FORMATION OF SUPERMOLECULAR STRUCTURES IN THIN POLYMER LAYERS

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ABSTRACT

Thin polymer films can be prepared by polymerization of a monomer in the gas phase. The polymerization may be initiated by light, pyrolysis, electron bombardment, or by glow discharge. The formation of polymers occurs mainly in the adsorbed monomer layer on a suitable support. The glow discharge technique is most effective.

It was originally considered that such films are rather amorphous irrespective of the support material, but later investigations on organosilicon compounds have shown that during polymerization, or immediately after, some supermolecular structures are formed.

Supermolecular structure formation was observed in the preparation of organic polymers by the glow discharge technique. Poly(benzene) films are at first amorphous but later exhibit birefringent areas and supermolecular structures. Similar phenomena were observed in other polymers. The origin of these supermolecular structure formations is not exactly known at this time. It is supposed that the local stresses due to further polymerization processes (related to trapped free radicals) and crosslinking enhance the structural changes.

With more polar monomers some orientation may occur during polymerization. The crystallinity of these layers is low.

The structure of thin polymer layers depends on the temperature and the kinds of support. Some characteristic features of epitaxial growth were observed for layers obtained on sodium chloride crystal surfaces. When metals are used as supports the capacity for supermolecular structure formation depends on the purity of the surface.

Typical spherulitic structures are not formed but hedrite-like structures may be observed.

The supermolecular structures in thin polymer layers obtained by glow discharge are compared with those found as the result of the polymerization of other monomers in solutions or melts by classical techniques, as well as with those formed in thin layers of molten polymers prepared in independent polyreaction processes.

INTRODUCTION

Various properties of a large number of thin polymer layers have been studied over the last ten years. Polymers obtained directly in the form of thin films display different properties from those prepared by classical methods of

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polymer synthesis. In particular they display different mechanical and thermal as well as electrical properties.

This is doubtless the reason for the considerable activity in recent years in studying methods of preparation and properties of thin polymer films which has been stimulated not only by the needs of the electronics industry but also by their use as coatings.

It has recently been found that some structuring of thin polymer films occurs during their formation or immediately afterwards. It is thus important to consider the mechanism of structure generation and its influence on physical properties.

For the purpose of this discussion we define a thin polymer film as one which has a uniform thickness of less than 3 000 nm (3 μ) and is of uniform chemical composition. Such films cannot usually be obtained easily by conventional methods, e.g. by evaporation of solvents from suitable polymer solutions or from polymer melts. However this last method may occasionally give thin, uniform films.

Thin polymer films can be prepared by polymerization of a monomer in the gas phase. Details of methods for obtaining thin polymer layers have been discussed recently in several papers[1-4]. The methods are given here in outline only.

Thin polymer films can be prepared from monomer vapours by polymerization initiated by light (photopolymerization), pyrolysis, electron bombardment or by glow discharge.

Thin films can also be prepared by vacuum sublimation. This method has been succesful for preparation of thin films of both inorganic and organic low molecular weight materials. The thermal evaporation of solid polymers and cathodic sputtering are not of great use in the formation of thin polymer films. These methods have been discussed in some reviews[5-7]. Thin films of polyethylene from 900 to 2 500 Å have been prepared by White[8] and other authors (e.g. ref. 9) from low molecular weight polymers. Some attempts have been made to obtain thin films of nylon and Teflon by this technique but most organic polymers decompose at the temperatures required for evaporation.

In the case of some monomers, e.g. ethylene, one can prepare continuous pinhole-free thin films by reaction between the monomer and an active surface[10]. This method is restricted to the production of thin films on surfaces which are able to react chemically with the monomer and initiate the polymerization reaction.

Interesting thin polymer films can be obtained by allowing a stream of heated di-p-xylylene (at 580°–620°C) to strike a surface at room temperature. The biradicals combine at the surface to form a solid film of good physical and electrical properties. Thin films of other poly-p-xylylene derivatives can be obtained[11 13] in a similar way.

The preparation of films by vapour phase pyrolysis has been little used since it tends to be accompanied by some carbonization, giving films of poor quality.

Thin polymer films are generally prepared by the interaction of monomeric or low molecular weight polymeric species in the gaseous form on the solid surface at which they are adsorbed in the presence of radiation energy, e.g. light of suitable wave length, ionizing radiation, electron bombardment or glow discharge.

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Photolytic reactions leading to the polymerization of many monomers are well known in polymer chemistry. It has been found that the optically excited molecule may be chemisorbed on the support leading to a shift of the frequency of light for activation of polymerization[14, 15].

Thin polymer films have been obtained by the photolysis of many monomers. Polymers prepared in this way show properties which are related to the bulk polymer and the parent monomer.

Without going into the details of the mechanism of photopolymerization in the gas phase and in the adsorption layer, which have been investigated by many authors, it should be emphasized that a very important step in these reactions is the physical or chemical adsorption of the molecules on the support where the free radicals produced during illumination (photolysis) react with other molecules[16].

Glow discharge in various organic vapours has also been used to prepare thin polymer films by d.c. as well as by a.c. techniques.

In recent studies using glow discharge polymerization it has been shown[17-24] that polymer films may be formed on electrodes or on suitable surfaces connected to these electrodes when a discharge is maintained in an organic vapour. It was also found that practically all organic materials can be used for the preparation of thin polymer films.

The d.c. technique has some disadvantages: relatively high pressures of gases are required and there is also considerable heating of the substrate. One observes that the films are not well defined geometrically and that the reproducibility of film structure and composition are not very good because of some contamination due to sputtering of parts of the system, and because of the variety of recombining species. Using the a.c. technique these problems are minimized. Other improvements have been proposed including electron injection into the gas phase and sustaining a glow discharge near the electrode[26], magnetic shaping of the discharge, and using a continuous process. Several different types of apparatus for the preparation of thin films by glow discharge have been described.

Detailed accounts of thin polymer film formation on the electrode surface in contact with an a.c. glow discharge in different monomer vapours have been given by many authors taking into consideration gas pressure, glow discharge current density, support temperature, etc. The detailed mechanism by which solid films are formed from a gaseous discharge is not known but many valuable suggestions have been made.

Recently investigations have been carried out concerning the structure of films prepared in this way. These films are quite different from conventional polymers prepared from the same monomers. They are crosslinked and have some degree of unsaturation. It was observed that increasing power dissipation in the discharge leads to discoloration of the films.

Electron beam induced polymerization of adsorbed monomer molecules on surfaces was first used for the preparation of polysiloxanes from different silicone oils[27] and then used for the preparation of other organic films from different materials[28, 29]. It was assumed that an electron interacts with an adsorbed molecule to create a reactive site which then allows the molecule to react with an adjacent molecule. Thus the kinetics of polymer film formation depend on the rate of arrival of oil molecules and their rate of adsorption, which

depend on the vapour pressure. The nature of the interaction with the support is also important. The detailed discussion of the mechanism of thin film formation by this technique which has been discussed by several authors is beyond the scope of this paper.

The properties of thin films obtained in this manner are usually similar to those prepared by the glow discharge technique using the same monomer. In some cases, however, distinct differences of structure and properties have been found.

The glow discharge technique is particularly valuable because of the possibility of varying the nature of the film by changing the conditions of preparation (vapour pressure, glow discharge current density, support temperature, etc.).

The kinetics and mechanism of polymer deposition in a glow discharge have been investigated by several authors[10, 11, 18, 19] and it is the subject of many recent interesting papers[30-36]. These studies lead to the conclusion that the general mechanisms involved in electron beam and glow discharge polymerization are quite similar and that the most important processes occur on the surface of the support where there is a layer of adsorbed monomer. The major differences between glow discharge and electron beam polymerization lie in the use of relatively high vapour pressures for the glow discharge and very low pressures in the electron beam technique.

A number of different species may be produced in the glow discharge technique and they may incorporate in the growing film. Free radicals seem to be most important in these polymerization processes. They are detected in the films by reacting with DPPH, and by epr. Ionic species or radical-ions are however not excluded by many authors. Recently more attention has been given to the gas phase reactions, which cannot be completely excluded as has been done by some authors.

From the above remarks it is to be expected that the nature of the polymer films will vary from support to support, just as films obtained by solvent evaporation differ from those obtained by cooling polymer melts.

It was considered originally that such polymer layers are without structure irrespective of the preparation conditions. However the latest investigations using organosilicon compounds have shown that during the polymerization process or immediately after it some structures arise. Similar effects have also been observed in films prepared by electron bombardment.

These phenomena of structure formation should be compared with those which have been found in thin polymer films previously prepared from other polymers or with those which are observed during some other polymerization processes.

GENERAL CHARACTERISTICS OF THIN POLYMER FILMS

The following remarks do not contain a deep discussion of all properties of thin polymer films. The aim of these few sentences is to give a general account of some of the characteristic features of these materials. We wish to limit our considerations to typical organic polymers excluding the organosilanes and other Si-containing films prepared by glow discharge, since these materials have been discussed extensively elsewhere.

As mentioned previously, thin polymer layers prepared by u.v. initiated polymerization resemble conventional polymers more closely because the u.v. light usually used is not of sufficient energy to cause ionization of monomer molecules. The energies employed in glow discharges and in electron bombardment give rise to some decomposition processes in the formed films. Thus many physical properties of films prepared by glow discharge depend on the experimental conditions under which they were prepared. At rather high monomer vapour pressure and low current density the films are transparent but soft[19, 20] which suggests incomplete polymerization. At low vapour pressure and high current density films are often discoloured, yellow or brown, and adhere well to the supports. When the current density is high and when the time of deposition is long the films are frequently degraded and loosely adherent. It has been assumed that this is due to hydrogen evolution. In addition it is possible that the high temperature of the substrate may lead to thermal degradation. Usually the films obtained at high current densities are highly crosslinked and insoluble in the solvents which are used for dissolving the conventional films produced from the same monomer. The soft films are usually more soluble.

Many investigators have shown that these films are substantially pinhole-free down to rather low thicknesses[37]. White[14] suggests that the reason is that the gas molecules adhere more strongly to the metal surface (support) than to the polymer surface already formed, which is in contrast to the situation found in thin film formation by evaporation techniques where film deposition proceeds through the formation of nuclei which grow with time leading to coalescence and films of variable thickness, where pinholes are very probable.

The chemical composition of thin films prepared by glow discharge technique is difficult to establish because of the small amount of material usually formed[33]. The i.r. absorption spectra of thin polymer films prepared by this technique have been studied by Jesch and co-workers[38]. Using many hydrocarbons they have shown that irrespective of whether the vapour was an aromatic or olefinic compound the films contain olefinic conjugated, unconjugated and fully saturated products as well as aromatic structures[39-41]. In air these films show a reactivity towards oxygen and moisture resulting in decreased solubility. An oxygen atmosphere also causes an increase in hardness and a gain in weight. These reactions are due to the formation of peroxides from the trapped radicals which cause further polymerization. The concentration of trapped free radicals depends upon the reaction conditions, e.g. time and power of discharge usually increase the radical concentration.

It was previously supposed that the structure of films prepared by glow discharge is more complex than those prepared by u.v. irradiation, but i.r. studies have shown that this is not always the case.

Interest in thin polymer films has been mainly due to their electrical properties: low conductivity, rather low dielectric permittivity and loss. In some cases however thin polymer films display semiconducting properties. The following remarks give the general characteristics of thin polymer films.

Usually they show small dissipation factors and high breakdown voltages. The value of dielectric constant (ε') sought depends on the type of practical application intended, but normally low values are required. Many studies of dielectric properties were carried out by White[14] on polybutadiene films, by

Stuart[42] on polystyrene films and by Hill on polydimethylsiloxane[43]. White showed that the polybutadiene films prepared by surface photolysis of adsorbed butadiene and by electron bombardment at room temperature are qualitatively similar. Polystyrene films obtained by a glow discharge technique give ε' values which are largely independent of frequency and temperature, and similar to that of conventional polystyrene. The rather high values of tan δ are probably due to the presence of oxygen or of trapped free radicals which can subsequently react with oxygen.

The dielectric properties of polymethylsiloxane films obtained by electron bombardment and hot glow discharge techniques depend on the type of starting monomer and energy of polymerization. They exhibit some aging reactions when exposed to the oxygen and moisture in the atmosphere. The films prepared from epoxy resins by electron bombardment are stable at room temperature[29] and show good dielectric properties.

The electrical conductivity of polymer films prepared by the discharge technique has been investigated by only a few authors. Bradley and Hammes[30, 44], have published the results of conductivity measurements on polymer films obtained from many organic substances. The absolute magnitudes of the dark conductivity at rather high temperatures (150°C) ranged from 10^{-17} to 10^{-13} Ω^{-1} cm^{-1}. Most of the values of the thermal activation energy were close to 1.36 eV. These authors suggested, that the conductivity of glow discharge polymers is determined by some gross features of the film structure which seem to be common to many polymers obtained in this manner. Probably the degradation and crosslinking of the materials which may occur during the discharge process or the contamination of the growing films with species produced in the discharge reaction may be responsible for the similarity of conductivity. When the films of polymer were prepared by photopolymerization the conductivities varied from 10^{-11} to 10^{-14} Ω^{-1} depending on the monomer used.

Electrical properties of thin films obtained from dimethylsiloxane[43] do not depend upon the starting monomer and are similar to those of other organosilicon films. Thin films prepared from silicone oil of thickness between 50 Å and 250 Å have been investigated by Christy[45a] and Mann[45b]. They found non-ohmic conductivity for all these films and Mann suggested that the conductivity for films in the thickness range 500 to 2 500 Å is related to Schottky emission or tunneling or to a mixture of both.

Hill[43] has shown that for films of thickness up to 5 000 Å, obtained from dimethylsiloxanes by electron bonbardment, the conductivity is related to Schottky emission which seems to be rather an unexpected result. Gregor and Kaplan[46] who investigated a thin film of epichlorohydrin of thickness 100 Å, came to the conclusion that the observed current–voltage characteristics could be related to a combination of tunneling and either the Schottky or the Frankel-Poole mechanism.

At the moment no conclusive results are available concerning the influence of the three basic external factors governing the conductivity process, that is, temperature, electric field strength and film thickness. The same situation exists concerning the dependence of conductivity of polymer thin films on their chemical composition and physical structure. This is why many authors have now undertaken investigations into thin film conductivity taking into consi-

deration a well-defined range of thicknesses, electrical field strengths and the chemical composition of the specimens. The purpose of these studies is to relate the electrical properties of thin polymer films to those concepts of electronic, or hole, conductivity which have been recently elaborated for thicker polymer layers[47, 48]. They must take into account all the factors resulting from considerations of models for disordered materials[49], such as injection of current carriers, trapping, etc., since polymer films are amorphous or at most only partially crystalline. One would expect that for very thin films the tunnel mechanism[50, 51] would dominate and at higher fields and film thicknesses the Richardson–Schottky mechanism would be significant[52–54]. Studying thicker films one can expect the appearance of space-charge limited currents[51, 55] or the Frenkel–Poole mechanism which is related to the volume of the sample[56–60].

If the applied voltage is high and the concentration of trapping sites and donor and acceptor sites is large one can anticipate a change of conductivity mechanism from Richardson–Schottky to that of Frenkel–Poole, and even for thicker films the appearance of space-charge limited currents may be expected[61].

Thin polymer films also have interesting properties at high electric fields because their thickness is very small as compared to other dimensions. They sustain field strengths well beyond those at which the bulk materials undergo dielectric breakdown. This increase of dielectric strength with decreasing thickness is well known and has been discussed in many monographs (e.g. ref. 62) in terms of the decrease of avalanche effects and thermal breakdown. Thin polymer films also show interesting self-healing phenomena which are of great importance in their application as condenser materials. These processes are not to be expected in conventional thick polymer films.

In addition to the electrical properties of thin polymer films one should mention their advantageous physico-chemical features. Many polymer films undergo plastic deformation when a stress is applied, minimizing the residual stress in the film. The residual stress in epoxy thin polymer film, obtained by electron bombardment, has not been detected, being of the order of 10^7 dyne cm^{-1}. Other mechanical properties such as hardness, tensile strength, elastic limit, etc. are difficult to measure on thin, supported polymer films. The only published data are for free poly-p-xylylene films and indicate that mechanical properties are directly related to their structure, which is generally asssumed to be amorphous.

Polymer films are usually poor thermal conductors but thin polymer films show special thermal properties, e.g. larger thermal resistivity than glass due to short correlation length or to greater variation in elastic constants, both factors being related to the structure[63].

Summarizing, the properties of polymer films are determined firstly, by the deposition process and secondly, by the monomer or starting material, but their chemical composition varies widely and individual films must be considered in order to explain their chemical behaviour, e.g. the aging processes, which might be of great importance. The same applies to the chemical inertness, thermal stability, oxidation resistance, permeability to gases, etc.

At the present time the most practical thin polymer film preparation process

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is the glow discharge technique. The use of electron bombardment also appears to be convenient for applications in microelectronics.

Much progress is being made in the production of films of high thermal stability either by the use of aromatic starting materials or by the incorporation of inorganic atoms.

Before discussing the formation of supermolecular structure entities in these polymer films it is necessary to mention the main areas of their application since in the different uses one takes advantage of their different chemical and physical properties.

The use of thin polymer film for insulation is most important, particularly in those applications where a high capacitance per unit area is required.

The application of thin polymer film directly on semiconductor surfaces to replace the conventional oxides and glasses does not seem to be of great interest at present because of the high temperatures employed in metallization and sintering. The silica or glass films which are adapted for insulating the different parts of metallic interconnecting films from each other are very useful but although they have high chemical stability and good thermal resistance they are brittle and build up stresses. Thin polymer films which show an ability to undergo plastic deformation in response to stresses may be extremely useful in this field. An important application of thin polymer film at present is the production of thin-film circuits. Polymer layers suit all the requirements: they are very thin, of uniform thickness and able to withstand the stress imposed by different thermal conditions[64]. They can be deposited in the form of patterns of a high degree of resolution, even using the same equipment as is used for the deposition of metallic film elements for complex circuits.

Some of these thin polymer films may be dissolved in suitable solvents thus permitting the etching of an underlying metal film. The remaining polymer can then be removed after this treatment.

It is not possible to enumerate and discuss here all the very interesting applications of thin polymer films in modern electronics but it should be mentioned that they have been used as gate insulation in silicon field-effect transistors and in thin-film field-effect transistors. Different peculiarities of electrical conductivity of thin polymer films may be used for obtaining thin-film active devices (hot electron triodes, tunnel devices, negative resistance elements, etc.). Although these devices are not yet largely used in practice, one may expect that with the development of fabrication techniques and controlled modification of thin film properties they may be very useful in this field.

Finally one should mention that thin polymer films are very good materials for fundamental research concerning the mechanism of conductivity in organic amorphous or partially crystalline solids, the influence of high electric fields on their optical properties, etc. These thin polymer layers may also be very good models for biological materials.

The possibilities of synthesizing different polymer films by the glow discharge technique or by other techniques mentioned earlier are very large and may lead to many interesting new materials. However it should be emphasized that the properties of thin polymer films depend not only on their chemical composition but also on their physical structure, an aspect which has been frequently neglected in many investigations.

STRUCTURE AND STRUCTURE FORMATION IN THIN POLYMER FILMS

The preparation of thin polymer films always requires suitable supports. This fact is characteristic for all the above-mentioned methods of obtaining thin polymer layers, because the polymerization process occurs mainly in the film of molecules adsorbed from the gas phase. The same is true for conventional methods of film casting or film pressing from the melt. Supports normally used are mostly metals, salts and dielectrics like quartz, glass or even polymer films. It is natural to expect that support materials may influence the structure of the polymeric material formed as has been found for films cast from solution, especially when the polymers used are able to crystallize. It is also known that introduction of solid crystalline particles into a polymer solution or into a polymer melt may enhance the crystallization process at a suitable temperature (e.g. refs. 65–67). Analogous behaviour has been found on the addition of amorphous solids of different melting points from that of the crystallizing material, or even liquids. The growth of strongly oriented material on the surface of a different material is known as epitaxy. Usually the addition of solid particles to polymer solutions or polymer melts does not cause an epitaxial growth of the parent material. The influence is only on the size, kind and kinetics of supermolecular structure element formation. These facts have been carefully investigated by many authors who have shown that in addition the nucleation type and crystallite growth rate have been affected[68, 69]. These phenomena have also been used for the regulation of the supermolecular structure of many polymers.

Independently one should consider the influence of support material on the structure of the resulting films. Let us first consider the conventional methods of film preparation from conventional polymers which have been synthesized in an independent process. When amorphous polymers are used one usually gets structureless films. However many authors have recently found that even in these 'amorphous' materials some order exists and different supermolecular entities may be found[70–72]. In the case of high molecular weight substances which are able to crystallize, many supermolecular structure elements have been observed. Their kind, shape, size and order depend on the kind and nature of the support as well as on the molecular weight of the polymers investigated. It has been established that the most important part in these phenomena is played by the adsorption layer in which a change of growth kinetics occurs which in turn results in a change of structure with film thickness; for example, it was found that in very thin molten polypropylene films no spherulites were formed although the same material gave distinct supermolecular entities in thicker layers[74, 75].

In these studies glass was mainly used as the support material. Thus it is not simple to evaluate its influence on the type of structures being formed or to give more definite suggestions on the mechanism of the interactions of support material with high molecular weight substances.

The epitaxial growth in polymer films was found after the discovery that many low molecular weight organic substances exhibit this type of crystallization. The first high molecular weight substance which showed epitaxy was polyethylene when crystallized from solution on rock salt[76-79]. Later, other

polymers were found to give epitaxial layers[80-82] from solutions and from melts[83].

Epitaxy in polymeric systems was established by optical and electron microscopy and some basic relations between the polymer unit cell and support unit cell have been found. These studies and those concerning biological polymers, e.g. polyaminoacids and polypeptides[84, 85] have also made it possible to draw some conclusions on the mechanism of epitaxial growth[86] in which the electronic interaction between support and crystallizing molecules must be taken into consideration.

Those interactions which modify the nucleation processes should not lead to very large deformations of molecules and thus epitaxial growth should be observed on many supports. However some differences exist between epitaxial growth of polymers from solutions and from melts. They consist in the influence of solvent on the conformation of the macromolecules which in turn determines in some way the capacity for oriented growth.

The rather small interaction forces which are needed for epitaxial crystallization suggest that this type of crystallization can also be expected when the support material is nonpolar, high molecular weight material. Indeed it was found that polyethylene crystallizes in an epitaxial form on oriented polyoxyethylene films[87]. Kargin and co-workers[88] have established that isotactic polypropylene exhibits different morphological forms when crystallized on the surface of polyester, polyamide and polytetrafluoroethylene films. When the crystallizing substance is separated from the polymeric support, e.g. by a thin layer of gold, the form of spherulites and degree of crystallinity of a polyethylene sample are changed[89].

It should be clear from the above remarks, without going into further details, that in any discussion of polymer film formation, the nature of the interaction between polymer molecules and the molecules of the support and the possibility of epitaxial growth must be considered. It is also important to consider the processes whereby crystallization occurs during the polymerization process. These have been reviewed by Wunderlich[90] and will only be summarized here.

In the past only two steps in the crystallization process have received much attention and all crystallization studies have concerned ready-formed, randomly-coiled polymer molecules. It requires energy to obtain oriented chains from randomly-coiled polymer molecules in solution or in the melt and hence the process of crystallization is kinetically hindered. Thus only metastable crystals of small dimensions are formed initially, much longer polymer molecules being accommodated by chain folding. Crystallization may occur during polymerization simultaneously or successively. In the first case monomer molecules are added to the growing chains and covalent bonds as well as secondary bonds are made immediately. This process occurs in a similar way to ordinary crystallization. In the second case polymerization is followed by crystallization before the molecule is completely polymerized. One could also expect polymerization to occur followed by crystallization. This is the normal situation, but it is somewhat more complicated when the molecules are formed in a particular conformation, e.g. a helical conformation, and crystallize before conversion into a random form.

Crystallization during polymerization by both simultaneous and successive processes is known for many organic monomers which are capable of stepwise

polycondensation and for monomers polymerizing by a chain reaction mechanism (addition to multiple bonds or ring opening). Step polymerization reactions are of less interest since all thin polymer films prepared at the present time are assumed to be formed by a chain reaction mechanism.

Step polymerization reactions lead to the formation of a high concentration of oligomers in the dissolved or molten state which can nucleate the crystalline polymer phase. These reactions produce polymer chains which may react with monomer on both ends and crystals may be formed. This type of reaction is also found in biological polymers (e.g. cellulose, Colvin[91]) and inorganic polymers[92].

It has been shown that several chain reaction polymerizations may also lead to crystal formation. The crystals must be nucleated so that an activated surface is the site for crystallization during polymerization, which means that either only narrow fibrils with a limited number of active sites are produced or that chain reaction polymerization leads to succesive, separate polymerization and crystallization. Successive polymerization and crystallization results in the formation of polymer molecules which crystallize at a certain distance from the active centres. Thus the morphology of the resulting crystals and supermolecular entities depends on the density of active centres and on the support medium or solid surface.

In the case of radical polymerization in solution (or in the gas phase at elevated pressures) in the presence of initiators, isolated molecules make up separate crystals or they are added to already formed crystals. It is also necessary that the active ends of growing molecules be protected from termination, as is the case in solid state polymerization where radicals are stabilized in the monomer crystal. Free radical polymerization in the solid state (i.e. in the crystalline monomer) does not usually lead to a crystalline polymer[93].

There are however some exceptions as recently reported by Wagner[94]. A special case is the radical polymerization of monomers introduced into clathrates of different types. It cannot be compared with those conditions which might be expected in thin polymer film preparations so it may be neglected in this discussion.

For ionic and coordination polymerization one would expect mainly successive polymerization and crystallization. These reactions have been investigated for many monomers and it has been shown that crystallization during polymerization may give rise to a large variety of morphologies. Some crystalline cyclic monomers seem to be capable of topotactic polymerization reactions which should be considered as simultaneous polymerization and crystallization. In some cases, for example for helical polymers in solution, an influence of nucleation and ordered structure on polymerization rate was observed which may also be considered as simultaneous polymerization and crystallization.

Most of the studies have however been devoted to the investigation of structure formation in heterogeneous chain-growth polymerization. Without quoting the many papers on this subject we should like to mention that successive polymerization and crystallization are particularly important when using heterogeneous catalysts. Due to unequal polymerization rates of different molecules, Keller and co-workers[95] expected chain folding in addition to a secondary formation of globules and other supermolecular structures.

To summarize and to draw some conclusions which may be useful for the

elucidation of processes of thin film formation, we should like to consider nucleation and the growth of structures.

Crystal growth can start only after nucleation, in contrast to a chemical reaction which may proceed on any encounter of two molecules (reaction partners). This difference between chemical reactions and crystallization processes in which secondary bonds are involved means that crystal nucleation is of fundamental importance for elucidation of the resulting structural entities. Wunderlich[90] has given an analysis of the crystallization phenomena during polymerization involving five different nucleation processes. A coupling of crystallization and polymerization occurs if the ceiling temperature of both processes is below the melting or dissolution temperature of the crystals.

By supersaturation at high enough concentrations oligomers are formed which may be of the critical nucleus length (sometimes 20 atoms). The thermodynamic parameters for polymerization are then changed usually resulting in an increase of reaction rate. If the molecular weight of polymer being formed is large, and if secondary nucleation of new chains on the growing crystal is slow, the crystals resulting have a fibrous habit. When the secondary nucleation is fast it leads to lowering of molecular weight, for example by occlusion of a previously nucleated chain in the interior of the crystal. In some cases the reversibility of polymerization and crystallization causes a rejection of defects and formation of perfect crystals. At lower temperatures it is still possible to obtain good crystals but at really low temperatures many imperfections may be metastable and they do not disappear by reversible rearrangement.

When polymerization and crystallization are very slow or hindered successive polymerization and crystallization are to be expected. The oligomers are not able to crystallize but leave the active centres in the amorphous phase. Due to complicated phenomena of crystallization in the amorphous portion and on the surface of the crystals, fibrous morphology is to be expected.

When the interaction of oligomers with nuclei is impossible only a folded chain nucleus can be produced—an intermolecular process—which may undergo a further increase. Such intermolecular nucleation may be followed by successive or simultaneous polymerization and crystallization.

From remarks given above it follows that during the polymerization in the adsorbed molecular layer one might expect structure formation when the concentration of oligomers and of monomer molecules is sufficiently high and when energetic requirements (temperature) for nuclei formation are fulfilled. These conditions are rather critical. Thus crystallization during polymerization at the support surface is not very probable, but this does not mean that completely structureless layers are formed in the preparation of thin polymer films.

STRUCTURE OF THIN POLYMER LAYERS

As was mentioned before, many authors have reported that thin polymer films obtained by direct polymerization on different supports are amorphous. This conclusion has been on the basis of x-ray diffraction patterns. However in the case of vacuum deposited, preformed polymers, it has been found by

Miyoshi and co-workers[9] that one obtains highly crystalline materials. They showed that the evaporated PE thin film was crystalline.

Non-fractionated PE was evaporated onto a single sodium chloride crystal or a collodion film at 5×10^{-5} Torr. The temperature of the polymer sample was kept in the range 603–623°K and the surface of the support was varied in the range 293–373°K. The thickening rate of PE-film was about 200–300 Åh^{-1}. It was shown by electron diffraction that thin films of the thickness $d = 200$–300 Å obtained in this way have the same structure as the single crystals obtained from solution by the precipitation method. It was also observed by x-ray diffraction that thicker films ($d = 2000$ Å) prepared by the same method show polycrystalline structure. It is interesting to note that the molecular weight of PE in these thin films is a little lower than that of the original sample. It seems that the decomposition of the starting material was very low. There are no further data on the mechanical and other, e.g. electrical, properties of these films, but it is clear that oriented growth is possible. The data concerning the epitaxy of these films are not given by these authors. However, some influence of the support material may be expected.

In order to see whether similar behaviour may be observed we have undertaken investigations of structure formation in thin films prepared from benzene, diphenyl and styrene using the glow discharge technique. Special attention has been given to polybenzene, which could be similar in structure to polyphenylenes which are known to be semicrystalline solids[96]. Very thin polybenzene layers have been reported to be structureless[97] and have been recommended for replica preparation in electron microscopy investigations[98].

All investigated thin films were obtained by glow discharge in vapours of the given monomer. The frequency of discharge current was 10–15 kHz and the power supplied to the discharge was about 40 W. Thin films were obtained on carefully polished stainless or chromium plates (electrodes) which were separated by a distance of 2 cm. Before each preparation they were cleaned with acetone, located in a bell jar, and the whole system was evacuated to $5 \cdot 10^{-5}$ Torr. A suitable monomer pressure was then achieved by introducing an appropriate amount of the compound to be polymerized.

The thickness of the resulting thin films could be regulated and controlled by changing monomer vapour pressure and the reaction time (time of discharge). The actual thickness of films was estimated by the multiple-beam interference method. Usually the times of reaction were chosen to be 1, 2 and 5 s, after which the specimens were removed from the monomer vapour atmosphere.

The surface of the samples obtained in the above way was investigated by electron microscopy as well as optical microscopy to study the morphological structure. All experiments described here were carried out at room temperature. The data concerning heat treatment of these thin films (using a hot stage) will be given in a forthcoming paper.

The electron micrographs were made immediately after preparation (1h). In order to establish the changes of the film structure as a function of time of storage in air they have been investigated with an electron microscope after 3 or 10 days or other known times after preparation.

The electron micrographs were made from carbon replicas shadowed with platinum and palladium under an angle of 30°. The replicas were then stripped off with polyacrylic acid and prepared in the usual manner for electron

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microscopy. The time needed for replica preparation was 1h, thus the films investigated have been considered as non-aged since the contact time with air between removal from the polymerization bell and placing in the replica preparation apparatus was also short.

For optical microscopy studies samples were prepared on glass slides previously covered by a vacuum-deposited thin transparent gold layer.

The investigation, which will be discussed below, concerned a number of thin polymer layers prepared by the glow discharge technique of which only some will be analysed in detail.

As polybenzene films were the main object of this study, the description of structure formation in thin polymer films will start with this polymer.

POLYBENZENE

None of the thin films of polybenzene (PB) in the thickness range 100–800 Å showed particular structures either by optical or electron microscopy. They were homogeneous, quite transparent and colourless. Electron micrographs of these films showed clearly the fissure structure of the supporting plates which leads us to expect a homogeneous structure with some very small grains or nodules.

When the thickness of these films was higher (due to longer discharge time) and was of about some 10^3 Å the films were very slightly birefringent and looked homogeneous when observed between crossed polarizers even at high magnification. The thicknesses of the PB films prepared at 1 Torr pressure of benzene vapour increased with polymerization time and were equal to 3.2×10^3, 5×10^3 and 7.2×10^3 Å for 2, 5 and 10 s polymerization times respectively.

Figure 1 shows an electron micrograph of a sample of thickness $d = 3.2 \times 10^3$ Å. Large hemispherical structures of the nodular type were
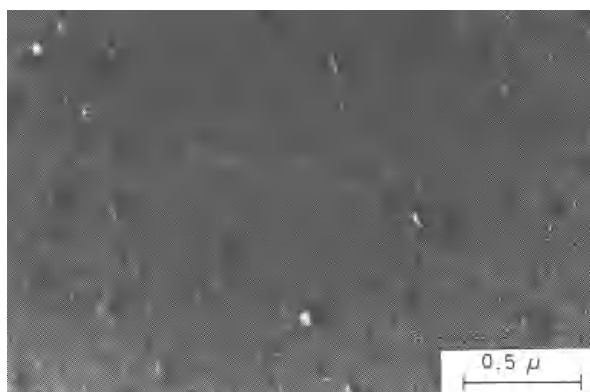
Figure 1. Electron micrograph of polybenzene (PB) obtained in 2 s polymerization time. Electron microscope studies made 1 h after finishing the polymerization reaction. Sample thickness d 3 000 Å

found. Their average diameter is 550 Å and their height is of the order of 250 Å. The concentration of these structural elements is rather low reaching a number $4 \times 10^5/cm^2$. In *Figure 1* the fissure structure of the support plate can be seen which suggests that the areas between these nodules are covered by a homogeneous film above which project some hemispherical structures.
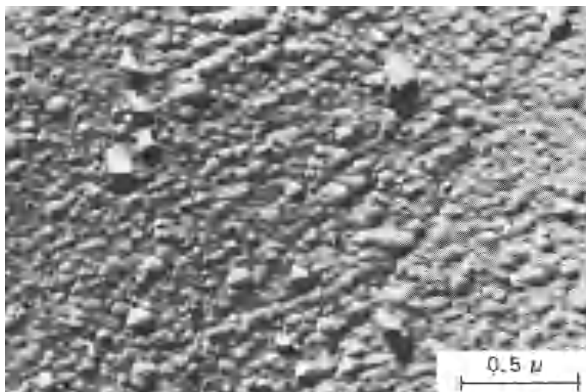
Figure 2. Electron micrograph of the surface of PB layer of thickness 5000 Å (preparation conditions as for *Figure 1*)

The increase of the polymerization time and the increase of sample thickness (to 5000 Å) causes an increase in the number of surface structures which cover the whole surface of the specimen without change of their dimensions, see *Figure 2*. It is also interesting to mention that the range of sizes of these entities decreases. The diameters of these structures are of 520 ± 30 Å. This value is the average diameter and the standard deviation is taken from a large number of measurements. Barely visible in this micrograph is the grainy or nodular structure of the larger structures. The surface concentration of these larger structural elements is $5 \times 10^{10}/cm^2$. *Figure 3* shows an electron micrograph obtained from the sample prepared by 1 s polymerization time (thickness $d = 3000$ Å) after 3 days aging in air. No distinct differences in appearance of the hemispherical structures can be seen.

Electron diffraction experiments do not show any regular patterns which could be attributed to regular structures of crystalline or mesomorph order.

Different structures have been observed in still thicker samples prepared in the same way. For PB samples of thickness 3 μ (3×10^4 Å) distinct supermolecular structures of the spherulite type have been seen.

These samples had a whitish appearance due to spherulites visible under the optical microscope. The spherulites are not formed directly during polymerization, that is, during glow discharge. They also appear in thinner films so studies on the thickness dependence of spherulite formation have been undertaken. For this purpose a sample with a thickness gradient was prepared by a suitable change of electric field inhomogeneity during glow discharge. The supermolecular structures formed were investigated in the thickness range 1 to 6 μ. It was
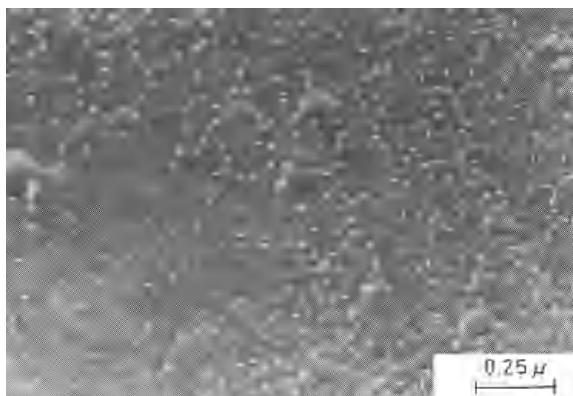
Figure 3. Electron micrograph of the surface of PB film after a further 3 days in air (the same film as in *Figure 1*)

found independently that spherulites exist even in thinner films of thickness $d = 7000$ Å (*Figure 4*). From *Figure 4* it appears that apart from small spherulites the whole surface of the investigated layer shows some folding. The details of these folded structures are shown in *Figure 5*. The folded structure is quite similar to a regular knitted twist whose density is different in different samples. The thickness of this knitted twist is however constant for a given sample but is different for samples prepared under different conditions. At present no definite reason for the appearance of this structure can be suggested. It seems, however, that in these thin films a further polymerization process occurs. This process is very likely because of the rather soft, viscoelastic, nature of the film immediately after its preparation. It is known[4, 19] that all films prepared by the glow discharge technique contain trapped radicals which in the presence of atmospheric oxygen may lead to peroxide formation. These compounds are able to initiate further polymerization or further crosslinking
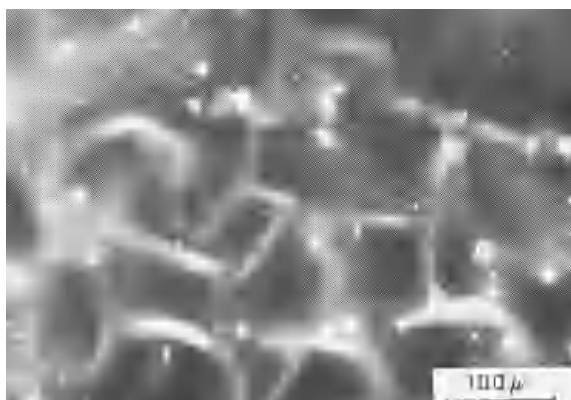
Figure 4. The spherulitic structure of thin PB film of thickness d 7000 Å (optical micrograph)

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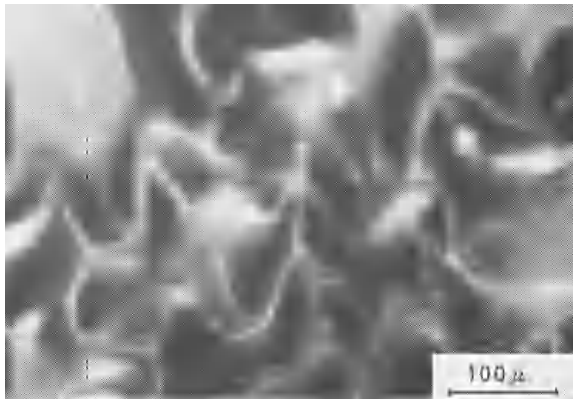
Figure 5. Details of knitted twist structure of PB thin film (optical micrograph)
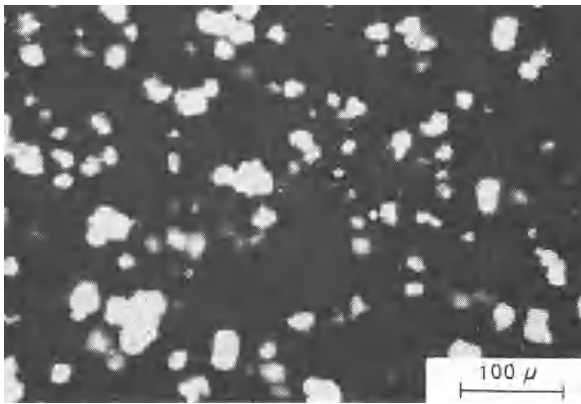
Figure 6. Optical micrograph of 1 μ thick PB film with spherulites whose diameter is of the order of 10 μ
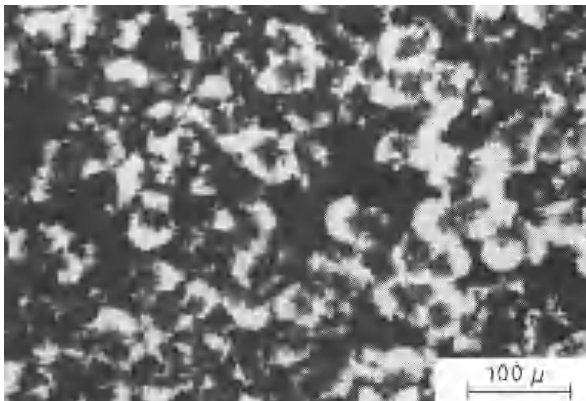
Figure 7. Optical micrograph of 4 μ thick PB film with spherulites whose diameter is of the order of 30 μ
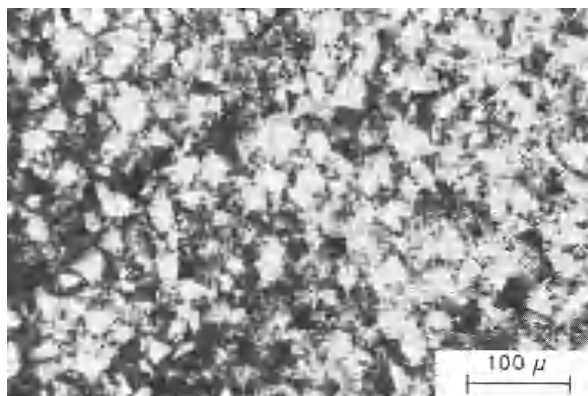
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Figure 8. Optical micrograph of PB film (thickness $d = 6$ μ) with large spherulites

reactions of adjacent macromolecular chains. As a result of these reactions some parts of the films are contracted leading to convexities in some places and concavities in others, which are probably responsible for the observed knitted twist structure.

In very thin parts of this wedge-type layer no spherulites were found, only the hemispherical structures shown in the electron micrographs above. From *Figures 6, 7* and *8*, obtained by optical microscopy, it appears that the increase of film thickness causes the spherulite size increase. The diameter of spherulites grown in PB films of thickness $d = 4$ μ is 30 μ and for still thicker samples, one observes still larger spherulites. From investigations of the dependence of spherulite dimensions on film thickness it was found that there is a sharp limit of thickness below which no spherulites could be formed. It is estimated to be of the order of 1 000 Å.

At present when no direct investigations of the kinetics of spherulite formation in PB films have been carried out it is not possible to estimate the type of nucleation mechanism, that is, whether homogeneous or heterogeneous nucleation occurs.
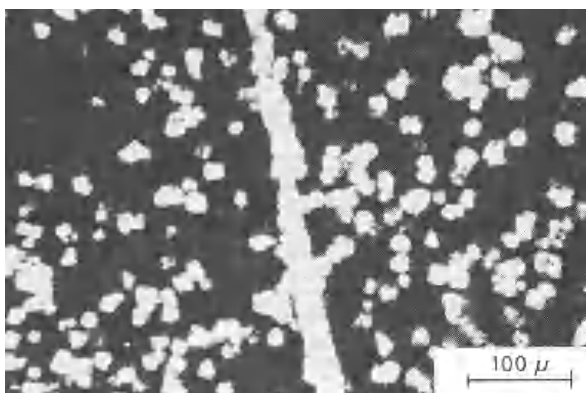
Figure 9. Optical micrograph of spherulites grown along a fissure in the support plate
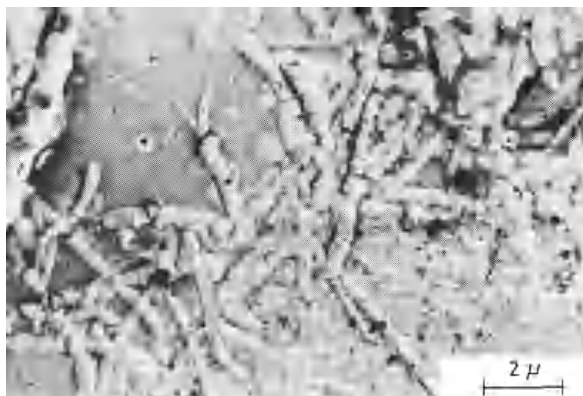
Figure 10. Electron micrograph of the centre of a spherulite shown in *Figure 7* grown in PB thin film

Optical microscope observations shown in *Figure 9* indicate that spherulites grow along the fissures in the support plate which suggests heterogeneous nucleation.

The areas in these samples without spherulites also show the knitted twist structure.

Optical microphotographs of spherulites formed in PB layers indicate that they are less regular than typical spherulites. Electron micrographs of the centre of one of these spherulites show that it is not built up of regular bundles, and sheaf-of-leaves aggregates are hardly detectable (*Figure 10*). The spherulites in PB are built up of fibrils of less regular arrangement than other spherulites. The fibrillar structure of PB spherulites is clearly shown in *Figure 11*. From this micrograph one can estimate that these fibrils project above the film surface for about 800–900 Å and are up to 5 000 Å across. Their length is rather great, and may be several microns in some cases.
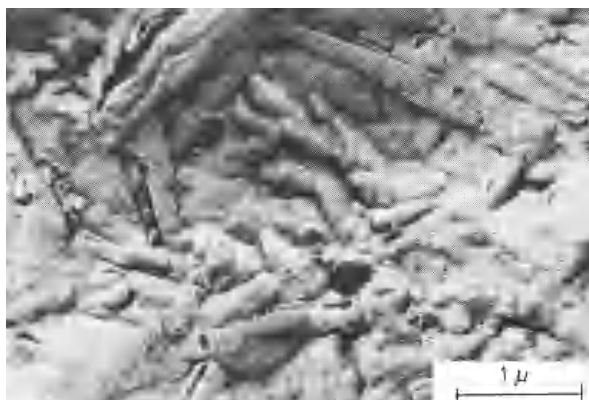
Figure 11. Electron micrograph of a part of PB spherulite showing its fibrillar structure (see *Figure 7*)

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It seems interesting to note that the appearence of spherulites almost excludes the hemisphere structures found in all thinner films.

POLY(DIPHENYL) AND POLYSTYRENE LAYERS

The investigations of the supermolecular structures formed in poly(diphenyl) films and in polystyrene films obtained by the glow discharge technique in the vapours of corresponding monomers have been more fragmentary.

As with very thin PB films. in the thickness range 100 to 1 000 Å. no supermolecular structures of any kind were found using optical and electron microscopy. They were transparent and without any trace of birefringence.

In the case of slightly thicker films obtained during 2 s glow discharge (film thickness $d = 2\,500$ Å) only a few. small. hemispherical structures could be found. Their average diameters are of the order of 500 Å. The major part of the films display a homogeneous structure reflecting all the support inhomogeneities. The density of these supermolecular entities is of the order $2 \times 10^4/cm^2$. (See *Figure 12*).
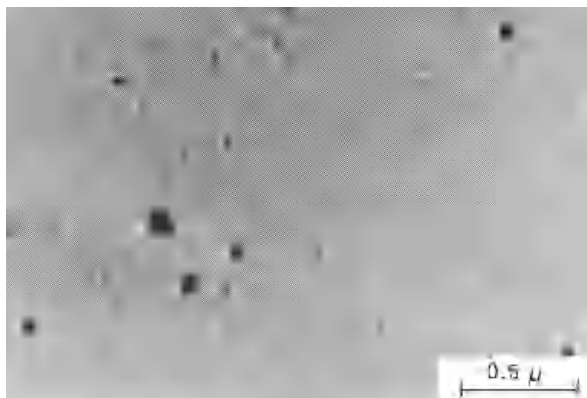
Figure 12. Electron micrograph of the surface of poly(diphenyl) thin film (film thickness $d = 2\,500$ Å)

All poly(diphenyl) films were devoid of knitted twist structures even after a long period of aging in air.

When a thicker sample ($d = 5\,700$ Å) obtained in 5 s glow discharge was investigated after 3 days aging in air. the concentration of the hemispherical entities had not increased. *Figure 13* shows also that the structures formed during the preparation do not change in an appreciable manner in this short time of aging. However in the case of PB films this treatment has already produced serious changes of structure. Thicker samples ($d = 6\,500$ Å) exhibit different structures. After similar aging times one can find quite strange structural entities in the form of truncated conical pits with small faults inside. In addition to these structures (see *Figure 14*) one can also find a few of the small. hemispherical structures observed in thinner samples.
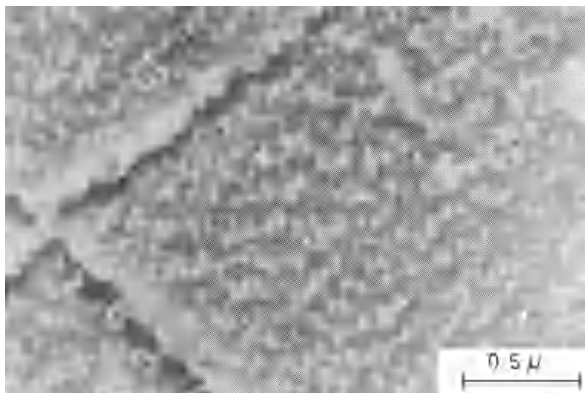
Figure 13. Electron micrograph of the surface of poly(diphenyl) thin film as in *Figure 12* but after 3 days aging in air
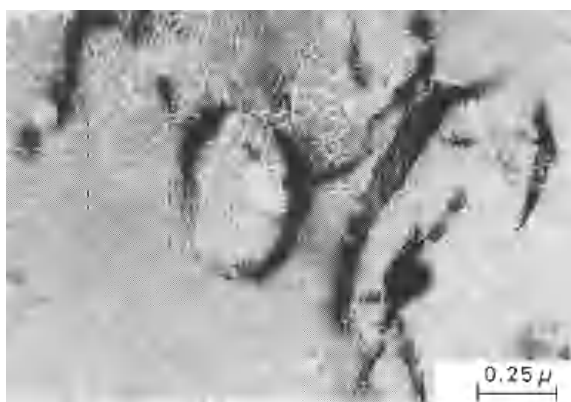

Figure 14. Electron micrograph of poly(diphenyl) thin film ($d \simeq 6\,500\,\text{Å}$) after 10 days of aging in air. Conical pits are present in addition to hemispherical structures
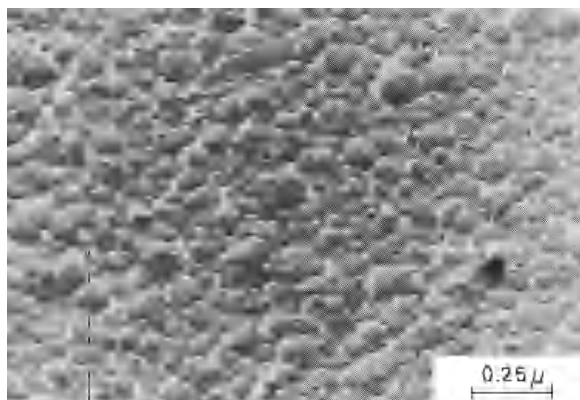

Figure 15. Electron micrograph of the surface of thin polystyrene film ($d = 8\,000\,\text{Å}$) with hemispherical structures

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For polystyrene films of thickness $d = 8\,000$ Å the hemispherical structures have also been found (*Figure 15*). They cover the surface of the film closely, being 700–800 Å in diameter and about 200 Å in height.

Some preliminary studies of the surface structures of poly(N-vinylcarbazol) thin films prepared by the glow discharge technique gave results in line with those discussed above, that is, completely structureless films for specimens of thickness less than 800 Å and nodular structures for thicker specimens.

SUMMARY AND CONCLUSIONS

Our results concerning the processes of structure formation in thin polymer films obtained by the glow discharge technique cannot be compared with many other results published by other authors. As was mentioned before, all workers describing the thin layers obtained from different monomers, using different methods of direct preparation from the gas phase, claimed that these specimens were amorphous, that is, without any structure.

The results on PB films given in ref. 97 and our own work on very thin PB films agree that in thin films no structure can be detected by electron microscopy. However, in thicker films nodular structures are formed, and in still thicker layers spherulites are formed.

PE thin films prepared by Miyoshi *et al.*[9] were highly crystalline and built up from oriented crystals. They cannot however be compared with films which are prepared during polymerization and not from already-formed polymer. In the former case one deals with polymerization and structure formation as simultaneous or separate processes, in the later case one has only a separate crystallization phenomenon.

Poll and Hinze[99], investigating the structure of thin polymers layers obtained by glow discharge from hydrocarbons, also observed nodular structures (see *Figure 16*). They carried out very careful x-ray diffraction studies of the resulting materials which suggested amorphous distribution of atoms with only short range order. IR spectra lead to similar conclusions showing some chain branching and inclusion of foreign atoms, the most important of which were oxygen atoms incorporated into these layers due to reactions of oxygen with trapped radicals.

Very interesting studies of the morphological structure of poly-*p*-xylylene crystallized during polymerization have been carried out recently by Kubo and Wunderlich[100]. However these authors have studied rather thick film of the order of 20 μ prepared by pyrolytic polymerization on solid surfaces, maintained at temperatures in the range 17°–30°C. These authors found spherulites of different sizes in their films. They concluded that spherulites and non-spherulitic portions or polymer films consist of folded chain lamellae. The poly-*p*-xylylene films cannot be compared directly with those prepared and discussed by us because of differences in thickness and technique of preparation.

The results which are presented above enable us to make some suggestions concerning the mechanism of structure formation in thin polymer films as prepared by the glow discharge technique from the gas phase:

(1) The thermal degradation of these films due to heating of the support plates may be neglected since they were cooled during polymerization. However, the possibility cannot be excluded that some thermal polymerization

caused by trapped free radicals occurred after the completion of the glow discharge.

(2) The chemical structure of these thin films, as determined by ir spectroscopy, is related to the starting monomer. However, many other chemical bonds and atomic groupings, which are not detectable in the monomers, were present.
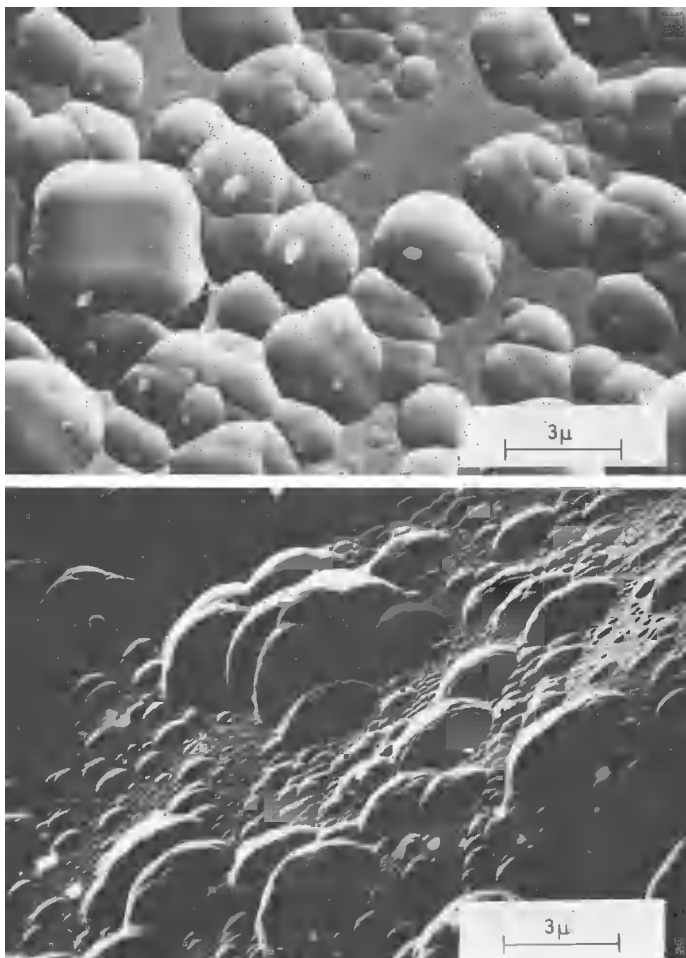
Figure 16. a and b Scanning electron micrograph of the fluorhydrocarbon polymer layer obtained by the glow discharge technique by P. Hinze and H. U. Poll (film thickness $d = 3$ μ). This layer covers small inorganic crystals dispersed on the support.

In the case of polybenzene films one might expect that benzene oligomers would be formed and would be able to crystallize, and could thus be responsible for the observed supermolecular structures. It seems, however, that the concentration of these entities in our films is too low to explain the observed structural units. The higher molecular weight polyphenylenes are quite insoluble and do not swell in organic solvents. Our films were insoluble, too, but they swell in aromatic solvents which is evidence against the presence of a sufficiently large

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concentration of oligomers. Preliminary thermal stability investigations of our films lead to the same conclusion.

(3) The formation of nodular hemispherical structures on the surface of thin films during the glow discharge polymerization process seems to be related to the random distribution of free radicals, resulting in areas of higher radical concentration which are trapped in the film material when the film thickness becomes slightly larger. They can react with the monomer molecules in the gas phase leading to a local increase of polymerization rate. This results in local internal stresses and nodule formation. It seems also that the observation of rather sharp edges to these hemispherical structures, tends to support these suggestions. In addition local overheating of these areas cannot be excluded from consideration.

(4) It seems that the twisted knit structure observed in aged films is due to internal stresses caused by further polymerization in the presence of peroxy-radicals formed from trapped radicals. Because of crosslinking, internal stresses are created. Polymerization and crosslinking reactions usually lead to an increase of density which in material which is still soft may be responsible for these structural inhomogeneities.

(5) The spherulites seem to grow in samples which contain rather regular chemical structures and where—at first—the internal stresses lead to some aggregations of macromolecules being formed. It may be expected that these aggregations could form nuclei which could lead to structure formation. The probability of formation of these elementary aggregations is larger at irregularities in the structure of the support (fissures), which may be sites of nucleation. These phenomena occur in rather soft areas of material where rearrangement of molecules is still possible. Crosslinking restricts the movement of the molecules so the spherulites being formed are not perfect but consist of irregular fibrils. Kinetic studies of spherulite growth are needed in order to obtain more information on the mechanism of their formation.

So far we have no evidence that in the nonspherulitic region of the films some orientation of the chains occurs as was found by Wunderlich. Thus at this stage it is not possible to discuss why the folded chain structure appears and not extended crystals, as one could expect for polymers which crystallize during polymerization.

The only conclusion that can be drawn from these experiments is that these nodular structures are formed during the polymerization process in films of medium thickness, and that these structures are further changed by aging in air, depending on the nature of the investigated material. It is probably due to further polymerization reactions which at first lead to density inhomogeneities and then to structure formation.

Further systematic study and analysis is needed with regard to other monomers as substrates, investigation methods, conditions of glow discharge polymerization and conditions of structure formation, dependence on support structure, etc.

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