

## Polyethylene: A Multicomponent Alloy

Paul H. LINDENMEYER

*Polymer Sciences Laboratory, Boeing Scientific Research Laboratories,  
Seattle, Washington 98124, U.S.A.*

(Received November 5, 1971)

**ABSTRACT:** In exploring the analogy between crystalline polymers and metallic alloys it becomes necessary to allow for the differences in size and anisotropy of the crystallizing entity. As a consequence of the size and anisotropy of crystalline polymers their diffusion constant is several orders of magnitude smaller than metals. The anisotropy of the polymer molecule also gives rise to a tertiary or intramolecular nucleation process which does not occur in metals. The dispersion of molecular lengths which is common in high polymers makes it necessary to compare even the purest polymer with a multicomponent alloy. The combination of low diffusion constants and the tertiary nucleation process gives rise to a multitude of metastable equilibrium states as well as kinetically inhibited transitions which tend to complicate the phase diagrams. Nevertheless when all of these factors are considered it is possible to qualitatively account for much of the observed structural behavior of crystalline polyethylene by direct analogy to multicomponent metal alloys.

**KEY WORDS** Polyethylene / Phase Diagrams / Nucleation /  
Multiple Melting Points / Alloys /

A polymer molecule differs from a metallic atom in at least three important aspects. In the first place the polymer molecule is  $10^3$  to  $10^6$  times as large as the metal atom. In the second place its length to width ratio falls in the same range (*i.e.*,  $10^3$  to  $10^6$ ). This anisotropy is by far the most unusual feature of a polymer molecule and its responsible for most of the unique properties of high polymers. The third aspect which we shall consider here is the fact that polymer molecules are almost never available as pure materials. By a pure material in this case we mean one in which substantially all the molecules are identical. Even if the polymerization reaction is a "clean" one which has no possibilities of branching or misplaced chain substituents there still will exist a distribution of chain lengths. The sharpest molecular weight fraction or the so-called "mono dispersed" polymers made from "living" chain catalysts contain hundreds of slightly different molecular length chains. Such preparations are frequently considered to be chemically pure but when one considers the packing of such molecules into a crystal lattice it is immediately apparent that their physical differences in length are important

and one has the problem of growing mixed crystals—not the crystallization of a pure material.

The principle thesis of this paper is that if one properly takes into account these three important differences, then the structure and properties of a completely crystallizable homopolymer such as linear polyethylene are not unlike those of a multicomponent metallic alloy.

One might reasonably ask, even if we are successful in developing a complete analogy between polymers and metals and can satisfactorily explain all of the differences, what is the advantage? My answer to this lies in the use of phase diagrams. The metallurgist has a tremendous advantage over the polymer chemist or physicist because he can sketch a phase diagram of his alloy and predict not only phase changes but composition, fine structures, micro- and macro-segregation and the accompanying changes in physical properties which go with such structural changes. Even in a complicated multicomponent alloy effects can be illustrated qualitatively on a pseudobinary phase diagram. A pseudobinary phase diagram shows the effect of varying the composition of one component in a multicomponent alloy while the other components main-

tain the same ratio. If one adds to the pseudo-binary diagram the possibility of drawing various metastable or kinetic phase diagrams then one can illustrate many of the same things for high polymers that the metallurgists do for alloys. Thus the objective of this paper is to try to make available to the high polymer physicist some of the methods which have long been used to advantage by the metallurgist.

#### MOLECULAR SIZE AND DIFFUSION RATE

As mentioned earlier one of the most obvious differences between a polymer molecule and a metal atom is the size. This difference in size manifests itself in a number of ways but perhaps the most readily apparent way is the effect upon the diffusion rate. The diffusion of polymer molecules in the liquid state have been discussed by a number of authors<sup>1</sup> and we shall not repeat or even summarize their results here. For our purposes all we need is the conclusion that the diffusion rate constant for a polymer molecule is inversely proportioned to the number of segments in the polymer molecule in the event that molecular entanglements can be neglected. If the concentration is such that entanglements cannot be neglected the effective number of segments is increased. Thus for purposes of comparison between polymers and metals we can say that the diffusion constant of the former are  $10^3$  to  $10^6$  times smaller than the latter as a direct consequence of molecular size and flexibility. As we shall see this difference in diffusion constants can be used to explain a number of differences between polymer and metallic structures. For example, it has been shown<sup>2</sup> that the crystal growth front in a metallic alloy will break up into a number of cells each having the approximate diameter of the so-called "characteristic diffusion distance" given by

$$\delta = D/G$$

where  $D$  is the diffusion constant and  $G$  is the crystal growth rates. This same expression has been used<sup>3</sup> to explain the structure of spherulites. In general the cell sizes in metallic alloys range from a few microns to hundreds of microns whereas the crystallite size in crystalline polymers ranges from a few angstroms to hundreds of

angstroms. Since the growth rates observed in polymers and metals are not greatly different, this difference in size can be directly attributed to the difference in diffusion rates.

Consequently, the first major point to remember in comparing polymers to metals is that the diffusion rate constants of the former are three or four orders of magnitude smaller than the latter. This factor alone accounts for many of the major differences in the observed structure of crystalline polymers and metals (*e.g.*, why metal alloys crystallize in the form of dendrites and polymers in the form of spherulites).

The characteristic diffusion distance,  $\delta$ , is an approximation to the dendrite arm spacing. When this spacing becomes very small, the dendrite becomes a spherulite.<sup>3</sup> Figure 1 shows spheru-

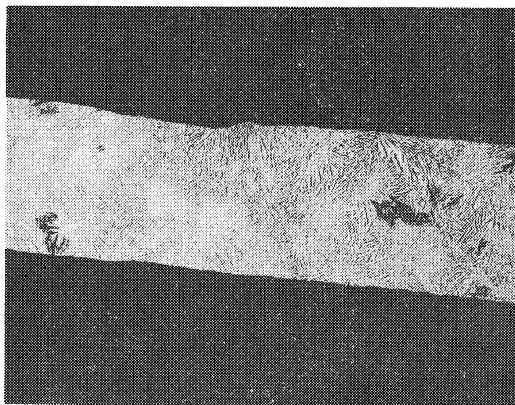
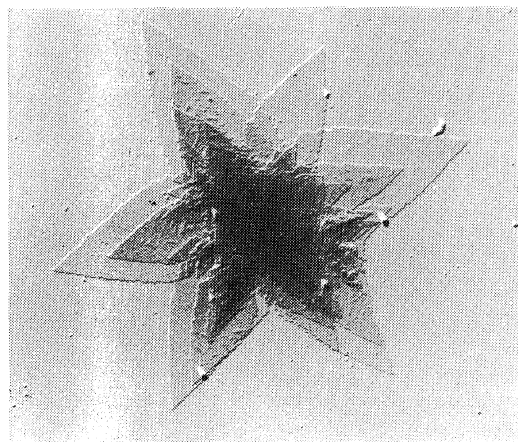


Figure 1. Spherulites in an aluminum—15% iron alloy cooled at  $10^4$  degrees per second.

lites grown in an aluminum—15% iron alloy where the cooling rate was approximately  $10^4$  degrees per second. Here the low value of  $\delta$  was obtained by greatly increasing the crystal growth rate rather than decreasing the diffusion constant as is the case with polymers. Similarly it is possible to grow dendrites in polymer crystallization when the diffusion rate is increased sufficiently by diluting with a solvent, see Figure 2.

#### NUCLEATION PROCESSES

The second major difference between polymers and metals is the anisotropy of the former compared with the isotropy of the latter. This anisotropy has a great many aspects and it will



**Figure 2.** Polyethylene dendrite grown from dilute solution.

not be possible to even mention many of them in this paper. However, we will be concerned with an attempt to show how the anisotropy of the polymer molecule can explain why polymers, in contrast with metals, do not crystallize from the melt in the vicinity of their melting temperature even when suitable crystalline nuclei are present.

When a metal alloy is cooled below its liquidus temperature, crystallization begins almost immediately unless care has been taken to remove heterogeneous nuclei and to isolate the melt from container walls. With sufficient care it is possible to cool an alloy below its liquidus temperature—sometimes as much as a few hundred degrees. However, as soon as solidification begins it proceeds very rapidly and the latent heat of fusion which is released is sufficient to raise the temperature back to the equilibrium melting point. This is not the case with crystalline polymer. Here, even in the presence of seed crystals it is necessary to lower the temperature 10–15°C below the melting point and then crystallization proceeds at a very slow rate. The latent heat of fusion which is released does not raise the temperature and if the temperature is raised by some external source the crystallization process slows down or even stops completely. The explanation of this phenomenon is in the nucleation processes which must occur during the crystallization of a polymer molecule.

Nucleation processes have been studied in

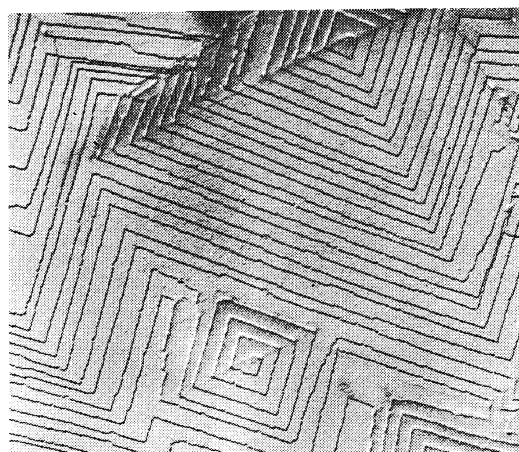
various system by a number of workers for many years. As a result a number of different methods of classification have arisen and since it is my purpose to add still another type it is necessary to review some of the previous classifications. In the transformation from one phase to another the essential driving force is the difference in free energy between the initial and the final phase. However, when the first small particles of the final phase begin to form, their free energy is somewhat higher due to the fact that those atoms located at the transition region do not have the same environment as those in the interior. Thus the first very small particle of the new phase, called the nucleus, requires a somewhat higher driving force for its formation than does the transformation after the nucleus has grown large enough for its surfaces to be neglected. The formation of the first small particle of a new phase we shall call primary nucleation and it must be present in all phase transitions from liquid to solid.

Primary nucleation may be further classified into heterogeneous or homogenous nucleation depending upon whether or not a third phase (impurity or container surface) takes part in the process. In general one can distinguish between heterogeneous and homogenous nucleation by the fact that heterogeneous nuclei form and begin to grow immediately when the temperature is lowered to the sufficient degree of supercooling, whereas homogenous nuclei form sporadically with time as a consequence of random thermal fluctuations. Unfortunately the above is not conclusive evidence since certain heterogeneities may simply catalyze nucleation with the final nucleus requiring thermal fluctuation and hence occurring randomly with time. Also there exists the possibility of athermal nucleation in which very small particles of the new phase (embryos) which are unstable at one temperature may be promoted to stable nuclei upon sudden cooling. Strictly speaking, such athermal nuclei are homogenous nuclei but since they begin to grow immediately upon cooling they may be confused with heterogeneous nuclei.

In crystallization one can encounter a somewhat different type of nucleation which we prefer to call secondary nucleation. This type of nuc-

leation occurs when a large perfect crystalline surface is exposed to liquid or vapor. In order that crystallization continue, it is necessary that a monolayer nucleus must first form on the surface of the crystal. This nucleus can then increase in size until the whole monolayer is completed and then a new secondary or two-dimensional nucleus must form. This secondary nucleation process requires a driving force in the form of a free energy difference between the liquid or vapor and the crystal. For many years the problem in metallic crystallization was to explain why this driving force was so low or apparently nonexistent. Crystals could be grown at the melting point or with only a very small fraction of a degree of supercooling. All estimates of the driving force necessary for second nucleation were much higher. The explanation for this apparent lack of a secondary nucleation process in metallic systems came with the discovery of the growth screw dislocation and other crystal imperfections which permit the continuous growth of an edge or step to build up the crystal face perpendicular to the screw dislocation.

In the crystallization of polymers we have almost the opposite problem. Very large supercooling is required for secondary nucleation and this process has been extensively investigated in an attempt to explain the chain folding phenomena. However, in spite of the fact that growth screw dislocations have been clearly observed in polymer crystals, (see Figure 3) growth does



**Figure 3.** Spiral growth dislocations in polybutene-1 grown from dilute solution.

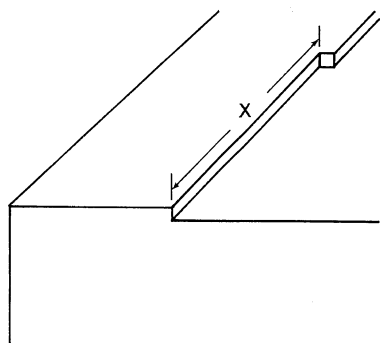
not occur unless supercooling of some 10–15°C exists. This suggests that there may exist still a third nucleation process in polymer crystallization which must be overcome before crystallization can occur even in the presence of crystal nuclei with a suitable self-perpetuating edge around a screw dislocation.

The usual way of approaching the problem of nucleation is to treat the very small nucleus in exactly the same way as one would a macroscopic mass. The transition region between the crystal nucleus and the liquid is considered to be a geometric surface and is assumed to have an excess surface energy. The mass of the nucleus is assumed to undergo a free energy change equivalent to that in the interior of a large mass. This is obviously a gross simplification since there is no reason to believe that the surface energy appropriate to a nucleus only one molecule in thickness is the same as the surface energy appropriate to a macroscopic particle. Nevertheless, this approach seems to yield results which have proven to be quite useful in the past. In the case of crystallization in the presence of a self-perpetuating edge, the classical approach would predict no tertiary nucleation.

#### TERTIARY NUCLEATION

The origin of the tertiary nucleation does not lie in the classical approach to the problem but one must take into account the unique of the long flexible polymer molecule. As with any other molecular or atomic solid its melting point is defined as that temperature at which the liquid has the same free energy as the crystalline solid.

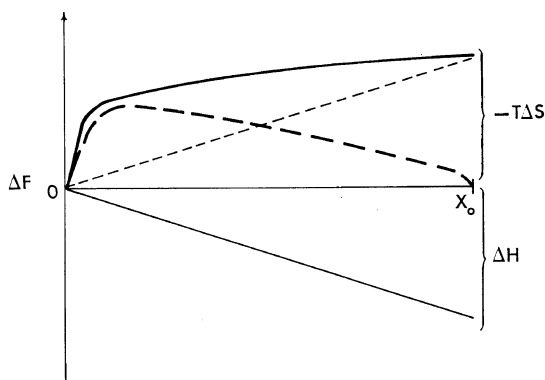
According to the well known principles of classical nucleation theory a crystal nucleus having a growth edge as depicted in Figure 4 should grow even at the equilibrium melting since no new surfaces must be created. The tertiary nucleation process arises from the fact that, although enthalpy decreases approximately linearly with the number of segments of the molecule which have crystallized, the entropy does not change linearly. In other words, even though the free energy of the molecule in the liquid is exactly the same as the free energy of the molecule in the crystalline state, crystallization will not occur because in the process of changing from a ran-



**Figure 4.** Ideal nucleus for crystallization of an extended chain molecule of length  $X$

dom coil conformation in the liquid to the extended chain conformation in the crystal, the molecule must assume conformations which have a higher free energy than either the liquid or the crystal.

This effect has been shown most clearly by Zachman<sup>4</sup> who points out that the number of conformations available to a molecule which is attached to a crystal face is less than the number available to a free molecule in the liquid due to the large excluded volume to the crystal. Similarly Flory<sup>5</sup> has pointed out the entropy change for pairing of chain ends which is required in order to adopt results derived from considerations of an infinite chain to the finite chain lengths found in practice. In transforming from liquid to crystal the molecule decreases its enthalpy linearly with the number of segments which take on the conformation of the crystal. However, we cannot assume that entropy also decrease linearly with the number of molecular segments which have entered the crystal. The entropy decreases much faster than the enthalpy as the molecule begins to crystallize and thus the free energy goes through a maximum of exactly the same kind which is associated with a nucleation process. The effect is illustrated qualitatively in Figure 5. A quantitative evaluation of this maximum depends upon whether one follows the methods of Flory,<sup>5</sup> Zachmann<sup>4</sup> or Peterson and Lindenmeyer<sup>6</sup> and at the present writing there is some reason to question all of these methods. However, qualitatively there can be no question but that the entropy is more or less drastically decreased at the beginning of crystallization and it does not approach the linear



**Figure 5.** Free energy as a function of number of molecular segments which have crystallized, illustrating the origin of the maximum in free energy.

extrapolation line until the last few segments enter the crystal. As a consequence the free energy change for the transformation of a molecule from liquid to crystal at the melting temperature as a function of number of segments in the crystal begins and ends at zero but undergoes a maximum during the process. Thus in order for molecule to transform from liquid to crystal at the equilibrium melting temperature, even in the presence of a crystal with an edge so that no excess surface generation is required, it must still adopt molecular conformations having free energies which are higher than either the crystal or the liquid. Consequently, crystallization of polymer molecules does not occur at the melting point even in the presence of "ideal" crystalline nuclei. A driving force of supercooling is necessary and each molecule must undergo an "intramolecular" or "tertiary" nucleating process. Since nucleation is always a relatively slow process compared to growth it follows that on the average each polymer molecules will complete its crystallization before the next molecule begins.

This tertiary nucleation process is unique to high polymers and follows directly as a consequence of the long chain flexible nature of the polymer molecule. Its existence permits us to understand why polymers require such high degrees of supercooling and why they do not heat up to their melting point once crystallization does begin.

This requirement that each polymer molecule undergo a nucleation step before it can crystallize and the associated high degree of supercooling required adds to the probability that crystallization of polymers may occur in non-equilibrium or metastable equilibrium forms.

In addition to the free energy barrier resulting from the nonlinear change in entropy with the number of segments in the crystal, we can also make an argument for crystallization occurring one molecule at a time on the basis of rate of energy transfer. The kinetic energy of the molecule must not only supply any activation energy necessary to cause nucleation but it is also the source of the latent heat of crystallization. Thus the process of crystallization consists primarily in the transformation of kinetic energy of the molecule into heat which must be absorbed by the surroundings. The kinetic energy of a long chain molecule consists of translational, rotational and vibrational energy. The frequency for each of these processes is roughly an order of magnitude faster than the preceding one (*i.e.*, vibrational processes are about 100 times faster than translational). Suppose we imagine the wall of a container to be a heat sink and we further suppose that the wall plays no other role in the crystallization process. One of the molecules having segments near the wall will be the first to have one of its segments translate into thermal contact with the wall. We wish to compare the probability that this single molecule will transfer sufficient kinetic energy to the wall so that it can by itself form a nucleus (obviously it will be a folded-chain molecule) with the probability that say ten molecules will translate to the wall, lose one tenth of the necessary energy and then translate into the proper position to form a bundle-like nucleus composed of portions ten molecules. It would seem that since rotational and vibrational transitions are much faster than translational transitions the first process would be appreciably faster than the latter. The same reasoning can be applied in the formation of secondary and tertiary nuclei. Thus there are purely kinetic reasons to expect polymer molecules to crystallize one molecule at a time. Once a molecule begins to crystallize it can proceed much faster than a neighboring mole-

cule which is not yet attached to the crystal because it can make use of rotational and vibrational processes to transfer energy whereas the unattached molecule must await the relatively much slower translational process.

#### PHASE DIAGRAMS

A phase diagram is a plot of temperature versus composition upon which lines are drawn to separate various phases (crystalline, liquid, etc.). The simplest binary phase diagram occurs when the two components crystallize into the same crystal structure and form a continuous series of solid solutions as illustrated in Figure 6. Such

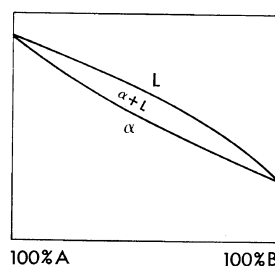


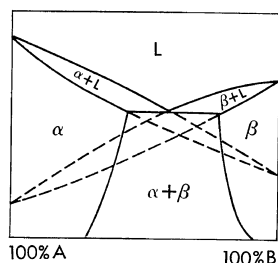
Figure 6. Simple binary phase diagram with complete solubility.

a simple phase diagram is composed of two lines separates liquid from solid and the lower solidus line separates solid from liquid. The region between these two lines represents compositions and temperatures in which a liquid may exist in equilibrium with a solid. The composition of the liquid and the solid which can exist in equilibrium is given by the horizontal tie line.

In textbooks on high polymers one frequently finds statements to the effect that "a crystalline polymer differs from a polycrystalline low-molecular-weight solid in that it shows evidence of a very broad melting range rather than a sharp first-order transition." Metallic alloys are "polycrystalline low molecular weight solids" and they also exhibit a broad melting range (from the solidus to the liquidus line in the phase diagram). The essential point here is that everyone apparently compares crystalline polymers with pure low molecular weight materials. This is not a valid comparison since as indicated in the introduction polymers are not pure materials but have

many different components (*i.e.*, molecular lengths).

Moving on from the simple solid solution case in Figure 6 the next most complex situation is where component B can form a somewhat different crystal  $\beta$  which is higher melting than the  $\alpha$ -crystal when B is present in high concentration. This situation is illustrated in Figure 7 which



**Figure 7.** Binary phase-diagram with solubility gap or eutectic.

shows a binary alloy which forms two different solid solution regions and a miscibility gap (or eutectic) in the solid solution. The dotted lines show how this phase diagram is related to the simple continuous solid solution case in Figure 6.

There are of course many and much more complicated phase relationships which may be encountered in alloys systems but these two will suffice to illustrate all the effects we require in this paper. Rather than illustrate more complicated effects we turn now to the difference between equilibrium phase diagrams, metastable equilibrium phase diagrams and kinetic phase diagrams. Unless otherwise specified it is generally assumed that a phase diagram is an equilibrium phase diagram (*i.e.*, it is assumed that the phase indicated would be those which exist when equilibrium has been attained.) This is not always the case and to illustrate some alternative possibilities we shall consider an example from metallurgy (*i.e.*, the iron—carbon diagram).

#### METASTABLE OR KINETIC PHASE DIAGRAMS

When iron which contains small quantities of carbon is cooled under normal conditions it undergoes a well-known eutectoidal transition of 723°C in which austenite ( $\gamma$ -iron) decomposes into

pearlite (a mixture of ferrite ( $\alpha$ -iron) and cementite ( $\text{Fe}_3\text{C}$ )). This is the transition which is normally shown on phase diagrams for steel since it is the transition which occurs under the cooling rates normally encountered in practice. However, it is well known that this is not an equilibrium transition since  $\text{Fe}_3\text{C}$  is thermodynamically less stable than iron and graphite. Consequently if steel is annealed for long periods of time between 723°C and 738°C it decomposes into  $\alpha$ -iron and graphite. Thus the true equilibrium phase diagram would show a horizontal line at 738°C marking the transition of  $\gamma$ -iron to an iron + graphite and cooling must occur extremely slowly in order to observe a transition at 738°C. Thus we can have metastable equilibrium diagrams as well as equilibrium diagrams. Finally, if steel is cooled rapidly the transition at 723°C can be displaced to significantly lower temperatures. Thus we can have equilibrium phase diagrams, metastable equilibrium phase diagrams and kinetic phase diagrams. The difference between metastable and kinetic phase diagrams being due solely to the rate of temperature change whereas the difference between equilibrium and metastable equilibrium involves a structural difference which was caused by the rate of temperature change.

In order that an alloy may be formed strictly in accordance with the deductions which may be made from the equilibrium phase diagram, it is necessary to assume complete diffusion in both the solid and the liquid. For example, as the melt for a given composition alloy is cooled to the point where it crosses the liquidus line, solid alloy will form which has the composition given by a horizontal tie-line to the solidus curve. As the temperature falls the composition of the liquid changes along the liquidus line and the composition of the solid changes along the solidus line. For complete equilibrium, additional solute must dissolve into the solid. Under normal conditions of melt casting this cannot occur rapidly enough to maintain complete equilibrium throughout the casting. Thus for fairly rapid cooling a reasonable "nonequilibrium" condition is to assume that no diffusion occurs in the solid but that the equilibrium concentrations are maintained at the interface between the solid and the melt. Thus if the solidus line is taken to re-

present the "average" solid composition then in a "kinetic" phase diagram the solidus line must be shifted towards reduced concentrations of solute in the solid, (*i.e.*, solubility is decreased as illustrated in Figure 8). On the other hand it is possible that cooling can occur with sufficient speed so the diffusion in the liquid also limits attainment of equilibrium. In this case since the composition of the liquid is richer in solute than that of the solid, a departure from equilibrium conditions sufficient to restrict diffusion in the melt would enrich the solid and cause the solidus curve to move in the opposite direction as illustrated in Figure 9.

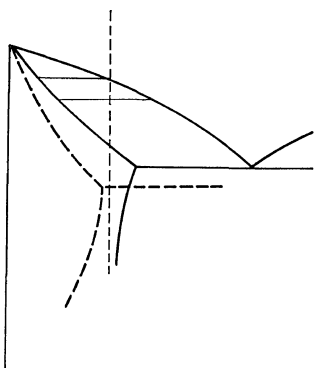


Figure 8. Deviation from equilibrium in which solubility is decreased.

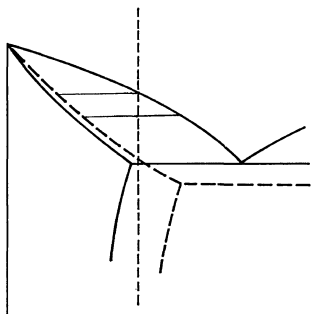


Figure 9. Deviation from equilibrium by very rapidly cooling so that solubility is increased.

In either event the eutectic temperature is depressed—and in the latter case the solubility limit is increased—sometimes even to the point of completely suppressing the eutectic structure. Thus for certain compositions a rapid cooling

can form a eutectic or two-phase structure as a departure from equilibrium but at still greater departure can increase solubility and eliminate the two-phase structure.

#### MULTICOMPONENT PHASE DIAGRAMS

In order to compare a high polymer such as polyethylene with an alloy we must use a multicomponent alloy not just a binary alloy. Unfortunately we cannot draw phase diagrams for multicomponent alloys. However, considerable progress can be made with the use of a pseudobinary phase diagram. A pseudobinary phase diagram is one which shows the variation in composition of one component with the assumption that all other components retain their same ratio. To be specific we can illustrate the pseudobinary phase diagram by considering a vertical crosssection through a tertiary phase diagram. The tertiary phase diagram can be visualized as a three-dimensional plot with composition being plotted in a triangular diagram and temperature along the mutually perpendicular axis. (Figure 10).

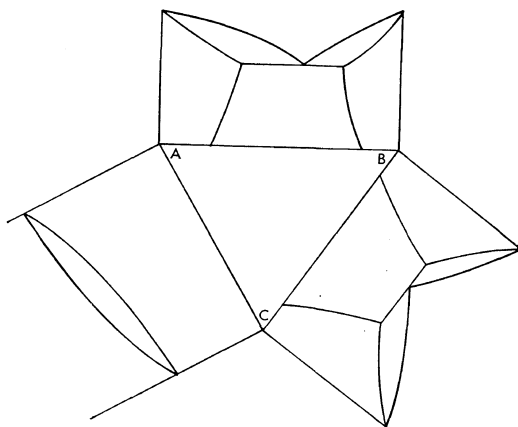


Figure 10. Ternary phase-diagram with the accompanying three binary diagrams.

Let us assume a ternary alloy consisting of components A, B, and C in which A and C form solid solutions in all proportions but in which there exists miscibility gaps (eutectics) in the two binary systems AB and BC. Let us further assume that there exists only two different crystal structures  $\alpha$  and  $\beta$  so the A and C crys-



tallize in all proportions into crystal  $\alpha$  while B crystallizes into structure  $\beta$  with only a limited amount of A and C. The phase diagram for such a system may be visualized by means of Figure 10 which shows a triangle with the three binary phase-diagrams layed out on its respective sides and by Figure 11 which shows an isometric drawing of the solid diagram.

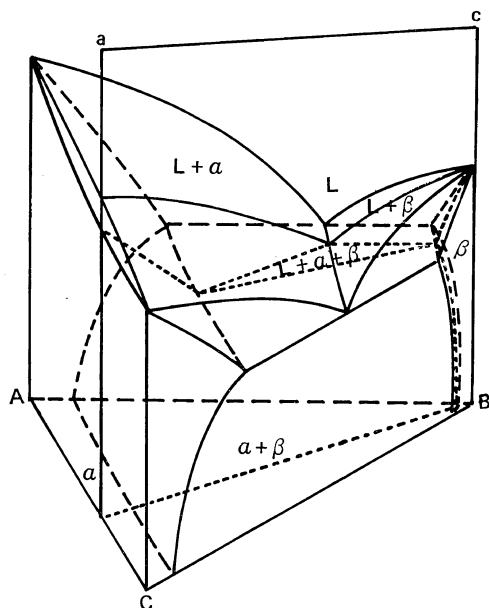


Figure 11. Three-dimensional ternary phase-diagram.

Now consider a vertical crosssection through such a phase diagram. Such a crosssection [ $a-c$ ] represents the complete variation in component B from 0—100% with the ratio A/C remaining fixed at the ratio established at point  $a$ . This vertical crosssection (Figure 12) is an example of a pseudo-binary phase diagram. It differs from a true-binary diagram in two important aspects. In the first place the liquidus and the solidus do not converge at the composition  $B=0$  since there still exists two components A and C so that the composition of the liquid and the solid need not be identical as they would be in a single-component material. Secondly, and most importantly, the eutectic line connecting the most soluble  $\alpha$ - and  $\beta$ -crystal is broadened into a triangular temperature and composition

region in which both  $\alpha$ - and  $\beta$ -crystals can exist in equilibrium with the melt. A ternary alloy with a composition which falls into this region will exhibit two melting ranges which corresponds to the melting of the  $\alpha$ - and  $\beta$ -crystals.

## POLYETHYLENE

In order to illustrate the application of such a phase diagram to polyethylene let us assume that instead of a continuous distribution of molecular lengths we have only three. Let us further associate the very long molecules with component A and the very short molecules with component B and those of average size with component C. Thus in the ternary diagram we assume that the  $\alpha$ -crystal represents a folded-chain crystal which can accommodate any composition of long and average length molecules but only a limited amount of short chain molecules. The  $\beta$ -crystal is the extended-chain crystal which can accommodate unlimited amounts of short chains but only a limited amount of average or long chains. (In the case of an actual polymer, one would have many different components all soluble in the  $\alpha$ -crystal and instead of one  $\beta$ -crystal there would be a whole series of extended-chain crystals. Nevertheless the three components already described permit illustration of some important principles).

If the composition of our hypothetical three-component polyethylene is such that it falls into the region where both  $\alpha$ - and  $\beta$ -crystals can exist in equilibrium with liquid, then it should exhibit two melting points corresponding to the melting of the two different kinds of crystals (*i.e.*, folded-chain and extended-chain). According to the diagram either the  $\alpha$ - or the  $\beta$ -crystal might be the lower melting crystal depending upon the actual composition. If one varied the composition, one could cause variation in melting temperature of the two different crystals and even effect a crossover between the crystal which had the lowest and the highest melting temperature. Alternatively, instead of varying the composition it is possible to conceive of a series of metastable equilibrium diagrams similar to Figure 12 with the lines shifted in such a way as to effect the same results. By changing the heating and cooling rates one can change the particular

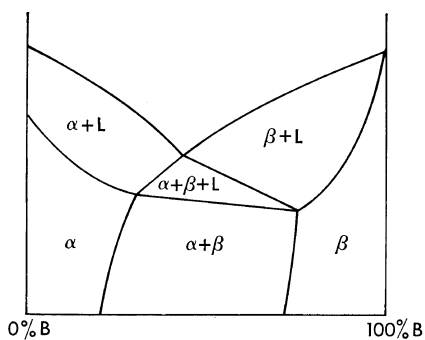


Figure 12. Crosssection through Figure 11.

metastable diagram which should apply and thus qualitatively account for the double melting phenomena which have been observed.

Thus it seems that at least qualitatively one can account for the observed melting behavior of polyethylene by considering it to be a multi-component alloy capable of existing in a series of metastable equilibrium states which depend upon the heating or cooling rates. Furthermore,

these conclusions have been reached by appealing only to the physical attributes of the polyethylene molecule (*i.e.*, size and anisotropy) which are common to all polymer molecules. Consequently, one could apply the same reasoning to any polymer molecule subject only to such modifications as might be necessary by the chemical nature of the polymer.

#### REFERENCES

1. F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York, N.Y., 1962.
2. J. W. Rutter and B. Chalmers, *Can. J. Phys.*, **31**, 15 (1953).
3. H. D. Keith and F. J. Padden, *J. Appl. Phys.*, **34**, 2409 (1963); **35**, 1270 (1964).
4. H. G. Zachmann and P. Spellucci, *Kolloid-Z.*, **213**, 39 (1966).
5. P. J. Floy and A. Vrij, *J. Amer. Chem. Soc.*, **85**, 3548 (1963).
6. J. M. Peterson and P. H. Lindenmeyer, *Makromol. Chem.*, **118**, 343 (1968).