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ORIGINAL CONTRIBUTION

O. Darras
R. Séguéla

Crystallization-induced gelation of ethylene/1-butene copolymers over a wide crystallinity range

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O. Darras · Dr. R. Séguéla (✉)
Laboratoire de Structure et Propriétés
de l'Etat Solide, Bat. C6
Université des Sciences et
Technologies de Lille
59655 Villeneuve d'Ascq Cedex, France

Abstract The crystallization-induced gelation from decalin solutions of a series of ethylene-butene random copolymers covering the range of crystal weight fraction 0.32–0.74 and having nearly equal molar weights has been investigated as a function of concentration. Swollen as well as dried gels have been characterized by means of differential scanning calorimetry, mechanical tests and scanning electron microscopy. The critical concentration for gelation is shown to be strongly dependent on the crystallinity of the polymers. On the contrary, the critical concentration for chain entanglement is quite invariant. A liquid-liquid phase separation phenomenon prior to the crystallization upon cooling is disclosed for the more crystalline materials. The better solubility of the co-unit rich copolymers is ascribed to a more favorable interaction parameter towards decalin with increasing co-unit content. Common aspects of the gelation process of the copolymers with that of atactic amorphous and isotactic semi-crystalline polystyrene are discussed.

Key words Ethylene copolymers – thermo-reversible gelation – chain overlaping – chain entanglement – critical concentration – liquid-liquid phase separation

Introduction

Thermoreversible gelation of semi-crystalline polymers has received increasing attention in recent years from both fundamental and industrial standpoints. On the one hand, new information about the morphological and topological habits of semi-crystalline polymers has been provided from investigations dealing with the phenomenological aspects of thermoreversible gelation. A good number of the studies have been focused on polyethylene (PE) [1–17] which is available in a great variety of molecular architectures and over a wide range of crystallinities owing to long-chain branching (high-pressure free radical polymerization) or copolymerization (low-pressure Ziegler–Natta catalysis). On the other hand, gelation of semi-crystalline polymers from solution has proved to be an efficient route for processing high-modulus high-strength fibres. The strong disentanglement of the chains which takes place in solution indeed allows an improved unraveling of the chain-folded crystals upon drawing of the gels. Successful endavors have been reported in the case of drawing of swollen or dried gels of polypropylene [18, 19], polyamide 6 [20], poly(4-methyl-1-pentene) [21], poly(ethylene terephthalate) [22] and poly(vinyl alcohol) [23, 24]. But most of the investigations have been focused on ultra-high molecular weight polyethylene (UHMWPE) for which this process gives spectacular results [25–32], the ultra-drawn fibers having Young modulus in the range 150–220 GPa and tensile stress at break as high as

3–5 GPa. It is noteworthy that these figures are close to the theoretical values for the stiffness and the strength of a methylene chain [33].

Cooling very dilute solutions of homopolyethylene and ethylene copolymers is well-known to generate isolated lamellar crystals or crystal aggregates that separate from the solvent through sedimentation. Besides, it has been recognized that high dilution promotes intramolecular crystallization with regular chain folding [34–36]. With increasing polymer concentration, intermolecular crystallization can occur giving rise to interconnected chain-folded crystals [4, 36, 37]. There is a concentration threshold beyond which the solutions turn into continuous gels upon cooling. This critical concentration for gelation of semi-crystalline polymers basically relies on the threshold for chain overlap in the solution prior to crystallization since a molecular connectivity of the crystallites is necessary for the formation of a continuous self-supporting gel [16].

This study is a contribution to the general understanding of the physical gelation of semi-crystalline polymers. Ethylene/1-butene random copolymers have been investigated over a wide range of concentration in decalin solutions. Particular attention has been paid to the intermolecular crystallization threshold and the chain entanglement threshold which have been briefly discussed in a previous paper concerned with a low crystallinity copolymer [38].

Experimental part

Materials, preparation and characterization

The materials investigated in this study were unfractionated industrial grade ethylene-butene copolymers having similar number-average and weight-average molar weights. Table 1 shows the characteristics of the polymers. The characterization methods are described elsewhere [39].

The gels were prepared from decalin solutions, the solvent being a 99% pure blend of *cis* and *trans* isomers. The concentrations are given in polymer weight fraction. The solutions were molded into 2 mm-thick films using an injection molding device described in the previous paper [38]. The molding temperature was between 160° and 190 °C depending on the concentration of the solution. Crystallization was performed by quenching the mold into cold water. The solvent was subsequently extracted from the swollen gels in a methanol bath for 48 h under stirring. A final drying was performed under vacuum for 48 additional hours at room temperature. During the extraction and drying treatment, the films were maintained between two loosely fastened grid plates in order to avoid curling and twisting.

Table 1 Characteristics of the materials: Weight- and number-average molar weights, M_w and M_n, average co-unit concentration, ε, density, ρ, and crystal weight fraction, X_c, of the compression-molded bulk materials

Materials	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	ε (mol %)	ρ (g/cm^3)	X_c†
PE-1 Alathon	146	33	nil	0.960	0.74
PE-2 Eltex	157	30	0.8	0.950	0.69
PE-3 Marlex	178	19	1.5	0.943	0.62
PE-4 Lotrex	136	31	2.7	0.932	0.55
PE-5 Lotrex	140	29	4.5	0.922	0.46
PE-6 Norsoflex	160	32	7.6	0.910	0.36
PE-7 Norsoflex	148	26	13.0	0.900	0.32

† from DSC measurements

Scanning electron microscopy

A morphological investigation of the films was performed by scanning electron microscopy (SEM) using a Cambridge Stereoscan microscope Model 250MK3 operated between 5 and 15 kV. The cryofractured samples were carbon-coated on aluminum holders before examination.

Ball-drop experiments

The critical concentration for gelation was determined by the ball-drop method, using 2 mg steel balls according to Matsuda et al. [14] Appropriate amounts of polymer and solvent together with a steel ball were first sealed in glass tubes under vacuum. Dissolution was performed by stirring the tubes in a glycerol bath at 160 °C, then crystallization was carried out by cooling the tubes in air. The steel ball was gently dropped on the surface of the crystallized solution owing to a magnet. The critical concentration for gelation of every polymer was determined accurately by preparing several concentrations at intervals of 0.25% in the region of the gelation threshold. The change from a ball-supporting gel to a deeply ball-penetrating gel occurred readily within a 0.25% concentration interval.

Thermal analysis

Differential scanning calorimetry (DSC) measurements were performed on a DSC-Delta calorimeter from Perkin Elmer. The crystallization and melting behavior of the swollen gels were studied using tightly closed cells. The gels were previously prepared in sealed glass tubes following a procedure analogous to the ball-drop experiment preparation. Amounts of gels of about 25–35 mg were quickly transferred from the opened tubes into the DSC cells at room temperature. The cooling and heating scans were performed at a scanning rate of 20°/min. The specific heat of melting of perfectly crystalline polyethylene was taken as $\Delta H_f = 290$ J/g [39].

Results and discussion

Critical concentration of gelation

An endeavor of modeling the physical gelation can be made by assuming that, at the threshold of chain overlap, the swollen coils form a close-packed array of spheres impinging into one another. One can thus derive the following equation for the critical concentration of gelation

$$C^* = \sqrt{2}M/N_a \rho_s d^3 , \tag{1}$$

where M is the molar weight of a chain, N_a is Avogadro's number, d is the distance between the centers of mass of two close-neighbor coils and ρ_s is the density of the solution. Table 2 affords comparison between the half mean distance of the swollen coils, $d/2$, computed from Eq.(1) for the seven copolymers and the unperturbed radius of gyration of these coils, R_G, in the assumption that the chains are close to θ conditions at the very moment when gelation takes place. Indeed, we shall see below that the more crystalline copolymers are prone to phase separation before crystallization. This supports the discussion of chain overlaping in terms of unperturbed chain dimensions. Under these considerations, the radius of gyration can be assessed from the following relation

$$R_G = 0.040 M^{1/2} , \tag{2}$$

where R_G is expressed in nanometers if M is given in g/mole. The coefficent involved in Eq. (2) is derived from the relationship which gives the unperturbed quadratic end-to-end distance of the chain, (r^2), for polyethylene as a function of the molar weight [40], owing to the correlation between the two parameters

$$(r^2)^{1/2} = \sqrt{6}\, R_G . \tag{3}$$

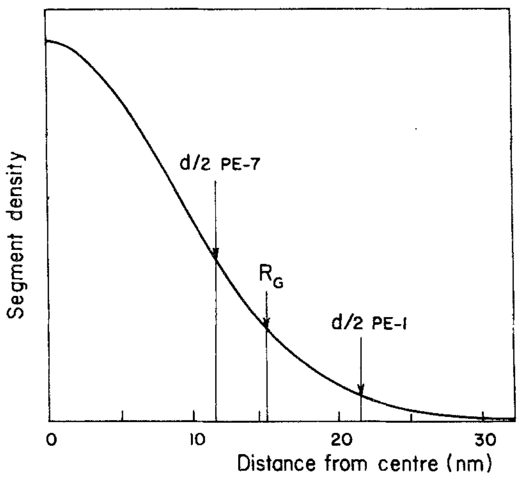
Table 2 Parameters of the gelation: critical concentration, C^*, unperturbed radius of gyration, R_G, and half mean distance of swollen coils, $d/2$

Materials	$C^* \times 10^2$	R_G(nm)	$d/2$ (nm)
PE-1	0.5	15.3	21.5
PE-2	1.0–1.25	15.8	17
PE-3	1.0–1.25	16.8	17.5
PE-4	2.0–2.25	14.7	13
PE-5	2.25–2.5	15.0	12.5
PE-6	3.0–3.25	16.0	11.5
PE-7	3.25–3.5	15.4	11.5

Considering now that the large coils begin to impinge mutually before the small one and that they are randomly distributed throughout the material, the calculations have been based on the weight-average molar weight which takes more into account the large molecules. The most relevant feature of Table 2 is that $d/2$ for the most crystalline polymer PE-1 is significantly greater than R_G. This gives evidence that a faint overlap is required for gelation to occur in this case since, as disclosed from the radial distribution curve of the chain segments of Fig. 1, only 2% of the segments are located outside the sphere of radius $d/2$ while 6% of the segments are located outside the sphere of radius R_G that is commonly considered to be the sphere enfolding the major part of an unperturbed coil. Moreover, as the crystallinity of the polymers decreases, the $d/2$ values become closer to the corresponding R_G values, then became smaller than R_G (Table 2). In the case of PE-7, 10% of the chain segments are outside the sphere of radius $d/2$ (Fig. 1). This is relevant to the necessity of a greater chain overlapping for the physical gelation of the copolymers when the co-unit concentration increases in order to counterbalance the concomitant reduced propensity of crystallization of the copolymers. Chain overlaping at the critical concentration for gelation is depicted in Fig. 2 for the extreme cases of PE-1 and PE-7.

Several authors have developed scaling laws for the critical concentrations for chain overlap, C_0 (see for instance refs. [42–44] and references cited therein). The usual

Fig. 1 Radial distribution of the segment density of an unperturbed random coil of molar weight $M_W = 1.5 \times 10^5$ g/mole after [41]



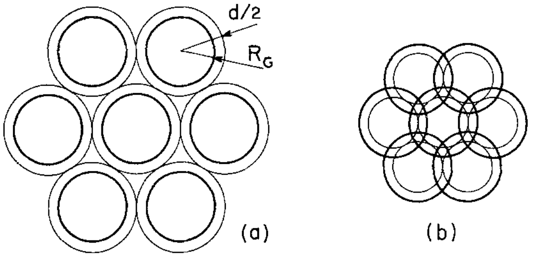


Fig. 2 Schematic model of chain overlapping for (a) PE-1 and (b) PE-7 at the critical concentration for gelation

form of C_0 under θ conditions as a function of the molar weight, M, is

$$C_0 = KM^{-1/2}\,, \tag{4}$$

where the constant K is specific to the polymer species. Borrowing the value $K = 2.1$ assessed by Takahashi et al. [45] for polyethylene, a value $C_0 = 0.006$ can be estimated for the present series of polymers. The data of Table 2 show that in the case of the homopolymer PE-1 having a high crystallization potential, C^* is remarkably close to C_0. However, as the crystallinity decreases, the critical concentration for gelation of the copolymers strongly deviates from C_0, indicating that the gelation process requires an increasing chain overlap. This is an additional evidence that the increase of the critical concentration for gelation with decreasing crystallinity is governed by the requirement of a sufficient number of intermolecular crystallization events in order to set up a physically crosslinked network.

Studying the physical gelation of atactic polystyrene (aPS) in carbon disulfide over the concentration range 10–60 vol%, Hiltner et al. [46, 47] emphasized that the requirement of coil overlap in solution does not necessarily entail chain intertwining. That is, the depth of interpenetration of the coils should be just enough to allow segmental interactions through sideway diffusion of chain loops in the peripheral regions of the coils only. The occurrence of intermolecular entanglements which involves diffusion through reptation is not required *a priori*. Besides, the above authors [47] have shown that chain intertwining occurs at much high concentration than chain overlapping, both thresholds being dependent on molar weight.

It is not necessary that all the chains overlap and that all the crystallites interconnect with each other for the formation of the gel; in fact, a tenuous molecular continuum throughout the sample is only required to prevent the collapse of the whole structure. In other words, the critical concentration for gelation is that which involves enough molecular connectivity between the crystals at the completion of crystallization for the build up of the physically crosslinked network. In this connection, the study by Okabe et al. [15] of gels in various aromatic solvents of ethylene-butene copolymers containing about 25 short branches per 1000 methylene units and having a weight-average molar weight $M_W = 110 \times 10^3$ g/mole deserves a particular attention. These authors reported critical gelation concentrations at room temperature close to 0.01, using the ball-drop method. In parallel, they observed a sudden increase of the slope of the shear modulus-concentration plot at a concentration of about 0.03 which interestingly corresponded to a change of structure from isolated microcrystallites to interconnected large dendrites. This perfectly supports the idea that the critical concentration for physical gelation C^* is governed by the occurrence of a slack molecular-crystallite network and not necessarily a crystalline continuum. It is to be mentioned that Mandelkern and coworkers [48] have first assigned the gelation mechanism of polyethylene to the extensive overlap of crystalline superstructures. However, they acknowledged later that the necessary condition for gelation is that a network structure develops through the physical crosslinking effect of the crystallites, every chain being involved into at least two different crystallites, on the average [11, 16]. An additional support is provided from a study by Phuong–Nguyen and Delmas [49] of a UHMWPE solution of 0.2 vol% in decalin which disclosed the presence of free and strained chain-folded crystals by means of thermal analysis. The authors concluded that the co-crystallization of the network with chain-folded crystals is at the origin of gel formation.

The build-up of the slack molecular-crystallite network can be intuitively associated with a percolation process. Okabe and Matsuda [50] have recently shown that this is effectively the case, by plotting the static shear modulus versus (C-C^*) for gels of low density polyethylenes in tetralin in the concentration range 0.4–1.2 wt%. This is the first evidence that physical gelation obeys a percolation model, whereas this phenomenon has been recognized long ago for chemical gelation [51, 52].

Critical concentration of chain entanglement

The skrinkage behavior of the gels upon drying has been studied through the change of the diametre to thickness ratio, D/e, of the dried discs as a function of the initial concentration. In the concentration range $0.2 < C < 1$, all the gels from the seven polymers shrink isotropically upon extraction of the solvent. This is disclosed in Fig. 3 excluding PE-3 for the sake of clarity. There are, however, two types of shrinkage behavior for the concentration range $C < 0.2$. On the one hand, the shrinkage of the three less

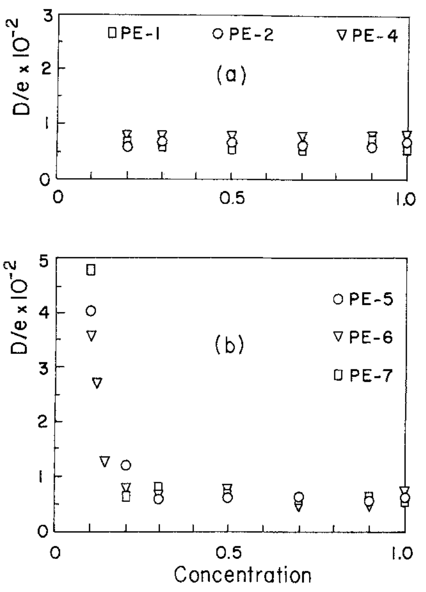


Fig. 3 Diameter to thickness ratio, D/e, of dried gels of (a) PE-1, PE-2 and PE-4 and (b) PE-5, PE-6 and PE-7 versus concentration of the initial solutions

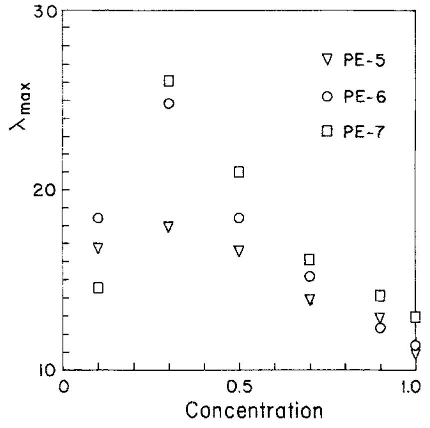


Fig. 4 Maximum draw ratio at 60 °C, λ_{max}, of dried gels of PE-5, PE-6 and PE-7 versus concentration of the initial solutions

crystalline copolymers PE-5, PE-6, and PE-7 is no more isotropic below $C = 0.2$ and turns gradually predominant across the thickness of the films (Fig. 3b). We have previously suggested [38] that the departure from isotropic shrinkage is relevant to the onset of the chain disengagement from the macromolecular network. As a matter of fact, we have shown that the drawing capacity of the dried gels from PE-6 begins to deteriorate for $C > 0.20$. A similar behavior is observed for PE-5 and PE-7. The plots of the maximum draw ratio of the dried gels of the three copolymers as a function of the initial concentration of the solutions reported in Fig. 4 indeed disclose a clear drop above a critical concentration $C \approx 0.2$. A rough estimation gives an average value of 2.5 entanglements per chain for $C = 0.20$, taking for the value of the molar weight between entanglements of the copolymers that of polyethylene in the melt, $M_e \approx 2 \times 10^3$ g/mole*, and considering a mean value, $M_n \approx 30 \times 10^3$ g/mole, for the number-average molar weight of the seven polymers studied. In an interesting study of fibers drawn from UHMWPE gels, de Boer and Pennings [56] have pointed out that the mechanical properties reach their maximum values for two entanglements per chain, with respect to the number-average molar weight of the chains. In the present case, the same choice of the number average molar weight for the estimation of the number of entanglement per chain relies on the assumption that the loss of mechanical properties should be effective as soon as a significant fraction of the chains, namely the shortest ones, no longer participate in the physical network. As a matter of fact, as can be seen from the molar weight distribution curves of PE-2 and PE-6 reported in Fig. 5, an amount of about 25% of the materials is composed of chains having a molar weight lower than M_n.

On the other hand, the dried gels from the more crystalline polymers PE-1 to PE-4 are powdery materials for concentrations $C < 0.2$ (Fig. 3a). They break into pieces when extracted from the mold and exhibit a typically brittle mechanical behavior after drying, so that measuring the D/e ratio becomes impossible below $C = 0.2$. Notwithstanding, it can be concluded that, down to this dilution level, there is a sufficient number of entanglements in the amorphous phase to allow an isotropic shrinkage of the gels upon drying, in spite of the phase separation.

We suspect that the final powdery texture of the films which crumble upon manipulation is the result of a liquid-liquid phase separation process during the cooling down of the solution, before crystallization takes place. In this instance, the lack of sufficient interconnections between the polymer-concentrated domains and the dilute matrix would be responsible for the collapse of the whole structure during evaporation of the solvent (i.e., the structure is

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* The assumption that the average molar weight between entanglements of the copolymers is roughly the same over the whole range of co-unit composition is founded on the fact that polyethylenes of very different architectures as well as ethylene copolymers with various co-units and various compositions have nearly the same melt density [53] and about the same radius of gyration dependency on molar weight [54]. Besides, the data of Carella et al. [55] show that the shear modulus in the rubbery plateau above the melting point of ethylenebutene copolymers in the co-unit range of the present study changes very little with composition, indicating a quasi invariance of the molar weight between entanglements.

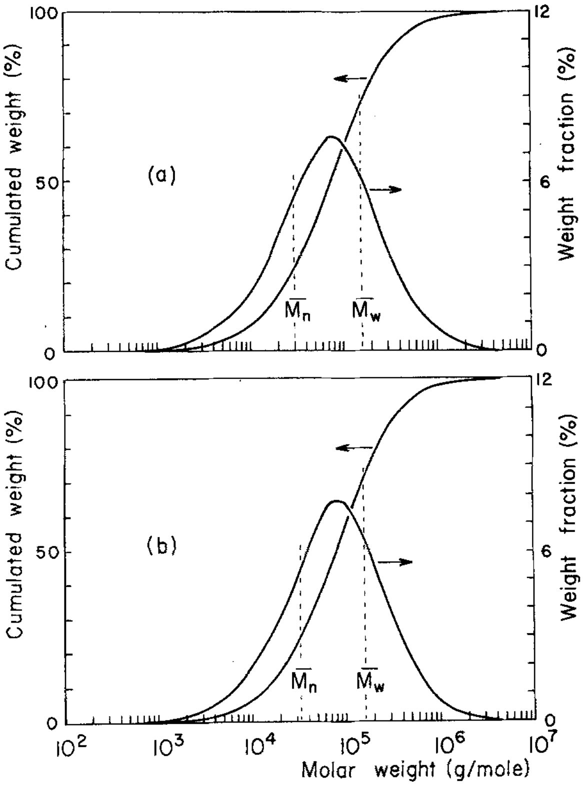


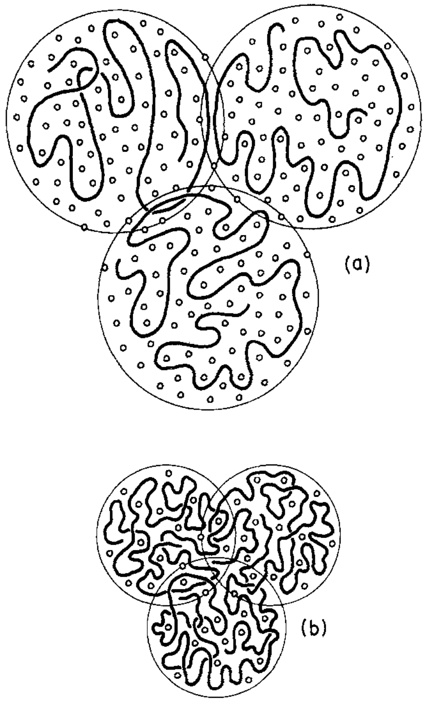
Fig. 5 Molar weight distribution curves of (a) PE-2 and (b) PE-6

no longer able to shrink isotropically). Besides, the gels from PE-1 and PE-2 display a milky appearance in the range of concentration $0.2 < C < 0.4$, indicating that the phase separation for these highly crystalline polymers is likely to occur over a larger domain than for PE-3 and PE-4.

The threshold of chain intertwining in the more crystalline samples could be biased by the liquid-liquid phase separation, the basis of which will be discused in the next sub-section. Nevertheless, the gels from PE-1 to PE-4 exhibit an isotropic shrinkage for $C > 0.2$ indicating that significant molecular connections exist between the phase-separated domains. It thus seems that the critical concentration for chain entanglement is much less sensitive to the crystallinity level of the copolymers than the critical concentration for gelation. According to Aharoni [42] and Kavassalis and Noolandi [44], the onset of chain entanglements occurs near $C_e = 0.20$ for chains having a number of main chain bonds $N = 10^4$ at θ conditions. This value is very close to the concentration threshold for isotropic shrinkage of the gels that we intuitively ascribed to the critical concentration for chain entanglement.

The intertwining of two neighboring chains in solution requires that the "depth" of mutual interpenetration of the random coils is at least equal to the average distance between entanglements at equilibrium in the melt, Indeed, if this condition is not fulfilled, the ends of every chain have little chance to experience an encounter with any of the neighbor chains and interchain entanglements are therefore unlikely. This argument is borrowed from Smith et al. [57] who provided an explanation for the very high drawability of virgin ultrahigh molecular weight polyethylene on the basis of a very low entanglement density inherent to the catalytic polymerization in suspension at low pressure and low temperature which involves a continuous crystallization of the nascent polymer chains. For the sake of illustration of this statement, Fig. 6 shows schematic pictures of neighbor coils at the threshold of overlapping, C^*, and at the threshold of intertwining, C_e. The ratio C^*/C_e was arbitrarily chosen at a value of 1/4 for reasons of convenience in the drawing, but it is actually of the order of 1/10. Besides, for sufficiently long macromolecules, both ends of a given chain can be independently involved into an intertwining process so that two entanglements per chain should occur simultaneously at the critical concentration. This critical concentration is merely the onset of entanglement behavior defined by Klein [58] as the point at which translational self-diffusion of a polymer molecule in a concentrated solution becomes restricted to reptation alone. Indeed, as soon as a chain experiences two entanglements with its neighbors, it can only diffuse by

Fig. 6 Pictures of polymer coils at (a) the threshold of chain overlap, C^*, and (b) the threshold of chain intertwining, C_e



reptation, the sideways motions being confined to the range of the chain gyration radius.

Phase separation

If the dried gels of the low crystallinity copolymers are macroscopically coherent over the whole range of concentration investigated in the present study, the situation is quite different for the high crystallinity materials. Coherent films are only obtained for high polymer concentrations. Increasing dilution leads to brittle films of powdery texture suggesting that liquid-liquid phase separation occurred prior to crystallization. In this connection, SEM micrograps of cryofractured surfaces of dried gels have been reported in Fig. 7. The PE-1 dried gels recovered from solutions of concentration 0.20 and 0.10 (Figs. 7a and 7b) show globular structures which are consistent with a liquid-liquid phase process. Conversely, no particular texture appears in the case of the PE-6 dried gel originating from a solution of concentration $C = 0.10$ (Fig. 7c).

Garber and Geil [59] have formerly observed globular structures arising when quenching, down to the crystallization temperature, a poly-3,3-bis(chloromethyl)-oxacyclobutane solution of 0.05 wt% in hot xylene. They suspected that the structure resulted from a previous liquid-liquid phase separation. An analogous phenomenon was reported later by Gogolewski and Pennings [20] in the case of polyamide gels in solvent-non solvent mixtures, for polymer concentrations in the range 50–90 wt/vol%. In this case, the loss of mechanical properties of dried fibers spun from the gels was ascribed to a strain-induced liquid-liquid phase separation phenomenon involving globular structures. Gelation of poly(vinylidene fluoride) [60] from butyrolactone solutions has also been reported to proceed through liquid-liquid phase separation over the concentration range 5–30 wt% and to give rise to interconnected spherulitic structures. The dense ball-structure of PE-1 crystallized from a $C = 0.20$ solution (Fig. 7a) seems to be the reminiscence of polymer rich microdomains embedded in a dilute matrix. At higher dilution, i.e., $C = 0.10$, a more open carnation-like structure made of intersecting lamellae occurs consecutively to a lower polymer concentration in the polymer rich microdomains (Fig. 7b). Schaaf et al. [61] have clearly demonstrated that globular structures appear in linear polyethylene gels as a result of liquid-liquid phase separation prior to crystallization in the case of semi-dilute solutions in the concentration range 1–5 wt% with relatively poor solvents. According to these authors, smooth ball-like crystalline structures are subsequently formed via homogeneous nucleation close to the liquid-liquid interface and further growth along the globule walls, while carnation-like structures are developed through heterogeneous nucleation within the globules and subsequent growth of radial lamellae. In a similar way, it seems likely that the carnation-like structures observed by Klein et al. [62] for isotactic polystyrene (iPS) grown from 30 wt%

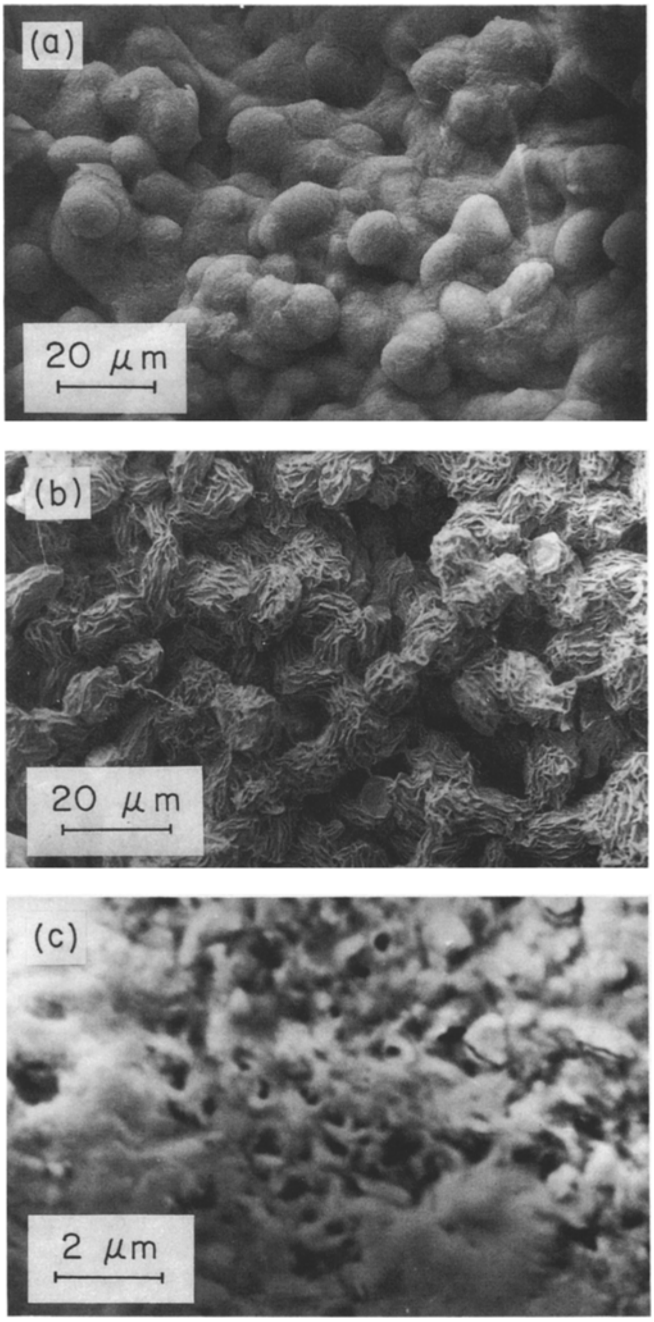


Fig. 7 SEM micrographs of dried gels recovered from solutions: (a) PE-1 ($C = 0.20$), (b) PE-1 ($C = 0.10$) and (c) PE-6 ($C = 0.20$)

decalin solutions, i.e., near the gelation threshold, is connected with the occurrence of a phase separation phenomenon that was previously reported by Guenet et al. [63] for the same system.

In the case of branched low density PE removed from slow cooled or quenched benzene solutions of 5 wt/vol% concentration, Matsuda et al. [14] have observed globular structures made of either spongy or carnation-like entities, but they did not even mention the eventuality of a liquid-liquid phase separation process. Mandelkern et al. [48] reported that linear homopolyethylenes and ethylene copolymers display the same trend for carnation-like structures for xylene solutions of concentration in the range 1–10 wt%. This was taken as an evidence that copolymers have a natural propensity to form chain-folded lamellae rather than fringed-micelles when crystallized from solution. Besides, these authors briefly discussed the case of poor solvents that involve liquid-liquid phase separation prior to crystallization. They emphasized that this situation precludes gelation, with white precipitates being formed instead of gels.

The last point mentioned above is quite consistent with the lack of coherence of the dried gels from the more crystalline materials studied presently. As a matter of fact, it is obvious that the brittle properties of the films having a powdery texture is relevant to a weak interglobular cohesion. It is an indication that little molecular connectivity exists between the globules because of the large difference of concentration between the globules and the matrix in the liquid-liquid phase-separated systems. However, this phenomenon does not prevent the occurrence of gelation threshold which has been effectively determined for polymers PE-1 to PE-4 (see Table 2). This should be relevant to the vanishing of the phase separation phenomenon in the high dilution range [63]. But the persistence of the gelation process in the concentration range where phase separation takes place is an evidence that significant molecular linkages lie between the microdomains. In this connection, it is noteworthy that the capability of colloidal gels of non-crystallizing aPS in cyclohexanol to shrink upon removal of the solvent for concentrations above 1 wt% has been ascribed by Keller et al. [64, 65] to the formation of molecularly ramified aggregates. The SEM micrograph of Fig. 8 reveals that, in the case of a PE-1 dried gel recovered from a solution of concentration $C = 0.20$, a few fibrillar interconnections exist between the globules. It suggests that the chains in the neighborhood of the interface of a polymer-rich microdomain and the polymer-dilute matrix can be shared between the two phases. Then, on evaporating the solvent, the chain portions pertaining to the dilute matrix collapse on the surface of the polymer-rich domains, except when they are anchored upon two neighbor domains. They are thus liable to form a few interglobular connections, probably associated with chain entanglements, that allow the gels to shrink isotropically upon drying, but do not prevent brittleness of the dried gels due to the heterogeneous globular structure. From these connections are certainly originating the interglobular fibrils observed in the micrograph of Fig. 8 as a result of the pulling out of the molecules from the globule surface during the cryofracture preparation of the sample. This standpoint is supported by Wellinghoff et al. [66] who claimed that phase separation in polystyrene as well as polystyrene/poly(phenylene oxide) blends from solutions of concentrations greater than 5–10 wt% in various solvents yields gels consisting of a continuous polymer-rich network physically crosslinked by glassy microdomains. Alternatively, the fibrillar interconnections could originate from the partial freezing-in of the liquid-liquid phase separation by the crystallization upon the fast cooling as suggested by Guenet et al. [63] in the case of iPS in decalin solutions.

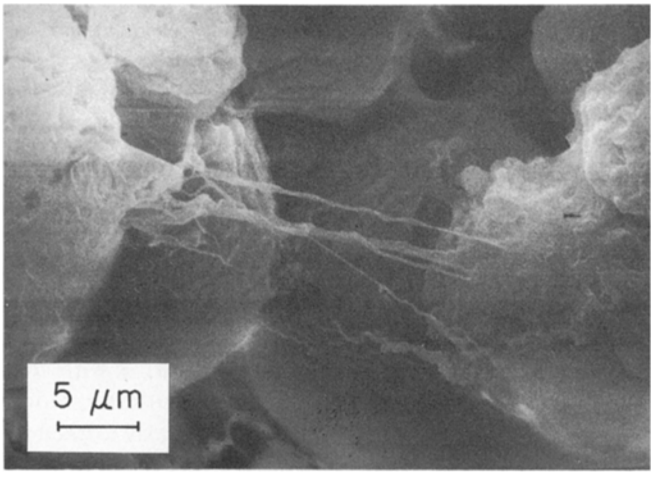
Notwithstanding the microdomain interconnections, the occurrence of a phase separation phenomenon supports our assumption that crystallization occurs close to θ conditions for the calculation of the unperturbed chain dimensions.

From the standpoint of thermodynamics, the phase separation capabilities of ethylene copolymers can be estimated through the solubility parameters calculated owing to the group contribution method. The following relation, which holds for random copolymers [67]

$$\delta = \phi_A \Sigma F_i / V_B + \phi_B \Sigma F_i / V_B , \qquad (5)$$

assumes an additivity of the contributions from the unlike species of volume fractions ϕ_A and ϕ_B, V_A and V_B being

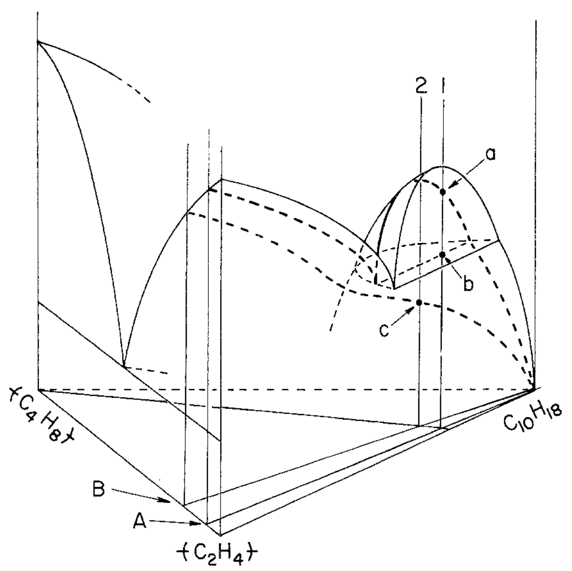
Fig. 8 SEM micrograph of a PE-1 ($C = 0.20$) dried gel showing close-up view of particle interconnections



their molar volumes, and F_i the molar attraction constants of the various groups in the monomer units. These parameters have been borrowed from recent refined calculations by Coleman et al. [68]. It is to be mentioned that the molar attraction constants under consideration agree much better with the values assessed by Small than with the ones of van Krevelen [69]. The solubility parameters thus calculated for the copolymers at room temperature fall from 8.0 to 7.6 $(\mathrm{cal/cm^3})^{1/2}$ when spanning the composition range from pure ethylene units to pure butene units. Comparison with the calculated value 7.1 $(\mathrm{cal/cm^3})^{1/2}$ for the solubility parameter of decalin clearly indicates an improved solubility of butene rich copolymers. This conclusion is thoroughly supported by isothermal calorimetric measurements of the heat of mixing, ΔH_M, reported for a linear and a branched polyethylene as well as for an ethylene-butene copolymer above the melting point [70], in the case of solutions with tetralin which is structurally and thermodynamically close to decalin ($\delta = 7.4$ $(\mathrm{cal/cm^3})^{1/2}$) . Indeed, the positive ΔH_M value for the linear PE about twice as large as those of the branched PE and the copolymer clearly indicates better solubility of the last two polymers.

Finally, it does not seem that the lack of mechanical coherence of the gels due to an early liquid-liquid phase separation in the solution disturbs the determination of a critical gelation concentration for the whole set of polymers studied presently because the former phenomenon is concerned with a range of semi-dilute solutions while the second one occurs at very low concentration. This is depicted on the schematic phase diagram of Fig. 9 drawn according to previous studies on the topic [61, 71]. The upper critical solution temperature (UCST) of the liquid-liquid equilibrium domain is consistent with a positive heat of mixing. For a highly crystalline copolymer containing few co-units (see A in Fig. 9), crystallization takes place from homogeneous solutions in both the high and the low concentration ranges. However, in the mid concentration range, the cooling pathway 1 involves phase separation prior to crystallization at points a and b, respectively. For the co-unit-rich copolymer (see B in Fig. 9), only crystallization from homogeneous solution is likely to occur over the whole concentration domain as depicted for instance by the cooling pathway 2 where point *c* indicates the onset of crystallization.

Fig. 9 Schematic ternary phase diagram of ethylene-butene random copolymers with decalin (see text for details)



The appearance of a reversible turbidity, the so-called cloud point, has been often considered as a characteristic hint for phase separation in polymer solutions or blends. The phenomenon may also be accompanied by a thermal transition due to absorption or release of heat. Atactic PS solutions with decalin or cyclohexanol have been reported to give rise to both effects [64, 72]. In the present case, no significant turbidity could be detected on cooling PE-1 solutions of concentrations in the range 0.02–0.40, prior to the strong whitening due to the crystallization-induced gelation. Besides, no clear-cut transition was observed in the DSC cooling traces of the same solutions before the crystallization exotherm. These negative results could be *a priori* taken as an evidence that phase separation does not occur in the PE-1/decalin system. However, two points deserve mentioning:

1) The first point is that the refractive index of molten polyethylene is $1.49 > n > 1.47$ for $100\,^\circ\mathrm{C} < T < 160\,^\circ\mathrm{C}$, while that of decalin is $n = 1.48$ at room temperature. This low refractive index difference is such that light scattering by phase-separated particles of polymer-concentrated solution dispersed in a polymer-diluted solution should be very weak. Indeed, a rule of thumb for optical transparency of heterogeneous polymeric systems with submicronic size domains is that the refractive index difference between the unlike species should be lower than 0.01 [73]. In this instance, it is worth mentioning that, in the course of gelation of poly(vinylidene fluoride) from butyrolactone solutions [61] and poly(4-methyl-1-pentene) [74] from cyclohexane solutions, phase separation has been reported to occur for concentrations above about 5 wt/vol% without loose of transparency of the homogeneous solution.

2) The second point is that the non-observation of the thermal transition that occasionally marks a phase separation process might be due to the concomitance of demixion and crystallization. As a matter of fact, the appearance of polymer-concentrated domains is likely to promote instantaneous crystallization at a temperature for

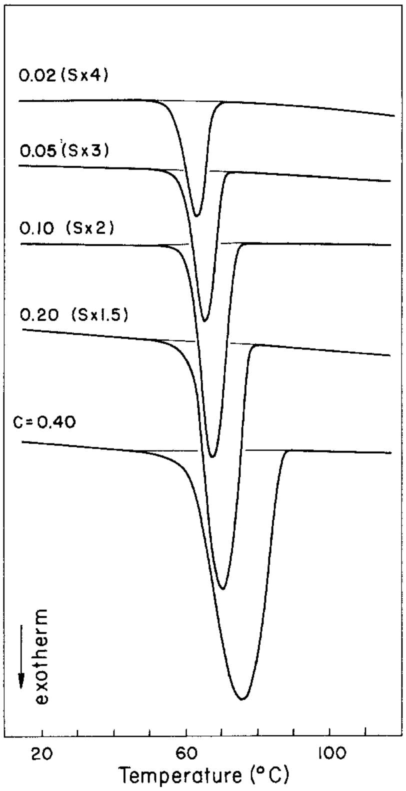


Fig. 10 DSC cooling curves of PE-1 gels as a function of concentration (*S* is the sensitivity)

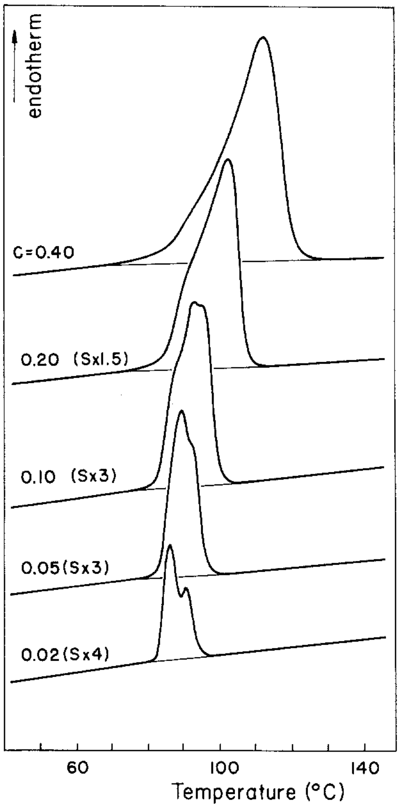


Fig. 11 DSC heating curves of PE-1 gels as a function of concentration for a cooling rate of 20 °C/min (*S* is the sensitivity)

which nucleation was impossible in the homogeneous dilute solution. The unique crystallization exotherm observed in Fig. 10, for PE-1 gels of various concentrations suggests that, in the proposed scheme of gelation, crystallization in the diluted phase must be initiated from the incipient crystalline polymer-rich domains. Indeed, the domain walls may act as nucleation agents owing to the strongly reduced molecular mobility at the motionless interface. This interpretation is consistent with the observation of smooth globules which, according to Schaaf et al. [61], originate from the crystal nucleation close to the domain interface and the subsequent crystal growth along the globule walls. It is also noteworthy that simultaneous liquid-liquid phase separation and crystallization has been reported to occur by Matsuo et al. [75] in the case of poly(vinyl alcohol) solutions with dimethyl sulfoxide/water mixtures over the concentration range 1–10 wt%.

Figure 11 shows that, contrary to the crystallization behavior, striking changes appear in the shape of the melting curves of PE-1 gels as a function of concentration. The gel of concentration $C = 0.40$ displays a broad melting endotherm, while double melting peaks are recorded for the gels of lower concentration. Besides, the low temperature melting peak grows gradually with increasing dilution at the expense of the high temperature melting peak. This is an indication that two types of crystals have been formed in the same temperature interval. Matsuda and coworkers have reported a similar melting behavior for gels of both linear low density [15] and linear high density polyethylenes [76] in 1-20 wt/vol% tetralin and 6 wt/vol% decalin solutions, respectively. Owing to parallel optical microscopic observations, these authors concluded that the gels were composed of two kinds of crystals, namely microcrystallites and large sheaf-like crystallites (*i.e.* dendrites) which melt in the low and high temperature endotherms, respectively. In addition, they suggested that the two kinds of crystals are issued from a solution-induced fractionation during crystallization of the polymer due to the co-unit concentration heterogeneity in the chains. But this explanation cannot hold for linear high-density polyethylene. Phase separation may be a possible cause for the double crystal population since two types of crystals can grow from the polymer-concentrated and the polymer-diluted phases, respectively. The improvement with increasing dilution of the lower melting point crystal population is indeed consistent with an increasing amount of the polymer-diluted phase. The DSC curves of Fig. 12 show that the cooling rate also affects the

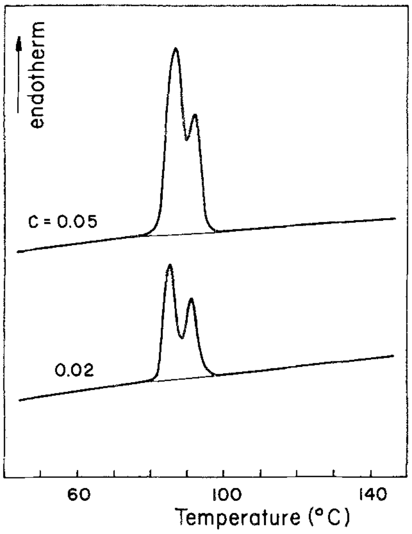


Fig. 12 DSC heating curves of PE-1 gels as a function of concentration for a cooling rate of 200 °C/min

melting behavior of PE-1 gels upon subsequent heating. For a given initial concentration, increasing the cooling rate improves the partition of the melting endotherm into two distinct peaks, in agreement with previous reports indicating that phase separation in moderately good solvents is more effective at high cooling rates [59, 61, 75]. The study of gelation of poly(4-methyl-1-pentene) in cyclohexane solution provides a valuable point of comparison [74]. Evidence of a liquid-liquid phase separation prior to crystallization has been claimed from the observation of two different crystal forms, the crystallites grown in the polymer-poor phase being dissolved at a lower temperature than those grown in the polymer-rich phase.

Secondary effects of crystallization from solution

Mandelkern et al. [11] and Matsuda et al. [14, 15] have reported that the critical concentration for gelation C^* is greater than the critical concentration for chain overlap C°, especially in the case of slow cooling. According to the above authors, this is merely an indication that chain overlap is not a sufficient condition for gelation. This would be a quite logical conclusion if crystallization did not involve chain reorganization within the randomly coiled chains, namely, regular intramolecular chain-folding (i.e., short-range chain rearrangements) and molecular disentanglement (i.e., long-range chain rearrangements) owing to the reeling effect of the chains. Indeed, in spite of the fact that a profound controversy exists concerning the rate of incidence of adjacent re-entry in chain-folded polymer crystals and the occurrence of chain disentanglement during crystallization (see, for instance, ref. [77]), there is no doubt that a real conformational upheaval occurs during the course of crystallization from solution.

As a matter of fact, the radius of gyration of the chains in single crystals is much smaller than that of the random coils in the melt or that of the chains in crystals grown from the melt [78, 79]. In addition, the well-known molecular segregation of polyethylene blends during crystallization, except quenching, due to molecular weight effects or to melting point differences between various species, either isotopic species or structurally different chains, is relevant to the occurrence of crystallization-induced long-range rearrangements of the chains and probably concomitant chain disentanglement. In this connection, the selective solvent-extraction of the lower melting temperature species suggests that no trapped entanglement remains between the chains of the segregated phases [80–82]. Therefore, it is obvious that the rearrangement of the chains during the course of crystallization from solution is likely to affect the conformation of the chains in the surroundings of the growing crystals. The chain overlap in the solution is thus expected to be strongly perturbed, notably by the fact that, every time a nucleation event occurs close to the center of mass of a solvated coil, the chain segments are dragged from the periphery of the solvated coil towards the growing crystallite. A depletion of the polymer segment density occurs consequently in the peripheral region and the critical concentration for chain overlapping changes as crystallization proceeds. This can be a reason why C^* is usually greater than C°, especially at slow cooling rates, because of the necessity to preserve a sufficient chain overlap at the ultimate stage of the crystallization.

An additional support to the above statement is provided by Odell et al. [83] who have pointed out that, in the case of transient networks, a range of critical concentrations for chain overlap can be defined depending on the time scale of the experimental testing method since unraveling of the coils can occur during the time of the experiment when no accompanying phenomenon is liable to set up the physical network.

Conclusion

Ethylene-butene copolymers covering the range of crystal weight fraction 0.32–0.74 display critical concentrations for gelation in the range 3.5–0.5%. This emphazises the combined effect of chain overlapping and interchain crystallization in the achievement of gelation. The critical concentration for chain entanglement is seemingly insensitive to the crystallinity level. Despite a little change of solubility of the various polymers in decalin, it is likely that the degree of swelling of the coils close to θ conditions is not significantly affected by the copolymer composition and, therefore, it is the same, for all the polymers studied, at the threshold of chain entanglement. This latter only depends on the chain length for a given polymer species.

Evidence has been given of a liquid-liquid phase separation in the mid concentration range for the more crystalline materials. The slightly better solubility of the co-unit rich copolymers in decalin compared with homopolyethylene and co-unit-poor copolymers is theoretically supported by both solubility parameter and heat of mixing data from the literature. A ternary phase diagram with a UCST domain is proposed for the ethylene-butene copolymers with decalin system. When phase separation takes place, it may perturb the overlapping and intertwining of the chains in the semi-dilute concentration range, but does not preclude gelation. It seems certain, that there is no significant perturbation at the threshold of gelation because it takes place in homogeneous solution, i.e., in a single-phase region of the equilibrium phase diagram.

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