

Thermoreversible Gelation of Low Molecular Weight Linear Polyethylene Fractions and Normal Hydrocarbons

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Received February 27, 1992; Revised Manuscript Received June 22, 1992

ABSTRACT: The thermodynamic and morphological features of thermoreversible gels formed by low molecular weight fractions of linear polyethylene and by *n*-hydrocarbons formed as a result of crystallization from dilute and moderately dilute solutions have been investigated. The critical concentration for gel formation, c^* , of the polyethylenes follows an unusual pattern with molecular weight. A discontinuity is observed at about $M = 4 \times 10^3$ followed by an initial decrease in c^* as the chain length is decreased. With a further decrease in molecular weight c^* becomes invariant. These unusual changes in c^* can be attributed to the formation of extended chain crystallites. The dependence of c^* on the chain length of the *n*-hydrocarbons follows a quite different pattern. In this case, the highest molecular weights overlap the corresponding polymer fractions. However, as the chain length decreases c^* continuously increases. The differences in gel formation between the two species can be attributed to the different morphological forms that develop. The thermodynamic properties of the gels and crystallites formed from dilute solution are very similar to one another.

Introduction

The thermoreversible gelation of polymers, without the formation of covalent bonds, is a well-established phenomenon.¹⁻¹¹ One established mechanism is gel formation as a consequence of crystallization from dilute or moderately dilute solutions. More specifically the gelation of linear polyethylene, and its copolymers, has been subject to many investigations.^{2-4,12} Studies using molecular weight fractions of the linear polymer and molecular weight and composition fractions of the copolymers have demonstrated that the size characteristics and thermodynamic properties of the crystallites in the gels and those formed from dilute solution, prepared under comparable conditions, are essentially the same for a given molecular weight.^{2,4} Contrary to some reports, stirring is not required for gelation since gelation can occur under quiescent crystallization conditions.¹³⁻¹⁵ There is a continuity in the gel melting temperatures, as well as in other thermodynamic properties, with increasing co-unit content despite major changes that take place in the supermolecular and optical properties.⁴ Gel formation in these systems results from intercrystalline connections and the overlapping of supermolecular structures. The formation of a fringed micellar crystallite is not a necessary condition for gel formation since gelation is observed for both lamellar and micellar systems.^{3,4}

The previous work with linear polyethylene, which lead to the above conclusions, encompassed the molecular weight range of approximately 10^4 – 10^6 . In the present work we have extended the gelation studies of linear polyethylene fractions to lower molecular weights. The lowest molecular weight fraction studied here was about $M = 6 \times 10^2$. The highest molecular weight fraction studied was 4.4×10^4 in order to overlap with the previous work. The gelation of the normal hydrocarbons has also been reported.¹⁶ However, detailed information about the thermodynamic and morphological properties of these types of gels was not made available. Because of our interest in the low molecular weight linear polyethylene fractions, we have also included a study of the *n*-hydro-

Table I
Characteristics of Linear Polyethylene Fractions

fraction	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
1	0.574		
2	0.785		
3	0.910		
4	1.1	1.2	1.10
5	1.7	1.9	1.15
6	2.9	3.1	1.10
7	3.9	4.0	1.06
8	5.6	5.8	1.08
9	8.0	8.4	1.05
10	8.9	10.0	1.26
11	21.6	23.3	1.16
12	41.0	44.0	1.16

carbons. Consequently, the thermoreversible gelation of the *n*-hydrocarbons from $C_{28}H_{58}$ to $C_{192}H_{386}$ was also investigated in the present work.

Experimental Section

Materials. The molecular characteristics of the linear polyethylene fractions studied here are listed in Table I. Samples 1–3 were fractions obtained from a whole polymer that was purchased from Polysciences, Inc. The fractionation procedure has already been described in detail.¹⁷ The number-average molecular weights were determined by proton NMR based on the end group analysis.¹⁷ Samples 4 and 5 were obtained from the Petrolite Corp. Samples 6–12 are narrow molecular weight fractions that were obtained from Société Nationale Elf Quitaine (SNEA). The *n*-hydrocarbons $C_{40}H_{82}$, $C_{44}H_{90}$, $C_{46}H_{94}$, $C_{50}H_{102}$, and $C_{80}H_{162}$ were obtained from Fluka A.G.; $C_{32}H_{66}$ was obtained from KBK Laboratories, Inc.; $C_{28}H_{58}$ was obtained from Aldrich Chemical. These samples were used as received. The $C_{34}H_{70}$ sample was obtained from the API Project courtesy of A. Dixon. The $C_{192}H_{386}$ was a gift from Professor G. Wegner and Dr. C. Kröhnke. The thermodynamic properties of this alkane have been reported previously.¹⁸

Procedures. The gels were made from toluene solutions. For linear polyethylene, typical concentrations ranged between 1% and 5% (w/v), depending on the molecular weight and temperature. For the *n*-alkanes, the concentrations varied from 0.3% to 8% (w/v).

Melting temperatures and enthalpies of fusion were determined with a Perkin-Elmer DSC 2B calorimeter operating at a heating rate of 10 K/min. The instrument was calibrated with indium. The melting temperatures were identified with the maximum of the endothermic peak in the thermograms. The nascent gels

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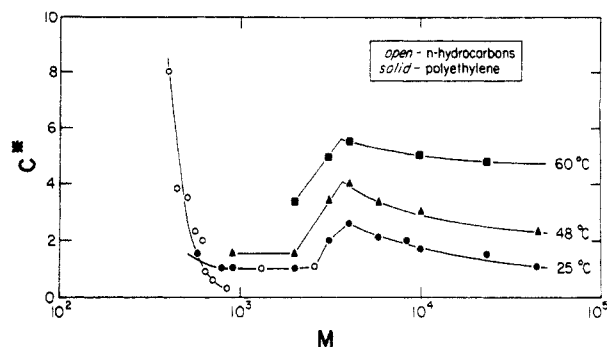


Figure 1. Critical concentration for gelation, c^* , against the log of molecular weight for the linear polyethylene fractions and n -hydrocarbons in toluene: n -hydrocarbons at 25 °C, \circ ; and polyethylene fractions at 25 °C, \bullet ; 41.3 °C, \blacktriangle ; and 60.8 °C, \blacksquare .

were confined to large-volume capsules sealed with O-rings. The enthalpies of fusion reported for these gels were based on the weight of the polymer. Small-angle light scattering (SALS) patterns were obtained using a photometer that has been described previously.¹⁹ The patterns were obtained at room temperature.

The polarized light microscopic studies of the undried gels were made at room temperature using a Leitz Ortholux II microscope equipped with a Leitz Orthomat-W automatic microscope camera.

Scanning electron micrographs (SEM) were obtained with a JEOL JEM-100CX II TEM SCAN operating at between 5 and 20 mV. Dried gels were placed on aluminum buttons and coated with a gold/palladium mixture to reduce sample charging. Reduced pressures and critical point methods were used to dry the samples.

Both the low-frequency longitudinal acoustic mode (LAM) and the internal model Raman spectra were obtained with a SPEX 1403 double monochromator operating with an argon ion laser at 514 nm. For the Raman LAM, the spectrometer was controlled by a SPEX Scamp. Dried samples were packed into a thin-walled capillary tube. The data were converted into ordered chain length distributions following the methods of Snyder and Scherer²⁰ and the Simanouchi relation²¹ taking 2.9×10^2 dyn/cm² as the appropriate modulus²². Raman internal models were recorded in the range 950–1550 Δcm^{-1} . The spectrometer was controlled by a SPEX Datamate. The procedure used to analyze these spectra in order to obtain the core crystallinity fraction, α_c , the liquidlike fractions, α_a , and the fraction of the interphase has been reported.^{23,24}

Results and Discussion

We find that thermoreversible gels are formed with the low molecular weight fractions in toluene, as well as other common solvents for polyethylene, at ambient as well as elevated temperatures. Thus, gelation can range from molecular weights of a few hundred to those in the multimillion range. All of the linear polyethylene gels are turbid. In general, they are mechanically weak but become more rigid at the high molecular weights.^{4,25}

An important quantity in analyzing the gelation process is the critical polymer concentration, c^* , that is required for gelation. This quantity is defined as the concentration at a given temperature, below which gelation will not occur. However, at concentrations less than c^* crystallization still takes place. The dependence of c^* on molecular weights and temperature is also very important. In Figure 1, c^* is plotted against the log of the molecular weight for different temperatures. The results in the higher molecular weight range studied here, 4×10^3 to 4×10^4 , are essentially a continuation of the earlier report with respect to both chainlength and temperature.⁴ Previously, the lowest molecular weight studied was about 4×10^4 . For the higher molecular weights, c^* decreases with molecular

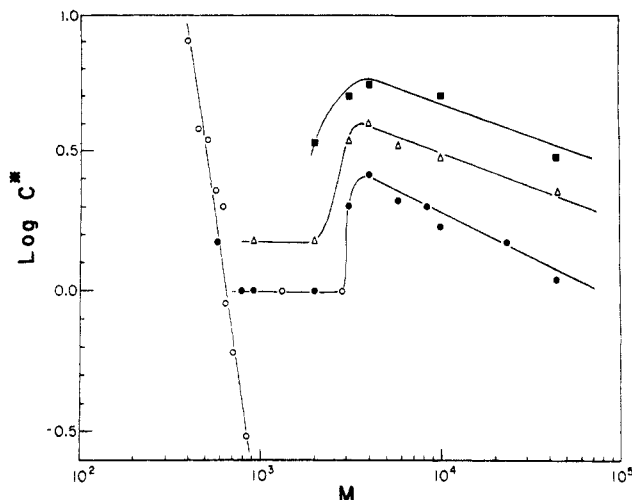


Figure 2. Double logarithmic plot of data from Figure 1 with the same symbols.

weight and increases with temperature. However, in the lower molecular weight range as the chain length decreases, a discontinuity is observed in the plot of Figure 1 at $M = 4 \times 10^3$. Here, the critical concentration decreases with a decrease in molecular weight to about 2.5×10^3 . With a further decrease in chain length, c^* remains constant to the lowest molecular weight studied, $M = 600$.

In order to understand this unusual dependence of c^* on M , it is instructive to examine the crystallite thickness in the molecular weight range of interest. This quantity can be obtained from the Raman LAM, and the values are listed in Table II. For $M_w = 3.1 \times 10^3$ the most probable ordered sequence length of the gel, L_R , is 0.27 of the extended chain length. Thus, the crystallite thickness is comparable to the extended chain length in this molecular weight range. This ratio increases to 0.6 for $M = 1.2 \times 10^3$. The three lowest fractions studied here are in almost completely extended form.¹⁷ Thus, the discontinuity observed, and the change of direction in the c^*-M plot, coincides with the molecular weight range where extended chain crystals are beginning to develop. The crystal concentration is essentially constant for the three lowest molecular weight fractions that are in almost completely extended form. To examine the molecular weight dependence of c^* in more detail, a double logarithmic plot of these two quantities is given in Figure 2. For molecular weights greater than about 3×10^3 , the data are linear in this plot and can then be expressed in the form

$$c^* = kM^{-a} \quad (1)$$

The constant a varies from 0.2 to 0.3. These values are the same as were found for the much higher molecular weight fractions.⁴ The discontinuity at about $M = 3 \times 10^3$ is more sharply defined in this plot as is the invariance in c^* at the lowest molecular weights. For chains in statistical conformation the concentration at which the molecular domains of the individual chains begin to overlap in dilute solution is expressed as $c^* \approx M^{-1/2}$. It is evident from the present, as well as previous,⁴ data that the constant a cannot be approximated by 0.5. Hence, we have now established that over the range $M = 3 \times 10^3$ to 2×10^6 molecular overlap is not a sufficient condition for gelation. Much higher concentrations are required. It has also been reported that the relative crystallite thickness influences the elastic modulus of the polyethylene gels.²⁵ For $M_w = 1.9 \times 10^3$, the elastic modulus is independent of chain length. However, as the molecular weight increases, so that the relative crystallite thickness also increases, the modulus increases.

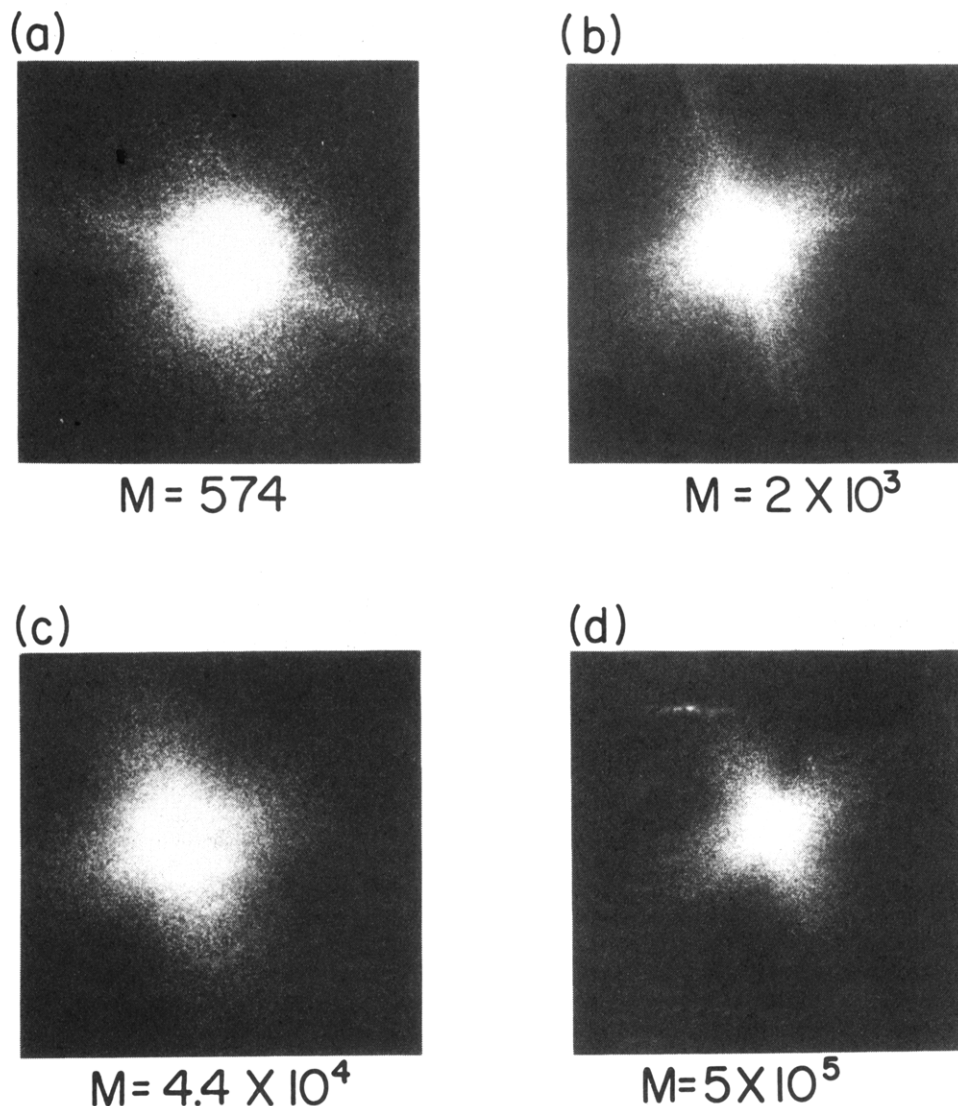


Figure 3. Small-angle light scattering patterns for gels of linear polyethylene fractions in toluene: (a) $M = 574$; (b) $M = 2 \times 10^3$; (c) $M = 4.4 \times 10^4$; (d) $M = 5 \times 10^5$.

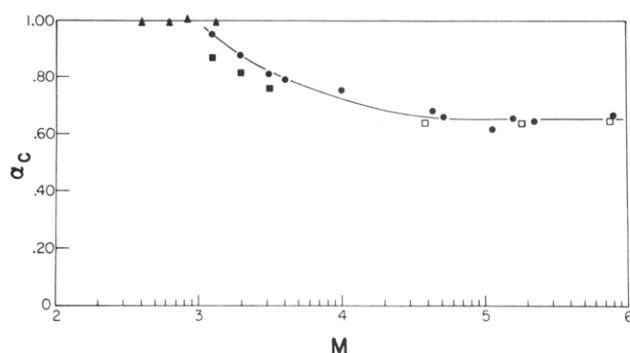


Figure 4. Degree of crystallinity, α_c , against the log of molecular weight for dried gels of linear polyethylene fractions and *n*-hydrocarbons formed at 25 °C: this work, Δ , *n*-hydrocarbon gels; \bullet , polyethylene gels; \blacksquare , polyethylene crystals formed in dilute solution; \square , from ref 26, polyethylene crystals formed in dilute solution.

In the lower molecular weight range, where extended-type crystallites are formed, the molecular chains can only participate in one crystallite in the crystallization, gelation, process. Therefore, there is no possibility of intercrystallite connections by a sequence of chain units. The gels must thus be formed solely as a consequence of the overlapping of the supermolecular structures.

The crystallites in the gels have a lamellar habit and are organized in supermolecular structures over the extensive molecular weight range that has now been studied. The SALS patterns of the low molecular fractions, which are given in Figure 3, demonstrate that the crystallites in the undried gels are arranged in a spherical pattern. However, it is also clear from these patterns that as the molecular weight decreases the spherulitic character becomes less well defined. Polarized light microscopy studies show that in the low molecular weight polyethylene gels the supermolecular structures are extensively overlapped.

The previous studies of the high molecular weight polyethylene gels have shown that the thermodynamic properties, phase structures, and size characteristics of the crystallites in the gels are identical to those formed in dilute solution for the same molecular weight under comparable conditions.^{2,4} It is, therefore, of interest to make a similar comparison with the low molecular weight fractions studied here. The data in Table III compare the dissolution temperature T_s and enthalpy of fusion ΔH for the two types of crystallites. We find that the dissolution temperatures are very close to one another while the ΔH values are just slightly higher for the gels relative to those of the solution crystals. A comparison of the Raman spectroscopy results is given in Table II. The LAM measurements show that the most probable crystallite

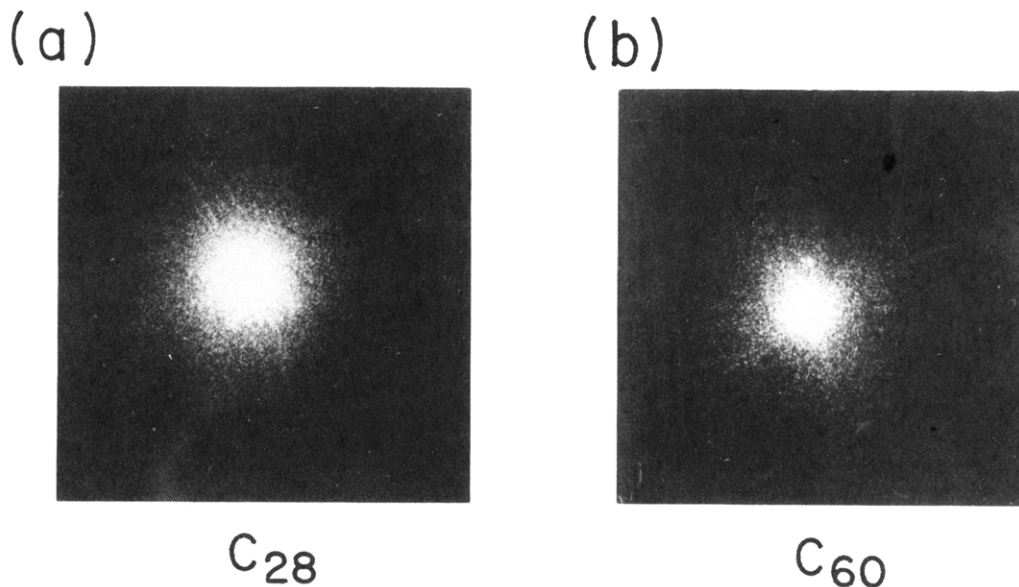


Figure 5. Small-angle light scattering patterns of *n*-alkane gels in toluene: (a) C₂₈H₅₈; (b) C₆₀H₁₂₂.

Table II
Crystallite Thickness and Phase Structure of Dried Gels and Dilute Solution Crystals of Linear Polyethylene

dilute solution crystals (0.1%)						gels					
$M_w \times 10^3$	$T_c, ^\circ\text{C}$	$L_R, \text{\AA}$	size range, \AA	$\alpha_c, \%$	$\alpha_a, \%$	$\alpha_b, \%$	$L_R, \text{\AA}$	size range, \AA	$\alpha_c, \%$	$\alpha_a, \%$	$\alpha_b, \%$
1.2	25	(97) ^a		87 ± 4	4 ± 3	9 ± 7	60	46–115	95 ± 2	5 ± 2	0 ± 4
1.9	25	(85) ^a		82 ± 3	13 ± 5	5 ± 8	75	51–116	87 ± 4	14 ± 4	-1 ± 8
1.9	60.8	131	101–156	87 ± 3	11 ± 3	2 ± 6	95	66–156	87 ± 4	10 ± 3	3 ± 6
3.1	25	79	57–117	76 ± 5	23 ± 5	1 ± 10	75	51–113	81 ± 3	21 ± 3	-2 ± 6

^a From ref 26.

Table III
Thermodynamic Properties of Dilute Solution Crystals and Gels of Linear Polyethylene^a

dilute solution crystals (0.1%)				gels	
$M_w \times 10^3$	$T_c, ^\circ\text{C}$	$T_s, ^\circ\text{C}$	$\Delta H, \text{cal/g}$	$T_s, ^\circ\text{C}$	$\Delta H, \text{cal/g}$
1.2	25	76.1 ± 2	50 ± 4	73.8 ± 2	54 ± 4
1.9	25	85.4 ± 3	49 ± 5	80.9 ± 2	53 ± 4
1.9	60.8	87.2 ± 2	50 ± 3	85.8 ± 1	55 ± 3
3.1	25	89.0 ± 1	51 ± 4	87.4 ± 1	55 ± 4

^a Comparisons were made at the concentration corresponding to c^* .

thickness, L_R , of the dried gels and their size distribution are comparable to those of the crystallites formed from dilute solutions. The quantitative phase structures, as determined from the internal modes, are also close to one another for both the gels and solution crystals. Thus, as was found with the higher molecular weight fractions,^{2,4} the crystallites in the gels have structural and thermodynamic properties very similar to those of crystallites formed in dilute solution.

With the data for the low molecular weight fractions now available, it is of interest to examine the molecular weight dependence of the core crystallinity for the gel and solution crystals prepared under comparable conditions. The results for the molecular weight range 10^3 to 8×10^5 are given in Figure 4.²⁶ The concordance in α_c between the solution crystals and gels over the complete range becomes immediately apparent. For the low molecular weights, 10^3 – 10^4 , there is a monotonic decrease in α_c from a value close to unity to about 0.65. However, with further increase in the chain length, α_c remains constant at this value as the molecular weight approaches 10^6 . These results reflect the change in crystallite thickness with molecular weight. It has been well-established that for molecular weights greater than 10^4 the thickness of a

crystallite formed in a given solvent is independent of molecular weight. It depends only on the undercooling at which the crystallization takes place.^{24,28,29}

***n*-Hydrocarbons.** The thermoreversible gelation of the *n*-hydrocarbons has already been noted in the literature.¹⁶ However, studies of the properties of these gels and an analysis of the gelation mechanism have not been reported. Since there is an overlap in molecular weights between the linear polyethylene fractions and the hydrocarbons, it is natural to extend the gelation studies to the alkanes. We have been able to observe thermoreversible gelation in the *n*-hydrocarbons ranging from C₂₈H₅₈ to C₁₉₂H₃₈₆ in toluene. All of the *n*-hydrocarbons form extended molecular crystals under the gelation (crystallization) conditions. The critical concentrations for gelation, c^* , of these species are also given in Figure 1.

The relation between c^* and M for the *n*-alkanes falls into several different categories. The critical concentration for the two highest molecular weight *n*-hydrocarbons, C₉₄H₁₉₀ and C₁₉₂H₃₈₆, fall exactly on the curve for the polyethylene fractions of comparable molecular weight. The critical concentrations for gelation of C₄₆H₉₄, C₅₀H₁₀₂, and C₆₀H₁₂₂ all lie very close to the polyethylene curves. However, for the hydrocarbon in the range C₄₄H₉₀ to C₂₈H₅₈ there is a very sharp increase in c^* with decreasing chain length. Since extended chain, molecular crystals are formed by all the *n*-hydrocarbons, the drastically different c^* -molecular weight behavior could be caused by the morphology or supermolecular structures that develop.

The conjecture with regard to differences in the supermolecular structures is borne out by direct microscopic and small-angle light scattering studies. For the *n*-alkanes greater than C₄₄H₉₀ (which obey the c^* - M relation close to that of the polyethylenes) spherulitic-type morphologies are observed. The spherulitic structures are very similar

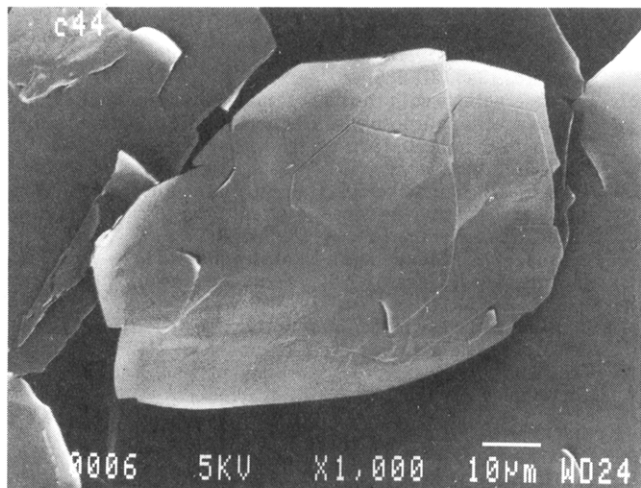


Figure 6. Scanning electron micrograph of the dried gel of $C_{44}H_{90}$.

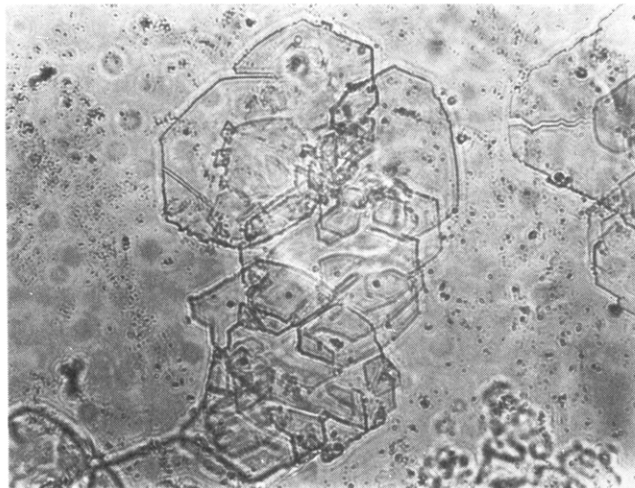


Figure 7. Polarized light micrograph of the gel of $C_{44}H_{90}$ in toluene.

to those of polyethylene fractions of comparable molecular weight. For the lower molecular weight samples, equal or less than $C_{44}H_{90}$, sheet or platelike superstructures are formed. The comparison of the SALS patterns for $C_{60}H_{122}$ and $C_{28}H_{58}$ that is given in Figure 5 makes this distinction clear. The SALS pattern for $C_{60}H_{122}$ indicates a poorly developed spherulitic structure. Polarized light and scanning electron microscopic observations confirm this conclusion. On the other hand, the lower molecular weight hydrocarbons have a quite different morphology as is illustrated by the SALS in Figure 5a for $C_{28}H_{58}$. The lower chain length hydrocarbons exhibit a circularly symmetric pattern indicative of some type of sheetlike structure.^{19,30,31} The formation of this structure is confirmed by electron microscopy. The scanning electron micrograph of the dried $C_{44}H_{90}$ gels in Figure 6 reveals quite clearly the platelike character of the crystallites and confirms the analysis of the SALS pattern. Polarized light micrographs of the same sample, as are illustrated in Figure 7, reveal the overlapping platelike superstructures in the gel. Similar type micrographs of the higher molecular weight sample show an overlapping of the spherulitic that are very similar to those already published.^{2,3} The gelation of the n -hydrocarbons gives a definitive example of a class of thermoreversible gels that are comprised of overlapping superstructures. A similar conclusion was reached with regard to the gelation of linear polyethylene.^{2,3} The unique c^*-M relation that is found with the n -hydrocarbons

Table IV
Comparison of Thermodynamic Properties of Dilute Solution Crystals and Gels of Hydrocarbons Quenched at 25 °C

	$C_{44}H_{90}$		$C_{60}H_{122}$	
	dilute solution crystals (0.1 %)	gels	dilute solution crystals (0.1 %)	gels
T_s , °C	51.3 ± 2	50.4 ± 1	65.9 ± 2	63.2 ± 2
ΔH , cal/g	57 ± 2	59 ± 2	61 ± 2	59 ± 2

reflects the strikingly different, chain length dependent superstructures that constitute the gels.

The structure and thermodynamic properties of the crystals formed in dilute solution and the gels are comparable to one another for either type of superstructure. Since the chains are extended, there is complete crystallinity in both cases. As is shown in Table IV both the dissolution temperatures and the enthalpies of fusion are also the same. Thus, we have developed the general proposition, for both n -alkanes and polymers, that there are no changes in crystallite properties during gel formation by a crystallization mechanism.

Gel formation of semifluorinated n -alkanes, $F(CF_2)_n(CH_2)_nH$, has been reported.³² However, detailed thermodynamic and morphological studies were not made. Therefore, the gel properties and gelation mechanism cannot be compared with those of the n -alkanes.

In summary, we have found that the gelations of the low molecular weight polyethylenes and the n -alkanes, where extended chain crystals are formed, have certain general features in common. Gel formation, manifested by a very large zero-shear viscosity, is a consequence of overlapping supermolecular structure. The type of superstructure that governs the c^*-M relationship is found to be quite different for the different situations. The low molecular weight polyethylenes, where extended-type chain crystals are not formed, are continuous with the previous work on the high molecular weight polyethylene fractions. The thermodynamic and structural properties of the crystallites in the different types of gels observed are the same as those formed in dilute solution.

Acknowledgment. Support of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

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- Registry No.** C₄₀H₈₂, 4181-95-7; C₄₄H₉₀, 7098-22-8; C₄₈H₉₄, 7098-24-0; C₅₀H₁₀₂, 6596-40-3; C₆₀H₁₂₂, 7667-80-3; C₃₂H₆₆, 544-85-4; C₂₈H₅₈, 630-02-4; C₉₄H₁₉₀, 1574-32-9; C₁₉₂H₃₈₆, 96123-38-5; polyethylene, 9002-88-4.