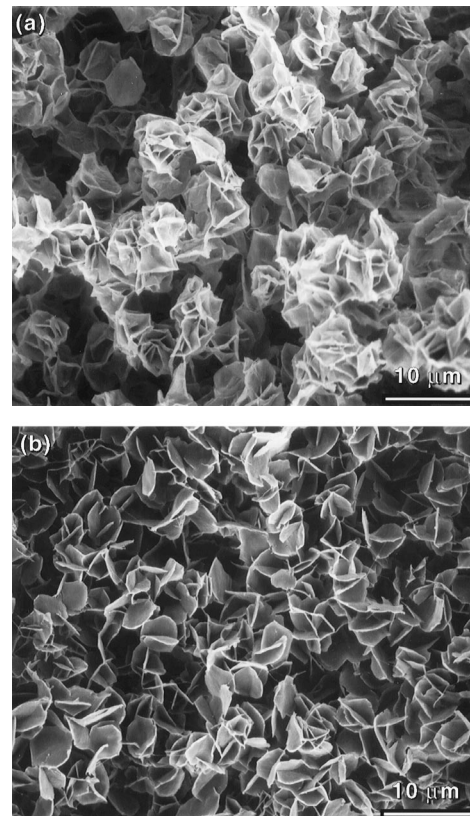
Figure 5 Scanning electron micrographs of dried gels formed by normal gelation of 5% polyethylene in decalin. Dissolution temperature (T_s) was 140°C; gelation temperatures (T_c) were (**a**) 70°C and (**b**) 20°C. Gels were freeze dried at 0°C after exchanging decalin with cyclohexane

gel became smaller still (about 1 μm), but the mechanical strength of the gel was similar to that of the gel cooled from 95°C. Again, most of the lamellae were nearly equal in size and were linked together by edge-to-edge joining.

The morphologies of the normal gels formed at the gelation temperatures of 70°C and 20°C from 5% poly-ethylene in decalin after cooling from 140°C are shown in *Figure 5*. On drying, the gel formed at 70°C (*Figure 5(a)*) shrank about 30% in each dimension. In contrast, the gel formed at 20°C (*Figure 5(b)*) shrank only about 10%, like the self-nucleated gels in *Figure 4*. (The more dense appearance of the dried gel in *Figure 5(a)* than that in *Figure 5(b)* is a result of its greater degree of shrinkage.) The gel formed at 70°C is composed of relatively dense multi-lamellar clusters. That formed at 20°C has more clusters but with fewer lamellae each (mostly two or three lamellae per cluster). The diameters of the crystalline clusters in the two dried gels seen in *Figure 5* were almost the same, about 4–5 μm.

DISCUSSION

When formed by self-nucleated crystallization, the mini-mum polymer concentration at which a gel will form under given conditions (the critical gelation concentration, C^*_g) was found for the polyethylene material studied to be about 0.8%, nearly independent of gelation temperature, T_c. C^*_g was found to be independent of the temperature to which the initial dispersion of crystals was heated, T_s, when T_s was in the range from the clearing temperature to 2°C above it (the most effective self-nucleation range). But at higher temperatures, C^*_g suddenly increased and became, at 6–8°C above the clearing temperature, the same as that when a polymer solution is cooled from a high temperature. Also, C^*_g was independent and the self-nucleation temperature range was relatively independent of the time, t_s, during which the initial dispersion of crystals remained in the self-nucleation temperature range. The self-nucleation tempera-ture range increased by at most 2°C when t_s was increased from 5 min to 30 min.

Critical gelation concentration and nucleation

The independence of C^*_g from T_c when self-nucleated and the strong dependence of C^*_g on T_c when not suggests that C^*_g depends on the number of primary nuclei. The main difference between the gels formed by cooling from the different temperatures is nucleation. With few hetero-geneous nuclei in solution, as when the dispersion was heated to high temperature to fully dissolve the polymer, gelation (or crystallization) waits for the formation of homogeneous nuclei, which is generally enhanced with decreasing temperature. But with self-nucleated crystal-lization, the large number of nuclei remaining from incomplete melting of previous crystallites is practically unaffected by homogeneous nucleation; the number of nuclei is controlled instead by the dissolution temperature[12]. The gelation time, which was noted qualitatively though not measured specifically in the present experiments, behaved like C^*_g. The suggestion that the gelation time depends on primary nucleation had previously been made by Girolamo *et al.*[19] Domszy *et al.*,[4] noting the same increase in C^*_g with increasing T_c for normal gelation, suggested instead that it arose from the dependence on temperature of the crystal growth kinetics and crystal thickness. Because nucleation was not separable from the overall crystallization kinetics in these studies, its role was not able to be ascertained. The

present results support the suggestion of Girolamo *et al.*[19] that nucleation plays the dominant role in the dependence of C^*_g on T_c. Other kinetic factors such as those suggested by Domszy *et al.*[4] may play a subordinate role, however.

The criticality of self-nucleation for gelation is indicated by the dependence of C^*_g on T_s and t_s. The clearing temperature, T_{cl}, occurs right at the end of melting, as measured by differential scanning calorimetry, for example, and the self-nucleation range extends upward by 6°C or so from T_{cl}. Presumably, the number of nuclei formed during self-nucleation decreases monotonically with increasing temperature. The independence of C^*_g from T_s over the range from T_{cl} to about $T_{cl} + 2$°C may arise then from there being an overabundance of nuclei when $T_s < T_{cl} + 2°$. But above $T_{cl} + 2$°C, the increase in C^*_g seen would seem to mirror the decrease in nuclei.

Although the dependence of C^*_g on t_s is small, it is not negligible. If the nuclei, usually thought to be higher-melting crystal fragments, were thermodynamically stable, the dependence of C^*_g on t_s would be negligible. But the lack of stability could arise from the small size of the nuclei and the effect on them of thermal fluctuations. Thus, the small dependence of C^*_g on t_s is not sufficient reason to think that the nuclei are not small pieces of higher-melting crystal fragments.

Critical gelation concentration and gel morphology

The morphologies of the various gels correlate well with their critical gelation concentrations. The gels in *Figures 4 and 5* were all formed from solutions containing 5% polymer. Like C^*_g for self-nucleated gels formed at $T_c = 20$°C and 70°C, respectively, the morphologies of these gels are essentially the same (*Figure 4*). Moreover, these gels make efficient use of the polymer. Most of the structural units are single lamella, and these are seen in the micrographs to often be joined at their edges. The lamellae are seen even to approach coplanarity with one another so as to enhance the length of the joint. (This was apparent as well in the previous micrographs of Blundell *et al.*[12–14]) By contrast, the individual structural units for normal gels (cooled from 140°C) consist of multiple lamellae in clusters (*Figure 5*). The unit for the gel formed at $T_c = 20$°C consists of two to three lamellae per cluster; that formed at 70°C, which was the gel having the highest C^*_g and was also the weakest, consists of many lamellae per cluster.

The number of lamellae per cluster for the 5% gels in *Figures 4* and *5* suggests how the excess polymer beyond C^*_g is distributed. For the normal gels, and especially that formed at $T_c = 70$°C, the excess polymer forms additional lamellae within the already formed unit or cluster; these lamellae seem to grow out from the original primary nuclei. There seems to be a paucity of primary nuclei elsewhere that can add structural units to further strengthen the gel beyond the minimum number of units needed for gel formation, which occupy ~16% of the volume[20]. In contrast, the self-nucleated gels, and to some extent the normal gel formed at $T_c = 20$°C, seem to add further structural units with the excess polymer above C^*_g. The spareness of these units seems to arise from there being a high enough density of primary nuclei producing primary lamellae that the solvent essentially becomes depleted of polymer before secondary lamellae are able to grow.

Bassett *et al.*[21] had previously suggested that secondary lamellae grow from molecular 'hairs' attached to primary lamellae and that the greater lamellar branching occurring at higher crystallization temperatures was because the

equilibrium length of the molecular hairs was longer. But now that the same single-lamellar morphology has been found at each of two gelation temperatures, differing by 50°C (cf. *Figure 4(a)* and *(b)*), the presence of hairs, short or long, seems not to dominate the initiation of secondary lamellae. However, Bassett *et al.*[21] also observed that at a given temperature, the number of lamellae per crystal cluster increased with increase in polymer concentration. This would be consistent with the above suggestion that the secondary lamellae arise from the excess polymer that remains in solution after the primary lamellae, growing from the totality of primary nuclei present, have merged to form a gel network.

A feature of the morphology of self-nucleated gels of particular note is the joining of the lamellae at their edges and the tendency for neighboring lamellae to be coplanar, allowing long lengths of the bond to develop. Other notable features of the morphology are the generally uniform size of the structural units or lamellae and the seeming independence of gel strength and lamellar size. These features are discussed in the following.

Edge-to-edge joining of near-coplanar lamellae

The tendency of the growing lamellae to join only at their edges is as if the edges were coated with a contact adhesive, an adhesive that adheres well to another similarly coated surface but is otherwise not very sticky. Since it is at the lamellar edges that lamellar growth occurs, the 'contact adhesive' that is attaching and even attracting pairs of lamellae would seem to be individual or entangled molecules that are being drawn from solution onto the growing surfaces of both lamellae. The secondary nucleation of molecules from solution onto the growing edge surfaces is analogous, then, to precoating with a contact adhesive.

To gain a long bond line between a pair of lamellae, the lamellae need not be coplanar, but the normals to the lamellae need to be in the same plane. But presumably the bond would increase in strength as the lamellae become more coplanar, because the crystallinity that forms the bond would become more perfect.

For a pair of lamellae meeting edge to edge, their normals are likely not to be in the same plane, let alone the lamellae being coplanar with one another. How is it, then, that so many of the lamellae in *Figure 4* appear to have their normals in the same plane as that of their nearest neighbors, if not even appearing to be coplanar? Are the crystallizing molecules that constitute the adhesive able to rotate the lamellae? Surprisingly, they are.

Consider the effect of a single molecule attached to the growing edge surfaces of a pair of lamellae and stretched between them (*Figure 6*). The dynamics of the mutual
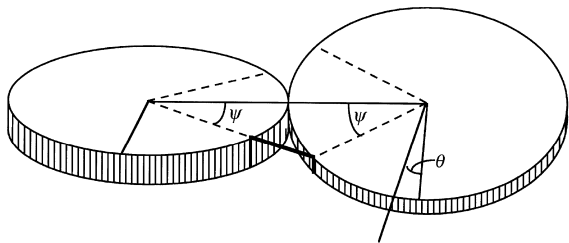
rotation of a pair of lamellae about an axis through their diameters can be described by

$$M = f\omega + I\dot{\omega} \qquad (1)$$

where M is the torque, f is the rotational frictional coefficient, ω is the rotational velocity, and I is the moment of inertia about the rotational axis. The solution to this equation is

$$\omega = M/f + (\omega_0 - M/f)\exp[-(f/I)t] \qquad (2)$$

where ω_0 is the rotational velocity at $t = 0$. The rotational frictional coefficient, for an oblate spheroid for which the radius, R, is much larger than the half-thickness, $h/2$, is given by[22,23]

$$f = (32/3)R^3\eta \qquad (3)$$

where η is the viscosity of the medium. The moment of inertia of a lamella of radius R and thickness h for rotation about a diameter is

$$I = (\pi/4)R^4 h\rho \qquad (4)$$

where ρ is the mass density. To estimate the coefficient in the exponential in equation (2), f/I, assume the lamellar radius to be 1.5 μm, the thickness to be 0.15 μm (the term 'lamella' is being used as a description of the morphology and is not meant to imply that the lamella is a single polyethylene crystal; the micrographs indicate that the radius is at least ten times greater than the thickness ($h \leq R/10$)), and the viscosity is that of pure decalin, about 1 mPa·s. The result is $f/I = 6 \times 10^7$ s^{-1}. Thus, the exponential is essentially zero within 0.1 μm, and the second term in equation (2) can be neglected, giving

$$\omega = M/f \qquad (5)$$

The effective force acting on a molecule from crystallization is the heat of fusion per unit length of chain. For polyethylene, the heat of fusion is 280 J/g; hence, the effective force acting on a single crystallizing chain is 5.2×10^{-11} N. For a molecule spanning the gap between a pair of lamellae to be able to apply the maximum mutual torque between the pair, the molecule needs to be attached as far away as possible from the point where the lamellae touch. Assume for each lamella that this is at the angle ψ away from the radial lines drawn to the point of lamellar contact, as indicated in *Figure 6*. Assuming that the maximum distance spanned by the molecule is equal to its root-mean-squared end-to-end distance, for polyethylene having a molar mass of 125 000, the maximum distance is about 40 nm. If the molecule spanning the gap between the lamellae is stretched to the length Z, the moment arm is given by $r = \partial Z/\partial \theta$, where θ is the angle to which the pair of lamellae are rotated away from coplanarity (see *Figure 6*). The moment arm depends on the orientation of the lamellae, the attachment points of the crystallizing molecule with respect to the pivot, and the lamellar radius. For $R = 0.5$ μm, $\psi_{max} \approx 5$–6° and $r \sim 0.04$ μm over a range of values of θ. The torque applied to the lamellae, then, is 2.1×10^{-18} N·m. Assuming the viscosity of the medium to be 1 mPa·s, the rotational velocity, according to equation (5), is 1560 rad/s. The time required for the lamellae to mutually turn through an angle of 45° is 0.5 ms. For $R = 1.5$ μm, $\psi_{max} \approx 2$° and $r \sim 0.05$ μm over a range of values of θ. The torque applied to the lamellae is now 2.6×10^{-18} N·m, and the rotational velocity, according to equation (5), is 72 rad/s. The time required for the lamellae to turn mutually through an

Figure 6 Diagram showing pair of touching lamellae, whose normals (not shown) are rotated away from being in the same plane, and a single polymer chain (darkened) that is attached at its ends to each lamella

angle of 45° is 11 ms. These very short times arise from a single molecule acting on lamellae in a medium having the viscosity of decalin, as would be appropriate if the solvent was on the verge of being depleted of polymer. At higher polymer concentrations, the viscosity would be higher, but presumably, more than just one molecule would be drawing the lamellae toward coplanarity, and the times could be equally short or shorter.

Lamellar size uniformity

The lamellae in the gel tend to all be roughly the same size. Although pairs of lamellae could presumably attach to one another at any time during their growth, their appearing in micrographs to all be about the same size suggests that most of them had joined together only after they had reached approximately their final size. This would occur if the nuclei were uniformly distributed throughout the solution and remained in fixed positions until the lamellae had grown large enough to join to form the gel. But the nuclei are not uniformly distributed at the beginning. With self-nucleation, the nuclei arise from the previous crystals. In the present experiments, crystal clusters were more or less uniformly dispersed in the solvent, but the nuclei arising from them would not be uniformly distributed. Crystallization from the nuclei without redistribution would just reconstitute the original crystal clusters. Hence, for gelation, the nuclei need to redistribute.

The mobility of a lamella can be estimated from the Stokes–Einstein equation for Brownian motion. The root-mean-squared translation of a particle during the time t is given by[24]

$$x_{rms} = \langle x^2 \rangle^{1/2} = (2Dt)^{1/2} \qquad (6)$$

where D is the diffusivity and for an oblate spheroid of radius R and thickness h, for $R \gg h$, is[23]

$$D = kT/(12\eta R) \qquad (7)$$

where k is Boltzmann's constant and T is the absolute temperature. η is the viscosity of the medium and is expected to depend on the polymer concentration, c. Assuming that a solution of polyethylene in decalin behaves like that of poly(vinyl chloride) in cyclohexanone[25], then

$$\eta = A \exp(\alpha c) \qquad (8)$$

where A and α are constants. When self-nucleated, the number of lamellae remains essentially constant during growth and their radii increase at the same rate while their thicknesses remain constant. Therefore, c can be related to the radius, R, decreasing as R increases. The initial concentration of polymer in solution can be denoted by c_0, when $R = 0$, and the solution can be assumed to have been depleted of polymer ($c = 0$) after the lamellae have grown to their final size, R_f. Since the volume of the lamellae increase in volume as R^2, then $(R/R_f)^2 = 1 - c/c_0$. Therefore, the viscosity can then be written as

$$\eta = A \exp\{\alpha c_0 [1 - (R/R_f)^2]\} \qquad (9)$$

The rms translation becomes

$$x_{rms} = (kT/6AR)^{1/2} \exp\{ -(\alpha c_0/2)[1 - (R/R_f)^2]\}t^{1/2} \qquad (10)$$

Examples of lamellar translation during 1 s are shown as a function of R in *Figure 7* for three different final lamellar radii. The diffusion is assumed to occur at 20°C. The polymer solution before crystallization has started is assumed to contain 5% polymer and to have a viscosity of 100 mPa·s,
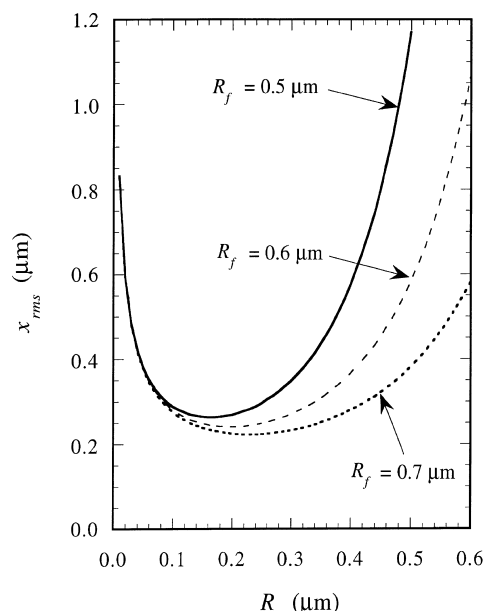
Figure 7 Root-mean-squared translation during 1 s in a polymer solution of a growing lamella of radius R. The radius approaches R_f as the solution becomes depleted of polymer
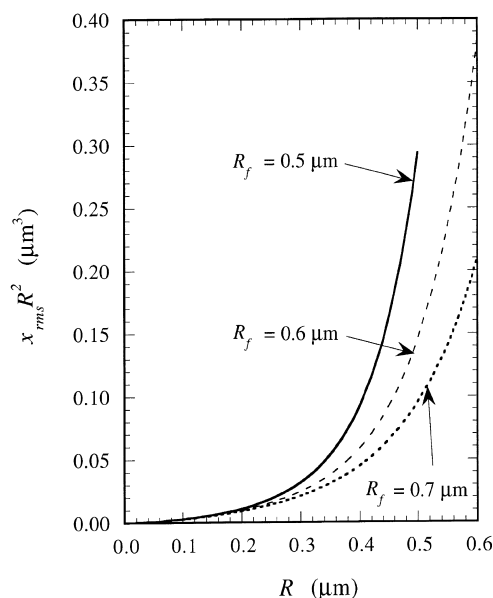
Figure 8 Probability of one lamella encountering a second lamella edge-to-edge, expressed as $x_{rms}R^2$, during 1 s in a polymer solution of a growing lamella of radius R. The radius approaches R_f as the solution becomes depleted of polymer

and this decreases to 1 mPa·s when the polymer has been removed by crystallization. The lamellae are seen to have high mobility as the nuclei begin to initiate crystallization. Thus, the nuclei are able to approach uniform distribution fairly quickly. As the nuclei grow, however, their mobility falls, though it is seen to increase again later with sufficient decrease in solution viscosity.

As the lamellae diffuse through solution, the probability that the growing edge of one lamella encounters the growing edge of a second lamella is proportional to R^2. (The lamellae translate most easily parallel to a diameter, and if a lamella typically collides with another that is turned away from the plane of the first by the angle θ, the effective collisional cross-section equals $R^2 \cos \theta$.) The probability that the
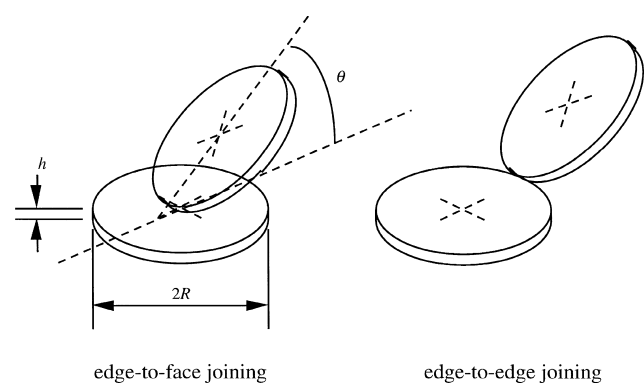
growing edges of a pair of lamellae encounter each other in the time t, then, is proportional to $x_{rms}R^2$. This quantity is plotted versus R in *Figure 8*, using the same assumptions as for *Figure 7*. The probability that a pair of lamellae encounter each other during translation and stick together is seen to be minimal while the lamellae are small but becomes increasingly likely as the lamellae increase in size. The size of the lamellae at which they begin to merge depends on the density of the nuclei or their average separation. The accelerating pace of merging with increasing size means that by the time roughly 10–20% of the lamellae have paired, the remaining 80–90% follow soon after with very little more growth, which causes the lamellae to seem to have the same size.

Lamellar size and critical gelation concentration

The critical gelation concentration of polyethylene/decalin mixtures seems not to correlate with the size of the lamellae forming the gel. When mixtures containing 5% polyethylene were dissolved at 94°C (T_{cl}) and cooled, the lamellae were about 1 μm in diameter, but when dissolved at 95°C ($T_{cl} + 1$°C) and cooled, the lamellae were 2–3 μm in diameter. But the gels seemed equally strong, and the critical gelation concentrations after dissolving at these two temperatures were about the same. The reason for the independence of $C*_g$ and lamellar size is probably related to the tendency of the lamellae to join together edge-to-edge.

The expectation that $C*_g$ and lamellar size should be dependent results from the following simple but incorrect analysis. If a gel forms by the joining together of randomly distributed lamellae all having the same radius R and thickness h as in *Figure 9*, any two lamellae are typically oriented at the average angle θ with respect to each other. The average excluded volume for each lamella, for $R \gg h$, is roughly $R^3 \cos \theta$. The excluded volume is the volume that cannot be occupied by the center of the typical neighboring lamella. The number of lamellae forming a gel in the volume V is then proportional to V/R^3, and the amount of polymer involved is proportional to $(V/R^3)\pi R^2 h$. Assuming h is constant, this is proportional to R^{-1}, according to which, gels with larger lamellae should have lower critical gelation concentrations. This was not seen.

The above model assumed that the lamellae could join edge-to-face as easily as edge-to-edge, but the former is rarely seen (Blundell *et al.*'s micrographs[12–14] and *Figure 4*). A more appropriate model is the following. Although each lamella in the gel may eventually join to many neighbors, when the gel first forms, it is sufficient for

each lamella to attach to just two neighbors. Thus, the sequence of lamellae forming the initial gel is similar to a polymer, with the lamellae as the repeating units. Also, since the sequence along the connected lamellae will be like a random walk, a volume of internal dimension L would have to be spanned by a minimum of n lamellae, where

$$L^2 = Kn(2R)^2 \tag{11}$$

and K is a constant, akin to the characteristic ratio for polymers. The concentration of polymer required to form the gel, $C*_g$, assuming each lamella has the radius R and thickness h, is

$$C_g^* \propto \frac{n\pi R^2 h}{L^3} \propto \frac{nR^2}{(nR^2)^{3/2}} = \frac{1}{n^{1/2}R} \tag{12}$$

But for fixed volume dimensions, $n \propto R^{-2}$, and $C*_g \sim R^0$, as observed. (Had h been allowed to scale with R in the first calculation, instead of being held fixed, $C*_g \sim R^0$ would have been obtained for that calculation as well.)

CONCLUSIONS

Self-nucleation of crystalline polymers in solution produces efficient gels that have a low critical gelation concentration and are relatively stronger at higher polymer concentrations than gels produced otherwise. The efficiency arises from the structural unit being a single lamella (but not necessarily a single polymer crystal) and by neighboring lamellae tending to rotate in solution to approach coplanarity, which allows an extensive attachment area between the lamellae. In addition, the lamellae in the gels appeared to all have the same size, and the critical gelation concentration was found to be relatively independent of the lamellar size.

Figure 9 Diagrams of edge-to-face and edge-to-edge joining behaviors of lamellae. It is assumed that the normals to any two lamellar planes form an average angle θ

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