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the polymerization of the two monomers.

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Registry No. C_8H_8, 100-42-5; C_8H_{14}, 695-12-5; $Al(CH_3)_3$, 75-24-1; $TiCl_3$, 7705-07-9.

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Thermoreversible Gelation and Crystallization of Homopolymers and Copolymers

R. C. Domszy, R. Alamo, C. O. Edwards, and L. Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306. *Received June 5, 1985*

ABSTRACT: The thermodynamics, kinetics, and structural features of gels formed as a consequence of crystallization from dilute and moderately dilute solution have been investigated. Major emphasis has been on the study of homopolymers and copolymers of ethylene. The melting temperatures and enthalpies of fusion of the gels are found to be continuous with counit content and independent of the chemical type, despite the fact that the supermolecular structure and morphology undergo major changes. It was also found that for a given polymer the thermodynamic and structural properties of a crystallite formed in dilute solution and in the gels are identical. From these types of measurements some of the general principles that govern gelation by a crystallization mechanism can be established. Preliminary experiments with isotactic and atactic polystyrene fractions indicate that these polymers also follow the same general principles.

Introduction

Gels, or network structures, that involve long-chain molecules can be formed by several distinctly different molecular mechanisms. A detailed description of the different types of known gel systems has been given by Flory.[1] Among these, gelation occurring as a consequence of the crystallization of copolymers from dilute and moderately dilute solution was recognized a long time ago.[1,2] In this type of gelation a three-dimensional network is formed where primary molecules of finite molecular weight are bound together, or connected, by crystallites. It differs from the more conventional type of network, where completely disordered chains are covalently linked together. Gelation as a consequence of copolymer crystallization has been actively studied for a long time.[1,2] It has been given serious quantitative consideration in a series of papers by Takahashi and co-workers.[3-9] The observation that vinyl type polymers, properly considered as copolymers from this point of view,[10,11] also form gels has given us an interesting set of new results.[12-20] However, the concept that crystallites are involved in gel formation is not new.[21]

It has also been recently shown that gel formation is a common feature of homopolymers crystallized under quiescent conditions at comparable polymer concentrations.[22-25] It needs to be emphasized in this connection that gel formation in homopolymers does not require flow, stirring, or even any type of prestirring of the solution, as has been repeatedly implied.[21,26,27]

When gelation occurs as a consequence of crystallization from dilute or moderately dilute solution, a very fluid solution is converted to a rigid medium of infinite viscosity. The polymer system pervades the entire volume. Gels formed by this mechanism are thermally reversible. They are formed on crystallization (cooling) and disappear on melting (heating). In this respect they are completely different from gels formed by covalently cross-linking amorphous chains, wherein the networks are thermally stable. The recent observations that gels are also formed during the crystallization of vinyl polymers, such as isotactic polystyrene,[12-14,20] poly(vinyl chloride),[15,17,18] and poly(4-methylpentane),[16,19] has rekindled interest in this subject. Unfortunately, in many cases these new results were discussed in a very limited context[21,28] so that the general aspects of the problem were not recognized. Consequently, serious misconceptions developed, and some limited ideas have been espoused. One example has been the concept that the crystallites in all gels are micellar in character.[21,28] In several of these systems polymorphic

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Table I
Characteristics of Linear Polyethylene Fractions

sample	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	$M_v \times 10^{-3}$	M_w/M_n
1	2.9	3.1		1.10
2	8.9	10.0		1.26
3	26.5	27.8		1.05
4	42.0	46.2		1.1
5	57.1	60.7		1.13
6	60.9	70.0		1.15
7	88.0	93.0		1.12
8	120.0	142.0		1.18
9	183.0	203.0		1.11
10	207.0	225.0		1.19
11	445.0	480.0		1.08
12			1050	
13			1620	
14			2490	
15			6090	
16[a]	7.5	180.0		24.2
17[a]			2000	

[a] Unfractionated polyethylene.

crystalline structures are formed. Although these crystallographic observations bring an additional complication to the problem, and are of interest in themselves, they do not bear directly on the gelation mechanism.

We have previously outlined some of the guiding principles which should govern gelation by the crystallization mechanisms of interest here.[25] These principles were based on our understanding of the crystallization behavior of polymers. Initial experimental studies were primarily concerned with the gelation from dilute solution of ethylene homopolymers.[24,25] However, studies with other homopolymers have substantiated the generality of the results.[25] These studies with ethylene homopolymers are extended in the present work. Extensive studies with ethylene copolymers, which cover the major portion of this work, will also be reported. These copolymers cover a very wide range in both counit content and chemical type. The main purpose of these studies is to develop in more detail the principles involved when gelation accompanies crystallization so that features that are unique to this particular gelation mechanism can be established. The new results thus allow for the development of a very general perspective of the gelation process and of gel properties.

In contrast to the work with the ethylene copolymers, the vinyl polymers that have been studied have, by necessity, been limited to a very narrow composition range.[10,12,13,29,30] Some specific experiments involving isotactic and atatic polystyrene were carried out in the present work. We were then able to assess the observed gelation behavior of these two polymers in terms of the principles outlined.

Experimental Section

Materials. A set of selected linear polyethylene samples was studied. Many of these polymers were also used in previous work that has been reported from this laboratory.[31-33] Their molecular weights and polydispersities are listed in Table I. Samples 1-11 are narrow molecular weight fractions that were obtained from Societē Nationale Elf Quitaine (SNEA). They were prepared and characterized by gel permeation chromatography. The highest molecular weight fractions, 1.05×10^6–6×10^6, samples 12-15, were obtained by liquid-liquid fractionation of high molecular weight whole polymers with methods that have been previously described.[34] Two unfractionated whole polymers of widely different molecular weights were also used. These were Marlex 6009 (sample 16) provided by the Phillips Petroleum Co. and Hifax-16 (sample 17) supplied by the Hercules Powder Co.

Two chemically different types of ethylene copolymers were also studied. Their molecular characteristics are summarized in Table II. One set of copolymers was the hydrogenated polybutadienes (HPBD) where the ethyl branch content ranged from 2.2 to 18 mol %. Samples prefixed by the symbol P were obtained from the Phillips Petroleum Co. The other samples, whose ethyl content ranged from 3.2 to 18.0 mol %, were kindly furnished to us by Dr. William Graessley.[34] Details of their synthesis and characterization have already been reported.[35-37]

Table II
Analysis of Ethylene Copolymers

fraction	$M_w \times 10^{-3}$	M_w/M_n	mol % branches	MD[a] ± 5	MD[a] (Bernoullian)
P16	16	1.14	2.1		
P108	108	1.31	2.2	97	95.6
P194	194	1.53	2.0		
P420	420	2.66	2.2		
HPBD4	160	1.05	3.20	96	93.6
HPBD5	180	1.05	4.50	88	91.0
HPBD7			4.40		
HPBD12			5.50		
HPBD6	150	1.05	5.75	79	88.5
HPBD11			7.25	87	85.0
HPBD8			13.0		
HPBD9			18.0		
EVAF9	70.7	2.07	1.12		
EVAF15	81.9	1.88	2.67		
EVAF35	105.5	2.64	4.14		
EVAF30	71.3	3.04	5.70		
EVAF29	63.6	2.46	6.60	83	88
1-EVA45-1			11.5		
2-EVA55-2	105.2	1.7	17.5		

[a] MD is the monomer dispersity = 100([EXE] + 0.5[XXE])/[X].

A series of molecular weight and compositional fractions of ethylene–vinyl acetate copolymers (EVA) were also studied. All of these fractions were obtained from commercial type copolymers. The fractionation procedure as well as the characterization of the lower counit samples have already been described in detail.[37] The two ethylene–vinyl acetate fractions having the highest branching content were obtained by the fractional precipitation of two whole copolymers (45 and 55% wt % vinyl acetate, respectively) from an acetone–*n*-hexane mixture at room temperature. The acetate branch content for the ethylene–vinyl acetate copolymers ranged from 1.12 to 17.5 mol %.

The branching content and sequence distribution of the copolymes were obtained from carbon-13 NMR measurements. The proton-decoupled spectra were recorded at 67.89 MHz with a pulse angle of 90° and a pulse delay of 30 s in a solution containing 10% (w/v) of polymer in deutierochloroform at 55 °C or trichlorobenzene at 120 °C. The choice of solvent and temperature depended on the polymer dissolution temperature and branching content. The ethyl branch content in the hydrogenated polybutadiene copolymers was analyzed by Randall's method.[38] The ethylene–vinyl acetate spectra were analyzed with literature assignments.[39,40] The ethylene–vinyl acetate copolymers always contained between 0.8 and 1.8 mol % butyl branches irrespective of the acetate content. In Table II, and in the subsequent discussion, reference is always made to the total branching content of these copolymers.

The sequence distribution analysis of the hydrogenated polybutadienes was carried out with the method developed by Randall.[41] The results obtained agreed with those reported by Graessley et al.,[35,36] who used the same method of analysis. As has been described previously,[37] the results, as summarized in Table II, indicate a slightly biased incorporation of comonomer (deviation of the random Bernoullian distribution) at the higher counit contents. The sequence analysis for ethylene–vinyl acetate are not nearly as extensive, although the trends appear to be similar.

The weight- and number-average molecular weights for these copolymers, which are also given in Table II, were obtained by gel permeation chromatography following conventional methods.[42]

In order to compare the behavior of the vinyl polymers with the general characteristics of ethylene copolymers, some specific experiments were performed with isotactic and atactic polystyrene. The isotactic polystyrene fraction used here was obtained from a whole copolymer supplied by the Dow Chemical Co. ($M_w = 1.9 \times 10^5$). The whole polymer was initially extracted twice with methyl ethyl ketone by precipitation of the hot solution at 20 °C in order to remove the atactic component. Carbon-13 NMR studies indicated that the extracted sample is highly isotactic.[10] The extracted sample (viscosity-average molecular weight 200 000) was further fractionated by the crystallization of a 2 wt % solution in decalin (Aldrich Chemical Co., mixture of cis and trans isomers) at 54 °C for 3 weeks. The crystals were separated at the crystallization temperature with approximately 40% of the polymer remaining in the supernatant. A fraction whose viscosity-average molecular weight was 1.62×10^5 was used. Viscosity measurements were made in a toluene solution at 30 °C with a Ubbelohde viscometer. A rate of shear correction was not necessary.

A series of atactic polystyrene samples, with molecular weights ranging from 2.4×10^4 to 1.1×10^6, were obtained from Polymer Laboratories Inc. For these anionically polymerized samples M_w/M_n was less than about 1.04.

Procedures. To prepare a gel, an appropriate amount of polymer and solvent was placed in a 1-cm-diameter glass tube and degassed before being sealed under vacuum. Typically, concentrations for the gels formed with linear polyethylene ranged between 0.5 and 5% (w/v), depending on the molecular weight and temperature. For the copolymers, the concentrations varied from 2 to 9% (w/v). Toluene was used as solvent for all the ethylene copolymers and for most of the linear polyethylene fractions, except for molecular weights greater than 4×10^5. For the higher molecular weights, either *p*-xylene or decalin was used for easier dissolution and homogeneity. The sample tube was initially maintained at temperatures between 120 and 160 °C for at least 30 min and then rapidly transferred to a bath set at a predetermined temperature, which was controlled to better than 0.1 °C. In order to determine the critical concentration necessary to form a self-supporting gel, the solutions were maintained at the desired temperature for about 10 h. After this time, the tube was inverted. The criterion for gel formation was taken as the point when the solution would no longer flow at the desired temperature. Mechanical melting points were determined with the ball-drop method, as described by Takahashi et al.[8] In this method a steel ball is placed on the gel, which is then slowly heated. The height of the steel ball, which weighed between 50 and 70 mg, was recorded as a function of temperature. When the gel melts, the ball descends. This breakup of the gel was taken as its mechanical melting temperature. For the specific determination of the mechanical melting temperature, the ethylene copolymer gels were prepared by quenching the molten solutions to −35 °C.

Thermodynamic melting temperatures and enthalpies of fusion of the undried, virgin gels, as well as those that were dried, 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.[43] Gels examined before drying were either formed in or confined to large volume capsules sealed with O-rings. The dried gels were prepared by washing thoroughly with methanol and drying under vacuum for at least 48 h. The thermal measurements of the dried gels were obtained in a conventional manner. The enthalpies of fusion were converted to degrees of crystallinity by taking the enthalpy of fusion of the perfect polyethylene crystal to be 69 cal/g at $T_m{}^\circ$ and ΔC_p of 0.0713 cal/g.[37] The values of the degrees of crystallinity derived from the thermograms of the undried gels were based on the weight of the polymer.

Small-angle light scattering (SALS) patterns, H_v, were obtained with a photometer similar to the one described by Stein.[31,44,45] A helium–neon laser (632.8 nm) was used as the light source. The sample-to-film distance was 15.5 cm. The patterns were obained at room temperature for both the dried and the undried gels of the ethylene copolymers. These gels were prepared initially by quenching at −35 °C. The undried gels were placed directly on microscope slides with covers. Films about 40 μm thick of the same gels in the dried state were obtained by allowing the solvent to evaporate under vacuum, washing repeatedly with methanol, and redrying under vacuum for at least 48 h. Silicone oil was used in the latter case to obtain homogeneous scattering. The nomenclature relating the observed SALS patterns to specific supermolecular structures has been described previously.[31,46] The term supermolecular structure is used to describe the arrangement of the crystallites relative to one another.[31,32]

Samll-angle X-ray scattering patterns (SAXS) of the dried gels and solution crystals were photographically recorded with a slit-collimated Rigaku-Denki camera and Cu Kα radiation. Exposure times were 48 h. The observed first-order maxima were converted to lamellar thicknesses by direct application of Bragg's law. The error in the thickness was ±4 Å.

Polarized light microscopic studies of the undried gels were carried out in a Leitz Ortholux II microscope equipped with a Leitz Orthomat-W automatic microscope camera. Samples were placed on microscope slides, as in the SALS studies, and examined at room temperature. Photographs were taken either with crossed polarizers or through a Zeiss 10× phase-contrast objective.

Scanning electron micrographs (SEM) were obtained with a Cambridge Model S4-10 stereoscan microscope operating at between 5 and 20 mV. Dried samples were placed on aluminum buttons and sputter coated with a gold/palladium mixture to reduce sample charging. Three methods of drying were tested: reduced pressure, freeze-drying, and critical point technique. It was found that the critical point drying technique, using carbon dioxide, had the least effect on the morphology.[25]

The low-frequency Raman longitudinal acoustic mode (LAM) was obtained with a SPEX 1403 double monochromator spectrometer operating with an argon ion laser (λ = 5145 Å) with the effective power at the sample being about 100 mW.[47,48] The raw data was corrected for temperature and frequency dependence so that it could be converted into the straight chain length distribution using the method of Snyder and Scherer[49,50] that has already been described in detail.[47,48]

Results and Discussion

Linear Polyethylene. We start the present discussion with an extension of the results previously reported[24,25] for linear polyethylene crystallized (gelled) from homogeneous solution, i.e., from one liquid phase. Molecular weight fractions covering the range 3×10^3–6×10^6 were studied. As has already been shown, linear polyethylene gels can be formed over the complete molecular weight range from solvents such as toluene, *p*-xylene, and decalin under quiescent conditions, i.e., without the necessity for any stirring or prestirring.[22-25] Cognizance must be taken of the fact that for a given set of conditions there is a critical polymer concentration necessary for gelation. The concept that some type of stirring is required is probably due to the use of an inadequate polymer concentration.[21,26] All the linear polyethylene gels are turbid. In general, these gels are mechanically weak and can be broken up by vigorous shaking. They become more rigid, however, at the high molecular weights.

An important quantity that describes the process is the critical polymer concentration that is required for gelation. Below this concentration, although crystallization definitely occurs, a gel does not form. In order to examine this quantity in more detail, the critical concentration for gel formation, c^*, is plotted against the logarithm of molecular weight in Figure 1 for different gelation temperatures. At a fixed crystallization (gelation) temperature, there is a monotonic decrease of c^* with M.[85] At higher molecular weights and lower temperatures, c^* depends only very slightly on M. At the lower molecular weights and higher crystallization temperatures there is, however, a somewhat more marked dependence of c^* on M.

In order to analyze the molecular weight dependence in more detail, it is convenient to present the data in the form of a double-logarithmic plot as in Figure 2. Except for the two highest temperatures, the data can be expressed in the form

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

The constant a varies from about 0.2 to 0.3. At the higher temperatures the data are no longer linear. However, at

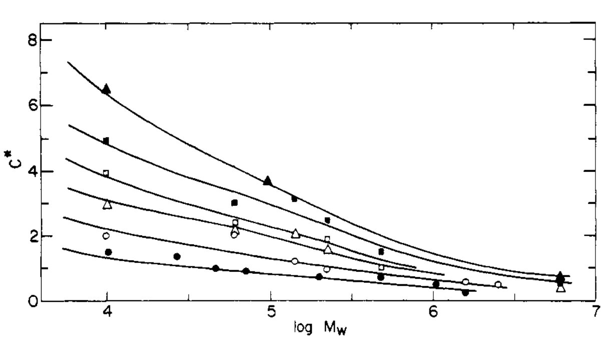


Figure 1. Plot of critical concentration for gelation, c^*, against log molecular weight for linear polyethylene fraction: At 25 °C in xylene (●); in toluene at 30.1 °C (○), at 41.3 °C (△), at 50.0 °C (□), at 60.8 °C (■), and at 86.0 °C (▲).

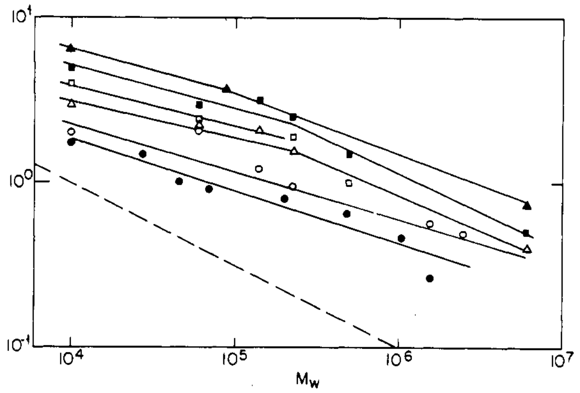


Figure 2. Double-logarithmic plot of data from Figure 1 with same symbols. Dashed straight line of slope −0.5 plotted for reference.

the lower molecular weights the constant remains about the same, but increases to about 0.4 at the higher molecular weights. These results for the molecular weight dependence of the critical concentration are of interest because of the concentration, c_0, at which the molecular domains begin to overlap in dilute solution. It is easily shown that for chains in statistical conformation

$$c_0 \sim M^{-1/2} \qquad (2)$$

For reference purposes a straight line, with slope −0.5, is also given in Figure 2. It is clear from the result displayed in this figure that for the wide molecular weight and temperature range studied here, the constant a does not equal −0.5. Thus, although molecular overlap is obviously a necessary condition for crystallization, it is not a sufficient one for gelation. The present data show that much higher polymer concentrations are required.

From a study of the gelation of atactic polystyrene in CS_2, it was reported that eq 2 was obeyed; i.e., the constant a equals 0.5.[30] It was implied that this was a general result for gelation. These results, and the conclusions derived therefrom, will be considered in more detail subsequently when copolymer gelation is discussed.

An important feature of Figures 1 and 2 is the temperature dependence of c^*. The changes in c^* are significant but relatively small at the very high molecular weights. However, they become much more marked as the molecular weight is decreased. For example, for $M = 10^5$ there is about a fourfold change in c^* as the temperature is increased to 85 °C. This change in c^* is enhanced even more with a further decrease in molecular weight. These temperature effects are quite important since they must be intimately related to the gelation mechanism. As will be discussed subsequently in detail, these experimental results for the temperature dependence of c^* explain in a straightforward manner the unique features that are observed in gelation kinetics.

It has been shown that gels formed from homopolymers, such as polyethylene and poly(ethylene oxide), possess lamellar type crystallite habits.[24,25] Gross morphological studies have shown further that such gels possess well-organized supermolecular structures. For a given molecular weight the same general structural features are observed at concentrations which are both above and below that required for gelation. The size of the structures is approximately the same over this concentration range. When gel formation occurs, however, the superstructures are significantly overlapped. Below the critical concentration these structures are relatively isolated from one another. In the extreme of a very dilute solution, the isolated plateletlike crystallite precipitates. A light microscopic examination of a linear polyethylene fraction, $M = 1.42 \times 10^5$, as a function of temperature at concentrations that cover the gel and pregel state, indicates no obvious change in superstructure with increasing temperature.

Linear polyethylene gels display varying amounts of syneresis, depending on the crystallization temperature. Although there is essentially no syneresis for low temperature rapid gelation, this effect becomes particularly marked in the isothermal crystallization region (approximately 80 °C for a 5% (w/v) toluene or p-xylene gel). At higher temperatures the c^* value continues to increase, but the gels are not coherent and exude solvent. Although some polyethylene gels can synerese, not all do. Thus syneresis is not a general phenomenon in the gelation of linear polyethylene, as had been thought.

Since the crystals formed in either dilute solutions or in gels show a lamellar habit, it is important to compare the crystallite properties of what superficially appear to be diverse systems. Since there is only an imperceptible difference between the equilibrium melting temperatures for a polymer concentration of 0.1% (dilute solution crystals) and those for the higher concentration typical of gel formation,[51,52] it is theoretically possible to prepare the dilute solution crystals and gels, from polymers of the same molecular weight, at an identical undercooling by crystallizing at a fixed temperature. Thus the properties of these two crystalline systems can be easily compared by crystallization under comparable conditions.

We have previously reported[25] that for a molecular weight fraction of linear polyethylene, $M = 4.45 \times 10^5$, thermodynamic properties, such as the enthalpies of fusion and the dissolution temperatures, are very similar for the dilute solution and gel crystallites. In addition, the small-angle X-ray diffraction maxima were very similar to one another. We have expanded this comparison in the present work by studying a more extensive molecular weight range, varying the mode of crystallization, and measuring the Raman low-frequency longitudinal acoustic mode (LAM) to determine the crystallite core thickness. Thus, we are now in a much better position to compare in detail the respective crystallite structures. The results of these new studies are summarized in Figures 3 and 4 for isothermal crystallization and in Tables III and IV for rapid, nonisothermal crystallization. Before these results are examined, it should be recalled that the thermodynamic properties and thickness of crytallites formed from dilute solution are independent of molecular weight. The enthalpy of fusion, density, and other measures of the level of crystallinity depend only on the crystallite thickness.[53-56] The crystallite thickness in turn depends only on the crystallization conditions.[53,54]

Table III
Comparison of Thermodynamic Properties of Dilute Solution Crystals and Gels of Linear Polyethylene[a]

crystals from dilute solution				gels			
$M_w \times 10^{-3}$	c, % (w/v) (p-xylene)	T_s, °C	$(1-\lambda)_{\Delta H}$	$M_w \times 10^{-3}$	c, % (w/v) (p-xylene)	T_s, °C	$(1-\lambda)_{\Delta H}$
194	0.105^f	96.2	0.62	194	1.98	98.3	0.65
225	0.107^d	98.4		225	1.4	99.6	0.60
225	0.1^f	99.3	0.72	225	4.2	98.6	0.65
2000^b	0.15^e	98.2		225	4.2^c		0.65
2000	0.1^f	100.3	0.73	2000^b	2.8	98.8	0.64
				2000	4.8	98.0	0.64
				2000	4.8^c		0.70

[a] Samples quenched at 23 °C. [b] Unfractionated sample, viscosity-average molecular weight. [c] Dried gels. [d] As made in p-xylene. [e] As made in decalin. [f] Dried solution crystals dilute in p-xylene.

Table IV
Crystallite Thickness of Dried Gels and Dilute Solution Crystals of Linear Polyethylene[a]

crystals from dilute solution				gels			
$M_w \times 10^{-3}$	c, % (w/v) (p-xylene)	L_R, Å	size range	$M_w \times 10^{-3}$	c, % (w/v) (p-xylene)	L_R, Å	size range
166	0.08	95	55–115	166	4	97	75–150
180^b	0.08	87	67–118	180^b	2	82	70–125
$2000^{b,c}$	0.08	100	80–155	$2000^{b,c}$	2	85	60–130

[a] Solutions quenched at 23 °C. [b] Unfractionated sample. [c] From decalin.

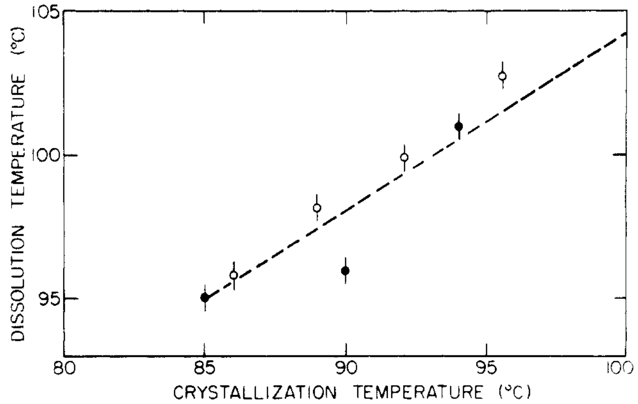


Figure 3. Plot of dissolution temperature against crystallization temperature for gels and dilute solution crystals of linear polyethylene. Dashed line dilute solution crystals from ref 53. Gels for $M = 4.8 \times 10^5$ from 2% solution (●), and 5% solution (○).

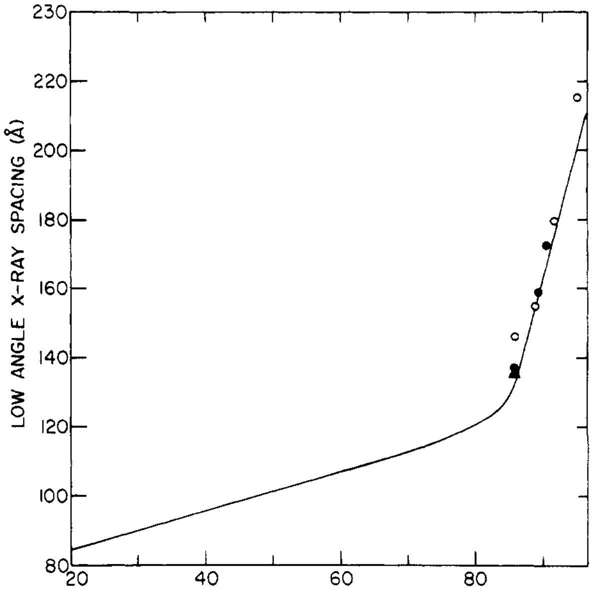


Figure 4. Plot of small-angle X-ray spacing against crystallization temperature for gels and dilute solution crystals of linear polyethylene. Solid line for dilute solution crystals from ref 53. For $M = 4.8 \times 10^5$%: dilute solution crystal (●); gels from 2% and 5% solution (○).

With this background we can analyze the new structural and thermodynamic data. For the isothermal experiments Figure 3 indicates that the dissolution temperatures, at different crystallization temperatures, are the same for the crystallites formed from dilute solution and those in the gel. The dashed line represents the data taken from the literature for the solution crystals.[53] The new data for the gels that are plotted in this figure fall on this same straight line. Similarly, Figure 4 shows that for a given crystallization temperature the small-angle diffraction maxima are also the same for the two systems. The solid curve in this figure represents the literature values for the solution-formed crystals.[53] The circles are the new data for the gels. The triangle is a new dilute solution data point. It is presented merely to demonstrate that the new data are consistent with the old for the dilute solution crystallites.

The results for nonisothermal crystallization follow a very similar pattern. The thermodynamic data for this crystallization mode is summarized in Table III. The level of crystallinity of the undried gels, $(1-\lambda)_{\Delta H}$, as calculated from the enthalpy of fusion, is essentially independent of molecular weight over the wide range studied. Moreover, the value of $(1-\lambda)_{\Delta H}$ of about 0.65 is the same for both the dilute solution crystallites and those characteristic of the gel. The dissolution temperatures are essentially the same for both systems and are also independent of molecular weight. The data indicate that the thermodynamic properties of the gels do not change upon drying and thus the crystallite properties remain unchanged.

The LAM measurements summarized in Table IV confirm the previous findings that for solution formed crystallites the lamellar thicknesses are independent of molecular weight. A similar conclusion is now reached for the dried gels. In this table L_R represents the most probable value of the crystallite thickness distribution. The range in crystallite thicknesses is also given, which is the more appropriate data for comparison. The results indicate that the dried gels and dilute solution crystals have very similar crystallite thickness distributions.

These new results represent more extensive confirmation of the earlier findings.[25] They make clear that the thermodynamic properties and size characteristics of the crystallites formed in gels and in dilute solution are essentially identical. Electron microscopic studies have demonstrated the lamellar-like crystallite habit in both cases. Hence the concept that a fringed micellar crystallite structure is necessary for gelation to occur by a crystallization mechanism is not in general correct.[2,13,21]

In the general discussion of gelation it was pointed out that crystallization from a heterogeneous system, i.e., where liquid–liquid phase separation occurs prior to crystallization, should properly be considered separately.[25] Crystallization (gelation) in this case can take place from the metastable region, i.e., between the binoidal and the spinoidal or in the unstable region within the spinoidal. In the metastable region, large fluctuations are required for liquid–liquid phase separation. In the unstable region, infinitesimal fluctuations will continue to grow and pervade the whole phase. Crystallization will then occur by a spinodal decomposition mechanism.[57] It has been proposed that spinoidal decomposition is a requirement for gelation.[29] However, crystallization from a dilute homogeneous phase is a nucleation-controlled growth process.[58,59]

The results that have been described so far were for a homogeneous system. Studies with heterogeneous systems were carried out with amyl acetate and two linear polyethylene fractions, M = 19 000 and 93 000, respectively. It is known that amyl acetate–polyethylene mixtures undergo liquid–liquid phase separation.[60] However, homogeneous solutions are formed after prolonged heating at 160 °C. Concentrations of 1–15% (w/v) were used for the lower molecular weight fraction. The cloud points were found at temperatures between 114 and 120 °C, which increased slightly with increasing concentration. Visible liquid–liquid phase separation was observed before crystallization occurred on slowly cooling the hot solution. However, a coherent gel did not form although crystallization occurred. The fraction M = 93 000 was studied by quenching a 4.1% (w/v) solution to 23 °C. A very white precipitate formed, which displayed pronounced regions of inhomogeneities. It clearly could not be classified as any kind of gel since it was not coherent and the aggregates broke up easily on gentle shaking. Crystallization from a very dilute solution (0.001%) of the same system resulted in rod-shaped superstructures. It was difficult to ascertain whether the liquid phase was homogeneous, although it is theoretically expected to be so at this dilution.[60]

The same kind of experiments were performed with a hydrogenated polybutadiene, P108 (2.2 mol % ethyl branches). The results were very similar to those obtained with the linear polyethylene fractions. Thus there is no indication of gel formation upon crystallization of this copolymer from the heterogeneous solution. These results indicate quite clearly that liquid–liquid phase separation, and spinoidal decomposition, is not a requirement for gel formation for either copolymers or homopolymers of ethylene. In fact for the polyethylenes gelation is retarded. However, for other systems gelation has been demonstrated to occur in liquid–liquid phase-separated systems.[20,29,30,86]

Copolymers. The extensive set of data that is now available for the gelation of the linear polyethylenes can serve as a basic frame of reference for the study of the gelation of copolymers. The major effort in this work was the study of the hydrogenated polybutadiene series and the compositionally fractionated ethylene–vinyl acetate copolymers. In some specific instances, in order to understand the relation between different chemical types, the gelation of both isotactic and atactic polystyrene was investigated.

Before undertaking a more quantitative analysis of their properties, certain characteristic features of the ethylene copolymer gels should be noted. The quenched or rapidly crystallized gels are stable essentially indefinitely. The copolymer gels formed isothermally are very elastic and only display syneresis over a very long time period.

Table V
Characteristics of Ethylene Copolymer Gels

sample	mol % branches	appearance
	Hydrogenated Polybutadienes	
P108	2.20	turbid
HPBD4	3.20	turbid
HPBD5	4.50	faintly turbid
HPBD6	5.75	clear
HPBD11	7.25	clear
HPBD8	13.0	clear
HPBD9	18.0	clear
	Ethylene–Vinyl Acetate	
EVAF9	1.12	turbid
EVAF15	2.67	turbid
EVAF35	4.14	faintly turbid
EVAF30	5.70	clear
EVAF29	6.60	clear
1-EVA45-1	11.5	clear
2-EVA55-2	17.5	clear

The macroscopic, or overall appearance, of the gels was examined at ambient temperature after quenching a 9–10% (w/v) solution in toluene to −35 °C. The results, for this comparable crystallization procedure, are summarized in Table V for the hydrogenated polybutadienes and the compositional fractions of ethylene–vinyl acetate. The results are the same for both types of copolymers. Characteristically, there is a gradual loss in turbidity with increasing branching content. At about 4–5 mol % branch groups, the gels become clear or transparent to the eye. A similar result has been previously reported with gels formed from unfractionated ethylene–vinyl acetate copolymers.[25] In analyzing these kinds of observations, care must be taken to distinguish as to whether the turbidity is due to inherent structure within the gel or to liquid–liquid phase separation, which can coincide with gelation. In the present case, since the crystallization is from a homogeneous solution, the changes in optical properties must reflect changes in the morphology and structure of the polymer. On the other hand, there are examples where the crystallization occurs from a two-phase system.[20,29,30] In this case the distinct possibility exists that the turbidity does not originate from morphological features of the polymer. The gelation of isotactic polystyrene in several different solvents demonstrates this point quite clearly.[20]

Thin section, transmission electron miscroscopy of these types of copolymers, when crystallized from the pure melt, shows that the loss of the well-defined lamellar crystallite structures occurs in the range 3–4 mol % branches.[61] For crystallization from dilute, or moderately dilute solution, the counit content corresponding to the loss of lamellar structure would be expected to be slightly higher. Therefore, it can be anticipated that some type of structural or morphological change, related to the lamellar structure, is the cause of the turbidity changes that are observed in the ethylene copolymers.

The concept outlined above is supported by the polarized light micrographs of Figure 5. Here the gelation conditions are the same as for the samples described in Table V. For both the 2.2 and 4.4 mol % hydrogenated polybutadienes, a spherulitic type supermolecular structure is observed. However, this structure degrades with increasing counit content. Well-defined, highly birefringent spherulites are found in the 2.2 mol % copolymer, with average radii of about 6.5 μm. This size is reduced to about 2.5 μm for the 4.4 mol % hydrogenated polybutadiene, and

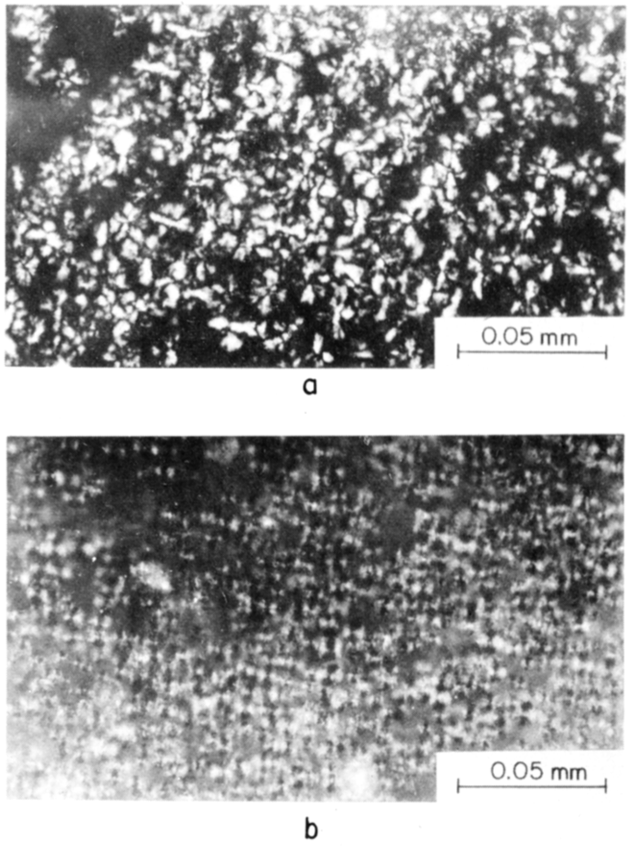
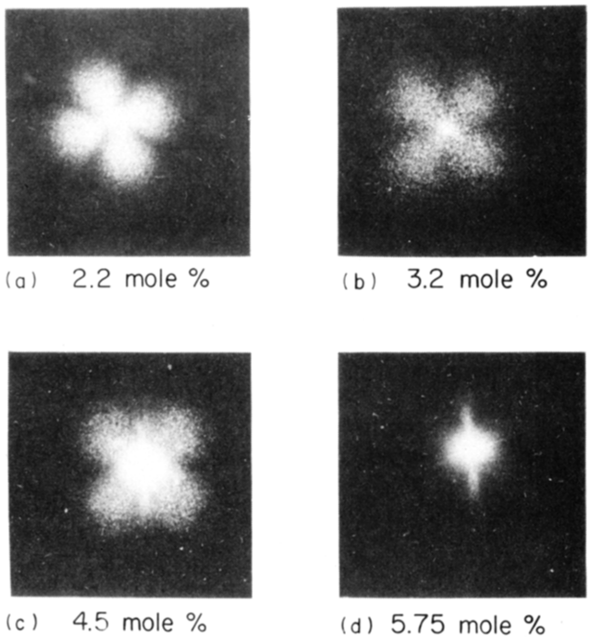
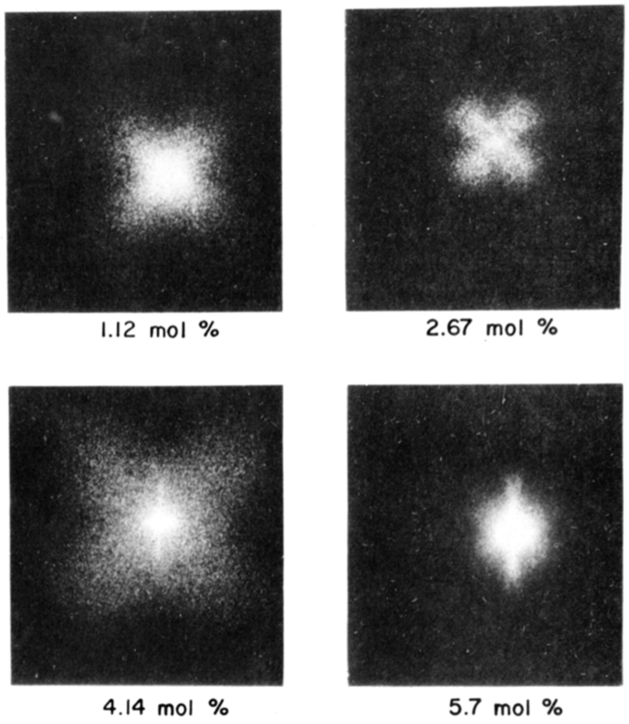


Figure 5. Polarized light micrographs of gels: (a) hydrogenated polybutadiene with 2.2 mol % branches, 9% (w/v) in toluene quenched to −34 °C; (b) hydrogenated polybutadiene with 4.4 mol % ethyl branches, 9% (w/v) in toluene quenched to −34 °C.


(a) 2.2 mole % (b) 3.2 mole %

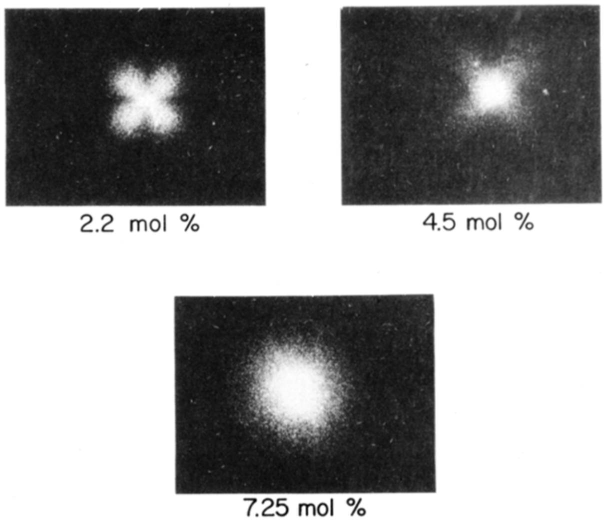
(c) 4.5 mole % (d) 5.75 mole %

Figure 6. Small-angle light scattering pattern for hydrogenated polybutadiene (undried) gels. Mole percent ethyl branches indicated. 9% (w/v) in toluene quenched to −34 °C.


1.12 mol % 2.67 mol %

4.14 mol % 5.7 mol %

Figure 7. Small-angle light scattering pattern for ethylene–vinyl acetate (undried) gels. Mole percent branches indicated. 9% (w/v) in toluene quenched to −34 °C.

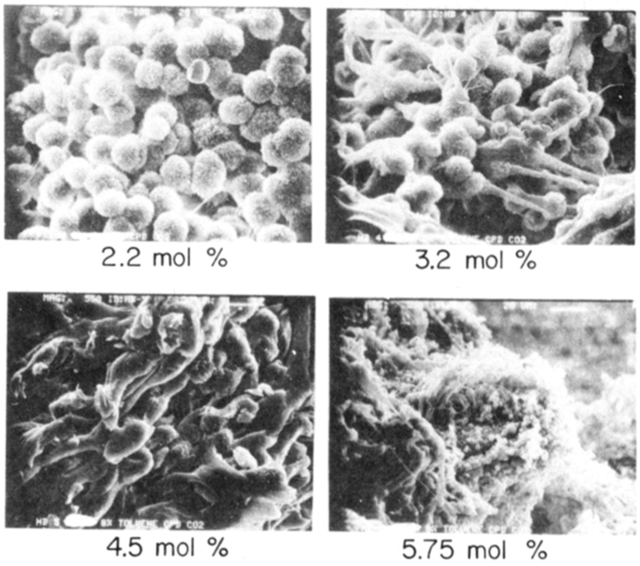

2.2 mol % 4.5 mol %

7.25 mol %

Figure 8. Small-angle light scattering pattern of dried hydrogenated polybutadiene gels. Mole percent branches indicated.

the spherulites are not nearly as well-defined. The 5.75 mol % copolymer (HPBD6) does not show evidence for the development of any kind of supermolecular structure. These results are consistent with the changes in turbidity that are observed visually (see Table V) and with the degradation and loss of lamellar structure. Insofar as lamellar-like crystallites are a necessary, but not sufficient, condition for spherulite formation,[62,63] there is a good self-consistency between the observation of lamellar structures, the formation of spherulites, and the gross optical properties.

These conclusions with regard to the supermolecular structures are given strong support by the series of small-angle light scattering patterns (SALS) that are illustrated in Figures 6 and 7 for the undried (wet) hydrogenated polybutadiene and ethylene–vinyl acetate gels. The typical clover leaf spherulitic pattern is found for either type copolymer of low counit content. The SALS patterns clearly demonstrate the continuous degradation of spherulitic order with increasing counit content. For the 5.7 mol % copolymer, of either type chemical side group, there is no distinct light scattering pattern. This result indicates the complete loss of supermolecular structure. These morphological features are still main-



2.2 mol %

3.2 mol %

4.5 mol %

5.75 mol %

Figure 9. Scanning electron micrographs of dried hydrogenated polybutadiene gels. Mole percent branches indicated.

tained when the gels are dried, as is shown in Figure 8 for the hydrogenated polybutadienes. Similar results are also obtained for the dried ethylene–vinyl acetate gels. Besides the degradation in structure, the spherulite radii decrease continuously until the superstructure is lost. Thus the polarized light micrographs and SALS patterns are consistent with one another and indicate a continuous and significant change in supermolecular structure. We have also found from SALS measurements that the undried gels of isotactic polystyrene do not give any indications of superstructure when initially formed.

Scanning electron micrographs of the dried hydrogenated polybutadiene gels, given in Figure 9, substantiate the conclusions that have been made with respect to the supermolecular structure. The 2.2 mol % copolymer forms very distinct spherical structures. The packing of the lamellae to form these structures can be seen in this micrograph, and their edges are clearly discernable. For 3.2 mol % ethyl branches, the spherulite structures remain. However, the overall impression that is obtained from the micrograph is that these structures are not nearly as well organized. For the still higher counit-content copolymers, the superstructure is not as well-defined and appears to be deteriorating. Qualitatively similar SEM results have been reported for dried, unfractionated ethylene–vinyl acetate gels.[25]

With these results of the morphological characteristics of the copolymer gels, we are in a good position to examine in a more quantitative manner the gelation behavior and gel properties of the copolymers. We consider first the factors that influence the critical concentration for gelation. A series of molecular weight fractions, 1×10^4–4×10^5, is available for the hydrogenated polybutadienes, each fraction containing 2.2 mol % ethyl branches. Therefore, this series of copolymers is well suited for the study of the molecular weight dependence of the critical concentration. This dependence is illustrated in Figures 10 and 11 for different crystallization temperatures. Figure 10 shows that there is a very strong dependence of c^* on M at all crystallization temperatures. In contrast, c^* for the linear polymers (Figure 1) does not depend very strongly on molecular weight at the lower crystallization temperatures. A significant molecular weight dependence is only found at the higher crystallization temperatures for the linear polymer. The double-logarithmic plot of Figure 11 indicates that in general the data cannot be described by the form of eq 1. It is also apparent that even if the data for a given temperature were represented by eq 1 over a limited molecular weight range, the value of the parameter a would still not be 0.5. It would vary from about 0.7 to 0.2 with increasing temperature. Thus, as was found for the homopolymers, molecular overlap is not a sufficient condition for gelation.

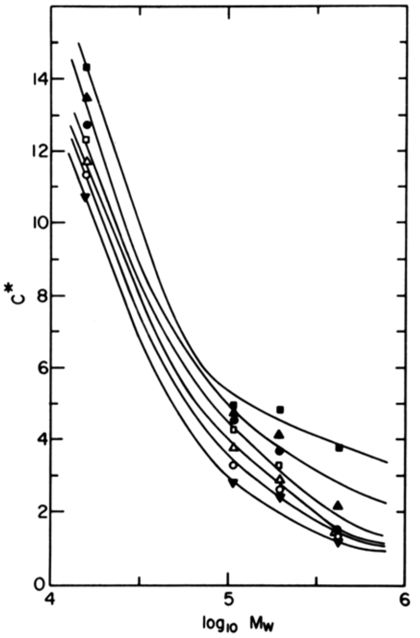


Figure 10. Plot of critical concentration for gelation, c^*, against log molecular weight for hydrogenated polybutadienes, 2.2 mol % ethyl: 20 °C (▼); 30 °C (○); 40 °C (△); 50 °C (□); 55 °C (●); 60 °C (▲); 63 °C (■).

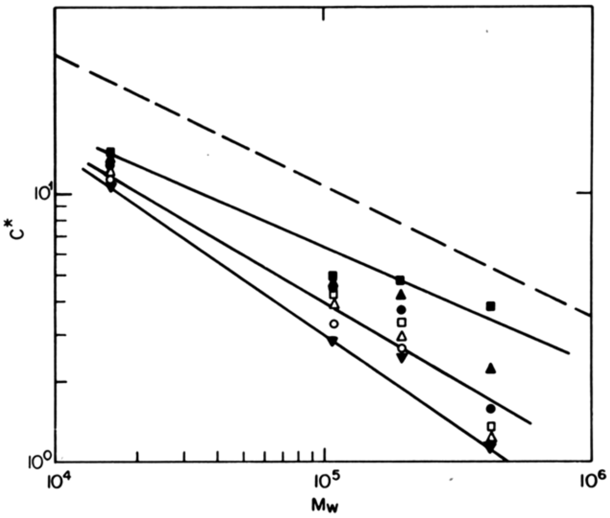


Figure 11. Double-logarithmic plot of data from Figure 10 with same symbols. Dashed line of slope −0.5 given for reference.

In contradiction to the conclusion just reached, Tan et al.[30] deduced from their study of the gelation of atactic polystyrene in CS_2 that eq 1 is obeyed over a wide range of molecular weights, with the constant $a = 0.5$. It was also assumed that these gels were completely noncrystalline. Hence, it was argued that molecular overlap was the sole requirement for network formation and gelation. However, the critical concentration used by Tan et al.[30] was not appropriate to the analysis and subsequent discussion. The value of c^* appropriate to eq 1 needs to be determined isothermally from a homogeneous solution. Confusion has resulted because atactic polystyrene in CS_2 can form a two-phase liquid–liquid system. Although gels can form

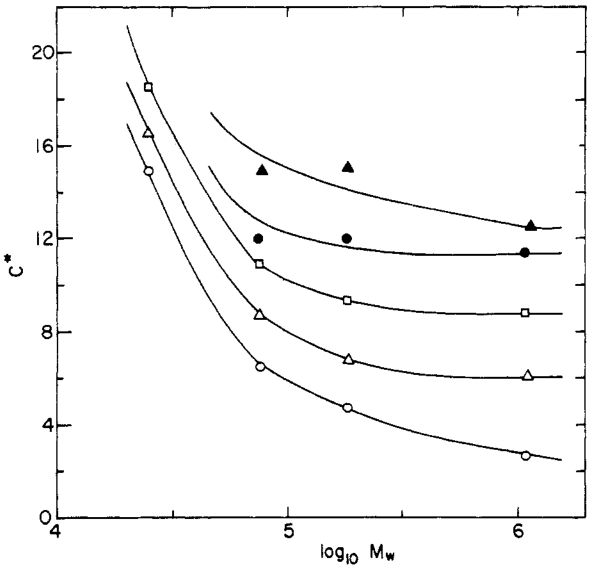


Figure 12. Plot of critical concentration for gelation, c^*, against log molecular weight for atactic polystyrene in carbon disulfide: −30 °C (○); −25 °C (△); −20 °C (□); −15 °C (●); −10 °C (▲).

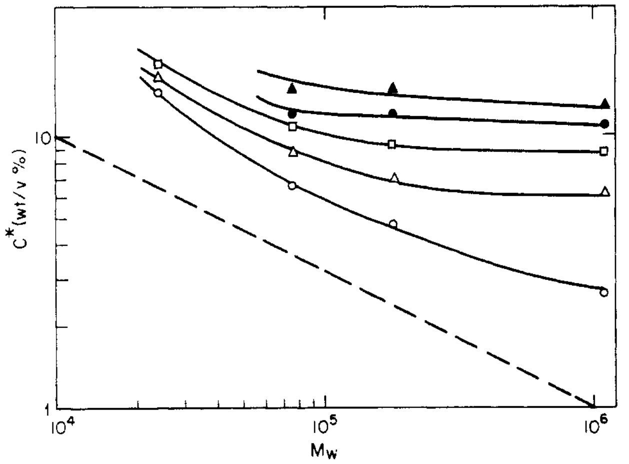


Figure 13. Double-logarithmic plot of data from Figure 12 with same symbols. Dashed line of slope −0.5 plotted for reference.

in this system from the one-phase liquid at temperatures above the binoidal, Tan et al.[30] arbitrarily defined c^* as the concentration at which a one-phase solution gels upon crossing the binoidal. Besides being theoretically inapplicable to the problem at hand, c^* determined in this manner must vary with temperature as the molecular weight changes.

Using a similar set of atactic polystyrene fractions, we have determined the critical concentration for gelation in CS_2 at fixed temperatures. The procedure followed was similar to that used for linear polyethylene and its copolymers. The results are plotted in Figures 12 and 13. The general character of the plots is very similar to that of Figures 10 and 11 for the hydrogenated polybutadienes. The critical concentrations involved are comparable. It is also clear that for this system, eq 1 is not obeyed. Even if it were fitted over a limited molecular weight range, the constant a would not equal 0.5. Thus, these new results strongly disagree with those previously reported for atactic polystyrene.[30] Consequently, we conclude that the gelation process for atactic polystyrene is not dependent on molecular overlap and the postulated entanglement mechanism.[87]

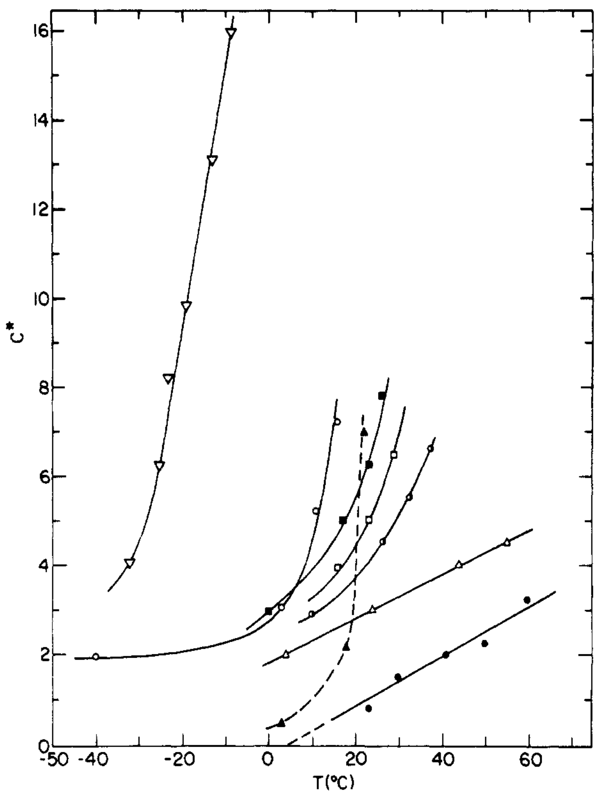


Figure 14. Plot of critical concentration for gelation against temperature. Linear polyethylene (●). Hydrogenated polybutadienes: 2.2% ethyl (△); 5.75% ethyl (□); 7.25% ethyl (○). Ethylene vinyl acetate: 4.14% acetate (◑); 5.70% acetate (■). Isotactic polystyrene (▲). Atactic polystyrene (▽).

The temperature dependence of c^* for the ethylene polymers is examined in more detail in Figure 14. Here we have plotted c^* as a function of temperature for a linear polyethylene fraction, $M_w = 1.4 \times 10^5$ and a series of hydrogenated polybutadienes and ethylene–vinyl acetate fractions. Also plotted are the results for the isotactic polystyrene fraction and an atactic polystyrene fraction $M_v = 1.8 \times 10^5$. All these samples have very similar molecular weights. Therefore, any differences that are observed between the samples can be attributed primarily to the chain structure. At a fixed temperature, c^* for the ethylene copolymers increases rather dramatically with counit content. For example, at 20 °C, c^* increases approximately threefold in going from the homopolymer to the 2.2 mol % ethyl copolymer. There is a rather substantial increase in c^* with a further increase in the side group content at fixed temperatures.

There is clearly a major change in the general character of the c^*–temperature plot between the low-counit samples and the higher ones. The linear polyethylene fraction and the 2.2 mol % ethyl branched copolymer behave very similarly. For both polymers there is essentially a linear increase in c^* with temperature. The main difference between the two is that higher values of c^* are required for the copolymer. On the other hand, the c^*–temperature relation (for both type side groups) is quite different for the higher counit content ethylene copolymers. Starting at about 0 °C there is a rapid increase of c^* with increasing temperature. The severity of this effect, as indicated by the steepness of the gradient, increases very markedly with counit content. Thus, for the 7.25 mol % hydrogenated polybutadiene an excessive polymer concentration would be required for gelation to take place at 25 °C.

The results for the isotactic polystyrene fraction are very similar to those of the higher counit ethylene copolymers. From the point of view of the c^*–temperature plot, isotactic polystyrene behaves as a typical copolymer. The appearance of a polymorphic crystalline form does not alter matters. The data for isotactic polystyrene indicates that an extremely high polymer concentration is necessary for gelation to occur at elevated temperatures, of the order of 100 °C or greater. At these temperatures it has been reported that although crystallization occurs, gelation does not take place.[10,13] The very large critical concentration that is required is a more rational explanation for the lack of gel formation than the argument that has been previously offered.[13,21]

Also plotted in Figure 14 are the results for a comparable molecular weight atactic polystyrene fraction. The general shape of the c^*–temperature plot is the same as for the other copolymers. However, the gelation process is shifted to lower temperatures and requires somewhat higher critical concentrations. This result is expected for a copolymer containing a very high counit content. The atactic polystyrene fraction fits this requirement. Therefore the results observed are a natural consequence of the chain structure.

The time required for gelation has an unusual temperature dependence, as was first reported by Keller and co-workers for the gelation of isotactic polystyrene.[13] We examine this phenomenon in more detail here. In Figure 15, parts a, b, and c, plots of the gelation time, for a fixed polymer concentration, are given as a function of temperature for three typcial copolymers: 2.2 mol % hydrogenated polybutadiene, 4.14 mol % ethylene–vinyl acetate, and the isotactic polystyrene fraction. It is quite clear that the curves for the three different copolymers, each at a fixed concentration, have essentially the same features. At the lower temperatures the gelation (crystallization) process is very rapid and the rate does not perceptibly change with temperature. However, there is a temperature at which the gelation begins to take a somewhat longer time. The process becomes sufficiently retarded with a further increase in temperature so that there is a dramatic upsweep in the time–temperature plot. Unduly long times are then required in order for gelation to occur at all. Thus, for a give concentration, there is a temperature above which gelation will not take place over any reasonable time period. For a given concentration there is a relatively narrow temperature interval over which gelation can occur and it does so relatively rapidly. The kinetic observations are a unique feature of the gelation process. They are independent of whether spherulites do (hydrogenated polybutadiene) or do not (isotactic polystyrene) form. They are not a consequence of nucleation kinetics, as has been proposed.[13,21] The narrow temperature interval that is available for gelation is solely a consequence of the temperature dependence of the critical concentration. As the temperature is increased, the required critical concentration approaches and then falls below the actual concentration. Gelation will thus be retarded and then completely prevented. Consequently, the gelation process is limited to a narrow temperature interval. The classical gelling system, gelatin–water, displays similar kinetic behavior. It is well-known that gelation takes place very rapidly at lower temperatures and is completely retarded at higher ones. It has also been well established that for this system a crystallization mechanism is involved.[1,65–68]

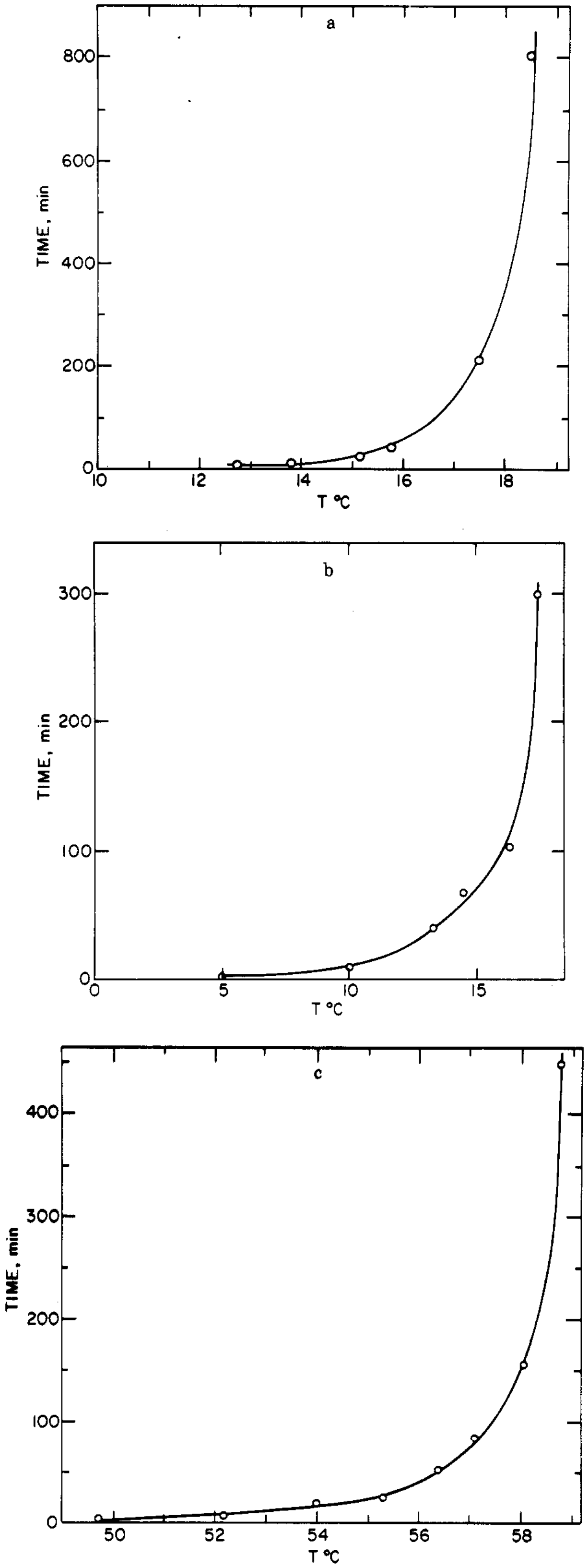


Figure 15. Plot of gelation time against temperature for representative copolymers: (a) ethylene vinyl acetate 4.14 mol % branches, 5.5% toluene solution; (b) isotactic polystyrene in *trans*-decalin, 2.2% solution; (c) hydrogenated polybutadiene 2.2 mol % ethyl, 4.4% toluene solution.

The similarity of the gelation time–temperature curves for the typical copolymers illustrated, and for the others studied as well, can be seen in Figure 16. Here the data from Figure 15 are replotted by merely shifting the temperature axis. It is clear that just by shifting the temperature scale, all the curves can be brought into superposition. The gelation kinetics, and hence the mechanisms, are obviously the same for all the samples. We thus find a universal gelation process for all crystallizable copolymers. The gelation time–temperature curves for linear polyethylenes are qualitatively similar to those illustrated for the copolymers. The main difference is that although for a fixed concentration there is a well-defined temperature region of rapid gelation, the interval for a finite rate,

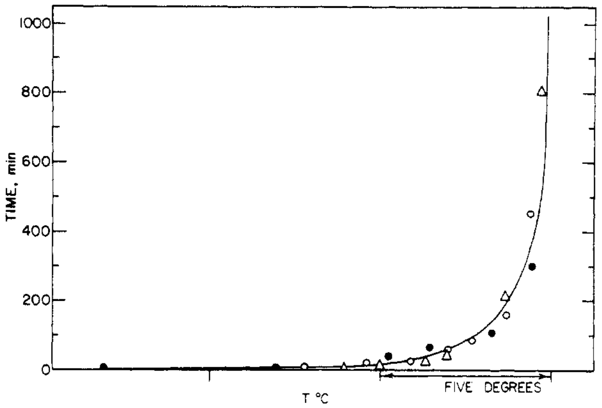


Figure 16. Superimposed plot of gelation time against temperature for data of Figure 15: 4.14 mol %, ethylene–vinyl acetate (△); isotactic polystyrene (●); 2.2 mol % hydrogenated polybutadiene (○).

before cessation of the process, is discernably smaller than in the copolymers.

Thermodynamic Properties. Two very important properties of gels are their melting, or dissolution, temperatures and enthalpies of fusion. The dissolution temperatures of the hydrogenated polybutadiene and ethylene–vinyl acetate gels were determined at a constant polymer concentration, 9.5% (w/v) in toluene, by differential calorimetry. Except for the highest counit copolymer, the samples were rapidly cooled to −35 °C, where crystallization ensued.[88] The melting temperatures were determined at a constant concentration to avoid the complication of the concentration dependence of the melting temperature. Beyond the dilute range there is, as is theoretically expected,[51,52] a monotomic increase of the dissolution temperature with increasing polymer concentration. The heating rate in these experiments was 10 K/min, and the temperature of the endothermic peak was taken as the dissolution temperature.

The melting temperatures determined in this manner are plotted in Figure 17 as a function of the branching content of the copolymers. The endothermic peak broadens considerably with increasing counit content, while the peak position is systematically lowered and the enthalpy of fusion is severely reduced. Hence, as is indicated in the plot, the experimental error becomes greater for the copolymers having the higher branching content. There are several very important features of the plot in Figure 17. Foremost among these is the observation that the melting temperature decreases in a continuous manner with increasing side group content. The results are the same for either the ethyl or acetate side groups. Data from the literature[69] for a set of random chlorinated polyethylenes are also plotted. They show good adherence to the results for the other copolymers. These melting temperatures may be slightly higher since this type counit behaves similarly to that of directly bonded methyl groups.[37] The melting point data of the gels given in Figure 17 extrapolate quite smoothly to the experimentally observed value for the homopolymer, linear polyethylene.[25] These melting, or dissolution, temperature data give no indication that the optical and morphological character of the gels change in the range 4–5 mol % branches. As we have already noted, in this composition range the initially turbid gels become clear. A major change in the supermolecular structure of the gels was also shown to occur. The very distinct spherulitic structures that are observed for the lower counit content copolymers disappear above 5 mol % branches. The observation of endothermic peaks for all the gels and the continuity of the melting point curve in Figure 17 clearly demonstrate that melting is taking place over the complete copolymer composition range.

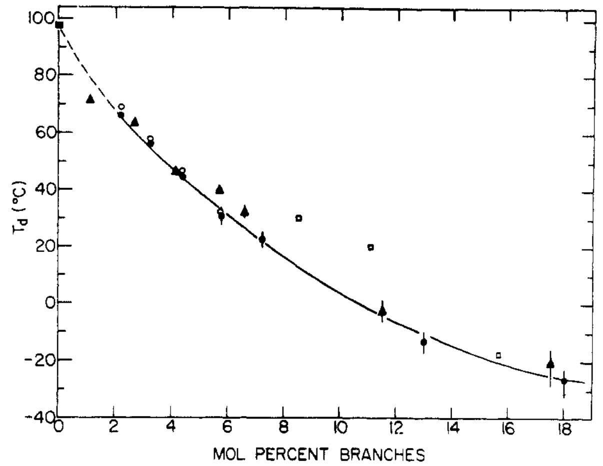


Figure 17. Plot of dissolution temperature (melting temperature) of 9% solution of gels and of dilute solution crystal against mole percent branches: hydrogenated polybutadiene gels (●); ethylene–vinyl acetate gels (▲); hydrogenated polybutadiene solution crystals (○); chlorinated polyethylene gels from ref 69 (□).

It is of prime interest to compare, at the same polymer concentration, the dissolution temperature of the gels with those of crystallites formed from dilute solutions. Such crystallites of hydrogenated polybutadiene with branch contents ranging from 2.2 to 5.75 mol % were crystallized and dried as described previously.[70] They were then suspended in toluene, at the appropriate concentration, in the DSC pan and the thermogram determined. The melting temperature of the suspensions (location of the endothermic peak) is also given in Figure 17. The melting temperatures for this type crystallite are essentially the same as those of the gels. This more extensive set of data strongly supports the previous conclusion[24,25] that the gel crystallites and those formed in dilute solution have the same thermodynamic properties. Lamellar-like crystallites have been observed by electron microscopy for a hydrogenated polybutadiene copolymer containing 1.8 mol % ethyl branches that was crystallized from dilute solution.[71] A lamellar structure in the gels can be inferred from the fact that spherulites are formed with copolymers that contain up to 4.5 mol % ethyl groups. Thus, in this counit-content range for the copolymer, as well as for the linear polyethylene, gelation does not involve a fringed micelle structure.

The behavior of the very high counit copolymers (17 and 18 mol % branches) was examined separately prior to the calorimetric studies. Starting with a solution of 18% (w/v) in toluene, which has a very high viscosity, it was possible to make self-supporting gels by quenching the solution to a temperature in the range −40 to −78 °C. Visual observations during heating indicated that the gel characteristics disappeared at about −20 °C. The result of a more quantitative study with a 16.6% (w/v) solution in toluene of HPBD9 (18 mol % ethyl) is shown by the DSC scan of Figure 18. Here, after quenching at −100 °C and heating at the rate of 10 K/min, a broad but distinct endotherm is observed in the range −33 to −20 °C. This dissolution temperature is in accord with the visible observations and adheres to the plot of Figure 17.

Analysis of the enthalpies of fusion leads to conclusions that are similar to those reached from the melting temperature data. The results are plotted in Figure 19. Again we note a continuity in the values of $(1 - \lambda)_{\Delta H}$ with the mole percent branching. The results are independent of

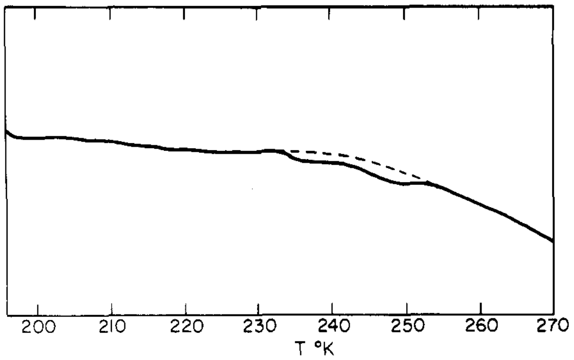


Figure 18. DSC thermogram for hydrogenated polybutadiene gel, 18 mol % ethyl branches.

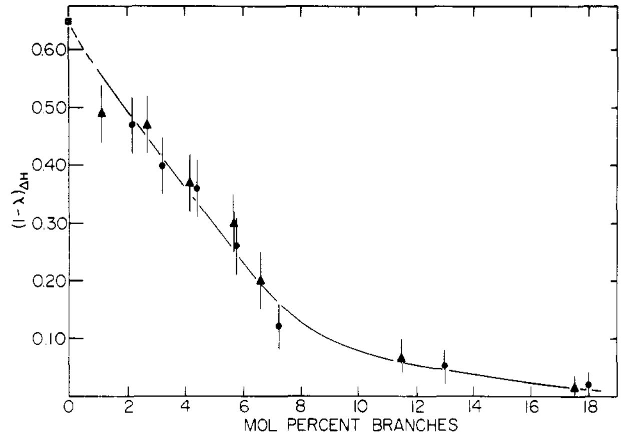


Figure 19. Degree of crystallinity calculated from the enthalpy of fusion of 9% gels plotted against mole percent branches: hydrogenated polybutadiene (●); ethylene–vinyl acetate (▲).

the chemical nature of the side group and extrapolate to the value expected for the homopolymer. The level of crystallinity is about 0.50 for a copolymer containing only about 1 mol % branches. It decreases to 0.10 when the branching content increases to about 7.5 mol %. For the high counit-content copolymers, as has been shown in Figure 18, a broad and weak, but quite distinct, endothermic peak is observed. The enthalpy of fusion in this case corresponds to a degree of crystallinity of about 0.03. Thus the major morphological changes that take place with increasing counit content have no effect on this thermodynamic property.

There would superficially appear to be an anomaly in the results for the higher counit copolymers. In the pure, or bulk, state ethylene copolymers with a total branching content of about 9 mol % and greater are not crystalline at room temperature after rapid crystallization from the melt.[37] For example, an ethylene–vinyl acetate copolymer containing 11 mol % branches melts at 27 °C after rapid cooling to −35 °C. However, it is well-known, and has been demonstrated, that crystallization from dilute and moderately dilute solutions enhances crystallinity. For example, about 10% crystallinity is developed in the 9 mol % copolymer after solution crystallization. Hence, there really is no anomaly in the fact that the gels formed by the higher counit-content ethylene copolymers are crystalline. The lack of understading of this point has lead to a serious misconception in the study of the gelation of chlorinated polyethylenes.[69] It was concluded that crystallization cannot be a condition for gel formation in this case because the copolymers were not crystalline in the bulk state. Such a conclusion is not warranted, and in fact, as is shown in Figure 17, the melting temperatures of the chlorinated polyethylene gels follow the pattern established by the other ethylene copolymers.

A similar situation appears to be applicable to the gelation of atactic polystyrene.[30] It has also been claimed that for this copolymer gelation cannot be due to crystallization. Furthermore, it was implied that a similar condition exists for the gelation of isotactic polystyrene. However, for atactic polystyrene in carbon disulfide a "heat of gelation" of 1–2 J/g was reported.[30] The characteristics of the endotherm are very similar to that illustrated in Figure 18 for the hydrogenated polybutadiene. For the atactic polystyrene, this excess heat capacity corresponds to a degree of crystallinity of about 1–2%. This value is quantitatively very similar to that for the 18 mol % hydrogenated polybutadiene, where the gelation is clearly a consequence of crystallization. Pure, bulk atactic polystyrene is noncrystalline. However, as has been pointed out,[20,64] the sequence distribution between isotactic and syndiotactic units provides a set of crystallizable units. These can, in principle, crystallize to a small extent upon dilution. Thus, from a thermodynamic point of view, the gelation (crystallization) characteristic of atactic polystyrene is very similar to that of a high counit-content ethylene copolymer. This conclusion is consistent with the similar molecular constitution of the two chains.

The thermodynamic data that have just been discussed for the ethylene homopolymers and copolymers are important in establishing a fundamental basis for understanding the properties of the gels and the gelation process itself. Since the particular gelation process under discussion here is a crystallization phenomenon, it is not surprising, from both theory[51,72] and previous experience,[37,73,74] that the gel dissolution temperatures are independent of the chemical nature of the side groups. The virtual correspondence of the melting temperatures, at a given counit content, for the gels and dilute solution crystals indicates that the crystallites have the same features in both cases. For the lower counit-content copolymer, therefore, the gels are still comprised of lamellar-like crystallites. The continuity of the melting temperatures and enthalpies of fusion, from that of the homopolymer through the wide range in copolymer composition, indicates that the gel properties and structure change in a gradual manner. They cannot be divided, even arbitrarily, into two distinct classes, as has been proposed.[21] Concomitantly, one observes gradual changes in the supermolecular structure, optical properties, and physical appearnace of the gels. These latter changes are reflections of the gradually changing crystallite structures, which range from well-developed lamellae to very small crystallites.[61]

One of the difficulties in directly establishing the basic principles involved in the gelation of the stereoirregular vinyl polymers, such as polystyrene, is the restricted counit-content range that is conveniently available for study. Usually, there is available only the highly stereoregular isotactic chain of low counit content or the atactic one of very high counit content. We have, however, found that these two extreme situations for polystyrene adhere rather closely to the patterns and principles established for the ethylene copolymers, where gelation by a crystallization mechanism is clearly established. There is no problem in understanding the gelation behavior of the polystyrenes from this point of view. Obviously, the study of polystyrenes having intermediate concentrations of structural irregularities would help in the quantitative understanding of the behavior of this polymer.

Table VI
Comparison of Thermodynamic and Mechanical Melting Temperatures of Ethylene Copolymer Gels

sample	mol % branches	c, % (w/v)	T_{mech}	T_{d}, DSC	morphology	physical appearance
P108, T_c = 52.8 °C (p-xylene)	2.2	5.1	65		spherulitic	turbid
		5.4		66.0	spherulitic	turbid
		6.8		66.0	spherulitic	turbid
		7.0	67.2		spherulitic	turbid
		8.8		67.0	spherulitic	turbid
		9.0	67.8		spherulitic	turbid
		10.4		68.0	spherulitic	turbid
		11.1	68.6		spherulitic	turbid
P108, T_c = 23 °C (toluene)	2.2	3.0	64.0	65.0	spherulitic	turbid
		4.0	66.0	65.2	spherulitic	turbid
EVAF35, T_c = −15 °C (toluene)	4.14	9.3	47.1	47.3	poor spherulitic	partly turbid
EVAF30, T_c = −15 °C (toluene)	5.7	10.0	40.3	38.5	nonspherulitic	clear

Gels display unique mechanical properties for the polymer concentration involved. A dilute or moderately dilute solution is transformed into a high viscosity, elastic medium. There has, therefore, been a focus on mechanical and elastic properties and the temperatures at which these properties undergo major changes corresponding to the sol–gel transformation. We shall designate this temperature as the mechanical melting temperature, T_{mech}. One method widely used to determine this temperature,[30,75–77] which was pioneered by Takahashi,[3,5] is the ball-drop technique. We have described this method in the Experimental Section. Surprisingly, there is no comparison in the literature between the melting temperature determined by mechanical methods and the thermodynamic melting temperature for the crystal–liquid transition. This is an important matter since it addresses directly the question of the relationship between crystallization and gelation. If the postulate that crystallization is not a requirement for gelation is correct, then the two different melting temperatures would not agree. According to this hypothesis, the gel structure should persist at temperatures above that for the melting of crystallites. The mechanical properties should be maintained above the thermodynamic melting temperature. It has also been postulated,[3] from a different point of view, that the melting temperature of the gel does not coincide with the thermodynamic melting temperature, since the sol was thought to still contain crystallites.

We have addressed this question by comparing the two melting temperatures for several copolymers that were gelled (crystallized) under different conditions and that also have different supermolecular structures. The results are summarized in Table VI. They are quite definite in demonstrating that, within the experimental error of 1 °C, the melting temperatures determined in the two different ways are identical with one another irrespective of counit type or supermolecular structure. Thus we conclude that crystallite melting and the loss of gel structure, with the change in mechanical properties, are concomitant processes. Molecular entanglement is therefore not a sufficient condition for gel formation; the key process is crystallization. Furthermore, the equality of the two melting temperatures indicates that crystallites do not persist in the sol.

Takahashi and co-workers have pointed out[3] that the melting temperature of a nonequilibrium crystallite can be obtained from the Flory formulation[51,72] for the free energy of fusion of a copolymer–diluent mixture. Their result can be expressed as

$$1/T_{\mathrm{m}} = \ln v_2 + C \qquad (3)$$

where C is a constant and v_2 is the volume fraction of polymer. The melting temperature of a large number of gel systems, from the classical work on gelation by Eldridge and Ferry[78] to atactic polystyrene in CS_2,[30] as well as many others,[3–9,75,79] obeys this relation. We have found that, except in the very dilute range, sample P108 (2.2 mol % ethyl) gelled under several different conditions also obeys this relation. Hence, this almost universal experimental result for the melting temperature–composition relation for gel systems can be explained on the basis of crystallite melting.

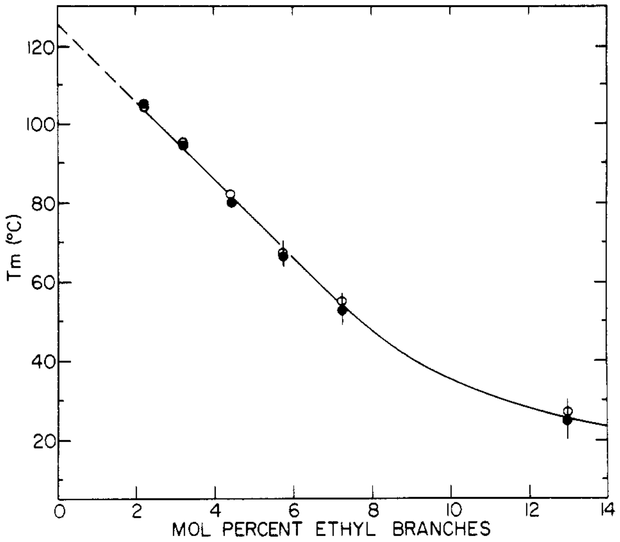


Figure 20. Plot of melting temperature T_{m} against mole percent branches for dried hydrogenated polybutadiene gels and solution crystals: gels (●); solution crystals (○).

Up to now, we have limited our discussion of gel properties to the "as-formed" system. It is also of interest to study the thermodynamic properties of the crystallites of dried gels and compare them with the properties of the crystallites formed in dilute solution and then dried. The results for the dried hyrogenated polybutadiene gels and solution crystals are given in Figures 20 and 21. For a given copolymer, the two types of crystallites give identical values for the melting temperature and for the enthalpy of fusion. We have found that the DSC melting of either of the copolymer crystal types is not complicated by the melting–recrystallization problem, which is of concern for homopolymers melting.[43,80] These thermodynamic quantities decrease in a continuous manner with increasing counit content. They extrapolate to the values expected for the rapidly crystallized homopolymer. We have already noted that the major changes in supermolecular structure with counit content are maintained in the dried gels. However, the thermodynamic quantities are again insen-

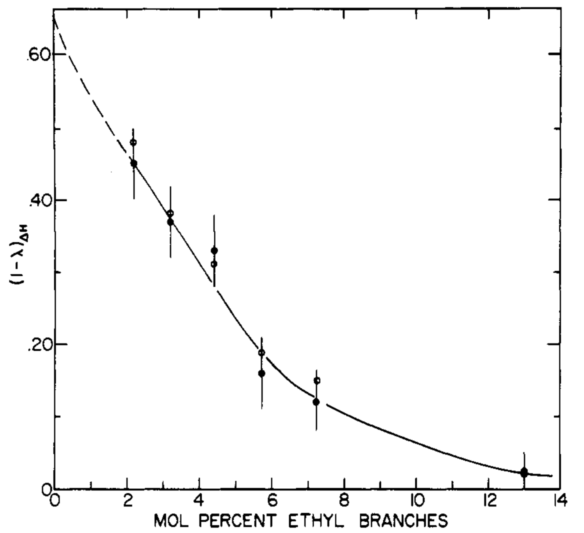


Figure 21. Plot of degree of crystallinity calculated from the enthalpy of fusion against mole percent branches for dried gels and solution crystals of the hydrogenated polybutadienes: gels (●); solution crystals (○).

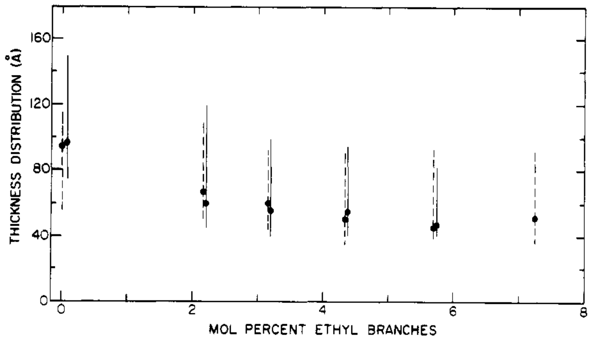


Figure 22. Plot of thickness distribution of ordered sequence length against mole percent branches for dried gels and solution crystals of the hydrogenated polybutadienes: gels (—); solution crystals (- - -).

sitive to these structural alterations.

Detailed studies of the low-frequency Ramany spectra of the hydrogenated polybutadiene copolymers crystallized from the bulk and from dilute solution have been recently reported.[70] Spectra of similar quality have been obtained for the dried gels. The distribution of ordered sequence lengths and the most probable value, L_R, are plotted in Figure 22 for both dilute solution formed crystals and for the gels. The value of L_R is indicated by the solid circle in the plot. Within experimental error, the size distribution of the ordered sequences is the same for a given copolymer, irrespective of whether from dilute solution or the gel. Morevoer, as has been noted previously,[70] the size distribution and most probable values are not very dependent on the counit content under these crystallization conditions. The values of L_R range from about 60 Å for the 2.2 mol % branched copolymer to 45 Å for the same type copolymer containing 5.75 mol % branches. Gels from sample HPBD11, 7.25 mol % ethyl branches, did not give a very reliable low-frequency Raman spectra. The results for the hydrogenated polybutadiene copolymers extrapolate very smoothly to the size distribution of linear polyethylenes of similar molecular weight crystallized (gelled) under comparable conditions. The results of these size measurements reinforce the conclusion that the structure of the crystallites formed in dilute solution and those involved in the formation of gels are very similar.

It has already been pointed out that the melting temperatures of the dried gels and the solution crystals are identical. Since, the size distribution is the same; the interfacial free energies characteristic of their basal planes must also be the same and identical with those previously reported.[70] Therefore, the interfacial free energy, σ_e, ranges from 1830 cal/mol for the 2.2 mo % branched copolymer to 2608 cal/mol for the copolymers containing 5.75 mol % ethyl branches. These results for the interfacial free energy reflect an increasingly distorted and thicker interfacial zone with increasing counit content. This type of structure results because of the rejection of the counits and their preferential accumulation in the interfacial region.

Summary

From the detailed studies of the gel properties of homopolymers and copolymers of ethylene that have been given here, it is possible to develop a rudimentary outline of the gelation mechanism. For the class of gels studied here the primary molecules are bound together, or connected, by crystallites. Takahashi has pointed out[3] that in order to develop a network structure a chain, on the average, must pass through at least two different crystallites. Thus the critical condition for network formation by this process is established. Although, in the range of interest, crystallization takes place continuously with concentration, there will be a critical concentrtion above which gelation occurs, i.e., when the aforementioned condition is satisfied. The critical concentration varies systematically with molecular weight, temperature, and counit content. However, the actual functionality of the junctions, or points of cross-linkage, are not obvious when they involve crystallites. Gels formed by this mechanism cannot be analyzed in the same manner as the classical case of networks formed by the covalent cross-linking of disordered chains.[1]

We consider first the gelation (crystallization) of homopolymers. In very dilute solution the well-known isolated plateletlike crystallites are formed. In this dilute range a molecule by necessity is restricted to participate in only one crystallite. As the polymer concentration is increased slightly, this tendency still prevails because of the problem of dissipating the flux of chains that emanate from the basal plane into the isotropic region.[81-83] This structural requirement is the basis for the formation of lamellar crystallites. It is accentuated in dilute soltuion since the chain flux in the isotropic region is severely reduced. Therefore, in this concentration range, all the chains will return to the crystallite of origin. However, as the concentration is increased further, some chains will be free to leave the crystallite of origin. They will then be in the position to participate in the formation of another crystallite. A partitioning of sequences will then take place between those that remain in the crystallite and those that leave, transverse the noncrystalline region, and are in a position to particpate in yet another crystallite. The structural basis for gel formation by a crystallization mechanism thus becomes clear. At a sufficiently high concentration the critical condition for gel formation, c^*, will be met; i.e., on the average a molecule will participate in more than one crystallite. Further understanding will require knowledge of the number of molecules participating in a given lamellar crystallite and the fraction of these that escape. These factors will be dependent on the molecular weight, crystallization temperature, and the not as yet understood specifics of the lamellar growth process. Neither theory nor experiment is sufficiently advanced at this time to allow for a more quantitative description. The crystallization process is clearly continuous with concentration. Gelation is superposed thereon. Therefore, the basic crystallite structure will remain the same irrespective of whether precipitated from solution or in the form of a gel. The detailed structure of the crystallite, beyond its lamellar character, must play a central role in gel formation.

Since gelation requires the participation of a given chain in more than one crystallite, the molecular weight will obviously be involved. However, as is shown in Figure 1, this factor is only significant in the low molecular weight range. For linear polyethylene c^* only increases moderately with the crystallization temperature. This may be due to crystallization kinetic requirements and the fact that an increasing crystallite thickness wil reduce the number of chains that are free to participate in more than one crystallite.

The outline of gel formation given above, as deduced from the experimental results for linear polyethylene, should be applicable to all crystallizable homopolymers. It has been observed that poly(ethylene oxide) also forms gels over the complete molecular weight range with properties very similar to those of linear polyethylene.[25] Other homopolymers should be expected to behave similarly. Low counit-content copolymers that form well-developed lamellae should also follow a similar pattern. This conclusion is substantiated by the results for the 2.2 mol % ethyl branched hydrogenated polybutadiene. The gelation properties of this copolymer are very similar to those of the linear polymer. Higher values for c^* are to be expected for this copolymer since the number of crystallizable sequences is reduced and more chains are involved in forming a crystallite.

In contrast to homopolymers, we can consider the other extreme of a high counit-content copolymer that is crystallizable and can thus form gels. Crystallization still occurs continuously with polymer concentration, and the crystallite properties do not change upon gelation. Because of the limited number of sequences that are available for crystallization in copolymers of this type, the crystallite thickness is small and its lateral extent severely restricted. These conditions have been directly observed by electron microscopy for the bulk crystallized copolymer[61] and should still be maintained for crystallization from solution. Although the relative number of chains emanating from a crystallite may remain the same, or even increase with decreasing lateral size, the concentration of crystallites that can be formed is sharply reduced. Therefore, a higher value of c^* will be required for gelation. The theory developed by Takahashi[3] would be most applicable for the extreme case where each chain participates only once in a given crystallite. As the crystallization temperature is increased, the number of available crystallizable sequences per chain will be reduced further.[51,72] Therefore, c^* will increase very rapidly with temperature, as is evidenced by the experimental results of Figure 14. It is this temperature dependence of c^* that leads to the unusual gelation kinetics that are observed. Copolymers having a lower counit content will behave between the two extremes that have been dicussed.

One of the key findings of this work is the observation that the thermodynamic properties of the gels are continuous from the homopolymers to the highly branched copolymers. At the same time, major changes are observed in the supermolecular structure. These changes reflect the gradual degradation of the lamellar crystallite structure. The changing supermolecular structure appears to be a consequence of the changing crystallite structure. It is an indirect result of the gelation process and not the cause, as had been originally postulated from a more limited set of data.[24,25] Thus it is not at all necessary to postulate two different gelation mechanisms as the chain structure is varied.

The principles that have been set forth should be applicable to the gelation of all types of crystallizable homopolymers and copolymers. We have seen from the preliminary experiments reported here that they are also applicable to the gelation of isotactic and atactic polystyrene, which are properly treated as copolymers. The polymorphic crystalline structure that is observed in isotactic polystyrene, as well as other crystallizable vinyl polymers, is not by itself fundamental to the gelation process. Thus the c^*–temperature relation for isotactic polystyrene is that expected for any crystallizable copolymer. For atactic polystyrene the c^*–molecular weight and c^*–temperature relations, as well as the enthalpy change that accompanies the melting of the gel, support the concept that the crystallization of a very high counit-content copolymer is involved. When the sequence distribution characteristics of the atactic polymer are recognized, these results and conclusion are not surprising.

It is hoped that some of the basic principles that have been established here, and elsewhere,[25] will be useful in guiding investigations of other gel-forming systems of flexible chains, without introducing unnecessary concepts and extraneous material.[19]

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Registry No. Polyethylene (homopolymer), 9002-88-4; (ethylene)·(vinyl acetate) (copolymer), 24937-78-8; isotactic polystyrene (homopolymer), 25086-18-4; polystyrene (homopolymer), 9003-53-6.

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(84) We thank Dr. Graessley for his generosity in supplying us with these samples and for helpful discussion concerning their properties.
(85) We should note that below 80 °C the crystallization (gelation) process is not isothermal.
(86) In analyzing such systems, it should be recognized that the concentrated phase will have a very high but finite viscosity. Thus, even noncrystallizable polymers can give the superficial appearance of being a gel or network. Therefore, a clear distinction needs to be made between the different situations.
(87) We should note at this point that atactic polystyrene in the bulk state is noncrystalline. However, even with a random sequence distribution it is theoretically crystallizable to a small extent.[20,64]
(88) Because of the very small enthalpy change and low dissolution temperature, the concentration of the 18 mol % copolymer was increased to 16% (w/v). The sample contained in the DSC pan was held at −45 °C for 30 min and then rapidly cooled to −100 °C prior to recording the thermogram.