Effect of Stirring on the Gelation Behavior of High-Density Polyethylene Solutions

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ABSTRACT: In an earlier work we reported that polyethylene solutions of ultrahigh molecular weight once stirred at temperatures above the dissolution temperature of normal crystals form gels on subsequent cooling, even in the quiescent state. Following this observation and the earlier recognition by Pennings of changes in the shear stress of a polyethylene solution during stirring at high temperatures, the present work was undertaken, fundamentally, to examine whether there existed a correlation between the shear stress and its different stages of development with stirring time at different stirring temperatures and concentration on the one hand and the gel formation on subsequent cooling in the quiescent state on the other. Indeed, clear-cut correlations were observed together with information on the associated relaxation times and on the strength and thermal stability of the gels. From this we could deduce the existence of a gel-forming association gradually building up across the fluid gap followed by its breaking up into gel particles which continue to impart gel-forming ability to the liquid when cooled after cessation of stirring. The underlying basic association itself, while temporary, is most likely to be of a crystalline nature and thus of relevance to flow-induced crystallization and shish kebab formation for which they are likely to be precursor stages. The detailed nature of the latter is to be explored. Our findings, however, should also be relevant to all conventional solution studies relying on chains being molecularly dispersed. We discuss this work in the light of similar observations on noncrystalline polymers made during the 1960s and some recent theoretical developments.

Introduction

The present work originated from the previous recognition[1] that stirring of solutions of ultrahigh molecular weight polyethylene at temperatures far too high for solution crystallization changes the state of the solution in a way that leads to interesting consequences. More explicitly, we reported that a solution of polyethylene in xylene at 135 °C, once stirred, would set as a gel on cooling, while in the quiescent state. This effect is particularly conspicuous when compared with the turbid but fluid suspensions resulting from the formation of familiar single crystals in solutions which had been cooled without any previous agitation. We found a correlation between the newly recognized mechanism of gel formation and the ability to produce fibers by solution crystallization techniques such as Zwijnenburg and Pennings' surface growth method.[2] The production of ultraoriented and ultrastrong fibers obtainable by the surface growth method consists essentially of the stretching of gel particles adhering to the surface of the rotor. Accordingly, we suggested that the adsorption-entanglement layer would be constituted of gel particles adhering to the rotor which, by the nature of the technique employed, become stretched. This recognition has reoriented current endeavors in the production of high-modulus fibers.[3-6] It has also directed attention to the production of the gel itself and to its stretching in both the wet state and the dried state. From the point of view of flow-induced crystallization it has drawn attention to the fact that many, if not all, past methods of growing shish kebabs could well have consisted of stretching of gel particles or localized networks.

The fundamental feature underlying all the above observations, however, is the origin and nature of the newly recognized gel itself, the issue to which the present work is directed.

The first point to note is that the formation of gels by polyethylene solutions at the concentrations involved in these works (0.05–1%) is most unusual: As already stated, in the absence of stirring only turbid suspensions of particulate crystals are obtained. Second, the gel, at least under these experiments[1] is not formed by the stirring itself; it is only after all stirring has *ceased* and *on subsequent cooling in a quiescent state* that the gel is observed. The gels form when the stirred solution is cooled to ~100 °C; at that temperature the gels are quite transparent (clear). When the gels are cooled below ~90 °C, they become turbid due to the onset of lamellar crystallization. Third, the effect induced by the stirring is only temporary; the gelling ability is lost after a lapse of sufficiently long time. Fourth, the stirring-induced memory, while transient, is surprisingly long-lived; it can persist over hours at temperatures as high as 130 °C, totally incompatible with the time scale of molecular processes. In brief, agitation at temperatures far beyond that of any known mode of crystallization produces some mode of molecular association.

The purpose of the present work is to obtain further information on the nature of this association, which, as already stated, while transient, is suprisingly long-lived and is the initiator of gel formation on subsequent cooling. During the cooling process all known modes of crystal formation, such as the formation of shish kebabs (no doubt some consequence of the initial stirring) and some isolated lamellae precipitating with the gel network, in addition to the formation of the gel itself, are recognizable.

The key for the present work is Figure 9 in the salient paper by Pennings,[7] which is similar to Figures 1 and 2 of the present paper. Here the apparent viscosity (or more directly the shear stress) of the solution at a temperature above that of normal crystal growth or fiber formation was recorded as a function of time. An initial rise followed by a drop in the shear stress was observed, which was interpreted as the building up and subsequent breaking down of a gel network. While in that work the actual formation of the gel itself during cooling under subsequent quiescent conditions was not reported, we perceived a potential connection between shear stress behavior in Figure 9 of ref 7 and our own observations on gelation described in ref 1, briefly recapitulated above. Consequently, we undertook to record shear stress and its variation with time during stirring at our original agitation temperatures and to see whether there is any correlation with the gelation phenomenon. We also extended the previous temperature range by using decalin (boiling point 183 °C) rather than

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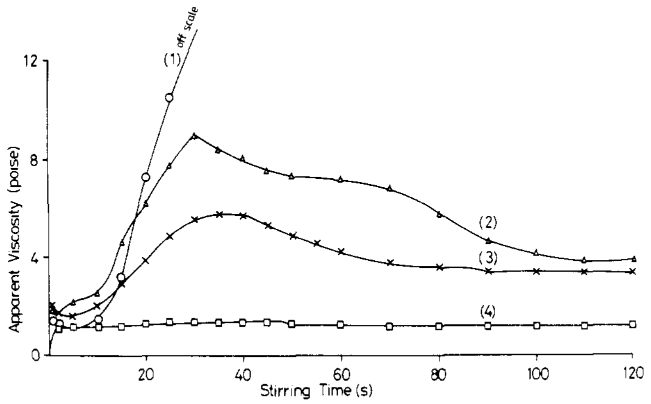

Figure 1. Apparent viscosity as a function of stirring time for a 0.6% (w/w) solution of high molecular weight polyethylene (M_w = 1.5×10^6) in decalin for a series of stirring temperatures (T_s): (○) T_s = 115 °C; (△) T_s = 120.8 °C; (×) T_s = 124 °C; (□) T_s = 140 °C. The annular gap between the inner and outer cylinders was 1 mm. Rotation speed = 15 rpm.

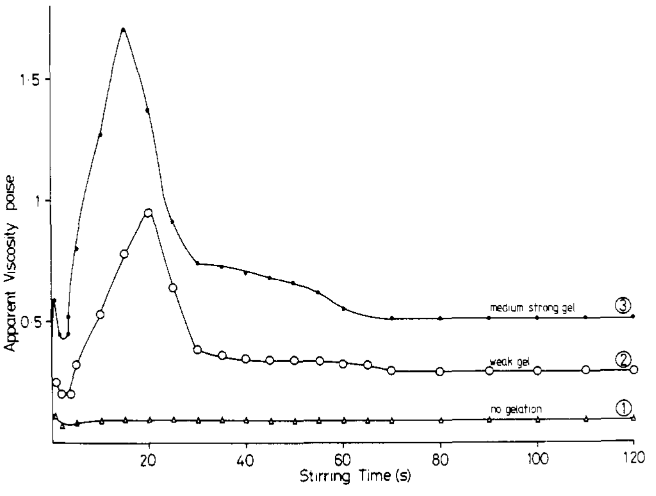

Figure 2. Apparent viscosity as a function of stirring time for a solution of high molecular weight polyethylene (M_w = 1.5×10^6) in decalin at 124 °C for a series of concentrations: (●) concentration = 0.4% (w/w); (○) concentration = 0.2% (w/w); (△) concentration = 0.1% (w/w). The annular gap between the inner and outer cylinders was 1 mm. Rotation speed = 64.1 rpm.

xylene (boiling point 138 °C) as the solvent.

We shall comment here, before describing our experimental work, on two sets of salient references which came to our notice after the completion of the work covered by this paper. First, observations of physical changes during flow featured frequently in the literature during the 1960s.[8-13] These observations include many examples where the viscosity passes through a maximum value during shearing for a variety of polymers.[11-13] While the formation of aggregates and even gelation are mentioned in several of these papers, the effects remained largely unexplained and do not appear to have been followed up. Second, recent theoretical work on concentrated polymer solutions, using the developments of the Yamamoto network theory,[14-16] has predicted a maximum in shear viscosity.[17,18] Indeed, Fuller and Leal[18] show that all current concentrated-solution theories[19-20] also predict such an effect, which is primarily due to a difference in the rates of creation and destruction of entanglements in stationary and flowing solutions. These authors also refer to recent experimental evidence for this effect.[21-23] It is interesting to note that some of this work[23] was carried out on Aroclor solutions of polystyrene, one of the systems used by Matsuo et al.[13] some 15 years earlier, though the authors seem unaware of the earlier work. Naturally, this large experimental and theoretical background unsuspected by us at the time of our experiments will affect the interpretation of our own experimental results insofar as it places them within a broader framework than envisaged initially. However, as we shall see, their implication for the explicit issue we set out to examine in the first instance remains unaltered. We shall return to a more detailed consideration in the Discussion.

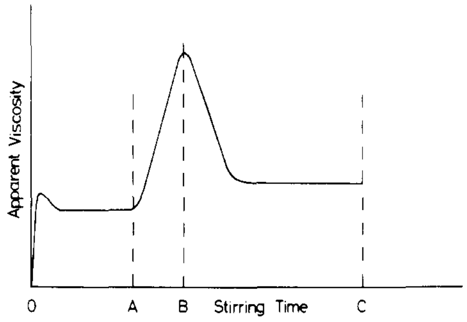

Figure 3. Schematic illustration of the apparent viscosity–time curve: (A) onset of peak; (B) peak; (C) arbitrary time after peak. Not to scale. Consult text for details.

Experimental Details

1. **Solution Preparation.** Solutions of Hostalen GUR (M_w = 1.5×10^6) were prepared in laboratory-grade decalin (supplied by BDH Chemical Ltd.) at about 150 °C. Antioxidant (*N*-phenyl-2-naphthylamine) was added to the solution at 0.02% (w/v) so as to minimize the chances of oxidation. After complete dissolution the solution was maintained at 170 °C for 1 h in order to destroy any memory of stirring during dissolution. The precise concentrations of the solution were determined by evaporating the solvent from known weights of the solutions and weighing the residues. The polymer solutions were transferred in their containers into a thermostatically controlled silicone oil bath at a preset temperature, and the viscometer cylinders, preheated to the temperature of the bath, were immersed in them with minimal mechanical disturbance.

2. **Description of Viscometer.** We used a Ferranti viscometer for the purpose of determining the changes in the apparent viscosity of the solution during stirring.

The viscometer consists of a rotating cylinder with a second cylinder mounted coaxially within it. The stress transferred across the gap between the cylinders is measured by the torque on the inner cylinder and reflects the apparent viscosity of the liquid in the gap. We use the term "apparent viscosity" since we expect the liquid to undergo structural changes during the stirring which may cause it to become inhomogeneous so that no true viscosity could be defined. The viscometer has interchangeable cylinders. We used an outer cylinder of 4.7-cm diameter with annular gaps of 1 and 4 mm. We used rotation speeds of 15 and 64.1 rpm. The actual gaps and rotation speeds for particular experiments are indicated in the legends to the figures.

3. **Measurement of Apparent Viscosity.** The system was allowed to reach thermal equilibrium (i.e., ~15 min) before the rotor was started. The solution was effectively stirred continuously by the rotation of the outer cylinder. The reading of the viscometer was recorded with time. The apparent viscosity during stirring is plotted as a function of stirring time for a series of temperatures and solution concentrations in Figure 1 and 2.

The various curves in Figure 1 represent the temperature (T_s) at which the solution was sheared. We found that in all cases where the solution formed a gel on cooling the corresponding viscosity–time curve shows a maximum viscosity before leveling again. We also found that at 140 °C (curve 4) there was only a hint of peak and that the gel formed was correspondingly weaker.[26] At 150 °C, however, only single crystal aggregates were formed on cooling.

To see if there is any correlation between the changes in the apparent viscosity during stirring and the ability of the polymer solutions to gel on cooling, the following tests were carried out.

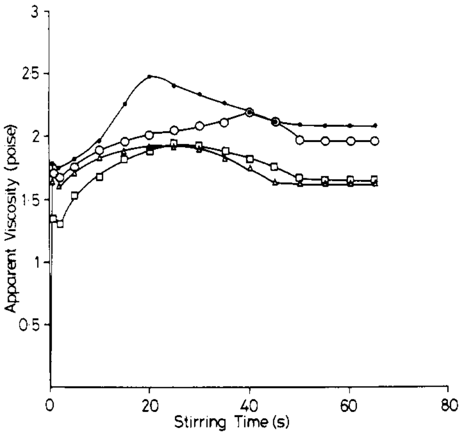

Figure 4. Apparent viscosity as a function of stirring time for a 0.5% (w/w) solution of high molecular weight polyethylene ($M = 1.5 \times 10^6$) at 124 °C for a series of resting time τ: (●) $\tau = 0$; (○) $\tau = 35$ min; (△) $\tau = 95$ min; (□) $\tau = 215$ min. Gap = 4 mm. Rotation speed = 64.1 rpm.

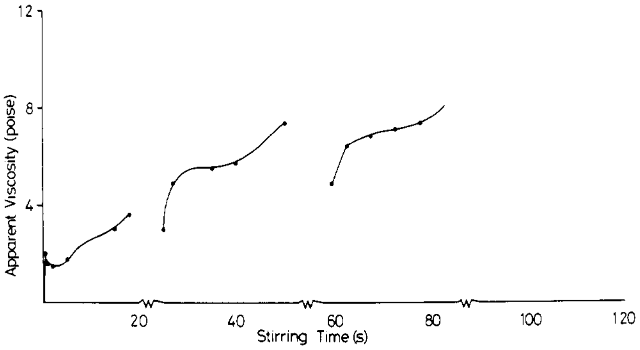

Figure 5. Apparent viscosity as a function of stirring time in region AB for a 0.6% (w/w) high molecular weight polyethylene ($M_w = 1.5 \times 10^6$) in decalin at 124 °C. Gap = 4 mm. Rotation speed = 64.1 rpm. Resting time = 120 s.

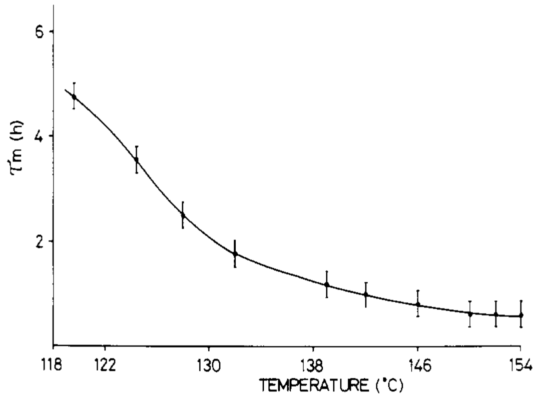

Figure 6. Time required to destroy memory of stirring effect as a function of solution temperature for high molecular weight polyethylene. Concentration = 0.6% (w/w). Total stirring time = 3 min. Gap = 4 mm. Rotation speed = 64.1 rpm.

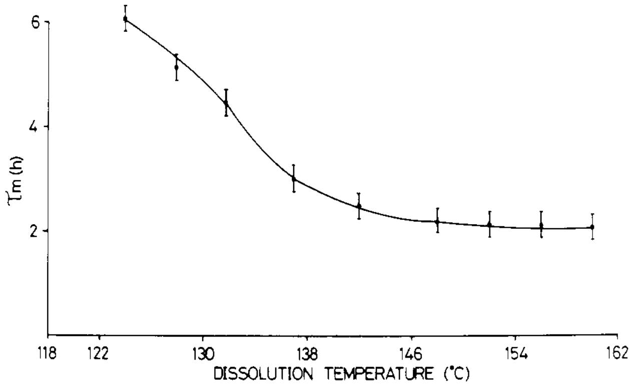

Figure 7. Time required to melt wet polyethylene gel as a function of the dissolution temperature. Gel was prepared as described in the text with $T_s = 124$ °C. Gap = 4 mm. Rotation speed = 64.1 rpm.

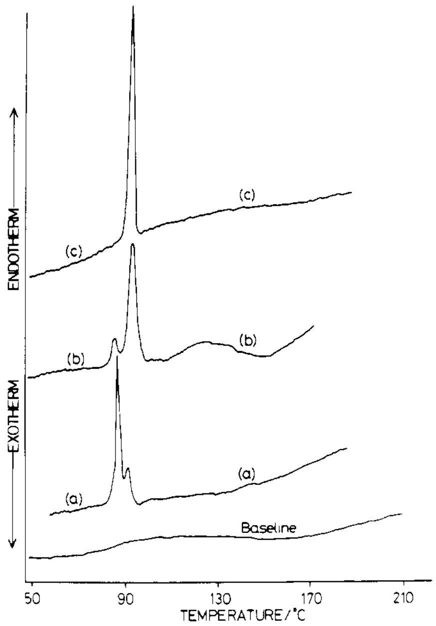

Figure 8. DSC thermograms for both PE single crystals and gels in decalin (in order to resolve the three peaks in curve b the highest sensitivity of the instrument was used): (a) single-crystal suspension; (b) gel in decalin; (c) same as (b) but gel kept at 150 °C for 2 h before cooling. Heating rate = 5 °C/min. Sensitivity range = 0.1 mcal s^{-1}.

We selected experimental parameters previously found to favor gelation after stirring (e.g., $T_s = 124$ °C, rotation speed = 64.1 rpm, concentration = 0.6% (w/w), and gap = 1 mm) and started the rotor as before. The stirring was then interrupted, and the solution was cooled to room temperature and examined to see if gelation occurred. The experiment was repeated for a wide range of stirring times. The results are summarized in Figure 3, where we sketch a typical apparent viscosity–time curve.

We found that gelation occurred in regions AB and BC and that the gels formed in region BC were stronger[26] than those obtained from region AB, whereas in region OA, only single-crystal suspensions were obtained when the solutions were cooled to room temperature.

The thermal stability of the network junctions and the gel-forming particles (or molecules) was also investigated by repeating the stirring process several times and interrupting the process for a series of time intervals: interruptions were made for both long intervals after long stirring times and short intervals after short stirring times. Examples of these experiments are shown in Figures 4 and 5. In Figure 4 we show what happens if the solution is first sheared for a long time (i.e., to point C in Figure 3) and then left unstirred for a time τ before repeating the original shearing experiment. On the other hand, we show in Figure 5 what happens when the shearing is stopped in region AB of Figure 3 and allowed to rest for 2 min before the shearing is restarted.

We also examined the memory effect on the stirred solutions by stirring the solutions at a predetermined temperature (T_s) for a measured time (τ), as before, and maintaining the system at this temperature until, on cooling, no gelation occurred. The minimum time (τ_m) required to store the solution when no gelation would occur on cooling was recorded as the time required to destroy the memory effect. τ_m is plotted as a function of the storage temperature T_s in Figure 6. Note under these conditions of speed and gap, gelation occurred up to 154 °C if the solution was stored at this temperature for less than 20 min. The memory effect was also determined by monitoring the dissolution of the wet gels. To this end, the time required to dissolve the wet gel

Table I
Optical Observations of the Thermal Behavior of Polyethylene Single Crystals and Gels in Decalin

T, °C	cooling an unstirred solution	cooling a stirred solution	on storing a previously stirred solution	heating a gel	heating single crystals
150-130	clear solution	clear solution	loss of gelation ability in 0.75-2 h	dissolution of gel in 2 h	clear solution
130-110	clear solution	clear solution	loss of gelation ability in 2 h to several days	break up of gel in ~6 h	clear solution
110-90	clear solution	clear gel formed		loss of turbidity	loss of turbidity
<90	onset of turbidity; single-crystal suspension	gel becomes turbid			

as witnessed by its return to fluidity was recorded and this was plotted as a function of the melting temperature (Figure 7).

4. Determination of Melting Points of Wet Gels. For comparison purposes the dissolution temperatures of both single crystals and gels of PE in the wet state were measured by the technique of differential scanning calorimetry using a Perkin-Elmer differential calorimeter (DSC 2) and recording the endotherm peaks as the melting points. The DSC results are shown in Figure 8.

Before the DSC measurements were made, however, a cursory visual observation of the melting behavior of the gels was carried out: A small quantity of the turbid gel was heated in a test tube in a bath preset at 150 °C. It was then found that at about 92 °C the turbidity disappeared completely, while a clear gel still remained in the solvent until 2 h later, when a complete solution was obtained. The disappearance of turbidity corresponds to the dissolution temperature of single crystals in suspension. Our visual observations of the melting behavior of both single crystals and gels in decalin are summarized in Table I.

Discussion

The work reported here shows many fascinating qualitative effects which are easily reproduced, although the detailed quantitative behavior may vary with the precise experimental conditions. The principal observations to emerge from this work are, first, that the changes in apparent viscosity of a polyethylene solution undergoing shear flow correlate with the ability of the solution to form a gel on subsequent cooling, second, that the structure formed during the shear flow, which causes the gelation, is itself remarkably stable, persisting for several hours in a quiescent solution, and, third, that these changes in the solution are strongly sensitive to the temperature at which it is sheared. These effects occur at all shear rates investigated in this work and at all concentrations greater than ~0.1%. Although we have not yet investigated different molecular weights, we expect the effects to rely on the presence of high molecular weight polymer since our experience shows us that only then will gels form.

It is convenient to discuss these results in two parts. First, we shall consider the relationship between the results presented here and the large body of relevant experimental data in the earlier literature on other systems and the recent theoretical work referred to in the Introduction. In the second part we shall present a model which accounts for the observed behavior and discuss, in detail, our experimental results in terms of that model.

The early experimental works[8-13,21] all involve high molecular weight polymer solutions undergoing shear flow. In addition, in some cases in order to produce detectable effects it was necessary to use solvents with high viscosity. We should note that these were also poor solvents although this is not always mentioned in the original papers. The maximum in the shear stress–time curves always occurred after ~50–100 s but its presence was found to depend on shear rate; no investigation of temperature dependence was made. The polymers were primarily poly(methyl methacrylate), atactic polystyrene, and poly(ethylene oxide). Only the last of these is normally regarded as crystallizable. All the authors have reported some sort of aggregation or gelation occurring during the flow. Our experiments reported here, in common with these earlier ones on different polymers, were performed with high molecular weight solutions and gave very similar results, including the time at which the peak occurs. However, we did not use high-viscosity solvents. The most obvious common elements between our experiments and the earlier ones are the shape of viscosity–time curves, the formation of aggregates or gels, and the fact that either a poor solvent was used as in the earlier works or, as in the present case, the most pronounced effect occurs at temperatures just above the equilibrium dissolution temperature. We may thus draw the tentative conclusion that all the solutions are liable to undergo some sort of segregation, which is induced by shear flow. The nature of the segregated parts is quite unknown but on the experimental evidence they would be expected to contain a larger degree of entanglement than the solution and to be comparatively stable when the flow field is removed.

The recent theoretical approaches to concentrated solutions which predict a maximum in the shear stress–time curves start by considering the stationary solution to have a network of entanglements which are being continuously created and destroyed. In the steady-state flowing solution there is again a network of entangled chains but the rates of creation and destruction are now different from their values in the stationary state. It is during the start up of the flow and the change from one equilibrium state to another that the maximum shear stress occurs. The theories as they are presently composed all assume either a net decrease in the number of entanglements[14-19] or a constant entanglement density.[20] The experimental evidence of aggregation and/or gelation found both by the previous workers[8-13] and by ourselves[1] suggests a net *increase* in the number of entanglements. Furthermore, the work presented here on the stability of the gel-forming structure suggests that the additional entanglements are of a more stable nature than any present in the initial stationary solution. In fact, the most salient feature of the observations in question is that entanglements are created on the time scale of tens of seconds while they decay on the time scale of several hours. This wide disparity of the relaxation times involved cannot be accounted for by geometric arguments alone but requires the endowment of the junctions created with special properties outside the scope of the theories quoted. This is not to say that it may not be possible to choose more appropriate functions for the creation and destruction of entanglements and insert them into Fuller and Leal's formation of Yamamoto's network theory[18] and, thus, mathmatically model the ob-

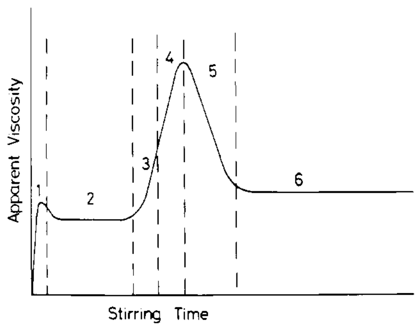

Figure 9. Schematic illustration of apparent viscosity–time curve. Not to scale. Consult text for details.

served behavior. However we prefer, at this stage, to offer a physical explanation of the behavior based on observational facts available so far for solutions of polyethylene. It is possible that an analogous explanation could be applied to PMMA, PS, and PEO. We shall not discuss them further.

In our previous work[1] on solutions of polyethylene in xylene stirred by the inner cylinder of a Couette-type apparatus, we were able to show that a layer of polyethylene, approximately 1–2 μm thick when dried out, was built up on the rotor surface. This buildup did not occur uniformly but only began after some incubation time. We proposed then that this effect was due to the buildup of small network particles during the initial stages of stirring which became attached to the rotor surface as one or more of the molecules involved in the network was adsorbed onto the surface. A similar mechanism can be used to explain the observations in this work. We divide the viscosity–time curve up into a number of segments (Figure 9) and discuss these separately. In region 1 we see a sudden increase in apparent viscosity with time; the small peak occurring in region 1, also seen in Figures 1, 2, 4, and 5, is an artifact caused by the inertia of the mechanical measuring device[24] and should not be associated with the theoretical predictions referred to above.[17-20] In region 2 the apparent viscosity is unchanged with time. We therefore suggest that in this region no discernible changes occur within the solution and we are measuring the viscosity of the polymer solution. In region 3 the viscosity starts to rise, and by the end of it the solution will form a gel when cooled. We therefore suggest that this corresponds primarily to the building up of network particles as we described previously.[1] We expect these network particles to start to stick to the inner and outer surfaces and, consequently, reduce the Couette gap and increase the apparent viscosity—this is what we believe occurs in region 4. As the gap is progressively reduced, so the shear stress on the adsorbed network particles increases. Eventually either the network will grow right across the gap or the shear stress on the adsorbed material will be so great that it will start to break up—this corresponds to the peak. N.B.: Using this model, we would expect the peak height to depend on the strength of the network and therefore the strength of any subsequent gel.) Now the network starts to break up and the apparent viscosity falls (region 5). However, it cannot be completely destroyed; otherwise the solution would lose its ability to gel. We propose that the adsorbed network now breaks up into particles which become homogeneously distributed throughout the solution and eventually reach an equilibrium distribution as reflected by the constant apparent viscosity—region 6.

We stated earlier in the Introduction that a curve of shear stress as a function of stirring time, showing features similar to those presented here, has been previously reported by Pennings,[7] although he did not correlate it with the particular type of gelation we have described. The mechanism he proposed is similar to that given above except that he envisages the complete destruction of the network in what we have termed region 5.

We may now examine the results of our study in the light of the model we have proposed. The model suggests several experiments, one of which is to stop the stirring in region 6 and to wait for various times before starting to stir again. If during the period of storage without stirring at the elevated temperature the particles have redissolved, this should be reflected by both a reinstatement of the original apparent viscosity–time curve, complete with its maximum, and the ability of the solution to gel when cooled. Figure 4 shows the result of one such experiment. There are several salient features in this figure. First, there is an overall tendency to lower apparent viscosities at longer times. We suggest that this is probably caused by degradation of the longest molecules (caused either mechanically by the stirring action or by the elevated temperatures used). Second, there is a change in the shape of the curves. The curve measured after 35 min of storage time shows a fairly constant value of apparent viscosity during stirring, with no peak (the slight hint of peak discernible at long stirring times is in fact within our experimental error). At longer storage times we begin to see the development of a peak although it is not until the longest storage times that we observe as clear a peak as we observed in the initial stirring experiments. We would, therefore, suggest that during the storage process network particles are progressively destroyed and that it takes 4 h at 124 °C to destroy them all. However, if a substantial number of them are redissolved, these dissolved molecules will form new particles on restirring as evidenced by the reemergence of the peak in Figure 4. A second experiment is to stop the stirring in region 3 or 4 for a short period and then restart, thus examining the stability of the original network particles prior to any breaking up. The result of the one such experiment is given in Figure 5. We see that after the resting periods the shear stress monitored by the viscometer falls slowly and rises quickly on restarting. There is no evidence for any significant breaking down of the particles within the time scale of the experiment, though there does appear to be evidence for an increase in the peak height if this prodcedure is followed. We propose that during the resting periods the few least stable network particles (i.e., those with the lowest number of junctions) are destroyed, which would not significantly affect the observed shear stresses. If on renewed stirring the initial gel particle distribution established itself again in the solution (i.e., nongel) portion of the system, the net result would be an overall increase of the number of stiffer network particles as compared to those created under conditions of continuous stirring; this would lead to a higher peak, as described above.

We now turn our attention to observations on the melting of gels. We have previously argued that the gels form on cooling by a process of coalescence of preexisting network particles due to crystallization. We have examined the structure of these gels, once formed,[1] and found that they consist primarily of shish kebab crystals with very large platelet overgrowths, plus some unattached platelets. However, none of these can exist in the initial network particles, since the temperature at which these particles are formed is far too high to form single crystals or even shish kebabs. The gels therefore have a different structure from the preexisting network particles, and great care must be exercised when comparing experiments on the melting of gels with the experiments on the destruction of the network particles after they have been cooled to form a gel.

Nevertheless, it is interesting to compare the results in Figure 6 and 7. In Figure 6 we plotted the time required to destroy the memory of stirring (i.e., to destroy most of the network particles formed by stirring) as a function of temperature, and in Figure 7 the time required to dissolve wet gels as a function of temperature. These two curves are surprisingly similar and suggest that the structure of the gel at these high temperatures may have reverted to that of the network particles. The DSC results in Figure 8 show two sharp peaks and one broad peak at a higher temperature. The two sharp peaks are probably due to the melting of platelet crystals (double peaks are often seen due to annealing during heating[25] and the broad peak is very similar to that seen in dry shish kebabs and is associated with the melting of the cores). However, as far as we know, there is no previous work on the melting behavior of shish kebabs surrounded by their mother liquor. The similarity of the memory effects of the gels of Figure 6 and 7 and the DSC results of Figure 8 allow us to speculate on the nature of the network junction zones as they are formed during shearing. The results quoted above strongly suggest that these junctions have a crystalline nature. Accordingly, we postulate that these may be localized regions of the flow field where the shear rate is sufficiently high to extend portions of the molecules. Such extended chain portions may then form crystals on coalescence with other locally extended chain portions nearby.

To summarize: We believe the work presented here shows that when solutions of high molecular weight polyethylene are stirred, network particles which can lead to gels on subsequent cooling are formed even at temperatures as high as 140 °C and concentrations as low as 0.2% (w/w). These particles once formed, although of a temporary nature, are nevertheless remarkably stable. They persist for as long as 5 h at 120 °C and as long as 0.75 h at 150 °C as can be seen in Figure 6. A gel once formed and reheated is even more stable as evidenced by Figure 7. Similar results have been reported for other polymers, and these may have the same underlying causes. If this were so, our work on polyethylene would correspond to a special case within a phenomenon of more overriding validity. This possibly special case has the advantage that we know that polyethylene does crystallize and we are familar with the temperatures of formation and melting of its various crystals morphologies. In any event, within its more confined limits, the relevance of the present results to crystallization, gelation, and fiber formation of polyethylene, the subject of our initial interest, remains upheld.

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Measurement of Diffusion in Polymer Films by Fluorescence Redistribution after Pattern Photobleaching

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ABSTRACT: Fluorescence redistribution after pattern photobleaching has been used to measure the translational diffusion of a small probe molecule in a glassy polymer film. A new method has been developed employing a pattern mask with submicron dimensions to allow very slow diffusion ($D \approx 10^{-13}$ cm^2/s) to be measured on a convenient time scale. The diffusion coefficient of a fluorescent dye, 7-(diethylamino)-4-nitrobenz-2-oxa-1,3-diazole, in a 1-μm-thick film of poly(methyl methacrylate) containing approximately 18% residual solvent (chlorobenzene) was found to be $D = 1.6 \times 10^{-13}$ cm^2/s at 25 °C.

Introduction

Recent progress in theories to describe the dynamics of polymer melts and concentrated solutions[1,2] challenges the experimentalist to make measurements of molecular dynamics in these regimes. A few experiments have already provided validation for scaling laws within certain limits.[3-5] There are many questions yet to be answered about molecular dynamics in these systems,[6] and new measurements

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