

MORPHOLOGY OF AMORPHOUS POLYMERS AND EFFECTS OF THERMAL AND MECHANICAL TREATMENTS ON THE MORPHOLOGY

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ABSTRACT

This report covers the experimental evidence of order and structure in three polymers, namely non-crystallizable atactic polystyrene (including amorphous isotactic polystyrene), crystallizable polyethylene terephthalate in its glassy amorphous state, and natural rubber in its near molten state. All the available evidence from diffraction and microscopy studies strongly indicate that there is a liquid-crystal type chain packing order contained within a nodular structure of limited size ($\sim 100\text{\AA}$) present in all three polymers. Effects of annealing and orientation give further support to the structure evidenced in the original polymer. The kinds of models which have been proposed for the amorphous state of polymers have also been discussed in order to clarify further the meaning of order in amorphous polymers and the presence of truly disordered regions.

INTRODUCTION

Considerable study of the morphology of crystalline polymers in the past decade or so has led to the development of the chain-folded lamella as a basic structural unit for both the undeformed¹ and deformed² polymers. Although there are still numerous questions concerning, e.g., the presence or absence of a truly amorphous phase inbetween the lamellae,³ the regularity of the fold structure,⁴⁻⁷ and the origin and extent of interlamellar links,⁸ the recognition of this basic, lamellar structural unit in crystalline polymers has led towards a much better understanding of the physical and mechanical properties of crystalline polymers.

In contrast, little is known concerning the morphology of amorphous polymers or polymers in their amorphous states (glassy, melt or solution). Clearly a better understanding of their morphology should also lead to a better description of the stress-strain behaviour of polymers in their rubbery state; a clearer understanding of ductility, crazing, and yielding behaviour of polymers in their glassy state; as well as possibly answering some of the questions raised earlier concerning the morphology of crystalline polymers.

A much more extensive review on the morphology of amorphous polymers has been written and will be published shortly.⁹ In this report we wish to review experimental evidence of order and structure in three polymers, namely noncrystallizable atactic polystyrene (APS) (including some results on crystallizable

isotactic polystyrene (IPS)), crystallizable polyethylene terephthalate in its glassy amorphous state and natural rubber in its near-molten rubbery state. The effects of thermal and mechanical treatment on the original amorphous morphology will also be presented to the extent that these effects are directly related to the original structure in the amorphous state of the three polymers. A brief review of the various models suggested so far for the amorphous state of polymers will also be included, hopefully to serve as a base for further experimentation and clarification of this controversial subject.

RANDOM COIL MODEL

Until recently, the random-coil model has been generally accepted by most polymer scientists as a fairly accurate description of the conformation of macromolecules in their amorphous state. This is schematically represented in *Figure 1*. In addition to the assumed total absence of order of any kind

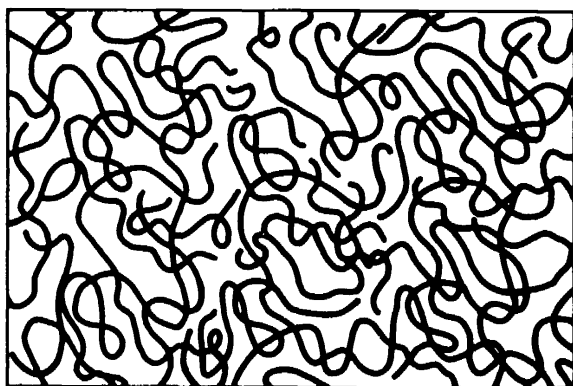


Figure 1. Schematic drawing of the random-coil model¹⁵.

(including 1- or 2-dimensional), the single-phase model assumes numerous chain entanglements and a great deal of free volume. Being statistical in character, the model has been very useful in the original derivation of the molecular theory of rubber elasticity. Although the limited applicability of this theory is known and has been pointed out from time to time, the questioning of this theory has only been taken seriously in recent years. The more successful and recent molecular theories by Guth¹⁰ and Blokland¹¹ have been developed by taking into consideration the presence of structure in rubber networks. Other suggestions which indicate the incorrectness of the random-coil model have come from the effects of solvents on the depolarization of light scattered from *n*-alkane solutions,¹² on the strain birefringence of swollen polymer networks,^{13, 14} and on the comparison of densities between calculated (based on the assumed random coil model) and experimental values of various polymers in their amorphous state.¹⁵

PRELIMINARY REMARKS ON TECHNIQUES

Evidence of order in amorphous polymers can be derived from analysis of x-ray or electron diffraction patterns either through the well-known Fourier analysis of the experimental scattering curves or through comparison between the experimental intensity function and a theoretically derived intensity function based on some assumed model. Indication of possible order may also be derived from semi-quantitative analysis of oriented (and/or thermally treated) and unoriented diffractions of the same amorphous polymer, this being the least time-consuming of the three methods of analysis.

A more direct technique capable of detecting order and/or structure in the so-called "amorphous" materials is done in an electron microscope using either dark field diffraction contrast or phase contrast microscopy. The Fourier analysis is then carried out automatically by the lens system, provided that the instrument has the resolution capable of detecting the size of the ordered region or the lattice spacing within a given ordered region. Neither the dark field nor the phase contrast technique has been used to any great extent to derive structural information on amorphous polymers, although the use of such techniques in studies on carbons has provided very informative data, e.g. ref. 16.

To date most of the electron microscope studies on amorphous polymers have been on shadowed or stained samples. With virgin specimens the contrast is mainly based on thickness contrast principle.

The evidence of order and/or structure in the three polymers which we have chosen for this lecture comes chiefly from our own studies, based primarily on electron microscopy and electron diffraction, and some on x-ray diffraction techniques. Whenever appropriate, comparisons with available data by others on the same or similar polymers will also be made.

POLYSTYRENE

Amorphous polystyrenes (atactic or isotactic) exhibit at least four diffuse rings in x-ray or electron diffraction patterns. An example is shown in *Figure 2*, which is taken of an unoriented pattern. The corresponding Bragg spacings (9, 4.78, 2.23 and 1.26Å) of these four rings are also indicated in the figure. The 4.78Å ring is the most intense of the four. The next most intense is the 9Å ring, followed by the 2.23 and 1.26Å rings. The 2.23 and 1.26Å rings can be easily assumed to result from intramolecular scattering. The distances between the C₁-C₃ and C₁-C₂ within the molecule are about 2.23 and 1.26Å. The origins of the 9.0 and the 4.78Å peaks have been elucidated by Krimm's study of oriented polystyrene.¹⁷ In the oriented pattern, of which an example is given in *Figure 3*, Krimm showed that the 9.0Å ring and the 4.78Å ring split into arcs and orient along the equator and the meridian respectively with essentially no changes in *d*-spacings. The split in the 4.78Å ring is barely detectable in *Figure 3*, as in most cases. Krimm concluded that the 9.0Å ring is intermolecular in origin, arising from scattering of atoms in neighbouring chains and that the 4.78Å ring is at least due to two different types of interatomic scatterings: those between atoms in alternate phenyl groups in the same chain and those between atoms in phenyl groups and main chain atoms in neighbouring chains.

Radial distribution curves of polystyrene have been obtained by Bjornhaug, Ellefsen and Tonnesen¹⁸ and by Kilian and Boueke¹⁹ from x-ray studies. Since no comparisons were made between the experimental distribution curves and theoretical radial distribution curves calculated from models of chain packing or from x-ray curves of crystalline polystyrenes, no definite conclusions were reached with respect to the possible packing order of polystyrene molecules in the solid state. However, Bjornhaug *et al.* did point out that the intensities of the

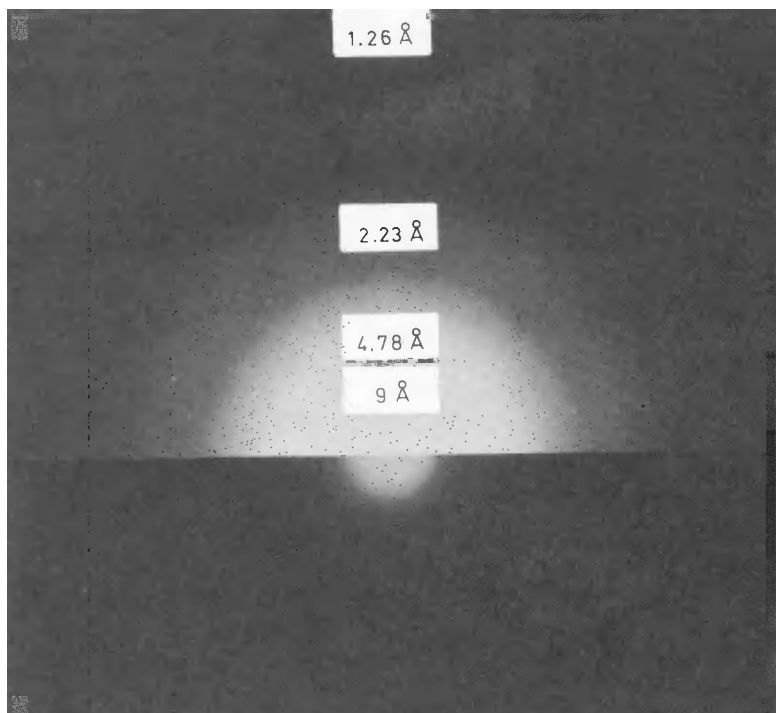


Figure 2. A typical electron diffraction pattern of fresh amorphous isotactic polystyrene. Atactic polystyrenes show similar 'amorphous' patterns²².

two experimental peaks, one at about 5Å and the other at about 10Å , were much higher than expected from a randomly packed chain structure, but that they could arise if neighbouring chain segments were assumed to have a parallel packing over some extended distance. 10Å is about the average intermolecular distance in polystyrene. (Therefore the very strong peak in the radial distribution curve at about 10Å can also explain the location of a diffuse ring with a corresponding d -spacing of about 9Å in the diffraction pattern).

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The suggestion of an orderly packing of polystyrene chain segments by Bjornhaug *et al.* was later verified by Katada's detailed electron diffraction studies of *p*-Cl-, *p*-Br-, and *p*-I-derivatives of atactic polystyrene.²⁰ Katada showed that the experimental intensity curves agreed very well with intensity

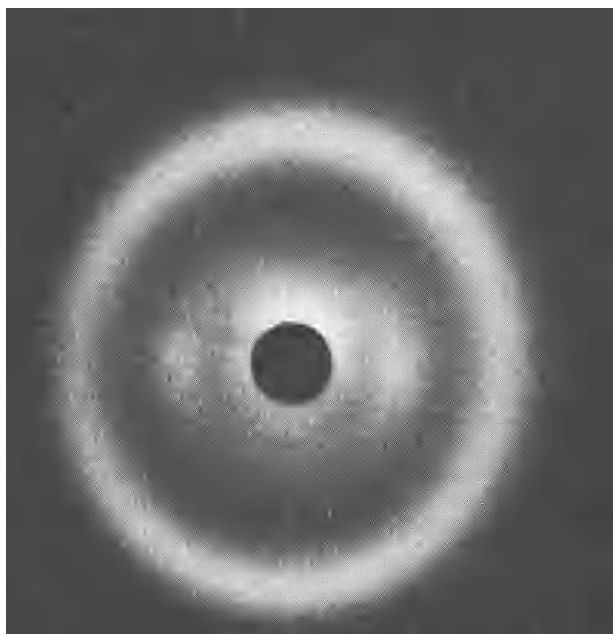


Figure 3. x-ray diffraction pattern of oriented amorphous polystyrene. Stretch direction vertical.

curves calculated from models which assumed an orderly packing of the styrene segments along the chain as well as a regular arrangement of the nearest neighbour styrene segments on neighbouring chain segments. In the assumed models the Cl-Cl, Br-Br and I-I distances between the 1st and 3rd phenyl rings were 4.84, 4.85 and 4.93Å respectively. This also indicates that the 4.78Å diffuse ring in the diffraction pattern is at least partially intramolecular in origin. The parallel chain packing indicated by Katada's studies can also give rise to a chain-to-chain distance of about 9 to 10Å. Furthermore, one finds from molecular model studies that the distance between atoms in phenyl groups on neighbouring chain segments also comes to about 5Å, suggesting that the 4.78Å diffuse ring can be due to intermolecular scattering as well.

The above analysis indicates that the molecules or segments of molecules in ordinary (atactic) polystyrene are packed with some order, nearly parallel to one another. Such ordered regions should reveal themselves in dark field electron micrographs. It also suggests that if such order is disturbed, e.g. upon crosslinking with fast electrons,²¹ the disturbance can be directly monitored in the diffraction pattern. Such studies have been carried out recently and the results will be summarized below.

Ordered regions as revealed by electron diffraction²²

First I would like to describe some changes in the diffraction patterns observed when freshly prepared thin films of atactic (three molecular weights: 4 800, 51 000 and 1 800 000) or amorphous isotactic polystyrenes were irradiated with increasing amounts of 80 kV electrons. *Figure 4* gives an example

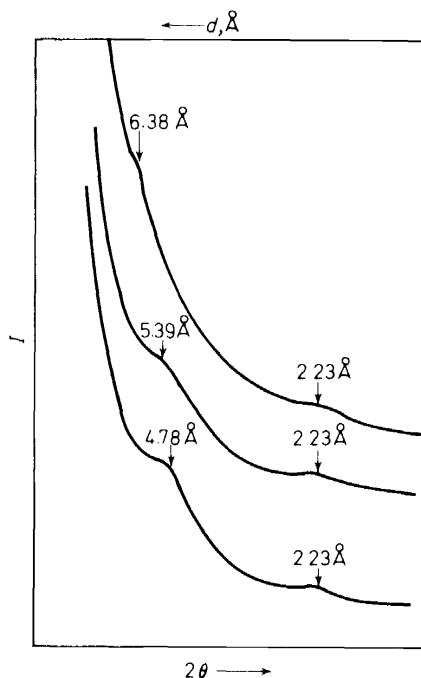


Figure 4. Densitometer tracings showing the changes in the 4.78 and 2.23Å maxima as a function of increasing crosslinking from bottom to top²².

of such changes in densitometer tracings. The major changes occur in the 4.78Å ring; changes in the 9Å ring were not monitored because of its closeness to the main beam and because of its much weaker intensity to begin with. Not only does the location of the 4.78Å ring change, corresponding to an apparent increase in d -spacing from 4.78 to 6.38Å with increasing time of exposure to the electrons (increasing degree of crosslinking), but there is also evidence of increasing line broadening as well as a decrease in intensity (after correction for the background scattering). These changes appeared permanent upon reexamination. No detectable changes, either in intensity, d -spacing, or line profile were observed in either the 2.23Å or 1.26Å rings.

The observed effects of electron irradiation clearly indicate that the 4.78Å ring arises from some kind of liquid-crystalline chain packing existing in amorphous polystyrenes. The ordered chain packing can be disturbed upon crosslinking by electron irradiation. The increase in disordering of the paracrystalline lattice results in the expected broadening of the peak, the expected shift of the peak position towards the main beam, as well as the expected decrease in peak intensity. Such changes are not expected to occur if the diffuse ring is due

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to interference caused by rigid particle scattering, as indeed was found to be the case with the 2.23\AA and the 1.26\AA rings, which are intramolecular in origin.

The findings were similar regardless of the molecular weight of the atactic polystyrene used. The same results were obtained with the isotactic polystyrene, MW 550 000. An exception was noted in the case of MW 4 800 atactic polystyrene, in that the 4.78\AA peak appeared to be somewhat sharper than those observed in others; the 2.23\AA and the 1.26\AA rings remained about the same as those found in other polystyrenes.

Size of ordered regions as revealed by dark field electron microscopy²²

Next I wish to describe some high resolution dark field studies that were

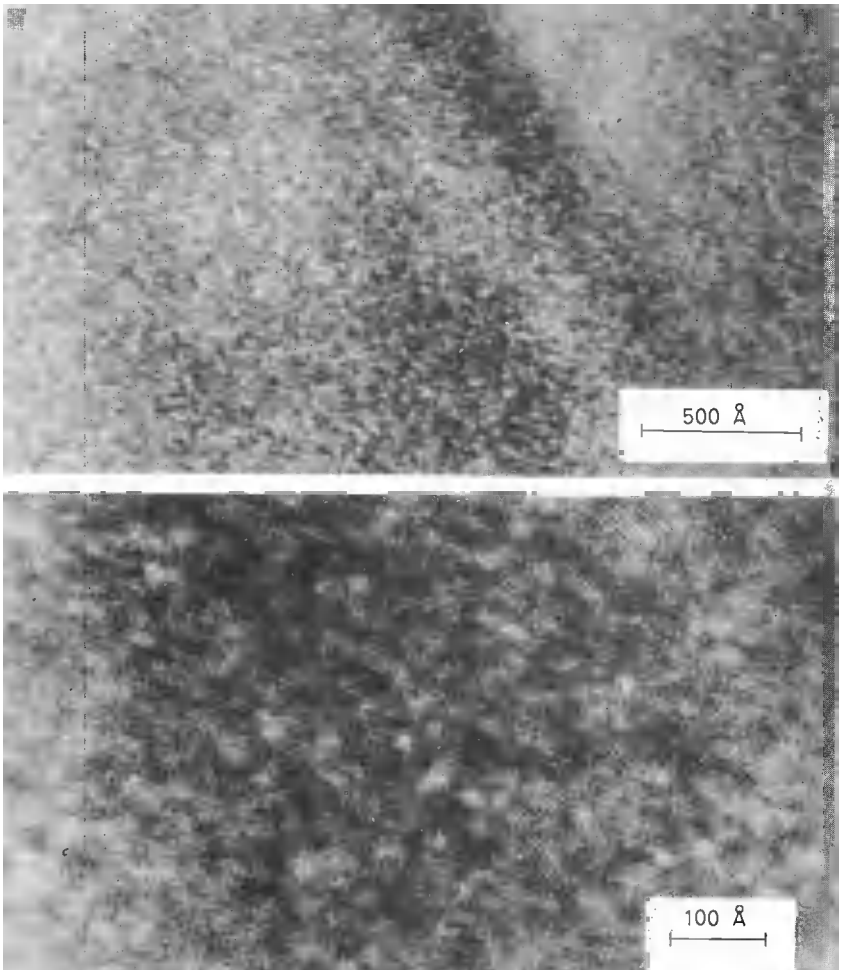


Figure 5. Dark field electron micrograph of an unshadowed thin film of atactic polystyrene (M.W. 1 800 000)²².

carried out on all the polystyrenes by using a portion of the 4.78\AA ring to project the image. The experiments were carried out in a Phillips electron microscope equipped with a beam tilt device and tested to have a resolution of better than 10\AA . The results confirm the presence of ordered regions suggested earlier from our own analysis of the changes in diffraction patterns (caused by increasing disordering of the ordered regions) and from analysis of diffraction studies carried out by others.

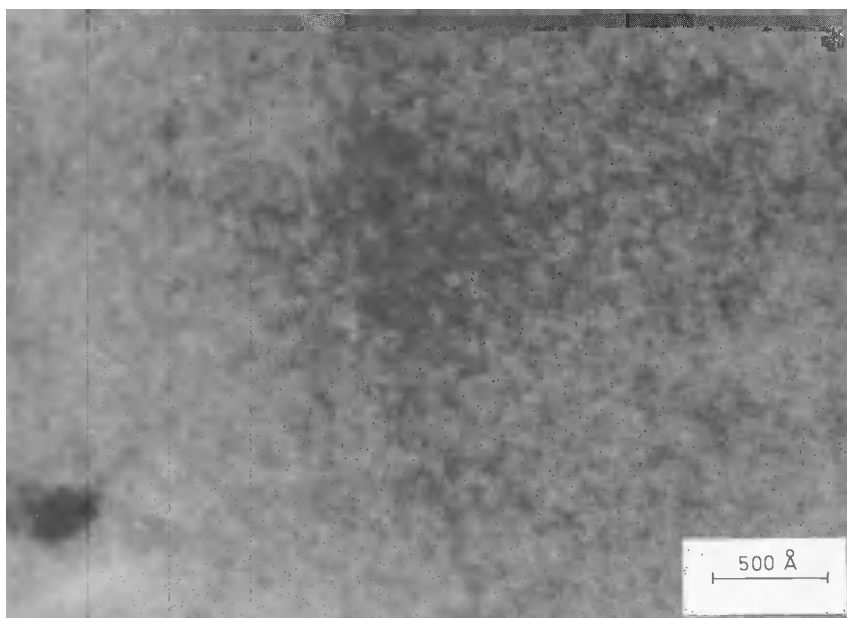


Figure 6. Dark field electron micrograph of an unshadowed thin film of amorphous isotactic polystyrene²².

Examples of dark field images obtained from two unshadowed amorphous polystyrenes, an APS of MW 1 800 000 and an IPS of MW 550 000, are shown in *Figures 5 and 6*. The ordered regions are readily observable as sharply defined, brightly diffracting spots against a relatively uniform dark field produced by background diffuse scattering. The size of ordered regions, averaging from some randomly selected diffracting regions in the dark field image, is about 27\AA for both types of polystyrene. Many "larger" ordered regions (~ 50 to 100\AA in size) can also be seen in the amorphous isotactic specimen. However, these "larger" regions are primarily caused by the tendency of the basic ordered regions to agglomerate, resulting in the apparent increase in size.

Nodular texture as revealed by shadowing technique²³

Carefully shadowed thin film specimens were made from several atactic

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polystyrenes of MW 4 800, 19 800, 51 000, and 1 800 000 and one isotactic polystyrene of MW 550 000, all of which showed a typical nodular texture (*Figure 7*). The nodules are much more distinguishable in an oriented specimen



Figure 7. Unstretched thin film of atactic polystyrene, Pt-shadowed.

(*Figure 8*). Many of the nodules can also be seen behind the shadows, thus removing the possibility that the observed nodules are due to the granulation of the shadowing material used. The size of the nodules is surprisingly similar



Figure 8. Thin film of atactic polystyrene stretched 100% on Mylar, Pt-shadowed.

regardless of the MW of the polystyrene used, or about 30\AA . In the only other work available for comparison, Schoon²⁴ reported some variation in size for his tertiary structure in stained thin films of various molecular weight polystyrenes. Two average sizes were reported. One was about 30\AA for structures seen in polystyrene with MW 8 000 and the other was about 45\AA in polystyrene with MW 700 000. A diameter of 45\AA gives an equivalent MW of only 40 000. Therefore we can conclude from both Schoon's studies and ours that high MW polystyrenes are expected to have molecules consisting of several of these nodular (or tertiary) structures with tie molecules running between them; whereas for low polystyrenes, a single nodule may consist of several molecules with fewer, if any, tie molecules between the nodules.

Changes in the nodular texture during annealing²⁵

Atactic polystyrene showed very little visible change, if any, when annealed

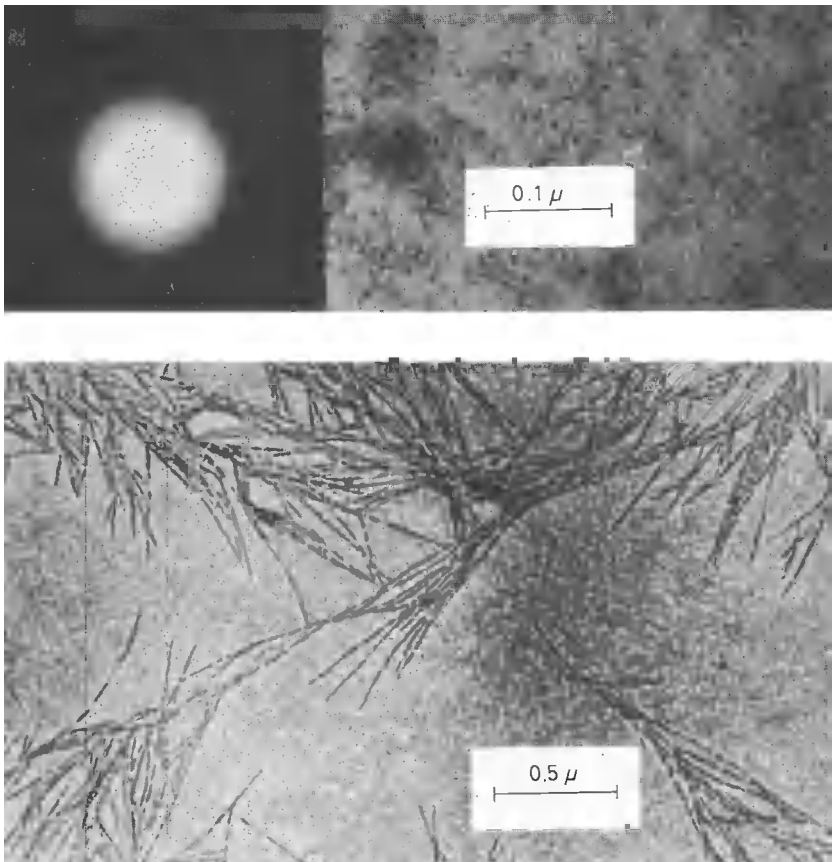


Figure 9. Bright field electron micrographs of an unshadowed, solution cast thin film of isotactic polystyrene after annealing at 125°C for one hour. The insert shows an electron diffraction pattern obtained from an area similar to the one shown on the right³⁵.

below or above T_g . This was expected since the polymer is noncrystallizable. Consequently isotactic polystyrene was used. Unlike polyethylene terephthalate²⁶ or polycarbonate^{27, 28} which showed a tendency for the nodular structures to aggregate or grow in size, isotactic polystyrene showed hardly any visible changes when annealed below T_g . On the other hand, distinct changes were detected when IPS was annealed above T_g . An example is given in *Figure 9*. The various stages of transformation from a nodular to a spherulitic texture are clearly discernible in this micrograph. Other results showed that the nucleation of a spherulite appears to begin with the crystallization of a liquid-crystal like nodule, or a group of nodules merging together to form a few fibrils, which eventually fan out from the nucleus by additional incorporation of maturing nodules.

POLYETHYLENE TEREPHTHALATE (PETP)

The major publications concerning the presence of order and/or structure in the amorphous state of this polymer are by Yeh and Geil²⁶ on the glassy state of PETP and by Ermolina *et al.*²⁹ on the molten state of PETP.

I wish to summarize their findings in the following.

Order as revealed by electron diffraction²⁹

Ermolina *et al.* analysed the electron diffraction patterns of PETP that were obtained at temperatures above and below the melting point of the polymer by means of Fourier analysis. They found that the experimental radial distribution curves are similar, each containing several maxima. The one at 4.45Å found in both crystalline and melt specimens was assigned as intermolecular in origin, due to scattering between atoms in neighbouring molecules which they suggested have a parallel packing arrangement. The size of the ordered region was not mentioned, nor could it be determined from their data. The disordered region was not mentioned either; but presumably it belonged to the boundary region surrounding the clusters of parallel molecules.

Ordered region as revealed by electron microscopy²⁶

Yeh carried out experiments on unshadowed thin films of glassy PETP (MW 15 000) at room temperature using bright field and dark field techniques. An example of a pair of bright field and dark field electron micrographs taken of the same area is shown in *Figure 10*. Regions of fair contrast of about 100Å which indicate the presence of order and/or structure can be seen in both micrographs. The dark field micrograph was obtained by using a portion of the innermost, which is also the most intense, diffuse ring with a Bragg spacing of 4.5 Å. The diffracting regions are suggested to have a paracrystalline packing of aligned chain segments with a constant chain-to-chain distance of about 4.5 Å.

In a shadowed specimen a distinct nodular texture was detected (*Figure 11*), the average size of the nodules being about 75Å. These structures are present in both bulk and thin films, and have been confirmed in a separate study by Klement.³⁰ The nodules have a fairly distinct boundary, indicating the majority

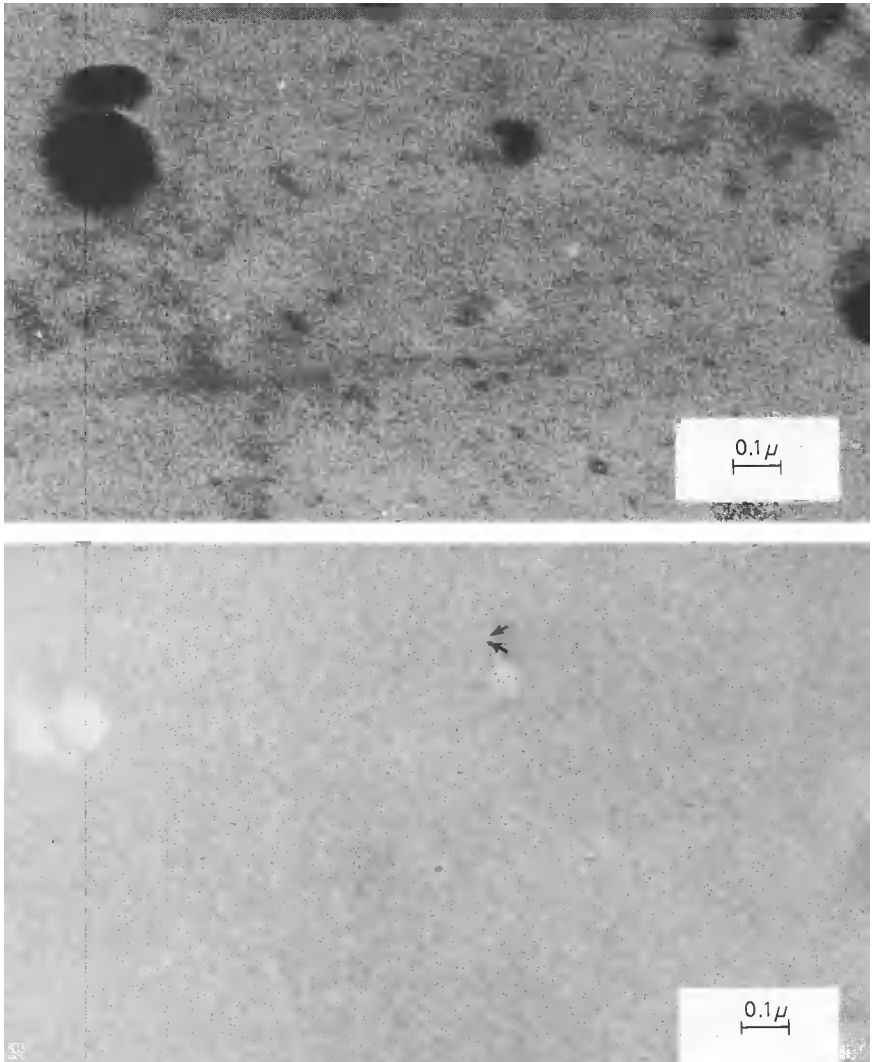


Figure 10. Bright field (top) and dark field (bottom) electron micrographs of an unshadowed thin film of amorphous polyethylene terephthalate.²⁶

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of chain segments being essentially contained within a given nodule. This, together with the parallel packing of aligned chain segments as indicated from dark field studies, would suggest the presence of some fold-backs at the nodular boundary, since the molecules are longer than the diameter of the nodules.

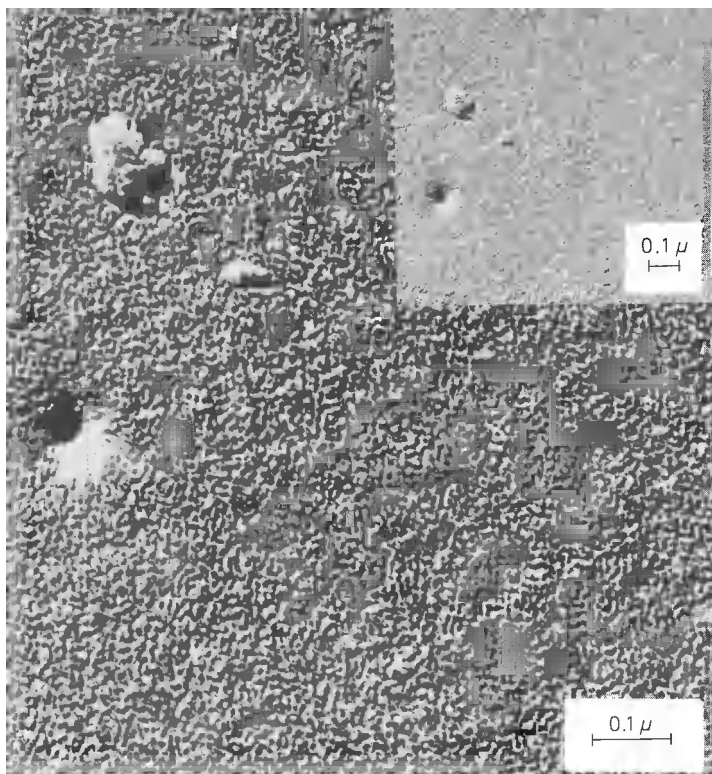


Figure 11. Surface replica of amorphous bulk polyethylene terephthalate showing the presence of nodular structures²⁶.

Upon annealing at temperatures about 10°C below T_g (T_g of PETP is about 65°C), a slight sharpening of the 4.5 \AA ring could be detected in the electron diffraction pattern. It became sharper when the sample was annealed at 60°C , indicating an increase in intermolecular order, that is, an increase in the packing order between parallel chain segments within the nodules. Other changes occurred in the morphology of the annealed specimens. Numerous aggregates (500 to 1000 \AA in size) of nodular structures (Figures 12 and 13) resulted throughout the annealed specimens. This suggests that a substantial amount of

molecular motion is occurring even at temperatures below T_g . These observations are to some extent similar to those reported by Frank *et al.*,³¹ Carr *et al.*,²⁷ and by Siegmann and Geil²⁸ for glassy polycarbonate upon annealing at

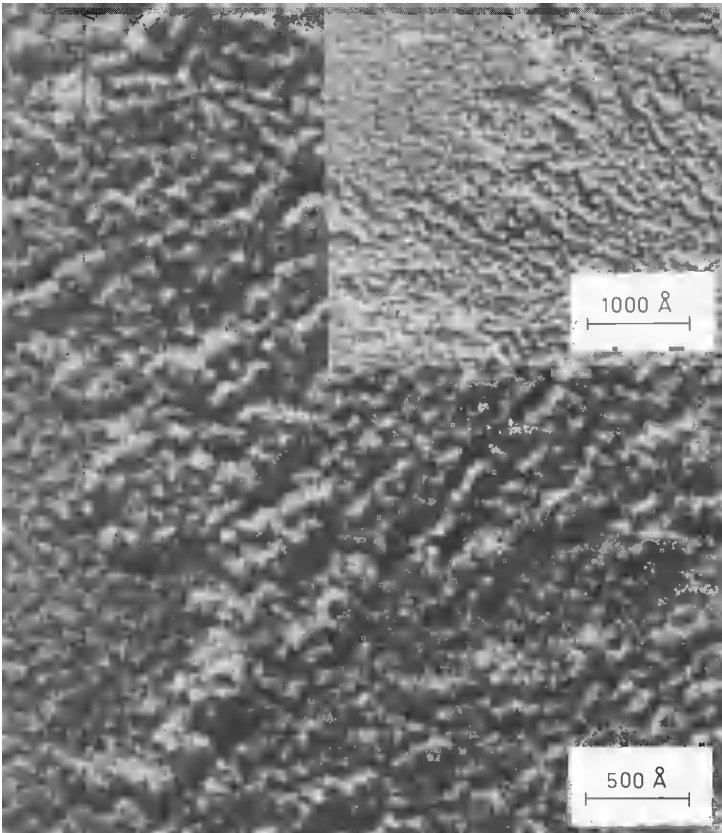


Figure 12. Surface structure of amorphous PETP after annealing at 56°C for 4 days²⁶.

temperatures below T_g . Whether this onset of nodular movement can be related to the onset of T_g in most polymers in mechanical relaxation remains to be seen.

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The nodular structures were again much more distinct in oriented specimens prior to heat set (*Figure 14*), after heat set at 260°C (*Figure 15*) and after heat set and restretch on a substrate (*Figure 16*). It is of interest to note that after restretching the heat-set specimen, the 3-dimensional order became destroyed, reverting back to a 2-dimensional smectic-type liquid-crystalline order originally present after the initial stretch.³²

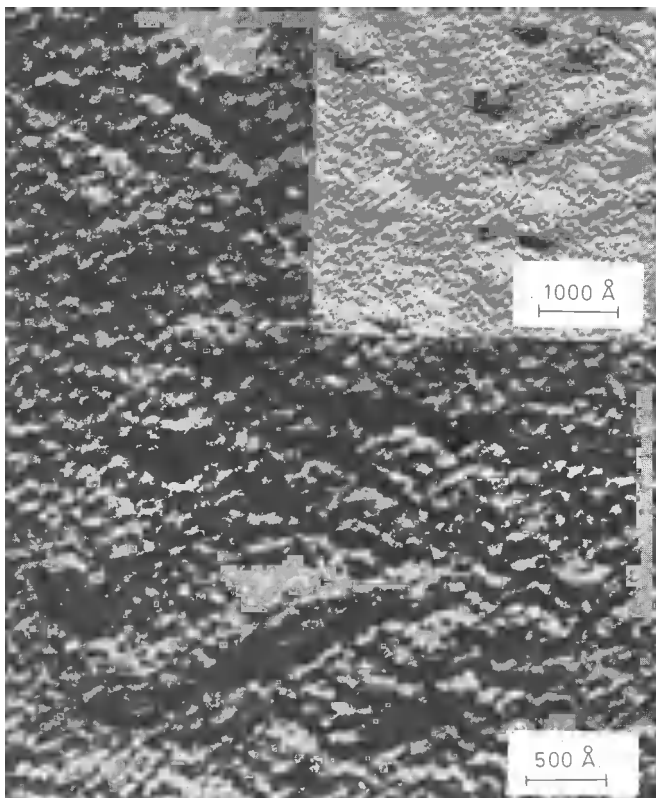


Figure 13. Surface replica of amorphous bulk PETP after annealing at 60°C for 6 days²⁶.

We concluded from these experiments that glassy amorphous PETP has a nodular texture; the nodules have a liquid-like crystalline order prior to thermal or mechanical treatment.

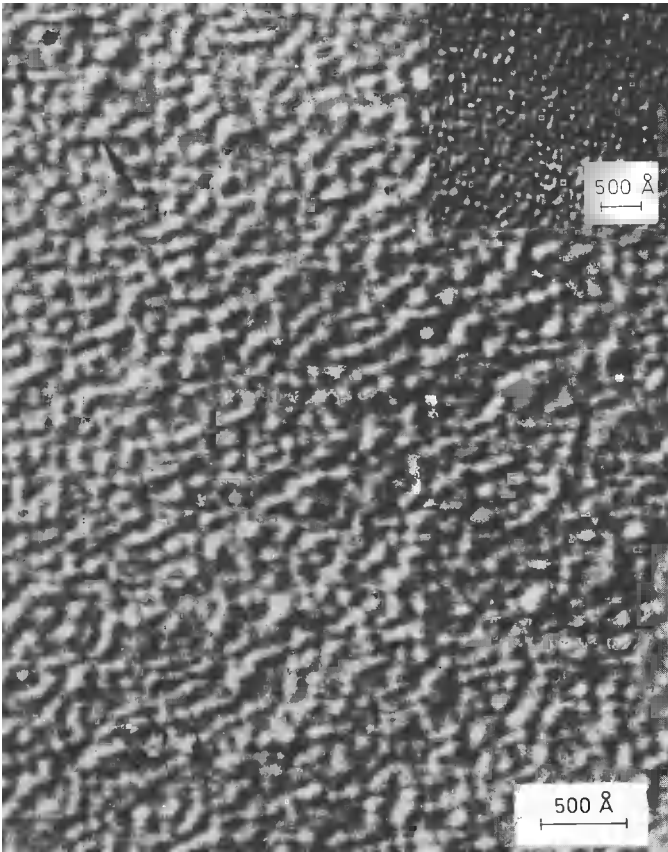


Figure 14. Thin film of PETP drawn at 65°C to 6 times its original length. The arrow indicates the draw direction³².

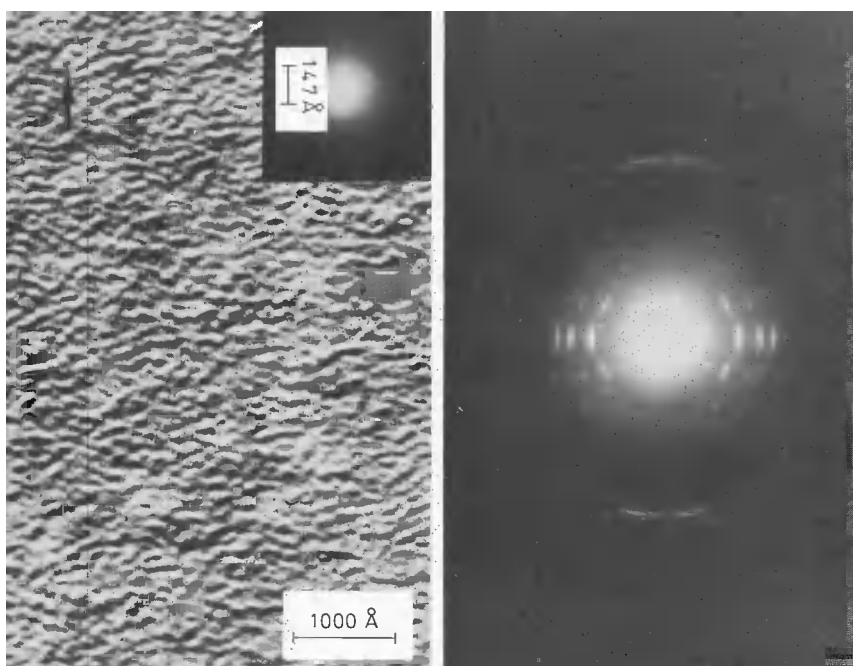


Figure 15. Stretched thin film of PETP after heat setting at 260°C for 15 minutes³².

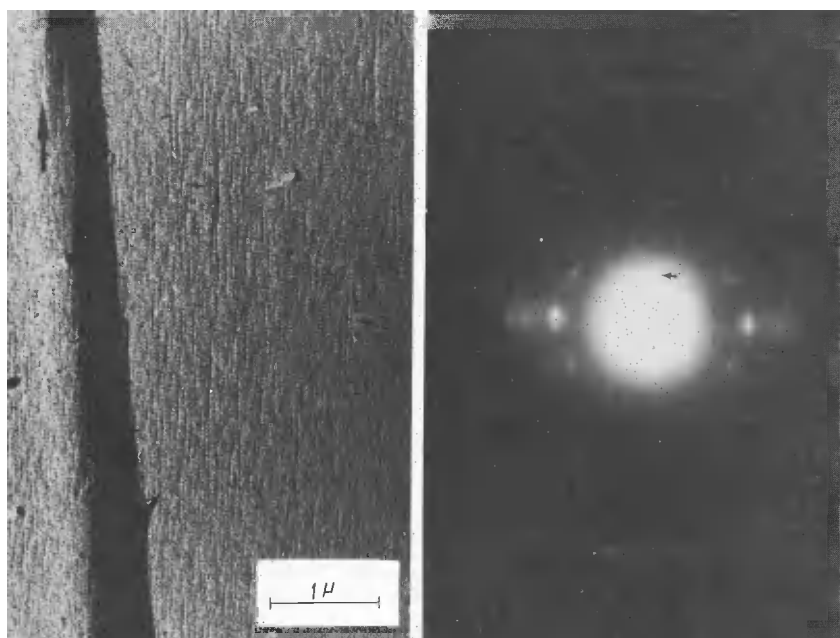


Figure 16. A heat-set stretched thin film after postdrawing 100% in a direction parallel to the original stretch direction³².

NATURAL RUBBER

Next to polyethylene, natural rubber is probably the second most investigated polymer. Yet very little is known concerning its morphology at room temperature in its most employed state.

Because of its high molecular weight (in the millions), it remains strong without crosslinking in its near-molten state at room temperature (T_m of natural rubber is about 25 to 28°C). Consequently structural studies can be conveniently carried out at room temperature in its amorphous molten state.

Structural order as revealed by diffraction techniques³³

Most of the x-ray diffraction studies on natural rubber have been on stretched, crystallized samples. Simard and Warren³³ are probably the only ones to have analysed in detail the x-ray diffraction of unstretched natural rubber obtained at room temperature by the radial distribution method. They showed that the corrected experimental intensity curve contained one very intense peak at $\sin \theta/\lambda = 0.104$ and two other much less intense peaks (at $\sin \theta/\lambda = 0.22$ and 0.41 respectively); the latter two are generally accounted for by intramolecular scattering of the carbon atoms, C_1-C_2 and C_1-C_3 . The intensity of the innermost one was about 7 to 10 times the outer two. (The origin of this peak is still considered to be unknown; its intensity, however, generally decreases with increase in orientation and finally disappears altogether upon further cooling in 'fully' crystallized stretched natural rubber.³⁴ The measured crystallinity for a 'fully' crystallized natural rubber is, however, seldom more than 30 to 35 percent).

In the radial distribution curve obtained by Simard and Warren, at least four peaks at $r = 1.52, 2.68, 4.0$ and 5.0\AA were observed. The first three were attributed to the first, second and third neighbour carbon atom distances. The location of the fourth peak was explained by its high intensity (concentration) due to an atom's nearest carbon neighbours in other chains, i.e., the distance from a carbon atom in one molecule to the first concentration of carbon atoms in neighbouring molecules which is about 5\AA . This high concentration of scattering, as pointed out by them, is responsible for the very strong peak at $\sin \theta/\lambda = 0.104$ in the experimental intensity curve. They did not explain, however, how that high concentration could arise if neighbouring molecules were not packed with any order. However, such concentration could arise if the neighbouring chain segments assumed a near-parallel alignment to one another.

Ordered regions as revealed by dark field microscopy³⁵

As we have indicated above, the most intense diffuse ring may be caused by intermolecular scattering of atoms between neighbouring chains that are more or less parallel to one another. This was proved by high resolution dark field electron microscopy using a portion of the innermost ring with a Bragg spacing of 4.5\AA (Figure 17). A similar image was reportedly obtained by Ban³⁶ in thin sections of crosslinked natural rubber. The interpretation of this dark field image is the same as for the ones obtained in polystyrene and polyethylene terephthalate. The size of the ordered regions averaged about 30\AA , which represents a time and space

average of a probably more stable diffracting region in the rubbery state of natural rubber.

More recently Luch in our laboratory has established a nodular texture in gold-decorated, lightly OsO_4 -stained and Pt-shadowed natural rubber specimens at room temperature.³⁴ *Figures 18* and *19* are some examples. The nodular size ($\sim 100\text{\AA}$) is distinctly larger than the diffraction regions. However, upon stretching, which results in crystallization, Luch showed that the nodules contained ordered regions about the same size as the nodules themselves (*Figure 20*).

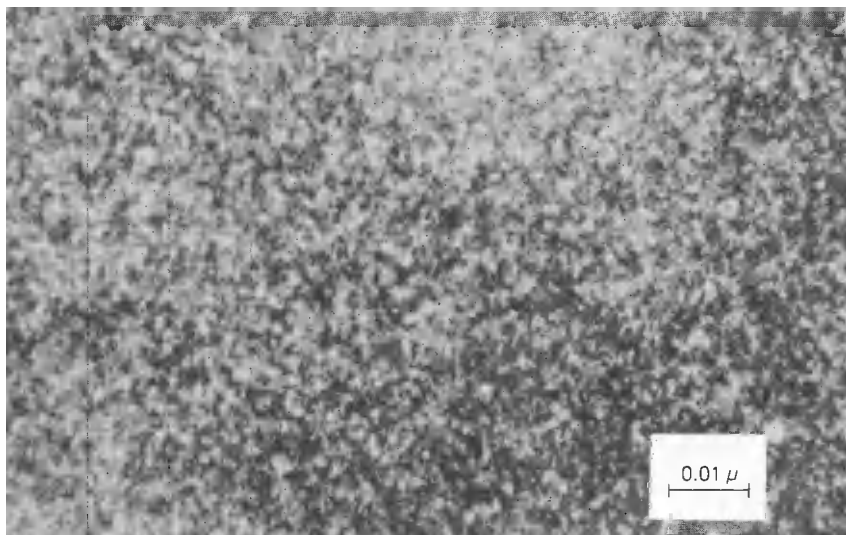


Figure 17. Dark field electron micrograph of an unshadowed thin film of natural rubber³⁵.

The nodular texture became much more distinct upon cooling to lower temperatures. An example is shown in *Figure 21*.

Another indication that the nodular structure is present in the molten state of natural rubber was proved by Luch by crystallizing a thin film which had been gold decorated *prior* to cooling. In the original uncrystallized specimen the gold particles tended to void the regions occupied by the nodules (see *Figure 18*). Upon crystallization similar gold-voided regions were observed to be present along the lengths of lamellae (*Figure 22*). This tends to suggest that lamellar crystallization from the melt, as in the case of crystallization of isotactic polystyrene,³⁵ polyethylene terephthalate,²⁶ or polycarbonate^{27, 28} from the glassy state, takes place by crystallization and packing of the nodules, which results in the observed crystalline lamellae.

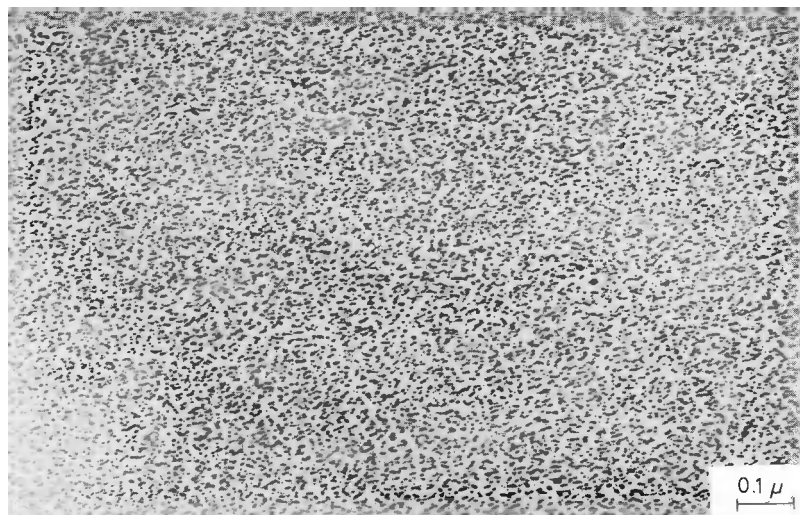


Figure 18. Thin film of natural rubber, gold-decorated at room temperature. Au-voided region $\sim 100\text{\AA}$ in size¹⁴.

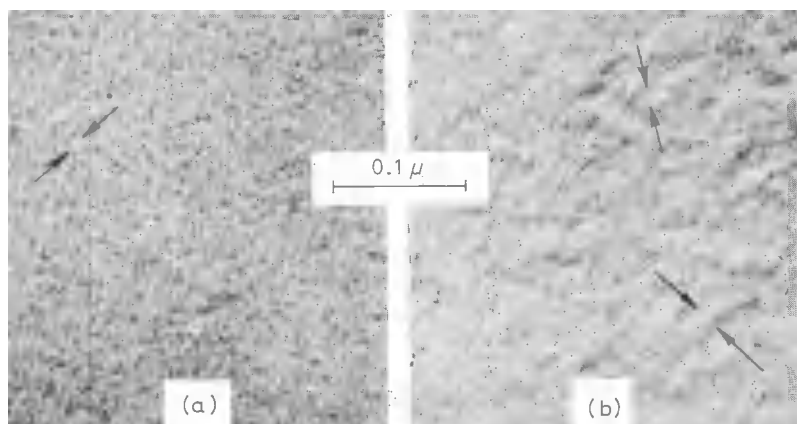


Figure 19. Thin film of natural rubber, Pt-shadowed at room temperature to bring out the nodular texture: (a) cast on water surface, (b) cast on glass slide¹⁴.

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Figure 20. Thin film of natural rubber stretched to about 700% and OsO₄ stained at room temperature³⁴.

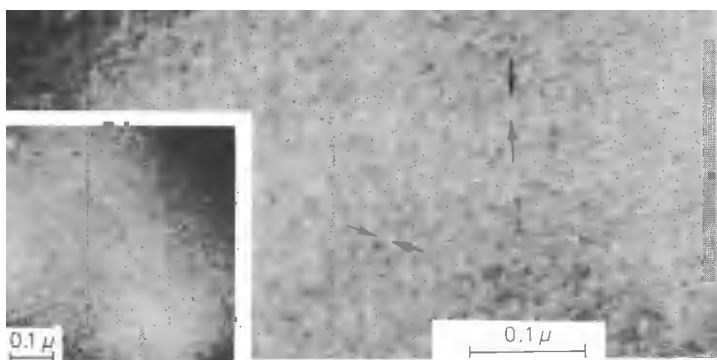


Figure 21. Uncrystallized region of natural rubber after cooling to a lower temperature showing the nodular regions, OsO₄ stained³⁴.

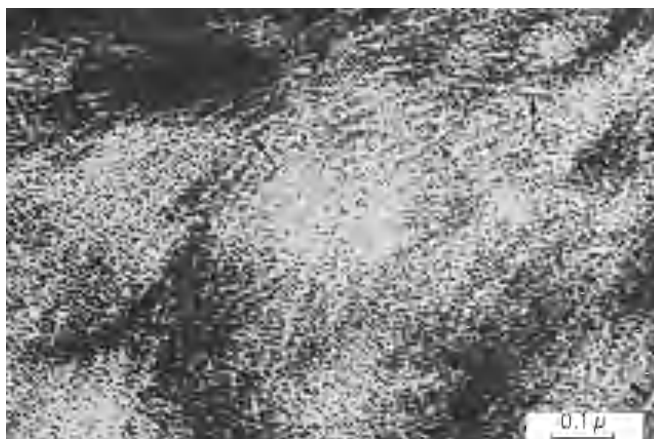


Figure 22. Natural rubber crystallized below room temperature. The thin film was Au-decorated at room temperature *prior* to crystallization and OsO₄ stained *after* crystallization.

STRUCTURAL MODELS OF AMORPHOUS POLYMERS

Various structural models have been proposed ever since the first suggestion of order in amorphous polymers by Katz in 1927. Some are based on structural studies while others are deduced indirectly. Some are also more specific than others.

Kargin proposed a bundle (or cluster) theory in 1957 based partly on x-ray studies of polymer melts showing high intensity of intermolecular scattering; and partly on bright field electron microscopy observations, showing spherulitic fibrils which remain undestroyed after destruction of crystallinity as well as fibrils that formed upon mechanical orientation.³⁵ Although the interpretation of such data, especially the electron microscope observations, may be somewhat questionable, the idea of parallel alignment of long chain macromolecules in the amorphous solid state appears reasonable and analogous to the swarm theory proposed originally by Bose in 1907,³⁹ and promoted later by Ornstein.⁴⁰ According to the swarm theory the interior of a nematic liquid is composed of clusters of molecules (10^4 to 10^6 molecules) with definite boundaries.⁴¹

In Kargin's bundle theory the parallel alignment of chain molecules is the essential feature; the size of the aligned region can fluctuate from a few segment lengths to lengths greater than fully extended chain molecules. The order is strictly intermolecular. The disorder is primarily in the boundaries between the bundles.

Hosemann⁴² suggested another model for the molten state of polymers (mainly polyethylene and polyethylene oxide). It is a one-phase paracrystalline model, based primarily on x-ray findings of disorder within lamellar crystals. With increasing temperature the disorder within the crystal is increased until finally at the melting point the lattice no longer has a 3-dimensional crystalline lattice; the chain segments, however, remain essentially parallel to one another. The folds originally present in the crystal are also suggested to remain in the melt. He pictured the melt as consisting of highly disordered crystals (see *Figure 16* in ref. 42).

Yeh³⁵ proposed a two-phase folded-chain-fringed-micellar-grain model for the amorphous state in general, glassy or molten. The model was based on structural evidence from electron diffraction and dark field microscopy studies of crystallizable and non-crystallizable polymers. The model contains two major elements as depicted in *Figure 23*. One element, which he called the grain (~ 30 – 100\AA), consists of an ordered domain of parallel chain segments brought about primarily by intramolecular folding of parts of a long chain molecule. The grains are generally connected to one another as in a string of beads especially for those molecules that are longer than can be contained within a single grain. Surrounding the grains are the second phase (~ 10 – 50\AA) consisting primarily of molecular chain segments in a truly disordered state, which may include low molecular weight molecules, chain ends or segments of molecules going from one grain to another.

A natural consequence of this model is the concentration of excess free volume in the matrix phase. A detailed description of this model and its possible relation to lamellar crystallization, rubber elasticity, viscosity, etc. have been covered in the same article.

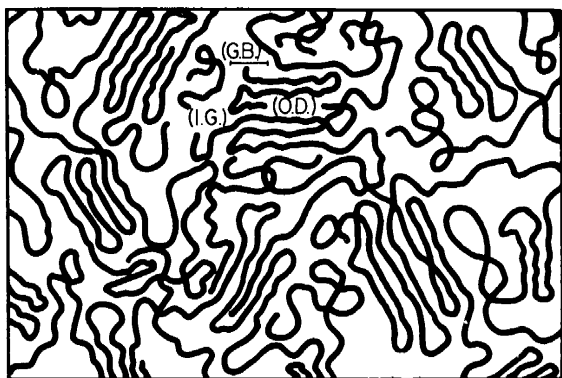


Figure 23. Schematic representation of the fold-chain fringed-micellar grain model showing the ordered domain (O.D.) the grain boundary layer (G.B.) and the intergrain region (I.G.)³⁵.

Another “two-phase” model which needs to be mentioned is the one being developed by Pechhold.⁴³ Starting with a nondefective (all *trans* conformations) bundle of molecules, by the introduction of more and more molecular defects (e.g. *gauche* conformations) into the system, Pechhold calculated from a simple thermodynamic treatment the mean radius of a meander curvature (disordered region). This radius came out to be about 50Å. His model is reproduced in Figure 24.

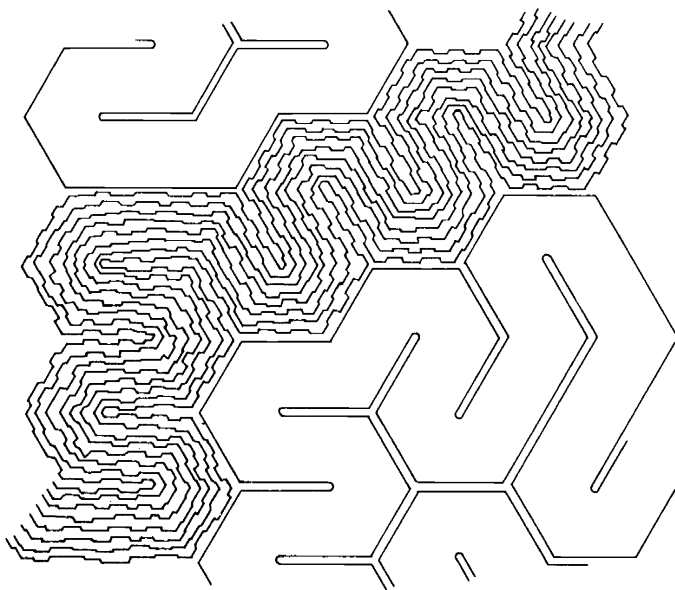


Figure 24. Pechhold's model for the amorphous molten state of polymers⁴³.

All four models have one major structural property in common. The molecules or segments of molecules tend to assume approximate parallel alignment over large regions compared to repeat units. Another common feature is that in none of the four models is there any extended region ($> 2-3$) of crystalline-type *trans* conformations remaining in the amorphous state. In two of the four (namely by Yeh and Pechhold) some definite regions of more highly disordered chain segments are included; while in three of the four (namely Hosemann, Yeh and Pechhold) some folded regions are also suggested.

We hope that the presentation and a brief discussion of these models here (all of which, we are sure, will be modified to a certain extent when more experimental evidence presents itself) may help to clarify the meaning of order (and/or structure) in the amorphous state of polymers. This may be of particular importance to those who wish to extend or improve these various models by calculations or experiments.

REFERENCES

- ¹ P. H. Geil. *Polymer Single Crystals*, Interscience, New York (1963).
- ² A. Peterlin. *J. Polymer Sci.* **9**, 61 (1965).
- ³ E. W. Fischer and R. Lorenz. *Kolloid-Z.* **189**, 97 (1963).
- ⁴ J. B. Jackson, P. J. Flory and R. Chiang. *Trans. Faraday Soc.* **59**, 1906 (1963).
- ⁵ T. Kawai and A. Keller. *Phil. Mag.* **8**, 1203 (1963).
- ⁶ M. Takayanagi, K. Imada, A. Nagai, T. Tasumi and T. Matsuo. *J. Polymer Sci.* **C 16**, 867 (1967).
- ⁷ T. Tasumi, T. Fukashima, K. Imada and M. Takayanagi. *J. Macromol. Sci.* **B1**, 459 (1967).
- ⁸ ^aH. D. Keith, F. J. Padden, Jr., and R. G. Vadimsky. *Science*. **150**, 1026 (1965). ^bH. D. Keith, F. J. Padden, Jr. and R. G. Vadimsky. *J. Polymer Sci.* **A2**, 267 (1966). ^cH. D. Keith, F. J. Padden, Jr. and R. G. Vadimsky. *J. Appl. Phys.* **37**, 4027 (1966).
- ⁹ G. S. Y. Yeh. *Morphology of Amorphous Polymers*, to be published in *CRC Critical Review in Macromolecular Science*.
- ¹⁰ E. Guth. *J. Polymer Sci.* **C12**, 89 (1966).
- ¹¹ R. Blokland. Ph.D. Thesis, University of Rotterdam (1968).
- ¹² K. Nagai. *J. Chem. Phys.* **47**, 4690 (1967).
- ¹³ K. Nagai. *J. Chem. Phys.* **49**, 4212 (1968).
- ¹⁴ A. N. Gent. *Macromol.* **2**, 262 (1969).
- ¹⁵ R. E. Robertson. *J. Phys. Chem.* **69**, 1575 (1965).
- ¹⁶ R. D. Heidenreich, W. M. Hess and L. L. Ban. *J. Appl. Cryst.* **1**, 1 (1968).
- ¹⁷ S. Krimm. *J. Phys. Chem.* **57**, 22 (1953).
- ¹⁸ A. Bjornhaug, O. Ellefsen and B. A. Tonnesen. *J. Polymer Sci.* **12**, 621 (1954).
- ¹⁹ H. G. Kilian and K. Boueke. *J. Polymer Sci.* **58**, 311 (1962).
- ²⁰ K. Katada. *Acta Cryst.* **16**, 290 (1963).
- ²¹ A. Chapiro. *Radiation Chemistry of Polymeric Systems*, Interscience, Wiley, New York (1962).
- ²² G. S. Y. Yeh. *Order in amorphous polystyrenes as revealed by electron diffraction and diffraction microscopy*, *J. Macromol. Sci.* **B**. In press.
- ²³ S. L. Lambert. Ph.D. Thesis, University of Michigan (1970).
- ²⁴ T. G. F. Schoon. *Brit. Polymer J.* **2**, 86 (1970).
- ²⁵ G. S. Y. Yeh and S. L. Lambert. *Mechanism of spherulitic crystallization as deduced from observations of partially crystallized glassy polystyrene*. Submitted for publication in *J. Macromol. Sci.* **B**.
- ²⁶ G. S. Y. Yeh and P. H. Geil. *J. Macromol. Sci.* **B1(2)**, 235 (1967).
- ²⁷ S. H. Carr, P. H. Geil and E. Baer. *J. Macromol. Sci.* **B2(1)**, 13 (1968).
- ²⁸ A. Siegmann and P. H. Geil. *J. Macromol. Sci.* **B4(2)**, 239 (1970).
- ²⁹ A. Ermolina, G. Markova and V. A. Kargin. *Study of structural changes in polyethylene terephthalate and polychlorotrifluoroethylene over a range of melting temperatures of crystals*, All-Union Symposium on Electronography, Moscow (1957).

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- ³⁰ J. J. Klement. Ph.D. Thesis, Case Western Reserve University (1969).
- ³¹ W. Frank, H. Goddar and H. A. Stuart. *J. Polymer Sci.* **B5**, 711. (1967).
- ³² G. S. Y. Yeh and P. H. Geil. *J. Macromol. Sci.* **B1(2)**, 251 (1967).
- ³³ G. L. Simard and B. E. Warren. *J. Am. Chem. Soc.* **58**, 507 (1936).
- ³⁴ D. Luch. Ph.D. Thesis, University of Michigan (1971).
- ³⁵ G. S. Y. Yeh. *A structural model for the amorphous state of polymers: folded chain fringed micellar grain model*, *J. Macromol. Sci.* **B**. In press.
- ³⁶ L. L. Ban. Private communication.
- ³⁷ ^aJ. R. Katz. *Z. Physik. Chem. (Leipzig)*, **A125**, 321 (1927). ^bJ. R. Katz. *Trans. Faraday Soc.*, **32**, 77 (1936).
- ³⁸ V. A. Kargin, A. I. Kitaigorodskii and G. L. Slonimskii. *Kolloidn. Zh.* **19**, 131 (1957).
- ³⁹ ^aE. Bose. *Physik. Z.* **8**, 513 (1907). ^bE. Bose. *Physik. Z.* **10**, 230 (1909).
- ⁴⁰ L. S. Ornstein. *Z. Krist.* **79**, 10 (1931).
- ⁴¹ L. S. Ornstein and W. Kast. *Trans. Faraday Soc.* **29**, 881 (1933).
- ⁴² R. Hosemann. *J. Polymer Sci.* **C20**, 1 (1967).
- ⁴³ W. Pechhold. *IUPAC Preprints*, 789 (1971).