Thermal Analysis and Model of Ultrahigh Molecular Weight Polyethylene Gels

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ABSTRACT: The traces of dissolution in decalin of nascent polymer and of gels equilibrated in different conditions are obtained at a low rate of heating (v = 1 K/h). The dissolution trace shows a gap between the low- and high-temperature endotherms (fractions I + II and fraction III, respectively). The equilibrium temperature of the end of dissolution depends on solvent and thermal history and can be as high as 165 °C. The heat flow during a slow crystallization reveals that two fractions grow separately in time/temperature. Since similar patterns were found in the melting and cooling traces of the solid, these results are interpreted along the same lines although other explanations may develop in the future. The high-temperature signals correspond to melting or crystallization under strain. A model for the ultrahigh molecular weight polyethylene gel follows readily from this interpretation: A strained melt network is stable in the solution at high temperature, and its cocrystallization with chain-folded crystals is at the origin of gel formation on quenching. The heat-resistant crystals take away from entanglements the key role in gel formation. A calorimetric characterization of crystallization as gel or single crystals is given. Procedures to reduce or raise the amount of network crystals are presented. Confirmation of the model by literature results and other techniques is discussed.

Introduction

Solutions of polyethylene (PE) of low or medium molecular weight have been prepared to grow single crystals on cooling. The thermodynamics of phase change of lamellae of different thickness, l, crystallized at different temperature, T_c, has been established.[1] Their melting points, T_m, or dissolution temperatures, T_d, correlate with l and allow the determination of $T_{m,o}$ and $T_{d,o}$, the values for infinite thickness (or extended chains). $T_{m,o}$ is 141 °C, and $T_{d,o}$ is 99 °C in decalin and 111 °C in p-xylene for instance.[1] T_d is lower (by 5–12 K) for thin lamellae.

Solutions of high or ultrahigh molecular weight PE have also been made to grow crystals, but crystals with a different morphology, the shish kebabs. These complex crystals are formed at high temperature (above $T_{d,o}$) in solutions under shear. The crystals which grow on a stirrer or in the gap of a Couette viscosimeter can form fibers with an unexpectedly high drawability. A large body of research has focused on the morphology of fibers, their thermal properties, and the relationship between drawability and mode of preparation.[2-6] The high modulus of extensively drawn fibers has given a high profile to the method of preparation involving a solution rather than a melt. Shish kebabs are easily superheatable due to their slow melting.[2-4] Drawn fibers[7] have an equilibrium melting temperature above $T_{m,o}$ when they are submitted to strain during melting, the normal entropy of melting being reduced by the constraints.

Dissolution behavior of shish kebabs, dried gels, and fibers indicates that they are also superheatable in the presence of a solvent. No equilibrium dissolution temperature has been measured in a calorimeter due to the lack of an adequate apparatus. However, from measurements on drawn fibers in p-xylene, Torfs et al. arrived at the conclusion that without external strain the equilibrium dissolution temperature T_d is very near $T_{d,o}$. Measurement of T_d was carried out visually or by measurement of the temperature of disappearance of stress for strained fibers.

On cooling, solutions form gels which can be drawn in a dry or wet state into fibers. The occurrence of gels from solutions of an easily crystallized polymer and other unusual features of solutions of high molecular weight PE (such as the effect of thermal and mechanical history on the state at room temperature) raised questions about the underlying association of macromolecules in a dilute solution.[9,10] The network structure recognized in fibers and nascent polymer[8,11,12] is thought to be at the origin of the gel cohesion, entanglements forming the stable junctions. In order to explain the long-time memory effects in melts and in noncrystalline solutions of long-chain macromolecules, especially the stable entanglements, the existence of tight knots was proposed. They could be generated during crystallization or in a sheared solution.[13] Crystalline junctions induced by shear were nevertheless postulated[9] although there was no support of an equilibrium melting endotherm at high temperature to give a final proof of their existence.

In recent work,[14] a missing part in the heat of fusion of nascent ultrahigh molecular weight polyethylene (UHMWPE) was found using a slow heating rate (v = 1 K/h) instead of the usual for the differential scanning calorimetry (DSC) analysis (600 K/h). It was called fraction III, fraction I being constituted by the crystals with a low melting temperature and fraction II by the main melting peak of unstrained chain-folded or extended-chain crystals. The strained crystals of fraction III are very stable in time/temperature; their melting does not occur below 200 °C if v is higher than 12 K/h. On cooling, the strained melted chains recrystallize at high temperature as a network in the melt.

The stability of fraction III in the presence of a solvent is the object of this paper. Its importance is due to the fact that it affects the properties of dilute solutions and of gels and also of dry gels. The conditions for maximum drawability which depend on the solution preparation (i.e., solvent, concentration, and maximum temperature reached) are still unclear. In this laboratory, investigation of the stability of fraction III has been made by intrinsic viscosity and calorimetry in a number of solvents (decalin, trichlorobenzene, normal and branched alkanes, and aromatic solvents) chosen for their solvent quality or their recognized advantage for characterization purposes (tri-

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Table I
Characteristics of Dissolution of Nascent (A, B) and Gels (C–G) in Decalin (0.2%) of PE GUR Having Different Thermal Histories

	thermal history	n	residence time[a]	v, K/h	T_d, °C	fractions I + II H,[c] J/g	fraction III $H_{3,a}$,[d] J/g	fraction III $H_{3,b}$, J/g	figure
A	nascent[e]	1		1	109.0	180 (105–114)	50 (128–144)	58 (145–165)	1
B	annealed[b,e]	1		1	109.0	180 (102–113)	88 (131–142)		
C	same as B[f]	>2	>3 days	1	96.0	260 (90–102)	20		
D	g	7	9 months	1	97.6	160 (92–100)	50 (100–120)	90 (130–158)	2
E	same as B	3	7 months	1	98.0	235 (92–101)	16 (119–127)	34 (127–141)	3a
F	4 days at 150 °C	2	2 days	1	97.4	230 (90–101)	60 (106–126)		3b
G	same as B	3	6 months	6	96.7	210 (92–102)	60 (108–198)		4a

[a] At room temperature, between the last crystallization and the dissolution. [b] One week at 90 °C in decalin (below T_d). [c] Interval of melting is noted in parentheses. [d] $H_{3,b}$ is included in $H_{3,a}$ when the two endotherms overlap. [e] First dissolution. [f] Typical dissolution trace after a network weakening treatment and a short residence time at room temperature. [g] From the solution of nascent GUR which was submitted to several cycles of dissolution–crystallization; T_{max} = 120 °C.

Table II
Characteristics of Crystallization and Dissolution of Single Crystals and Mixed Morphologies of PE GUR in Decalin (0.2%)

	crystallization						dissolution					
	n	v, K/h	T_c,[a] °C	fractions I + II H, J/g	fraction III H_3,[b] J/g	figure	n	v, K/h	T_d,[c] °C	fractions I + II H, J/g	fraction III H_3,[b] J/g	figure
H	3	6	80.3 (93)	230	62 (123–160)	4b	4	6	90.5–96.4	220 + 35	40 (115–185)	4c
I	3	1	83.0 (88)	267	15 (88–92)	5a	4	1	92.4–96.6	207 + 55	<15	5b
J							8	3	90–96.9	200[d]	[e]	6a
K							9	1	90–96.9	210[d]	[e]	6b

[a] The temperature of beginning of crystallization (fractions I + II) is in parentheses. [b] The interval of temperature is in parentheses. [c] The first temperature is the temperature of dissolution of single crystals, and the second temperature is the temperature of dissolution of gel. [d] Solutions were not submitted to a network weakening treatment. [e] T_{max} = 120 °C; it is too low to measure H_3.

chlorobenzene). In this first paper, only calorimetric results in one solvent in which an extensive study on gel formation[9] was carried out (decalin) will be presented.

The dissolution traces are analyzed as indicators of the morphology of crystals being melted or dissolved and in particular of their content in fraction III. The crystallization traces permit following the order of crystallization of the fractions which can be monitored by v, i.e., by the time left for relaxation. A relation between fraction III and gel formation is presented. A characterization of the gel/single-crystal mode of crystallization has been developed as well as the procedures to reduce or raise the amount of fraction III in the presence of a solvent.

Experimental Section

Polymer. A commercial grade Hostalen GUR with a nominal M_w equal to 0.9×10^6 was dissolved either as received or after a week-long annealing in a solvent at 90 °C. For the latter treatment, after the long contact with solvent, the polymer was quenched at room temperature and analyzed as a nascent sample.

Solvent. Decalin is the commercial mixture of isomers, used without purification.

Apparatus. The calorimeter is a sensitive differential calorimeter (Setaram, Lyon, France) which can accomodate large size cells. With a temperature ramp and v as low as 1 K/h, a signal of 10 μW above the background noise is measurable. The calorimeter can rotate by half a turn, six times per minute.

Preparation of a Solution. The polymer is placed along with the solvent (c = 0.2% by volume) in a glass tube which is sealed after careful elimination of oxygen. The first dissolution is always made at v = 1 K/h in a temperature ramp (70 to 160–170 °C) with stirring in the calorimeter. The solutions have been found less homogeneous than those prepared as described above when they were dissolved without the slow temperature raise. The quantities of the gel obtained after quenching and of the crystals are obviously dependent on the homogeneity of the solution.

Modes of Crystallization. The crystals are formed either by quenching a solution at room temperature (or at a higher temperature (T_c)) or by cooling in a slow temperature ramp. The maximum temperature before cooling is between 170 and 200 °C. A few heterogeneous gels are grown with a maximum temperature of 120 °C.

The main peak of the dissolution traces permits a clear identification of these different modes. Isothermal crystallization gives single crystals (or pseudosingle crystals) whose T_d–T_c relationship is very similar to that obtained for low molecular weight samples in the same conditions.[16] The temperature of the peak of the sharp endotherm of dissolution in decalin, T_d, is situated between 90 and 96 °C. For a gel, T_d is higher (96.5 and 98 °C) and the endotherm significantly larger. Both morphologies can be found by crystallizing at 80 °C in certain conditions. The high-temperature endotherm of the nascent polymer spread over 50 K since dissolution and melting occur successively. Conditions are found to reduce the range of temperature of this endotherm. In some cases, two distinct parts can be seen in the endotherm associated with the transformation of the strained orthorhombic crystals into the hexagonal phase and the melting of the hexagonal phase. These transformations seem to occur also in the presence of a solvent due to the slow randomization of the chains.

The definition of a gel in the absence of measurement of its mechanical properties is necessarily imprecise. We have found here that the endotherm of dissolution is a very reliable definition of a gel. As will be detailed below, cocrystallization of different morphologies leads to a gel and a very distinctive peak of dissolution.

Quantitative analyses are given in Table I for the dissolution traces of gels and Table II for the dissolution and recrystallization traces of single crystals and mixed morphologies. Each row is listed with a letter from A to G in Table I and H to K in Table II, and the corresponding history is detailed and labeled in the text. The rows H and I keep the same letter for the crystallization and dissolution traces. The different columns in the tables list the history of the sample, the number of dissolution–crystallization cycles previous to the reported trace n, the residence time, the rate of heating/cooling v, T_d and H for fractions I + II and fraction III, the range of dissolution/crystallization temperature in parentheses, and the number of the figure when the trace is given. When dissolution of fraction III occurs into two endotherms, IIIa and IIIb, the enthalpies are given separately.

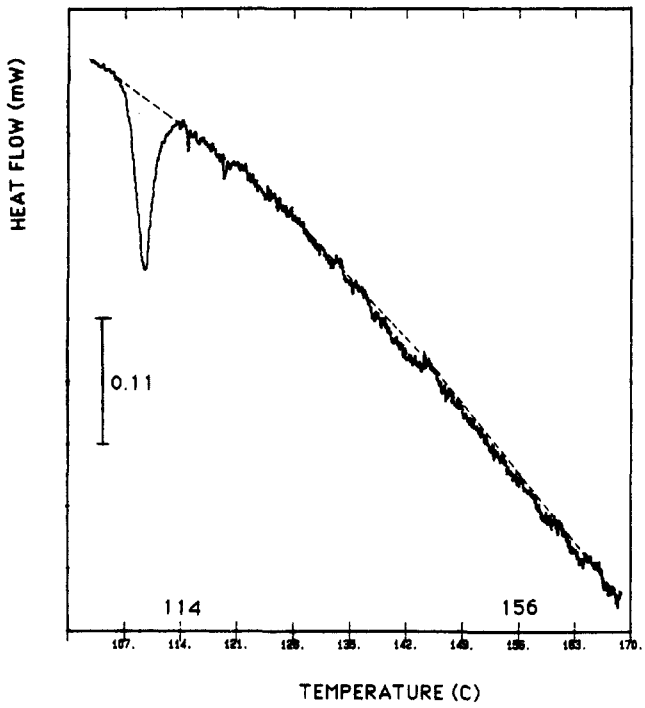

Figure 1. Dissolution trace of nascent GUR in decalin at 1 K/h (A).

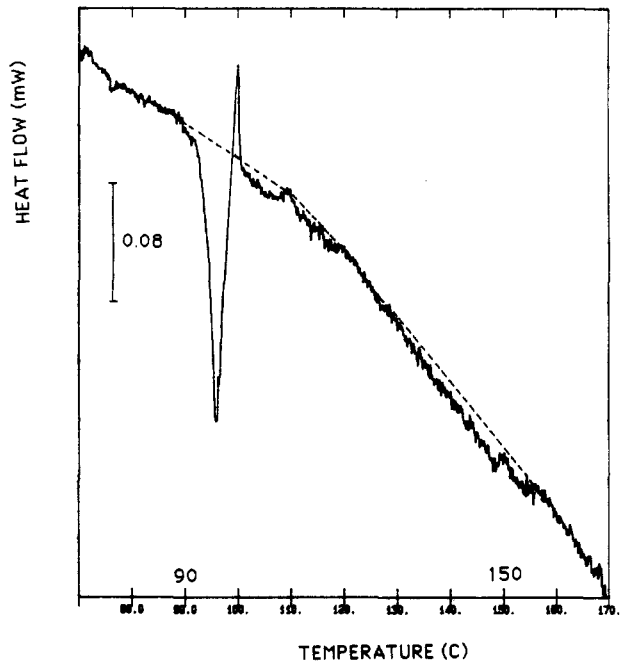

Figure 2. Recovery and stability of fraction III: dissolution trace of a gel equilibrated at room temperature at v = 1 K/h (D). The exotherm of recrystallization at 100 °C is a typical behavior of a heterogeneous gel.

Results and Discussion

Traces of dissolution and crystallization have been obtained under quite a variety of conditions. A few of them have selected and reported in Tables I and II and the figures. In order to make the reading of the tables easier, the point raised by each datum (A–K) will be listed below with a short explanation. Figure 1 (and A) shows the very slow dissolution of the strained crystals in the nascent. (B) illustrates the weakening effect of the solvent treatment on the nascent and (C) more of this effect on a gel. (A) and (B) are the only dissolution characteristics reported for the nascent, the others being those of gels. The comparison of (C) and (E) shows, on a solvent-annealed sample, the partial loss of fraction III and its recovery at room temperature with time. Figure 2 (D) is the trace of a heterogeneous gel obtained by quenching a solution with T_{max} = 120 °C. Spontaneous recovery at room temperature of strain of this sample submitted to a long thermal history is explained below. Comparison of (E) and (F) indicates the stability of fraction III after a high-temperature treatment (Figure 3).

The most striking result of this work is given in Figure 4 (G and H). The high-temperature exotherm obtained on cooling (Figure 4b) reveals that, during the dissolution of Figure 4a, total randomization has not taken place. The evidence of crystallization of PE at 160 °C from a dilute solution is noteworthy. The comparison of Figure 4a and c tells the story of the gel formation: The amount of gel in Figure 4c has been drastically reduced at the expense of single crystals because cocrystallization of the two morphologies has been prevented by the slow temperature ramp of Figure 4b. A slower crystallization (Figure 5a and I) allows for more relaxation and reduces fraction III at the next dissolution (Figure 5b). Figure 6 does not deal with fraction III since the maximum tempeature is 120 °C but shows dissolution traces of a mixed crystallization.

The analysis of the dissolution traces of UHMWPE and of its gels draws much from that of the melting traces (preceding paper in this issue). Although further evidence is needed to attribute unequivocally the high melting en-

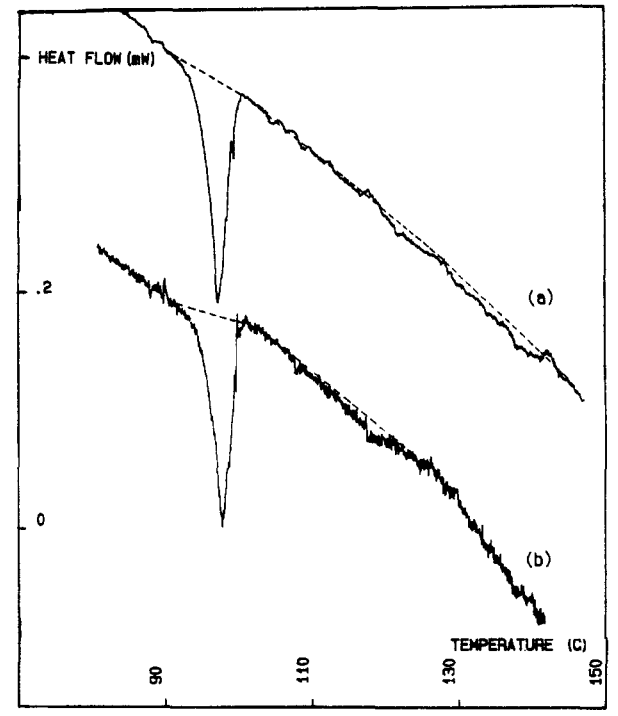

Figure 3. Recovery and stability of fraction III: (a) dissolution trace of a gel equilibrated at room temperature (E) and (b) dissolution trace of a gel obtained from a solution equilibrated for 4 days at 150 °C. v = 1 K/h.

dotherms to the dissolution and fusion of strained crystals, the terms of unstrained and strained crystals will be used because it is a convenient way to classify crystals with widely different temperature and kinetics of melting.

During the heating ramp, the unconstrained crystals (fractions I and II) are dissolved with a dissolution peak at T_d below T_m, the melting temperature; $T_m - T_d$ is 40 K for decalin. Before and during the dissolution of the higher MW molecules, the polymer not randomized in the solvent is a network whose junctions are the nondissolved strained crystals and the amorphous parts are the random

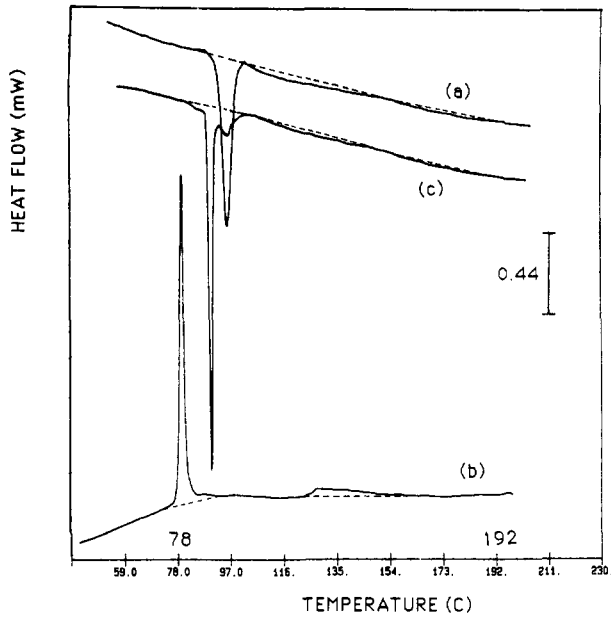

Figure 4. High-temperature crystallization of strained crystals: (a) dissolution of a room-temperature-equilibrated gel (G); (b) slow cooling in a temperature ramp, separate crystallizations of fraction III and fractions I + II (H); and (c) dissolution trace after (b) (H). v = 6 K/h.

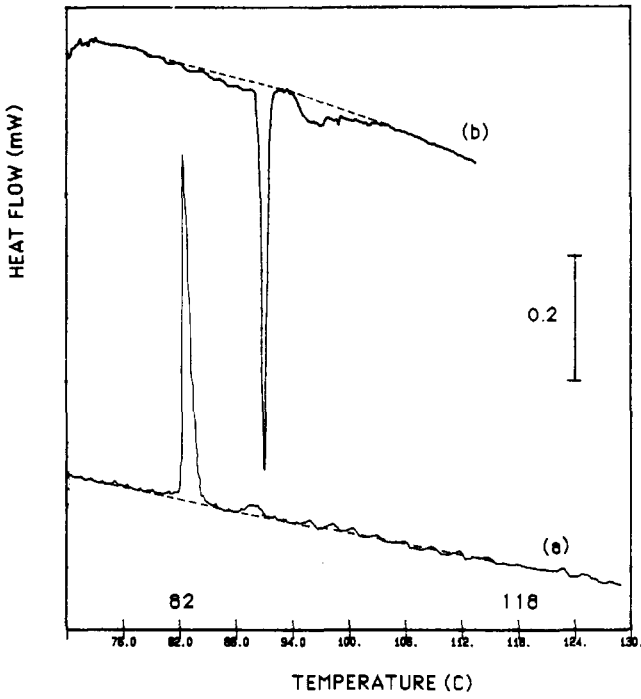

Figure 5. Relaxation of strained crystal/melt on cooling: (a) trace of crystallization of solution and (b) dissolution trace after (a) showing the typical endothem for pseudoisothermally grown single crystals. T_d is 92.4 °C for T_c = 83 °C. v = 1 K/h.

coils whose expansion in the solvent creates a strain on the crystals. This strain, which is expected to be higher in a good solvent than in a bad solvent, increases T_d for the remaining crystals. An arrested dissolution will occur similar to the arrested fusion of the dry polymer if the balance between the perfection of the crystals and the strain is adequate. When the temperature of the system reaches the dissolution temperature for the given strain, dissolution will be resumed if enough time is given in a temperature ramp. Dissolution occurs slowly because the perfected crystals, the core of the network, melt slowly[1] and over a large temperature interval in an equilibrium melting due to a range of strain in the sample. However, when the number of chains in a crystalline junction is large or when the perfection of the crystals is high, the strain to which the crystals are submitted during the course of dissolution increases. In that case, the randomization in the solvent does not occur at melting, and the dissolution endotherm is indeed a melting endotherm situated at the melting temperature of fraction III. If v is too high in comparison to the perfection of the polymer crystals, fraction III will not even melt or dissolve in the alloted time for residence in the temperature ramp between 70 and 200 °C. Intermediate situations will occur with the dissolution of less strained chains of fraction III and the melting of the more strained parts of the chains.

Strain in the Nascent Sample (Fraction II). The observation of the stability of strain in the presence of a solvent which gives rise to fraction III requires special melting conditions, but the effect of the strain on the melting and dissolution temperatures of the main peak (i.e., fractions I + II) is seen readily in a normal DSC run. An example is the effect on T_d of the strain in the nascent. The data of Table I give a quantitative evaluation of this effect. The dissolution temperature of the polymer dissolved once is lower by 11 K (rows C–G) than that of the nascent polymer (A and B). This difference is independent of v. However, the strain in fraction II, unlike that in fraction III, is not recoverable since T_d stays low whatever the treatment of the solution after the first dissolution. Differences in T_m between the first and second fusion of a nascent sample can be found in the literature without comment or attribution to strain. Although reports on T_d are few and deal mainly with the relationship between T_d (and lamellar thickness) and T_c, a lowering of T_d after the first melting is obsrved on HMWPE.[4]

Dissolution of the Nascent Sample. An example of the type of dissolution described above is given in Figure 1 (A). The temperature of the end of fraction III (165 °C) corresponds more to a melting than a dissolution. Dissolution is arrested due to strain and resumes at high temperature after the dissolution of fractions I + II (180 J/g), leading to the melting–dissolution of fraction III (~110 J/g). This trace was presented to illustrate the low fraction of the nascent polymer which melts in what could be named a generous time for a dilute solution (9 h from the start of the melting endotherm and 44 h from the beginning of the heating ramp with gentle stirring). The high-temperature part of this trace shows also that the interval of temperature needed for dissolution/melting has not been reduced by the presence of a solvent (preceding paper in this issue, Figure 1 or Table I). The dissolution/melting of fraction III is achieved between 128 and 165 °C (A) over 37 h. It is interesting to note that by contrast drawn fibers dissolve on a lower time temperature interval.[16] In consequence, the dissolution of behavior of the nascent resembles more that of fibers submitted to stress[8] than that of nonstrained fibers.

In trichlorobenzene (TCB) whose mediocre solvent quality brings about a reduced swelling of the dissolved chains, an almost normal dissolution takes place for the nascent sample. The endotherm of dissolution of the nascent polymer in fractions I + II (265 J/g) corresponds to about 95% of the whole polymer. In this solvent, the polymer succeeds in dissolving before buildup of strain on the crystals. In decalin, on the other hand, this type of dissolution can also occur but only after a specific treatment described below. Conditions can be found for a strained dissolution (i.e, H(I+II) < 200 J/g)) to take place in trichlorobenzene as well as in decalin.[15]

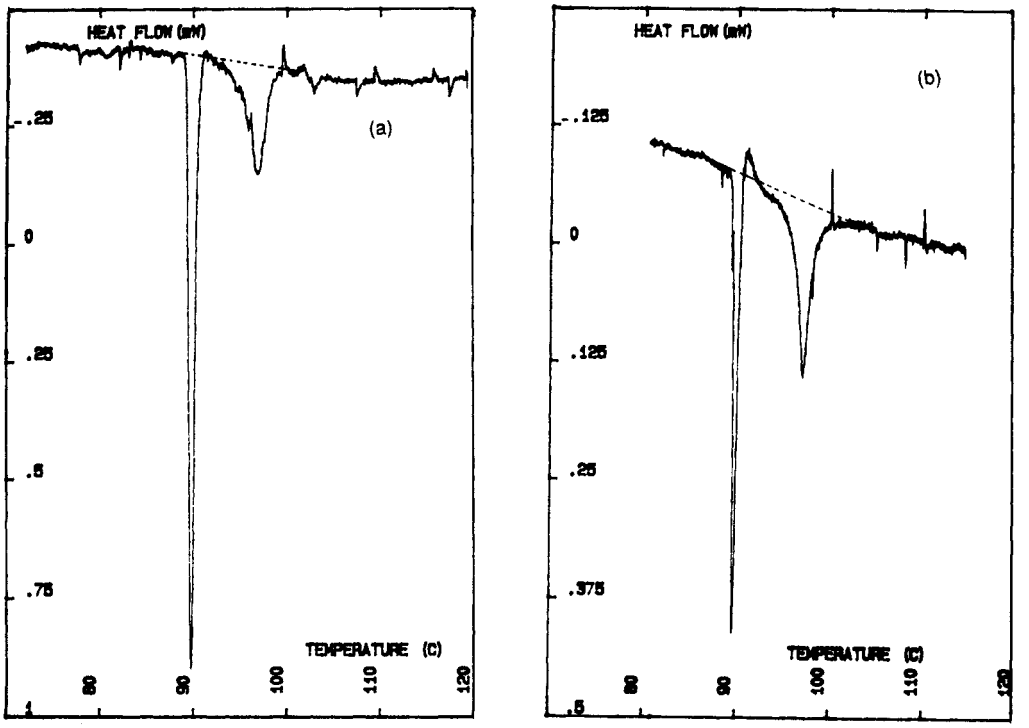

Figure 6. Dissolution traces of mixed crystals (fractions I + II) formed at T_c = 80 °C: (a) at v = 3 K/h (J) and (b) at v = 1 K/h (K).

The results of intrinsic viscosity measurements in several solvents will be reported later.[16] The high value of $[\eta]$ found in decalin and not in TCB is consistent with crystalline aggregates more stable in the good solvent than in the less good solvent. Understandingly, TCB has replaced decalin in the last decade for characterization in solution of PE.

Heterogeneity of Gels Obtained from Solutions Prepared at Low Temperature. The high intrinsic viscosities of decalin solutions prepared at 120 °C are stable during days. This observation supports the concept of arrested dissolution similar to arrested melting. The end of the dissolution endotherm noted below 115 °C was at the origin of the choice of T = 120 °C as a working temperature for solution properties. The heterogeneity of the solution however became apparent by calorimetry when it was found out that a succession of cycles of dissolution–crystallization increased the value of the enthalpy of the main endotherm. The history of the sample whose last dissolution is presented in Figure 2 included five cycles of dissolution and quenching (n = 1–5), a crystallization in a low ramp of temperature (n = 6), and a last dissolution at v = 1 K/h (n = 7). The first six cycles were performed within a short time while the gel was left nine months at room temperature between n = 6 and n = 7. For n = 1–6, T_{max} = 120 °C. The enthalpy of the main fraction which had increased to 260 J/g at n = 6 diminishes to 160 J/g for n = 7. This result is interpreted as follows: The successive crystallizations transform strained crystals into nonequilibrium unstrained crystals which melt with H_2 = 260 J/g. A long residence time at room temperature assures a more complete crystallization which entails the creation of strain on previously nonstrained crystals. It is not meant here to claim that strained crystals are more stable than unstrained ones, only that more complete crystallization in the presence of solvent including a combination of strained and unstrained crystals minimizes the free energy of the system as indicated by the effect of residence time at room temperature.

The dissolution trace with an exothermic peak at the end of the main endotherm is typical of nonhomogeneous gels and could be used as a test of solution homogeneity before quenching. The exotherm at 100 °C which lasts about $1^1/_2$ h obviously signifies the growth in solution of stable, thick crystals. The conditions of the experiment, presence of strained crystals, and slow heating are adequate for increasing the kinetics of recrystallization and separating the growth of crystals from their high-temperature melting. The different parts of the endotherm above 100 °C must correspond respectively to the melting of the network, melted in the previous cycles (100–120 °C), and to the first melting of some crystals (130–158 °C).

Network Weakening and Recovering. The next rows in Table I report the treatments made with two objectives, namely, (i) to weaken fraction III so that its melting will give a more compact endotherm and also (ii) to dissolve equilibrated gels, i.e., crystals equilibrated in a solvent rather than the nascent. A simple way of reducing the strain was found while doing preparation for viscosity work. A sample left in a solvent below T_d (to eliminate soluble impurities) was found to have a low and stable intrinsic viscosity. The same procedure (1 week at 90 °C) was applied to the nascent prior to a dissolution trace directly on the tube prepared for the calorimeter. The characteristics of the main peak (T_d, H) are the same as those of the nascent (A and B), but the endotherm of fraction III (128–144 °C) has gone from 50 to 88 J/g. The not-aged gel obtained by quenching such a solution has the largest nonstrained melting endotherm (260 J/g (C)) in decalin. Recovery of strain occurs after a residence time at room temperature since H (I + II) diminishes to 235 and H_3 increases to 50 J/g in a process similar to that found in the nascent (E). The difference in H(I+II) is meaningful, and the value of T_d for the gel (98 instead of 96 °C) confirms the increased strength of the gel after stabilization at room temperature. This trend is very similar to that observed on fibers for which a delayed crystallization of a minute amount of molten material is thought to be the origin of the increase of modulus with time.[17] Whatever the exact morphology of these last crystals (extended chain between the lamellae or extension of the lamellae by a thin edge which provides a better penetration of cohesion of neigh-

boring fibers), they have been perfected by an increment hardly noticeable in their total heat of dissolution (possibly within the limit of measurement of fraction III, about 10 J/g) but very significantly as far as their kinetics of melting are concerned.

The molecular reason behind the gel weakening by solvent treatment cannot be due to a simple beginning of crystal dissolution since the peak of T_d for the treated sample is the same as that of the nascent. The strain weakening at 90 °C may be thought of as the reverse process, at that temperature of the self-stiffening of the gel at room temperature. Evidence for the weakening of the crystalline "cement" between the shish kebabs can be found in the beginning of the dissolution trace which has been lowered from 105 to 102 °C after the solvent weakening treatment.

The change of entanglement concentration during the annealing at 90 °C is difficult to assess. Strained melting is not limited to very high molecular weight samples,[14] but the stability of strained crystals from low or medium molecular weight nor their dissolution behavior has been investigated. Further work will tell if extremely long chains have a specific and unique role in the balance of events which lead to a strained dissolution, i.e., the formation of a stable network and its recovery with time.

Temperature Stability of Fraction III. In order to test the stability of strain in the presence of a solvent at a temperature used as the dissolution temperature of the nascent in the literature, a solution was left at high temperature and then it was quenched and reheated again to measure H_3. Row F of Table I reports the results of the dissolution trace of a gel whose residence time at 150 °C was 4 days; Figure 3b is the dissolution trace of this gel after 2 days at room temperature. The amount of fraction III, although reduced compared to its value for the nascent sample, is still a sizeable portion of the total heat of fusion.

In Figures 2 and 3, the dissolution traces of gels give a dissolution peak at T_d = 96–98 °C. This temperature is 5–8 K higher than that of thickened crystals of low MW grown isothermally.[16] The cocrystallization of the network and of the chain-folded crystals is thought to be responsible for the higher T_d through numerous connections between crystals. Crystals grown isothermally from solutions of GUR have values of T_d lower than 97–98 °C as indicated by the narrow endotherm of Figure 6.

Network Weakening Treatment by Crystallization in a Temperature Gradient. If strain is conserved between melting and recrystallization, a separation of crystals according to strain is best done by a slow crystallization in a temperature ramp. Crystallization traces are shown in Figures 4b and 5a for two rates of cooling, namely, 6 and 1 K/h. These solutions underwent a similar thermal treatment, i.e., they were equilibrated gels made from solvent-annealed initial polymer. The last part of the thermal history was different, one gel being dissolved at 6 and the other at 1 K/h.

The important factors of strain release or strain conservation in the melt or in the presence of a solvent are the maximum temperature reached and the residence time between the beginning of formation of strained melt (about 100 °C) and the end of existence of strained melt on cooling (about 90–100 °C). The upward temperature ramp from 100 to 200 and downward from 200 to 100 °C is traversed in 33 h with v = 6 K/h. The residence time is however longer in the cycle made with v = 1 K/h and T_{max} of 170 °C. The crystallization and dissolution traces reflect without ambiguity the effect of the residence time in strained crystallization, gel formation, and persistence of fraction III.

Crystallization Traces. At 6 K/h (Figure 4b), strained crystals re-form between 160 and 123 °C with an enthalpy of crystallization about equal to that of the previous fusion. From this result, one can conclude that, on quenching a solution from a high temperature to room temperature, the usual mode of gel formation, the melted network will be a fortiori even less randomized than in a slow crystallization and will recrystallize as extended-chain crystals. The cocrystallization of the folded chains with the network on quenching is at the origin of the gel. The trace of Figure 5a, on the other hand, shows that the relaxation has taken place. The strained crystals contribute only to about 15 J/g to the heat of crystallization; a major fraction of the polymer grows as chain-folded crystals between 78 and 88 °C. The undulating baseline between 130 and 90 °C is not reproduced in Figure 4b or the other traces. It is thought that succession of small endotherm and exotherm could be related to the relaxation, i.e., to the melting on cooling of the already crystallized strained melt.

Dissolution Traces. The dissolution traces of Figures 4c and 5b and, in particular, the relative amount of fractions I + II and fraction III confirm the analysis of the crystallization traces. Fraction III (Figure 5b) is estimated to be about 15 J/g as in Figure 5a while it is still 40 J/g in Figure 4c which follows a more rapid crystallization. The endotherms of fractions I + II also reveal the difference in crystallization conditions: Both have two peaks, one for the chain-folded crystals and the other for the gel. The T_d of the chain-folded crystals, respectively, 90.5 and 92.4 °C, reflect the 2.7 K difference in the temperature of pseudoisothermal crystallizations T_c (80.3 for Figure 4b and 83 °C for Figure 5a). As observed previously,[1,16] recrystallization during heating being slower in solution than in the solid state leaves unchanged a fraction of crystals whose T_d and lamellar thickness reflect the original T_c. It is interesting to note that the gel fraction is still important after the slow crystallization at 1 K/h (55 J/g). One can visualize the change in the distribution of the crystals as a change in the amount of the core crystals of the shish kebabs. A diminution of fraction III would correspond to a diminution in the core thickness of the shish kebabs.

Characterization of Gel and Single Crystals through Fractions I + II. The two endotherms of fractions I + II in Figures 4c and 5b show that the temperature of the dissolution peak permits the distinction of free chain-folded crystals on one hand, and of crystals cocrystallized with the network on the other hand. The endotherms which are best separated in Figure 5b at v = 1 K/h will provide information on the amount of network in the solution, complementary but easier to obtain than that requiring the complete melting at high temperature of fraction III. Complex crystals, formed on quenching at low temperature, melt at higher temperature than crystals grown isothermally. This is in contrast with what happens in the absence of network where crystallization at low temperature leads to thin, metastable lamellae which melt at low temperature. As mentioned above, the raise in T_d (fractions I + II) due to cocrystallization is similar to the raise in T_d due to strain (nascent strain) described above, although more moderate.

Systematic isothermal crystallization at T_c has been made, and the crystallization and dissolution traces have been recorded for $80 < T_c < 90$ °C. The dissolution traces show a narrow peak (ΔT at demiheight = 0.5 K). The T_d–T_c relationship is similar to that obtained on low molecular weight samples,[16] T_d being higher by about 8–10 K than T_c. The crystals grown at $T_c < 72$ °C also dissolve

with a single peak which belongs to the typical dissolution peak of gel formed by quenching at room temperature as indicated by its T_d (97 °C) and its shape (ΔT at demi-height = 3.5 K). At somewhat higher temperature, 72 < T_c < 82 °C, the two morphologies grow simultaneously. No dissolution trace of a single crystal grown isothermally will be given since they are similar to the main endotherm (Figures 4c and 5b) of crystals formed in a pseudoisothermal crystallization (Figures 4b and 5a). The dissolution traces of Figure 6 are characteristic of a mixed crystallization made at 80 °C. The dissolution temperatures of the chain-folded crystals (90 °C) and of the gel (98.5 °C) are distinct. The dissolution traces at 1 and 3 K/h indicate no substantial changes in the distribution of crystals between the morphologies. In the slow dissolution (Figure 6b), the small exothermic peak followed by a shoulder between the two endotherms indicates recrystallization into thicker lamellae followed by the melting of these crystals. The amount of gel fraction depends on the amount of network in the solution, i.e., on the history of that particular solution. When isothermal crystallization takes place at a given temperature for two solutions, the gel morphology is increased for the solution which has not been submitted to the network reducing treatment. The melting of fraction III, not recorded here, should give about 70 J/g. It is believed that this method of characterization, which does not rely on the lack of flow but on the mode of crystallization, will permit an investigation of dilute gels obtained from homogeneous solutions. Analysis of gels, traditionally based on lack of flow of more concentrated solutions, is likely to be perturbed by inhomogeneity in the solution before quenching.

Gel Crystallinity. The preparation of a network-free solution entails several consecutive crystallizations in a temperature gradient, and their efficiency is judged from the enthalpy of fractions I + II compared to the overall enthalpy. In the present solution work, involving several solvents for UHMWPE GUR, it was found that the overall enthalpies of dissolution of gel, including the contribution of the three fractions, are always high (280–290 J/g). One can safely assume then that the enthalpy of fraction III is the complement to 280–290 J/g of the enthalpy of fractions I + II. Consequently, in a partial dissolution whose temperature has not been raised beyond 120 °C, the magnitude of the enthalpy of dissolution of fractions I + II is a precise indicator of the amount of network in solution, a low enthalpy (180 J/g) corresponding to a network-rich system and a high enthalpy to a homogeneous solution. The enthalpies of dissolution of fractions I + II reached after an extensive network weakening treatment are high (285 J/g) corresponding to a shrinking of fraction III and, consequently, an expected loss of gelation. However, when such a solution is quenched, the following dissolution trace is typical of a gel with a single large peak. The dissolution temperature, however, has dropped by 1–1.5 K, a sign of a weaker gel. This result shows that a small amount of fraction III corresponding to an enthalpy of fusion lower than 15 J/g is sufficient to lead to gel formation. It is noteworthy that such a small amount of network probably well dispersed into the solution is sufficient to assure a high crystallinity of the gel although, due to quenching, the first stages of crystal formation are rapid. Badly formed chain-folded crystals characterized by a low dissolution enthalpy could not be grown under the present conditions (0.2% in decalin and quenching from T_{max} = 180 °C).

Effect of Fraction III on Dilute Solution Properties. Characterization of high molecular weight PE[18,19] cannot be reliable if the existence of fraction III is not recognized. To avoid the high MW due to crystalline junctions, a network weakening treatment should be applied prior to analysis. Molecular weight distribution measured in decalin at 135 °C has been found to be skewed due to a too large amount of high molecular weight molecules.[18] Intrinsic viscosity[15] constitutes a sensitive way to follow, at constant temperature, the gradual loosening of the network observed by a slow diminution of the apparent molecular weight. At 120 °C, crystalline aggregates are stable during days or weeks depending on the concentration. In a temperature ramp between 100 and 120 °C, the crystalline aggregates do not melt even after several cycles of dissolution–crystallization as revealed by the dissolution trace given in Figure 2.

Molecular weight characterization (intrinsic viscosity and gel permeation chromatography) should be performed then on solutions submitted to the network reducing treatment with a limited time of the crystallized solution at room temperature to avoid crystal perfection and recurrence of strain melting. In the current work done in this laboratory on the measurement of MWD (molecular weight distribution) of GUR by turbidity at a LCST (lower critical solution temperature),[20] verification of the absence of crystalline aggregates is made by calorimetry prior to LCST measurements.

Stirring and Gel Formation. Stirring during crystallization induces more strain and entanglements in the crystals and leads to high-temperature dissolution traces.[15] The effect of shearing PE solutions prior and during crystallization on the morphology of crystals has been studied extensively. The present solutions use the same constituents at the same concentration as investigations into the precursors of gel made by Keller et al.[8] (1982) (except that our polymer has a lower nominal molecular weight). Thermal histories were also comparable since in the Bristol laboratory, the solutions were made at 150 °C, left 1 h at 170 °C, and quenched at various temperatures (115–140 °C) in a Ferrari viscometer to submit them to a shear and measure also the change of viscosity with time. Gel formation on cooling was found to be related to the maximum in viscosity found 20–40 min after the quenching–shearing treatment. The exotherm of crystallization of fraction III in Figure 4b which spreads between 160 and 123 °C, i.e., over 6 h in this particular experiment, illustrates the slow kinetics of crystallization and by consequence the memory effects on that range of temperature. The heat flow in Figure 4b indicates that, in the 1982 experiments, fraction III was either present or growing during the viscosity measurement. The observed changes of viscosity with time may constitute an indirect measurement of crystal formation in a shear. Gels are formed even when stirring is not stronger than that necessary for a good dissolution. However, the relation between gel formation and shear can be understood qualitatively. With a gentle stirring, the crystallized extended chains are well dispersed in the liquid and assure a wall to wall networking previous to the chain-folded crystal growth. With a higher shear, some random coils dissolved in the solution may be extended and caught in the crystallizing process, contributing to a stronger gel. The present work confirms, by a technique which is sensitive to slow crystallization, the previous conclusions concerning the likelihood of the crystalline nature of the gel-forming associations.[9] The difference between the former investigation and the present one residues in the definition of a gel and its consequences on requirements for gel formation. Since the present definition of a gel is based on its trace of

dissolution (high T_d, wide endotherm, and high enthalpy of dissolution), it includes not only the stirred solutions with a wall to wall cohesion on cooling but those formed from unstirred and dilute solutions which are either a flowing suspension of gel particles or a weak gel whose capacity to support its own weight does not resist to moderate shaking.

Conclusion

The dissolution traces of nascent samples and equilibrated gels have shown that, due to the stability of strained crystals, arrested dissolution occurs as arrested fusion. The lack of randomization of the melted network (fraction III), in the time of the experiment, causes recrystallization as extended-chain crystals on cooling of the strained melt. A thermoreversible gel is the result of the concomitant crystallization from solution by quenching of a dispersed but not randomized network together with dissolved random coils. The crystalline network takes away from entanglements the key role in solution network formation. Prevention of cocrystallization by slow crystallization in a temperature gradient leads to an almost network-free solution and a weak gel. The endotherm of fractions I + II permits an unambiguous characterization of a gel. The recovery with time at room temperature of strained melting in a gel crystallized from an almost network-free solution suggests that strained melting is associated with the presence of some amount of very perfect crystals. The slow dissolution and slow crystallization traces constitute a powerful means of investigating gelation processes. The mechanism proposed here seems to be general and to apply in particular to poly(4-methylpentene) gels.

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