

Gels and Foams from Ultrahigh-Molecular-Weight Polyethylene

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Crystallization–gelation of ultrahigh-molecular-weight polyethylene (UHMW PE) was used to make stiff gels that were supercritically dried to make low-density, small-cell-size foams. The effects of solvent and cooling conditions on gelation and morphology were investigated. X-ray diffractometry showed that the size of the crystalline lamellae in the finished foam decreased with increased cooling rate for foams made from UHMW PE in tetralin, but not in dodecane or decalin. This difference may be attributable to the greater expansion of the polyethylene chain in tetralin than in dodecane, as revealed by viscometry. However, the superstructure of the foam, which includes the pore sizes and homogeneity, was found to be affected by solvent as well as by cooling conditions.

GELS ARE FORMED BY CRYSTALLIZATION of polyethylene from solution (1, 2). For a time, the belief persisted that shearing of the solution was required for gelation of polyethylene (3, 4), but Edwards and Mandelkern (5) and Smith and Lemstra (6) showed that shearing is not required, and in fact, gels will form on cooling from quiescent solutions. In addition, crystals formed during gelation appear to be the same type as those formed from dilute solution, that is, lamellar rather than fringed micelle (5).

The variables involved in forming the crystalline cross-linked structures (several chains physically locked into the crystal) can be understood by looking at the process. As the solution is cooled, chains form crystalline lamellae that serve as reversible cross-links if chain entanglement in the solution was sufficient. Chain entanglement is sufficient if for each lamella, at least three chain ends leave and participate in the formation of another

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lamella. Several variables seem important in this process. The degree of entanglement of the chains prior to gelation will obviously affect the formation of the cross-linked system. A high-molecular-weight polyethylene with a narrow molecular-weight distribution would be expected to give the most entanglement. This hypothesis has been well proved by Domszy et al. (7), who showed that gel formation is proportional to molecular weight and concentration. Also, the expansion of the polyethylene chain in solution will differ depending on the solvent used. Thus, the aspect of gelation related to chain entanglement should be a function of the solvent.

The cooling rate, crystallization temperature, and solvent are important in the formation of crystalline nuclei. The formation of crystalline nuclei requires energy because new surfaces are being created, so a certain amount of subcooling is required, even though the crystalline form of polyethylene is more thermodynamically stable once formed (8, 9). Thus, the interfacial surface energy at the crystal face-solvent boundary strongly influences the rate of crystal formation and the crystallization temperature. Geil (8) pointed out that, for a given molecular weight and concentration of polyethylene in a particular solvent, the lamellar thickness is solely a function of the cooling conditions for dilute solutions. However, the lamellar thickness is changed by different solvents (10).

Given this background, we investigated the effects of the solvent, cooling rate, and crystallization temperature on polyethylene gel formation for ultrahigh-molecular-weight polyethylene (UHMW PE) over a narrow concentration range. To study the crystalline structure and more details of the morphology, the gels were dried to foams via a very gentle technique, supercritical drying. Cloud point measurements, viscometry, differential scanning calorimetry (DSC), optical microscopy (OM), scanning electron microscopy (SEM), and X-ray diffraction measurements (XRD) were used to investigate the effects of the processing parameters.

Experimental Details

Preparation of UHMW PE Gels and Foams. An entangled solution was made by injecting 3–30% (w/v) PE powder, 0.4% (w/v) antioxidant, and the solvent into a 10-mL ampule. Hercules PE 1900, a powder of about 30- μm diameter, with a molecular weight of 3×10^6 daltons, was generally used in the experiments. The antioxidant, 4,4'-methylenebis(2,6-di-*tert*-butylphenol), retards chain scission that would reduce the degree of entanglement. The filled ampule was then sealed to prevent evaporation of the solvent and reduce oxidation of the PE. The contents were shaken to disperse the PE powder and immediately placed in a 150 °C oil bath, where dissolution and/or melting occurred within 10 min. One to three days was given for complete disentanglement and randomization of the polymer chains. The solution was now cooled to crystallize and phase separate, during which the gel shrinks slightly.

The now-solid, white gel was slid into a Soxhlet extractor for 7 days of exchange with isopropyl alcohol. In the next step, isopropyl alcohol was replaced with liquid

carbon dioxide for critical point drying. The gel was placed in a pressure vessel, and the vessel was filled with liquid CO₂ at 14 °C and 900 psi. The CO₂ was replaced three to four times each day for 1 week. Then, the CO₂ level was dropped to half, the temperature was raised to 40 °C, and the pressure was raised to between 1200 and 1600 psi. (The critical temperature (T_c) is 31 °C, and the critical pressure (P_c) is 1100 psi). After 10 min, the pressure valve was cracked open, and the CO₂ was allowed to vent down to atmospheric pressure over 3 h without ever passing a liquid meniscus through the fragile foam material. The finished foam was cylindrical, white, and deformable. It shrank to 70–80% of its original volume when tetralin was the solvent.

Apparatus for Characterization. An Ubbelohde tube with Schott Gerate AVS 300 automatic dilution viscometer was used to determine intrinsic viscosities of the polyethylene samples. Gel points were determined via a Nametre oscillating viscometer. A Leitz Orthoplan-Pol polarizing microscope with Vario-Orthomat 2 camera attachment was used for optical microscopy. A Perkin-Elmer DSC-4 was used for the differential scanning calorimetry. The X-ray diffractometer consisted of a Norelco X-ray source with copper anode and nickel filter coupled to a Philipps scanning goniometer. Scanning electron micrographs were taken via the Hitachi S-800, generally at 10 kV.

Results and Discussion

Solvent Effects on Solution and Gelation. We screened 14 solvents for solubility and behavior during gelation. Cloud point and dissolution temperature measurements of the eight most promising solvents were made to determine the degree of subcooling. These were determined visually in the oil bath while the solutions were cooled at about 10 °C/h. The cloud point data are shown in Figure 1 as a function of solution concentration. The cloud points for *n*-alkanes are typically 10–15 °C higher than those for aromatic and hydroaromatic compounds. However, the degrees of subcooling (ΔT_m), that is, the initial dissolution temperature minus the cloud point, are virtually the same for both tetralin and dodecane at 2 wt % (where ΔT_m is 38 °C for tetralin and 41 °C for dodecane) and at 9 wt % (where ΔT_m is 31 and 21 °C), respectively. The lowered values of dissolution temperature and cloud point for PE in tetralin are probably related to its greater effectiveness as a solvent. But because the degree of subcooling is not changed by different solvents, this measure gives no indication that crystalline structure should be affected by the solvent.

We next investigated the effect of solvent on chain dimension via viscometric techniques. Tetralin and *n*-dodecane were chosen for further comparison of the aromatic compounds with the *n*-alkanes. Dilute solution capillary flow viscometry was used to measure the limiting viscosity number, $[\eta]$. In a good solvent, the chain is swollen with solvent and expanded, a condition that increases the viscosity. Einstein's viscosity equation (11)

$$\eta = \eta_0(1 + 2.5\phi) \quad (1)$$

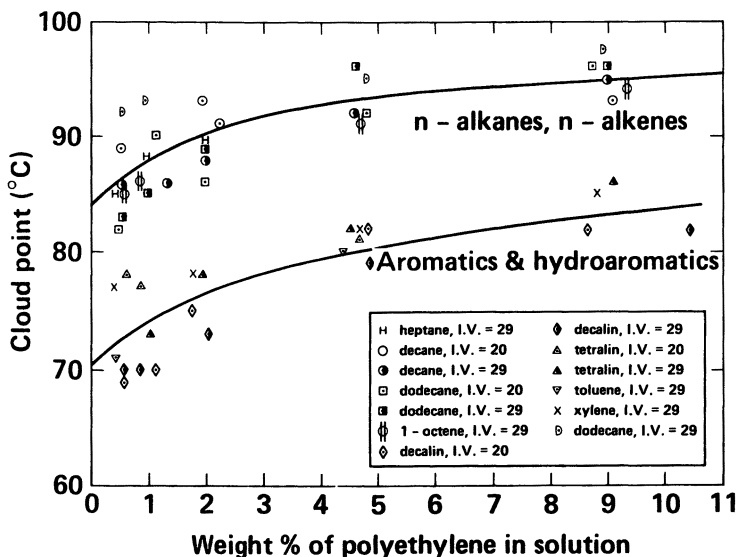


Figure 1. The effect of solvent and concentration on cloud point of solutions of UHMW PE. I.V. stands for intrinsic viscosity of the polyethylene. I.V.s 29 and 20 correspond to molecular weights of approximately 6×10^6 and 3×10^6 daltons, respectively.

relates the solution viscosity, η , to the solvent viscosity, η_0 , and the volume fraction of the particles, ϕ . This equation can be rewritten in terms of limiting viscosity number, partial molar volume of the polymer, v_2 , and the molecular weight, M (11).

$$[\eta] = \frac{2.5v_2}{M} \quad (2)$$

For the UHMW PE used here, the molecular weight had been determined to be about 3×10^6 daltons by applying the Mark-Houwink (12) equation to intrinsic viscosity measurements. The limiting viscosity numbers were 20 dL/g in tetralin and 5 dL/g in dodecane, corresponding to partial molar volumes of 3.98×10^{-15} and 9.99×10^{-15} cm³/molecule, respectively, as calculated from equation 2. If we assume the particles to be spherical, the radii are 9.83×10^{-6} cm³ in tetralin and 6.19×10^{-6} cm³ in dodecane, results indicating one-third higher expansion in tetralin.

The average radius of a polymer molecule can be calculated with the assumption that the polymer takes on a random flight configuration in solution. Then the mean square radius is

$$r^2 = nl^2 \quad (3)$$

where n is the number of repeating units, and l is the length of each bond (11). For PE chains with molecular weight of 3×10^6 daltons, n is 2.1×10^5 , l is 1.54×10^{-8} cm, and the mean radius is 7.06×10^{-6} cm, which is between the experimental values for tetralin and dodecane.

Actual molecules do not assume truly random flight configurations in solution because bond angles and steric effects restrict flexibility and tend to increase the size of the molecule in solution. The mean square radius of a chain with a bond angle θ is

$$r^2 = \frac{nl^2(1 - \cos \theta)}{(1 + \cos \theta)} \quad (4)$$

For PE in which the polymer is linked by C–C single bonds, θ is the tetrahedral angle, 109.5° . The mean radius was found to be 9.98×10^{-6} cm, almost exactly that found experimentally from analysis of the limiting viscosity data for UHMW PE in tetralin. This result suggests that PE is collapsed somewhat in dodecane relative to the unperturbed state.

Next, the concentrations and temperatures at which entanglement of the UHMW PE occurs were investigated with vibrational viscometry. The probe, a 0.5-in. diameter cylinder, oscillated at approximately 600 Hz with an amplitude of 25 μ m. The extremely low amplitude of oscillation avoided any stirring motion that may have induced polymer chain alignment. Figure 2 shows the rise in viscosity as the solutions were cooled from 150 $^\circ$ C to their crystallization temperatures. Viscosity increases sharply for solution concentrations high enough to produce chain entanglement and is determined by the amount of chain entanglement. The concentration at which the viscosity shows a sharp rise is defined as the gel concentration, c_g . If gelation is the condition when the polymer chains just touch, the chain radii can be calculated. With closest packing, the total polymer particle volume is then

$$V_p = 0.74V_t \quad (5)$$

where V_t is the total volume of the solution. The total polymer particle volume is also given by the product of the volume of an individual particle with the number of particles,

$$V_p = \left[\frac{4\pi r^3}{3} \right] \left[\frac{c_g V_t N_0}{M} \right] \quad (6)$$

where N_0 is Avogadro's number. Equations 5 and 6 can be combined to give

$$r = \left[\frac{0.177M}{c_g N_0} \right]^{1/3} \quad (7)$$

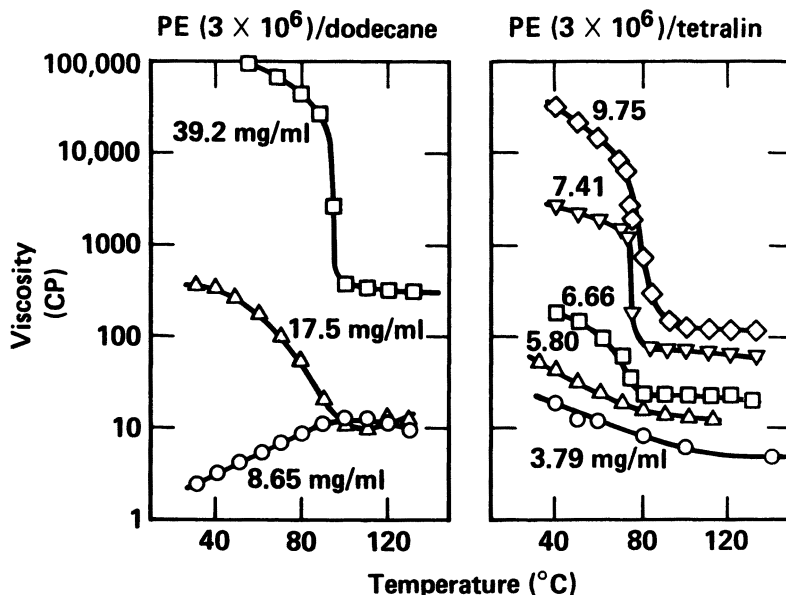


Figure 2. The effect of tetralin and dodecane as solvents on the UHMW PE gel concentration and temperature (gel point defined here as place where viscosity increases sharply) demonstrated via results of oscillating viscometry.

The critical gel concentrations were found to be approximately 0.74% (w/v) at 75 °C for tetralin and 3.0% (w/v) at 90 °C for dodecane. From equation 7, the polymer particle radius was found to be 4.88×10^{-6} cm in tetralin and 3.08×10^{-6} cm in dodecane, each approximately half the dimension found from analysis of dilute solution viscometry. The ratio of the radius in tetralin to that in dodecane is about 1.6, exactly that found from the dilution viscometry experiments. The higher solution concentrations may change the polymer dimensions, or the polymer chains may already be overlapping at our definition of critical gelation. Nevertheless, analyses and experiments show that entanglement should and does occur at a lower concentration in tetralin.

Conditions during Crystallization. The strength and structure of the PE gel depend directly on the crystalline structure induced during cooling to gelation. Previous work and theory (8) on crystallization from dilute solution indicated that a high degree of subcooling would result in a smaller crystal size. We therefore studied the effects on gel structure of cooling rate and crystallization temperature via DSC, OM, SEM, and XRD.

Heating and cooling cycles for a 5% (w/v) PE–tetralin gel were performed directly on the DSC. The sample was cooled at 0.1, 1, 10, 30, 60, 100, and 320 °C/min and then heated at 10 °C/min. The results for the

heating cycle, shown in Figure 3, were reproducible. A higher onset and melting point were obtained when the sample was cooled more slowly. A very fast cool (100 or 320 °C/min) resulted in double peaks, but a cool of 10 °C/min resulted in a left shoulder. This finding suggests that more rapid cooling may result in smaller morphology, or perhaps a dimorphism, where different size crystals are formed.

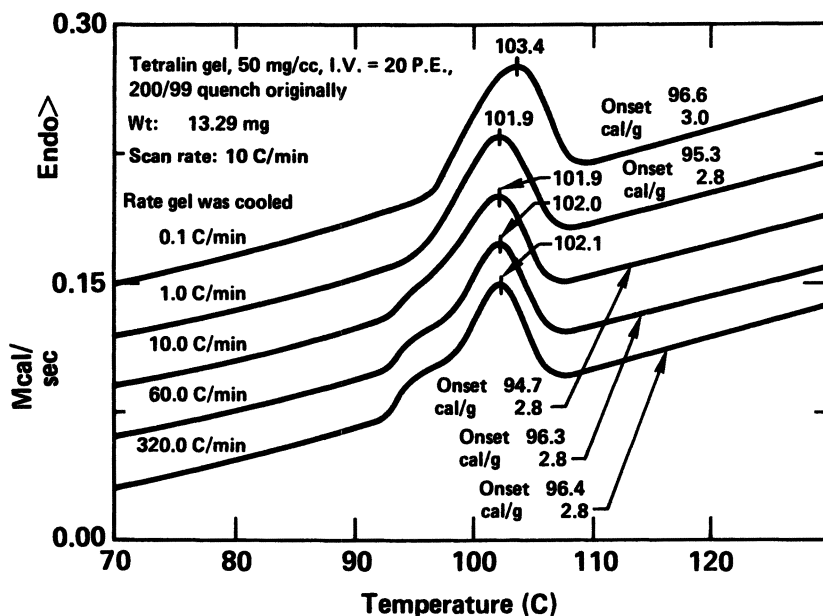


Figure 3. Effect of quench rate of UHMW PE gels on crystal size, as seen by differential scanning calorimetry.

However, the DSC scans of the gels permeated with isopropyl alcohol in the first solvent-exchange step and of the foams showed about 75% crystallinity and no substantial differences attributable to cooling rate effects. Probably, tetralin acts to stabilize the amorphous regions around the smaller crystals, and these amorphous regions crystallize to form larger crystals during exchange, considering that the PE–isopropyl alcohol gels do not show any differences.

If the rate of cooling is fast and the crystallization temperature sufficiently low, the crystal size and the degree of crystallinity in the gel are significantly reduced. Analysis of another series of 5% (w/v) PE–tetralin gel samples via DSC revealed that the heat of melting was 2.2 cal/g for a gel quenched to –5 °C, as compared to 5.7 cal/g for samples quenched to 45 and 99 °C. In addition, the gel quenched to –5 °C was noticeably less rigid than the others.

Optical micrographs of the gels and scanning electron micrographs of

foams made from those gels support the DSC results. Gels made from 5% (w/v) PE in tetralin, dodecane, and decalin were cooled by quenching to -5°C and by slower cooling rates of $5\text{--}8^{\circ}\text{C/h}$ and $2\text{--}3^{\circ}\text{C/h}$. These results are shown in Figures 4–6, respectively. For all three solvents, the structure is most homogeneous for the samples quenched to -5°C . With the PE–tetralin gels, optical micrographs of those more slowly cooled show spherulitic structures of about $200\text{ }\mu\text{m}$, but the quenched gel has a fine, homogeneous structure of $20\text{-}\mu\text{m}$ sliverlike crystals. These changes are reflected in the foams by an increase in homogeneity as seen in the SEMs. The gels from dodecane were influenced the least by the cooling rates, and those from decalin gave the most dramatic results as well as the most obvious relationship between the OM and the SEMs, as seen in Figure 6. At the slowest cooling rate, OM show large spherulites of approximately $100\text{ }\mu\text{m}$, and the SEMs show “sea sponges” near the same size. These structures

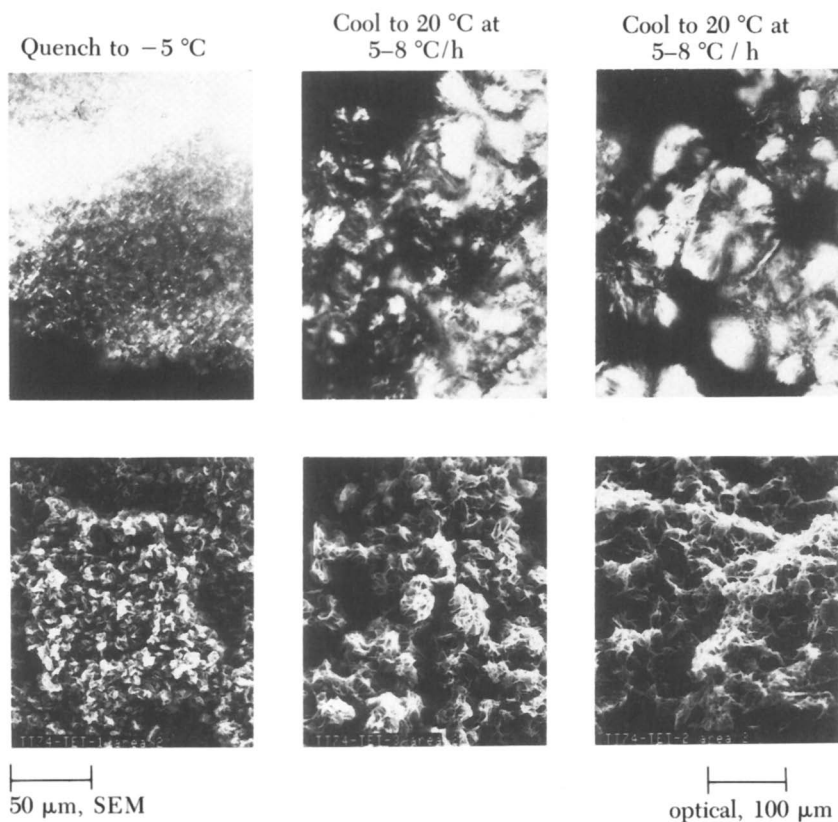


Figure 4. Optical micrographs (top) of 5% UHMW PE in tetralin gels and scanning electron micrographs (bottom) of the supercritically dried foams. Increased cooling rate decreases the spherulitic size and increases homogeneity.

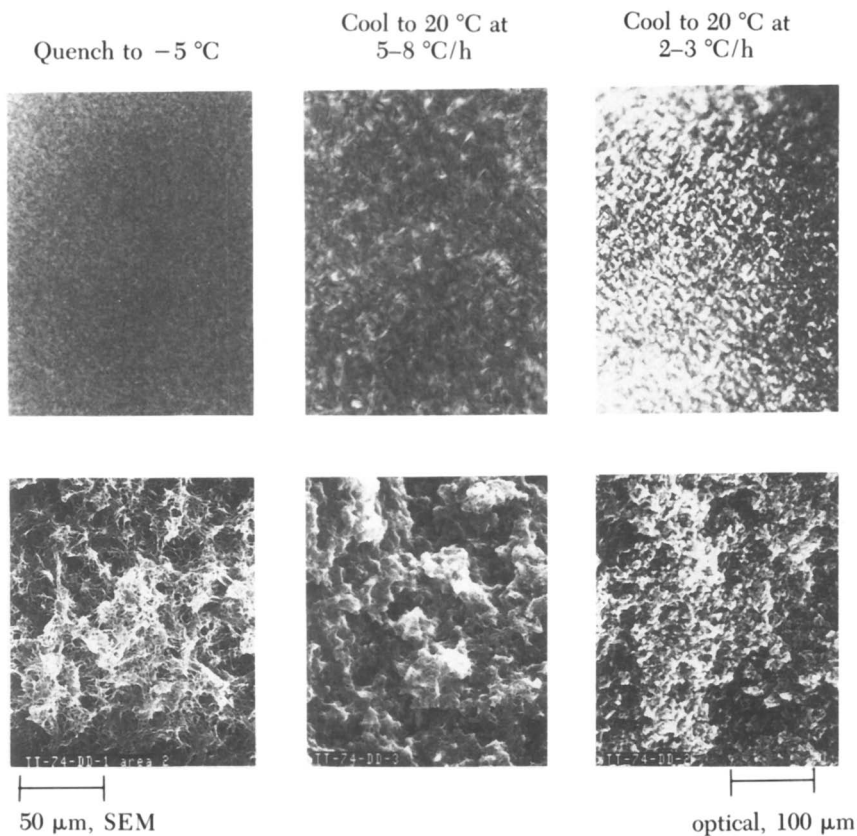


Figure 5. Optical micrographs (top) of 5% UHMW PE in dodecane gels and scanning electron micrographs (bottom) of the supercritically dried foams. Spherulitic size decreases slightly, and homogeneity increases.

clearly decrease in size as the cooling rate is increased, so that for the quenched sample, they are from 10 to 20 μm in diameter.

The thickness of the folded polymer chain lamella that make up the walls of the cellular foam can be measured by X-ray diffraction techniques. For a foam whose walls are relatively perfect crystalline lamella, the crystalline thickness can be calculated from the Scherrer equation (13),

$$L_{hkl} = \frac{K\lambda}{\beta_0 \cos \theta} \quad (8)$$

In the Scherrer equation, L_{hkl} is the crystallite dimension perpendicular to the hkl plane, K is a constant commonly set to unity, β_0 is the full width at half maximum intensity of the reflection occurring at a diffractometer angle of θ corresponding to the hkl reflection, and λ is the radiation wavelength.

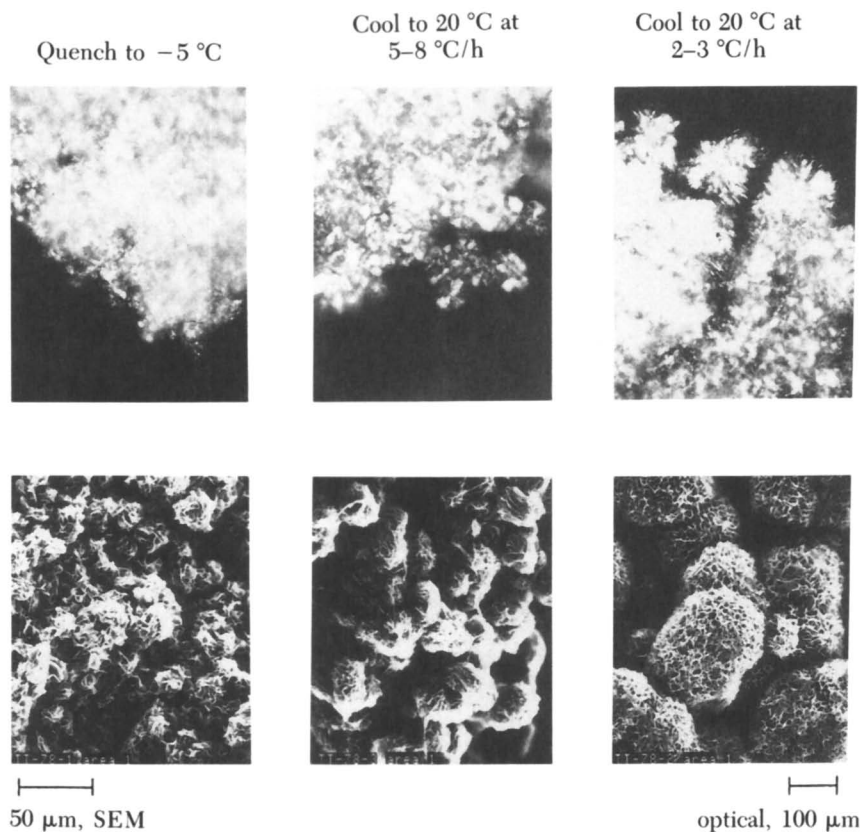


Figure 6. Optical micrographs (top) of 5% UHMW PE in decalin gels and scanning electron micrographs (bottom) of the supercritically dried foams. Increased cooling rate significantly decreases spherulitic size and increases homogeneity.

Accurate analysis of crystal dimensions by the Scherrer equation is complicated by the broadening caused by lattice distortions. However, comparisons between similar materials provide useful qualitative information on crystal thickness. The thickness of polyethylene lamella is a function of the magnitude of the undercooling during crystallization.

We first compared two samples of polyethylene with molecular weight 3.5×10^6 daltons: one was melted and slowly cooled as a film; the other was a foam prepared as a gel and then supercritically dried. Analysis of the diffractometer scans from the two samples gave a crystal thickness of 17 nm for the melt and 8 nm for the foam. Because of lattice distortion, both values may be low by a factor of 2. A cell-wall thickness of about 35 nm was previously calculated (14) from a foam structural model; therefore, the cell walls must be composed of two to four layers of polyethylene lamella.

Next, the gels prepared from tetralin, dodecane, and decalin under different cooling conditions as discussed were dried to foams. A thin slice of foam was mounted and scanned by the X-ray diffractometer. Analysis of XRD scans shows that crystal sizes of the 5% PE–tetralin foam, as determined from the 110 and 200 reflections, decrease with decreased crystallization temperature, as shown in Table I. However, no correlation is evident between crystallization conditions and crystal sizes for the foams made from dodecane or decalin.

Table I. Effect of Cooling Rate on Crystal Size As Seen by 110 and 200 Reflections

Cooling Rate (°C/h)	Tetralin		Dodecane		Decalin	
	110	200	110	200	110	200
2–3	14	13	10	10	11	11
5–8	10	8	14	13	12	9
–5 °C quench	7	6	14	12	13	11

NOTE: All values are given in nanometers.

Obviously, the combination of the SEM, OM, and XRD results suggests that the crystal lamellae forming the structure are affected by cooling conditions in the gelation process only for tetralin. But the superstructure that uses the crystal lamellae to form the gels is affected by solvent and cooling conditions. A further example of this effect is the fact that the percent shrinkage on going from gel to foam is different for both solvent and cooling rate. On the average, the percent shrinkage was 26, 37, and 47 for tetralin, decalin, and dodecane, respectively. And, for the 2–3 °C/h, 5–8 °C/h, and –5 °C quench samples, the percent shrinkage was 31, 36, and 43, respectively. This result indicates that the gels made in tetralin and cooled at the slowest rate, 2–3 °C/h, are the most cohesive and strong.

Summary

We studied the effects of solvent and cooling conditions on the structure and properties of crystallization gels and foams made from those gels by supercritical drying. Dilute and concentrated viscometric studies showed that PE is more expanded in tetralin than in dodecane, a necessary condition for entanglement and gelation. The effects of cooling rate on gel morphology were studied via DSC and OM. Increased cooling rate resulted in a more homogeneous and overall finer structure. Studies of the foams via SEM and XRD verified these results. Also, increased cooling rate and decreased crystallization temperature decreased the crystal size in foams made from PE–tetralin gels. However, some structural change may occur during the solvent exchange or drying process, considering that DSC of the foam samples shows no significant effect of cooling rate.

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