

THE EFFECT OF MODIFICATION OF SUPERMOLECULAR STRUCTURE ON THE PROPERTIES OF POLYMERS

M. Kryszewski

Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź 90-362, Poland

Abstract - The properties of polymers depend on their chemical composition and physical structure. Preparation of the new practically useful polymers by modification of their chemical composition is limited by the availability of pure monomers and the complexity of the polymerization reactions; consequently, a lot of work is currently devoted to the change of their properties by modifying their physical structure. It is shown that controlled modification of supermolecular structures by thermal treatment (rate of cooling) and drawing of low density polyethylene results in materials with different viscoelastic and electrical properties. A special spinning technique consisting in simultaneous stretching and twisting yields polypropylene fibres with highly modified properties. Finally it is shown that the kind and perfection of spherulitic structures in polypropylene films influence their thermal oxidative degradation. These four examples show that a detailed knowledge of the relationships between morphological structure and properties of semicrystalline polymers leads to progress in controlled modification of the properties of this important class of high molecular weight substances by physical treatment during processing.

INTRODUCTION

It is a well established fact that the properties of polymers depend on the chemical structure of macromolecules and on the physical structure of the forming system. It follows that the properties of polymers can be modified by changing the molecular structure of macromolecules; this can be effected by choosing appropriate monomers and polymerization conditions as well as by changing the supermolecular structure of the system, i.e. the spatial packing of macromolecules and phases arising in the material as a result of the different physical processes that take place during processing. The fact that many compounds can undergo polyreaction processes which lead to the formation of homopolymer molecules and various types of polymers makes it possible to obtain polymers of different chemical structure and properties. However, the availability and the usually required high purity of the monomers as well as the complexity of the polymerization process are all responsible for the fact that only a small number of polymers is manufactured on a large scale. Obviously, for special purposes one can, by choosing suitable monomers, polymerization process and manufacturing conditions, obtain polymers exhibiting predetermined properties, however complex the requirements may be. For this reason there has been increased interest in controlled modification of typical and well-known polymers effected by changing their physical structure. Such modification is usually performed by thermal treatment and the action of mechanical forces during processing. Another possibility which has claimed increasing attention is the modification of the properties of materials by using mixtures of polymers of different chemical structure. In this way one can obtain not only multi-component systems but also multi-phase ones, as when one of the components can undergo crystallization. Even though such systems are becoming increasingly more important from both the practical and theoretical points of view, the discussion in this paper will be confined to the modification of the properties of polymers of definite chemical structure, i.e. one-component systems. Modification of the physical properties of polymers is connected with the possibility of obtaining systems of definite molecular orientation of molecules and crystallinity, as well as definite geometrical arrangement of the ordered

phases. This makes modification of properties relatively easy to effect in the case of polymers which easily undergo crystallization or form anisotropic ordered structures already during synthesis, e.g. liquid crystal polymers. Amorphous polymers, where there is a total absence of ordering of molecules (cf. Ref. 1), easily undergo deformation at temperatures above the glass transition temperature. This is due to weak intermolecular interaction forces. The ordering of macromolecules brought about by their orientation or crystallization leads to a stiffening of the material and there by to decreased susceptibility to deformation. At the opposite pole from amorphous materials are crystalline materials with maximum molecular orientation and crystallinity. Here belong e.g. highly-crystalline polymers with extended chains of definite direction, e.g. orientation direction, brought about by external stress. The elastic moduli of such systems may be very high, especially in comparison with the moduli of isotropic amorphous polymers or elastomers. The basic structural entities of the crystal structure in partially crystalline polymers are more or less perfect lamellae which are particularly distinct in polyolefins. Lamellae over 100 Å thick are separated by the amorphous phase. They may exhibit distinct correlation of orientation and arrangement forming higher-order structures, e.g. spherulites, where the lamellae are radially arranged. The knowledge of the overall degree of crystallinity is not sufficient for the description of the properties of such complex systems. Also indispensable is some information about the shape, size and the degree of perfection of these basic crystalline entities as well as some information concerning the correlation of orientation and arrangement of these elements inside higher-order structures, e.g. spherulites, and finally, information about the size of spherulites. It is well known that the presence and size of spherulites determines many of the properties of partially crystalline polymers (cf. Ref. 2-4), and for this reason we will only give some basic examples. Polymers with large spherulites, produced by slow cooling have lower impact strengths than polymers with the same crystallinity which were cooled rapidly and have many small spherulites. Spherulites affect the impact strengths of films in a very pronounced manner when their diameter is comparable with the thickness of the film. Polymers with many small spherulites show higher yield strengths, higher brittle temperatures, lower ultimate elongation and greater tendency to break during cold-stretching than comparable polymers with large spherulites. The effect of spherulite size on the strength of polymers has been explained by an analogy to the effect of grain size on the properties of metals. This explanation takes into consideration the fact that dislocations at grain boundaries and at interfaces are more numerous in a material consisting of many small spherulites and due to this more stress is needed to influence plastic slippage. This explanation may be partially true, but it is not entirely adequate because fracture in spherulitic polymers follows spherulite boundaries and sometimes passes through individual spherulites.

The effect of molecular weight on the strength of spherulitic polymers is difficult to explain. Two polymer films with the same average spherulite size but with different molecular weight will have different impact strength. Crystalline materials show lower permeability to gases and vapours. Crystallinities are almost impermeable to small molecules and thus the presence of crystallinity and of supermolecular structures reduces both the solubility and diffusivity of small molecules. The low rate of diffusion in partially crystalline materials can be accounted for by assuming that the presence of nearly impermeable crystallites increases the length of diffusion paths by setting barriers which diffusing molecules must circumvent. When the barrier crystals or structures are elongated and oriented, e.g. by deformation, molecules diffusing perpendicular to the direction of orientation have longer diffusion paths than molecules diffusing in the direction of orientation.

There are already some quantitative relations established which describe diffusion of gases and vapours and crystallinity. Crystallinities which are completely impermeable to diffusing species cause solubility and diffusivity to vary inversely with the first power to the volume fraction of crystallinity and they cause the permeability to change inversely with the second power of volume fraction of crystallinity. It seems interesting to note that the impermeability to gases depends on the perfection of the crystallites or supermolecular structures. The above discussion leads to the conclusion that in highly crystalline polymers, e.g. polyethylene, diffusion takes place in amorphous parts (fringes and fold surfaces).

The size and size distribution of crystalline regions in partially crystalline polymers influence the optical properties, e.g. clarity. These effects are due to non-homogeneities that scatter light from the interior and from the surface due to the presence of grain boundaries and phase boundaries when there are differences in refractive indices. Fissures, voids, and inclusions of gases cause light scattering in both amorphous and crystalline parts.

The above remarks show that many studies, which cannot be cited here, devoted to the establishment of the relations between properties and structure have led to considerable progress in this field. This does not mean that all problems have been solved, or that our knowledge of these relations is sufficient to permit fully controlled and predictable modification of polymer properties. The complex structure of partially crystalline polymer samples and the various internal interactions between macromolecules and elements of higher-order structures are responsible for the fact that the experimental parameters describing the properties of polymers, especially the mechanical ones, are complex functions of many structural parameters. Deformation of a polymer containing spherulitic structures brings about changes in their shape, from spherical to ellipsoid. It follows that local elongation inside spherulites depends on the arrangement and orientation of lamellae relative to stress direction. Amorphous regions with lower moduli than the crystalline regions exhibit larger microscopic elongation when the two phases are arranged in series relative to external stress, e.g. in the polar regions of spherulites. If, on the other hand, the lamellae embedded in the amorphous phase are parallel to the direction of external stress, then they too shift parallel to the stress direction and the inter-lamellae regions undergo extensive shearing deformation. This shows that local deformation inside a polymer depends not only on the nature of the phases but also on the orientation of the larger structural entities in the sample.

Important information about the mechanical properties of spherulitic polymers in the range of small deformations can be obtained not only by analysing stress-strain curves and their correlation with the results of structural studies, but first of all by considering the characteristic of viscoelastic properties. Such information can be obtained by studying sinusoidally variable deformation which provides insights about the relaxation processes taking place in the different phases of the material under study and thus makes it possible to correlate properties and molecular processes.

To show how controlled modification of the morphological structure affects the viscoelastic properties of spherulitic polymers one has to describe in detail the structure of the sample under study and its changes during dynamic deformation. As an example we will present some of the results of studies conducted at our laboratory on the modification of the properties of low-density polyethylene (PELD) carried out by suitable thermal treatment.

THE EFFECT OF COOLING RATE ON THE MORPHOLOGY AND VISCOELASTIC PROPERTIES OF LOW-DENSITY POLYETHYLENE

Without going into a detailed description of the molecular parameters of the PELD used in the study - those parameters can be found in the literature referred to later on in this paper - we shall only point out that the samples (films) were obtained by melt-pressing and nonisothermal crystallization at different cooling rates of the melt. During sample cooling, at definite change of the temperature inside the sample there takes place growth of spherulitic structures whose kinetics were studied by the light scattering technique. Apart from that the arising structure of the samples was analyzed by optical and electron microscopy, small-angle light and X-ray scattering, as well as by X-ray diffraction technique. In this way we obtained information (Ref. 5 - 7) about the parameters of spherulite size distribution in the samples under study, about the internal arrangement in spherulites, and about changes in the size of lamellae and the degree of crystallinity in the function of the method of sample preparation. Some of the results obtained are collected in Table I below (after Ref. 8).

TABLE 1. Characterization of the samples (after Ref. 8)

Sam- ple N ^o	Bath tem- pe- rature C ^o	Cooling rate C ^o /s	Average rate of spheru- lite growth μm/s	R _v μm	σ ²	Degree of crystal- linity %	Long period nm	Spherulite perfection factor η
1	0	95	90	1.83	0.358	43.2	9.3	1.11
2	25	51	56	1.98	0.88	43.4	9.6	1.43
3	50	29.5	25	2.16	1.14	43.5	9.8	1.85
4	70	6.0	0.3	2.28	1.32	44.2	10.5	2.90
5	80	1.5	2.2	2.43	2.92	45.2	10.8	2.17
6	90	0.17	1.1	2.84	3.35	45.6	12.0	2.43

R_v - volume average of spherulite radii

σ² - variance of spherulite size distribution

It can be seen that the overall degree of crystallinity of the samples under study is, to all intents and purposes, constant, while the other parameters characterizing the sample structure change in a significant way. This makes it clear that slight changes in the way PELD was cooled lead to changes in spherulite size and the degree of their internal ordering, and to marked changes in lamellar size and orientation, the overall degree of crystallinity undergoing relatively small changes. These changes in the morphological structure occurring under different conditions of sample cooling, i.e. under different conditions of growth of morphological structures manifest themselves in the shapes of the stress-strain curves (Ref. 9) but the differences in their shape for fast and slow cooled samples are not very distinct and are difficult to interpret unequivocally.

More interesting results, ones that led themselves to a more detailed interpretation, were obtained in studies on the dynamic deformation of samples (Ref. 8). Deformation was conducted in a small range of sinusoidally variable strains at frequencies ranging from 0.003 to 20 Hz and the parameters of the mechanical properties of the films were determined. Also studied were changes in birefringence and changes in the intensity distribution of the light scattered by the spherulites at small angles (Ref. 8). Figs. 1a and b depict the frequency dependence of the real part of modulus E' and of $\text{tg } \delta$ of the samples under study. These dependences exhibit marked changes in sample behaviour which manifest themselves in shifts of two maxima, one of which appears at 0.2 Hz (a_2) and the other - at 10 Hz (a_1).

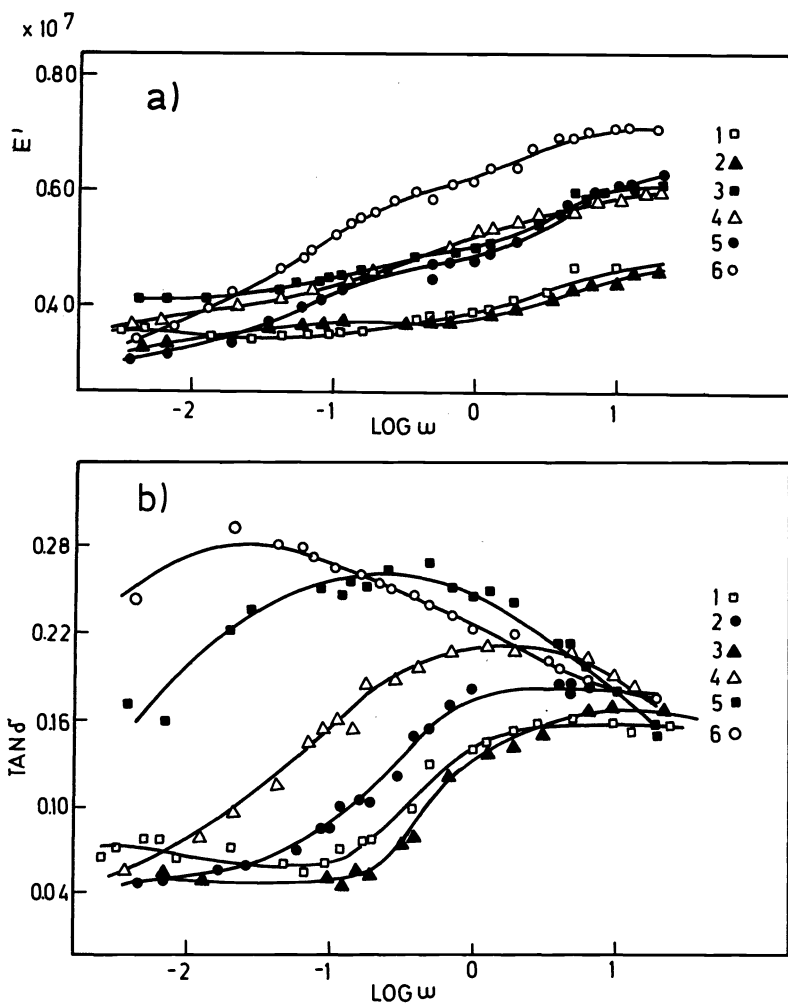


Fig. 1. Dependence of E' (a) and of mechanical loss ($\text{tg } \delta$) (b) on logarithm of deformation frequency at room temperature (Ref. 8)

It follows that the positions of these maxima on the frequency scale depend on the morphology of the samples. Apart from that the values of K' - the real component of the rheoptical coefficient, and of $\text{tg } \alpha$ (α - the angle of the phase shift of changes in sample birefringence relative to strain) were also determined by measuring the changes in the intensity of the light transmitted by the sample. These results (Ref. 10) confirm the earlier statements (the maxima

a_1 and a_2 are particularly distinct here). Measurements of the real component of modulus E' and of $\text{tg } \delta$ in the function of temperature (Ref. 9,10) made it possible to determine the activation energy of the observed relaxation processes. Fig. 2 depicts the dependence of $\log \omega_{\text{max}}$ for $\text{tg } \delta$ on the reciprocal of the temperature. The values of the activation energy are contained in the 30-45 kcal/mol interval. This means that in samples cooled under different conditions (lowest and highest temperature) one of the relaxation processes predominates (a_1 - characteristic of the amorphous phase, and a_2 - characteristic of the crystalline phase). The activation energy values determined by us agree well with those of Tanaka et al (Ref. 11) obtained in studies of dynamic X-ray diffraction.

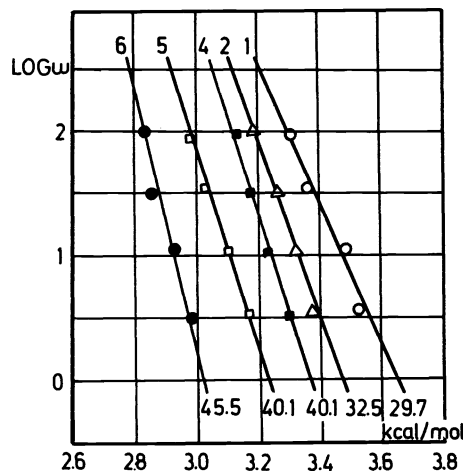


Fig. 2. Frequency dependence of $\log \omega_{\text{max}}$ for $\text{tg } \delta$ (Ref. 10)

These results indicate that the viscoelastic properties of PELD samples are closely related to the degree of internal ordering in spherulites which, in turn, is closely related to the size of the lamellae and their different correlation inside higher order structures.

Interpretation of the observed changes of the viscoelastic properties of PELD samples on the basis of the information about their supermolecular structure requires the adoption of a definite structural model which takes into account its heterogeneous nature and the specific correlations of the crystalline species inside radial spherulites (Ref. 12). The mechanical model, which permitted analysis of unhomogeneous strain and deformation inside the spherulites, was discussed in some detail in our earlier publication (Ref. 8) and was then extended in (Ref. 13); we will thus limit ourselves here to the most important conclusions. The results of calculations of strain and deformation distribution in different parts of spherulites carried out in accordance with that model have shown that the maximum a_2 increases with increasing spherulite ordering, and is related to increased strain in the polar parts of spherulites. This confirms the earlier mentioned correlation of the maximum a_2 appearing at 0.2 Hz with crystalline entities. Basing on experiments and calculations performed in terms of the model in question the experimentally observed decreased intensity of the maximum a_1 was attributed to strain relaxation in the surface layers of the lamellae oriented at 45° relative to external strain direction. Support for that conclusion came from an analysis of the dependence $\text{tg } \gamma$ i.e. of the spherulite elongation phase shift relative to the macroscopic elongation of the sample (Refs. 8,10).

It should thus be clear that a through-going structural analysis leads to an explanation of the effect of thermal treatment of the polymer on its mechanical properties, and the viscoelastic properties in particular. It should also be evident that by modifying the morphological structure one can significantly control the changes in the mechanical properties of partially crystalline polymers. It should be stressed, however, that we are here not talking here only about the effect of the size of the supermolecular structures - something that has already been pointed out - but also their internal structure which can also be controlled by suitable thermal treatment. In the case under consideration modification of the mechanical properties depended first of all on the morphological structure.

The properties of man-made fibers depend primarily on the orientation of the crystalline entities and on molecular orientation. Numerous studies on the correlation of structure and properties of synthetic fibers have been performed on systems in which definite mechanical properties were obtained by bringing about uniaxial orientation of the crystalline entities and macromolecules. Several important relationships between properties and morphology have been established.

They are of particular importance for the preparation of high modulus fibers (Refs. 14,15). It is well known that extensive modification of fiber properties takes place when the overall geometry of orientation is different from uniaxial (Ref. 16), e.g. helical (Ref. 17). This type of orientation was found in many natural fibers and it can be achieved in man-made fibers by the use of special techniques. As an example of controlled modification of the properties of partially crystalline polymers we will discuss some of the results of studies on the preparation and properties of synthetic fibers with internal helical orientation.

THE EFFECT OF INTERNAL HELICAL ORIENTATION ON THE PROPERTIES OF SYNTHETIC FIBERS

Some basic information about the method and conditions of preparing fibers with internal helical orientation can be found in (Ref. 18). Similar studies were also started by Andersen et al (Ref. 19). The method consists in setting in rotational motion about the fiber axis of the solidified part of the fiber (between the spinneret and the take up device). In this way the fiber is simultaneously drawn and twisted in the region where it is still in the molten state. After leaving the spinneret the filament of spinning fluid changes its diameter (as it travels away from the spinneret) and cools down. This is accompanied by changes in the viscosity of the melt. An analysis of the spinning dynamics during simultaneous drawing and twisting shows that the longitudinal gradients of the rate of mass flow $\delta v/\delta x$ in the nonsolidified part of the fiber and of the rotational flow $\delta \omega/\delta x$ are different depending on the distance away from the spinneret. This can be seen very distinctly in Fig. 3 which depicts distribution of the gradients $d\omega/dx$ and dv/dx in the function of the distance from the spinneret.

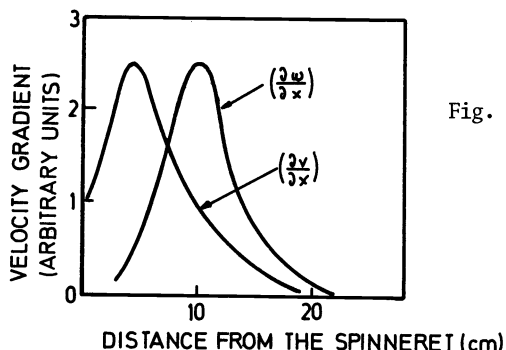


Fig. 3. Calculated rotational ($d\omega/d$) and longitudinal (dv/d) velocity gradients as functions of the distance from the spinneret (Ref. 18)

It follows from the well known fact that orientation in a fiber depends on the ratio of the mass flow gradient and orientation relaxation times related to local viscosity of the filament, that a shift in the maximum of rotational flow gradient velocity towards longer distances from the spinneret (where the filament has higher viscosity due to cooling) makes helical orientation relaxation more difficult. This orientation may then be preserved as the filament continues to cool down and solidify. Indeed, studies of the structure of polypropylene fibers obtained in this way have shown extensive helical orientation in them; polarizing micrographs of the fiber cross-sections show typical helical structures. The anisotropy is not constant along the fiber radius and reaches higher values towards the centre of the cross-section for fibers obtained at higher rotational speeds. Using wide-angle X-ray scattering to determine the orientation of the crystallites it was found that in the case of uniaxial orientation of the usually prepared fibers the distribution function of orientation in the (110) plane has a Gaussian shape, while in the case of twisted fibers it does not. It has two distinct maxima which are symmetric with respect to the fiber axis and are characteristic of the helical orientation. These distribution functions of orientation depend on the twisting rate ω . Thus, the parameters of the helical structure of the fibers obtained in this way depend on the fiber drawing speed and the twisting speed. The different ratios of these velocities make it possible to control the of the arising helical orientation.

As an example of the differences in the mechanical properties of such fibers consider the elasticity moduli (Fig. 4) determined along the axes of fibers obtained at constant drawing speed but at different twisting speeds. It can be seen that twisting gives rise to increased modulus, the maximum increase

occurring at a definite ratio of the two velocities, i.e. at a definite orientation geometry. It should be pointed out that a change in the overall orientation geometry from uniaxial to helical (at constant orientation degree) should lead only to decreased values of the modulus, while experimental evidence shows that the fiber deformation brought about by twisting leads to greater orientation than in the case when the drawing speed is the same, but there is no twisting.

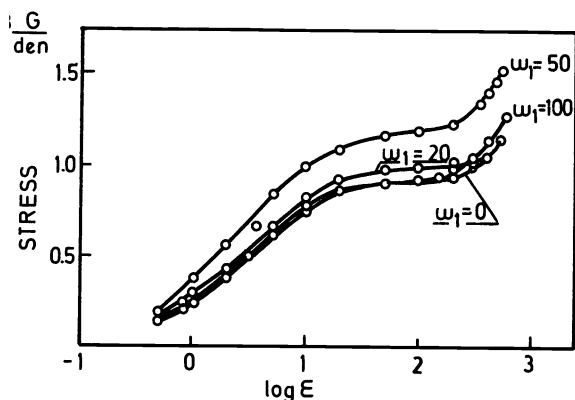


Fig. 4. Stress-strain curves for fibers obtained with different twist ratio (Ref. 18)

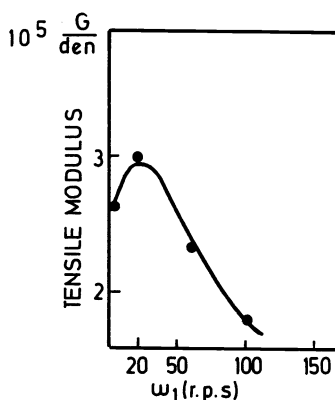


Fig. 5. Dependence of tensile modulus on rotational spinning velocity (Ref. 18)

The stress-strain measurements of fibers with various degrees of twist show that the elastic moduli calculated from these results, in the range of 1% deformation, are the highest for intermediate rotational velocity (cf. Fig. 5). The ultimate strength of twisted fibers is also extreme for fibers obtained with the same twisting speed. In spite of the increased elasticity modulus along their axes, fibers with helical orientation exhibit also higher susceptibility to bending. Work on the preparation and properties of fibers of this type is still in progress at our laboratory, but it seems that the results obtained thus far make it clear that appropriate conditions of structure modification will lead to a range of interesting new materials with a variety of properties.

Modification of the morphology by thermal treatment and controlled deformation also leads to changes in the electrical properties of partially crystalline, or even amorphous, polymers.

THE EFFECT OF ORIENTATION AND MODIFICATION OF MORPHOLOGY ON ELECTRICAL PROPERTIES

Orientation of polymer chains brought about by elongation may also cause changes in the electrical properties of such systems (Refs. 20,21). The mechanism of electrical conduction of such anisotropic materials is not fully understood yet, and the same applies to the relation between the superstructure and conductivity.

It is reported (Ref. 22) that uniaxial and biaxial elongation results in decreased electrical conductivity. The effect of orientation on the dielectric loss tangent ($\tan \delta$), short-term electric strength, and voltage endurance capacity of a number of polymers, e.g. polyethylene (PE), polyvinyl chloride (PCV), and polycaprolactam (PCAP) was investigated by Bagirov et al (Ref. 23) as well as by other authors. The relations between the change of fine texture and the electrical properties of uniaxially oriented materials are usually quite complex, as e.g. in the case of high density PE where drawing was found (Ref. 24) to cause an increase in the conductivity and a decrease of apparent activation energy, as well as of a.c. and d.c. breakdown strengths. Different relations were observed for PELD. It was established (Ref. 25) that the pulse breakdown strength increased linearly as the temperature, at which the elongation was carried out, increased. This effect was attributed to the c-axis orientation of crystalline lamellae as well as to the increased density in the amorphous regions.

The effect of uniaxial elongation on the conduction of PELD was recently investigated by Yahagi et al (Ref. 26) and also at our laboratory (Ref. 27). Both studies concerned additive free non-crosslinked material as well as to

films crosslinked with γ -rays (Ref. 26) and with dicumyl peroxide (Ref. 27). A certain degree of crosslinking was necessary to draw films at higher temperatures (about 120° C) without melting. Because the results of both these studies are to some extent similar, we would like to discuss them together. For the sake of convenience the work of Yahagi et al (Ref. 26) will be referred to as I, and our study (Ref. 27) - as II. Since the details of our conductivity studies have not been published yet, some information about sample preparation and the measurement techniques used is in order. The material used was PELD Lupolen S (BASF), $T_m = 110^\circ \text{C}$, density $\zeta = 0.918 \text{ g/cm}^3$ and $M_v = 28.000$. The number of CH_3 groups for every 1000 C atoms in the main chain was equal to 35. Films about 50 μ thick were obtained by melt-pressing at 130° C. The crosslinked films employed in II were obtained using less than 2 % of dicumyl peroxide and were cured in laboratory press, while the ones used in I were obtained by 20 Mrad irradiation under vacuum. The degrees of crosslinking were found to be 56 % (I) and 62 % (II) as established by gel fractions determined by weighing out insoluble polymer in toluene. The degree of PELD crystallinity determined before crosslinking amounted to 48 % in I (density measurements) and 45 % in II (wide angle x-ray diffraction). Uniaxial elongation by tensile stress was effected at 20° C and at 120° C with a drawing velocity of 7 mm/min in I and at 20° C and 120° C, with a drawing rate of 5 mm/min in II, until a given ratio of ϵ was obtained ($\epsilon = 1 - l_0/l_1 \times 100$, where l_0 and l_1 represent sample lengths before and after elongation). In some cases ϵ amounted to 300 %. In both studies the stretched films were investigated in metal frames to keep the ϵ values constant. Electrical conductivity measurements were carried out at room temperature (time dependence) or at rising temperature (activation energy measurements) 2-5 hours after the elongation. In I the measurements were carried out in the air using aluminium foil electrodes, and in II under vacuum using vacuum-deposited aluminium electrodes. During electrode deposition care was taken not to interfere with the structural changes which had been brought about by elongation. DC conductivity measurements were performed using a conventional electrometric system. The time dependence of currents was measured at field higher than $1.6 \times 10^6 \text{ V/m}$ in I, and at fields exceeding $0.5 \times 10^6 \text{ V/m}$ in II. In both studies current-voltage characteristic were determined 10 minutes after voltage application.

The time dependence of the transient current $I(t)$ was in both cases found to correspond to the expression $I(t) = A t^{-n}$ where t is time after the application of external voltage, A is a temperature dependent factor, and n is a constant. Similar relationships were found to hold for many other polymers. In I the values of n measured at 20° C were in the range of 0.76 to 0.92 for films drawn at 120° C the n values were in the 0.76 - 1.07 range. In our study (II) the n values were of the same order of magnitude for films deformed at room temperature, while in the case of films stretched at higher temperatures the n values were a little higher. Possibly, these differences are due to the fact that our study (II) was carried out under vacuum, and the absence of O_2 could be significant. The differences in the n values could be analyzed in terms of the different ways of crosslinking (γ -irradiation and chemical crosslinking), and in terms of the presence of by-products of peroxide decomposition. These differences are, however, small and the error in the determination of the n value too high to permit any definite conclusions about the role of the above mentioned by-products.

The details of the analysis of the $I = f(t)$ relations obtained in both studies will be omitted here. Let us only point out that stretching causes a faster current decay and the differences are more distinct for samples drawn at low temperature (20° C) because stretching has a greater effect on the changes in sample morphology, e.g. destruction of small spherulites, splitting of crystalline lamellae, than drawing at higher temperature (120°) at which PE is almost in the amorphous state and its structure does not depend on the ϵ values to such an extent.

The time dependence of the current can be interpreted by taking into consideration the ionic carriers (they can be accumulated at electrodes and cause a decrease of internal field with time) or electrons or holes which may be transported by random hopping through the sample. It seems that the conductivity changes with the draw ratio found in I and II and which are depicted in Fig. 6 favour electronic conductivity. This is due to the fact that the first decay of conductivity can be explained by the creation of new trapping sites by deformation until $\epsilon=60$ % and the further increase of conductivity at ϵ values reaching 300 % (observed especially for samples drawn at 20° C) may cause a conductivity increase due to decreased distance between the hopping sites. This interpretation is compatible with the density increase of highly stretched samples found both in I and in II, which was also reported earlier by other authors (cf. Ref. 28). In the case of ionic conductivity one could only expect a continuous decrease of conductivity with draw ratio.

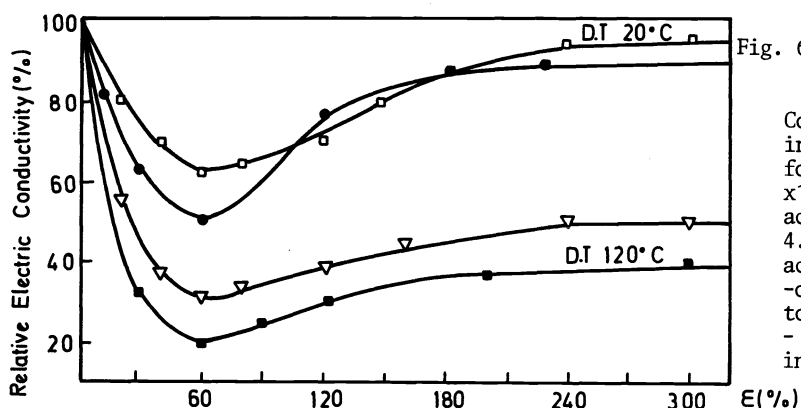


Fig. 6. Effect of uniaxial drawing on electrical conductivity of PELD. Conductivity is expressed in relative units, taking for undrawn samples $2.5 \times 10^{-15} \text{ (ohm cm)}^{-1} = 100$ according to Ref. 26, and $4.8 \times 10^{-14} \text{ (ohm cm)}^{-1} = 100$ according to Ref. 27. -o-o- and - - - correspond to results in Ref. 26, - - - and - - - to those in Ref. 27.

Interesting conclusions about the influence of conductivity changes related to structure modification by deformation can be reached from current-voltage characteristics which were studied both in I and in II. A characteristic feature of the $\log I \sim \log E$ curves (E is electric field strength) is the existence of two sectors: one corresponding to Ohmic behaviour, and the other - to space-charge limited currents (SCLC) injected into PE in the range of high E values. This type of I - E relation is typical of all high molecular weight dielectrics (Refs. 21,29). For films drawn at 120°C the I - E curves preserve their shape and are only shifted parallel to the lower values (for small ϵ) and later on - to higher values (for high ϵ), but never reaching the current values of unstretched films (cf. Fig.7). The transition from the Ohmic range to space charge limited currents (SCLC) does not depend on stretching which again favours the conclusion that smaller structural changes related to elongation at high temperatures have a rather small influence on conductivity. In the case of chemically crosslinked materials according to II the conductivity is higher probably due to the presence of by-products which may act as weak acceptors, releasing the trapped carriers at room temperature. In the case of I - V curves, there are more pronounced differences both in the shape of this relation and in

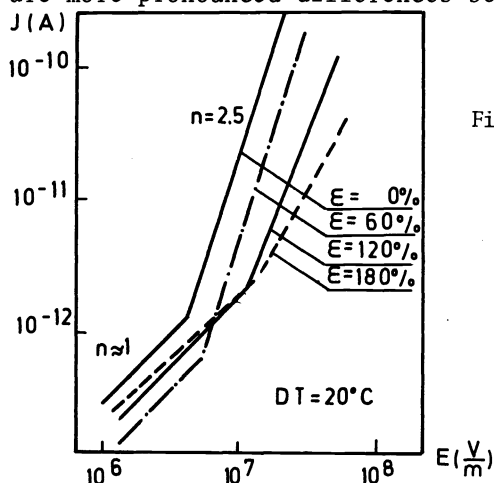


Fig. 7. Current-voltage characteristics for chemically crosslinked PELD films drawn at 20°C to different ϵ values. (presented schematically)

the current values for a given electrical field. Drawing affects the transition from Ohm's law to SCLC. It is shifted according to I towards higher fields with increasing elongation ϵ . This behaviour was also found for chemically crosslinked materials, but the Ohmic behaviour was extended to higher fields and the exponents n in $I \sim E^n$ are higher than those observed in γ -ray crosslinked materials. This difference may be accounted for by considering the fact that during the peroxide-induced crosslinking some $\text{C}=\text{O}$ groups are created (in addition to crosslinks) which enhance the conductivity. This confirms the conclusion of Look (Ref. 30) and of Fischer et al (Refs. 31a,b) that $\text{C}=\text{O}$ groups do not represent deeper traps than those already present in the pure material. It seems reasonable to suggest that $\text{C}=\text{O}$ groups represent localized centers by which hopping transport of injected carriers occurs. The average distance of these centres changes during uniaxial deformation thus influencing the conductivity. At small deformations these distances increase and the conductivity must be lower, while at higher deformations these distances decrease due to

increased density of the material as mentioned before. It can also be said, in favour of this suggestion, that the activation energy values E_a of conductivity for a given E value are similar for γ -crosslinked and chemically crosslinked PELD films, being of the order of $E_a = 0.7$ eV according to I, and 0.81 eV according to II, for $E = 0$. These values decrease for drawn samples as was found in both studies. Only for high E values do the E_a values increase again for samples stretched at high temperatures. This effect may be accounted for by the creation of new trapping sites brought about by stretching. Without going into a more detailed analysis of PELD structure changes during deformation which was the subject of several investigations and is discussed in I and in II, we can conclude that uniaxial drawing results in increased rate of current decay, and decreased Ohmic region of electrical conductivity. These changes depend on structural modifications occurring during stretching. Both studies also show that it is not only the final deformation value that is of importance, but so is also the temperature at which this deformation, i.e. structural changes are achieved.

In the above investigations the role of trapping sites was mentioned many times and it seems reasonable to add some remarks on the direct observation of traps by the thermally stimulated currents method (TSC). The technique has recently been shown to be very important and useful in studies of dipolar relaxations and trapping effects in polymers. Numerous publications have been devoted to different aspects of TSC application in polymers studies (cf. Ref. 32,33). We have recently applied this method to demonstrate the influence of spherulite size on the intensity of TSC and to show that this technique can be usefully applied in morphological studies of semicrystalline polymers (Refs. 33,34).

The study (Ref. 34) concerned additive free isotactic polypropylene (PP) ($M_v = 300,000$) in the form of thin films. Spherulites of different size were grown in PP films melted under pressure of 200 kg/cm^2 at temperatures above 190°C cooled at different rates. The heating of the PP melt at different temperatures and its subsequent cooling yielded films with different degrees of crystallinity (density), different melting point of the crystallites, and different spherulite diameters (optical microscopy). TSC measurements were carried out on films with vacuum deposited Al electrodes in standard equipment for this type of studies. The charging conditions - electrical field strength E_p and temperature T_p , were chosen in such a way as not to change the initial morphological structure ($E_p = 8 \text{ kV/cm}$, $T_p = 105^\circ \text{C}$). The heating rate in all TSC experiments was equal to 1°C/min . Films cooled from 220°C and 190°C contain spherulites of $8.0 \mu\text{m}$ and $6.9 \mu\text{m}$ in diameter respectively. The TSC curves for samples with small spherulitic specimens exhibit two maxima at 90° and 120°C , and those for larger spherulites have only one well-pronounced maximum at 90°C (Fig. 8). It can be seen that spherulite size influences the

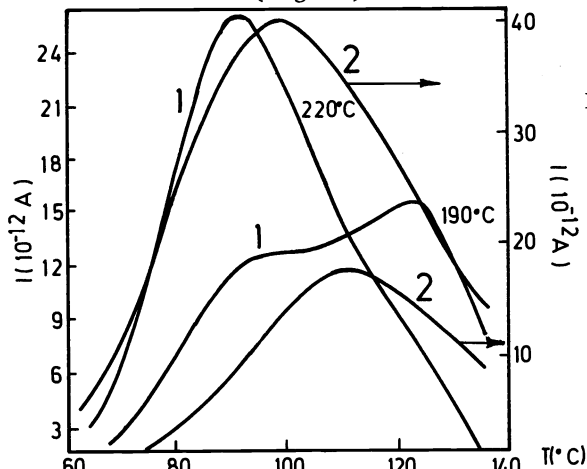


Fig. 8. Thermally stimulated depolarization currents for PP films crystallized from different temperatures, containing spherulites of different sizes. Curves 1 - samples polarized at $T_p = 105^\circ$, curves 2 - sample polarized at $T_p = 125^\circ \text{C}$.

intensity of TSC maximum. The rise of the charging temperature to 125°C causes a change in the shape and intensity of the observed maxima. The sample with smaller spherulites (obtained by cooling from 190°C) shows a more intense maximum at 90°C , and the one with larger spherulites exhibits a maximum at 110°C . The fact that charging conditions influence the TSC spectra is also related to their morphology. Independent conductivity measurements carried out at different temperatures for samples with varying degrees of crystallinity make it possible to determine the relative content of the amorphous and crystalline phases when simple Lichteneker logarithmic rule of mixing is assumed to be valid. The calculated conductivity values of both phases plotted in the function of temperature exhibit two maxima - one at 85°C for the crystalline phase, and one at 110°C for the amorphous phase (the overall conductivity increases

with temperature). This fact leads to the conclusion that the first maximum at 90° C is related to the crystalline phase, and the one at 110° C - to the amorphous phase. Polarization at 125° C seems to favour smaller spherulites which are less perfect and contain more amorphous phase, and there is no doubt that the borders between the spherulites are trapping centres. These few examples show that studies of the electrical properties using the TSC technique also lead to interesting conclusions about the relations between morphological structure and properties.

The different kinds of morphologies which can be formed in semicrystalline polymers influence not only their mechanical and electrical properties but also their thermooxidative degradation.

THE INFLUENCE OF MORPHOLOGY ON THERMOOXIDATIVE DEGRADATION OF POLYPROPYLENE

It has already been mentioned that the relative content of the crystalline phase and the morphological structure of semicrystalline polymers influence the solubility and permeability of gases and vapours. It has also been found that the rate of thermooxidative degradation of polyolefins depends on oxygen solubility and for this reason one can expect differences in sample crystallinity and morphology to have an effect on the degradation process. Studies have been carried out on the effect of crystallinity on the thermooxidation rate of PE (cf. Refs. 35,36), and of polypropylene (PP) (cf. Refs. 35,37-40), as well as of other parameters characterizing the physical structure of the samples, e.g. tacticity, sample thickness, on this reaction.

The IR absorption studies (the ratio of CH₂ group absorption in crystalline and amorphous regions), density measurements, and X-ray diffraction investigations have shown that the crystallinity of polyolefins increases during thermooxidative degradation. However, some differences in the interpretation of the results (especially of IR studies) have to be noted.

Much less attention has been given to the role of the morphological structures in thermal degradation of PP in the presence of air. Thus, knowing the influence of morphology on many properties of semicrystalline polymers it seemed interesting to conduct appropriate studies in order to elucidate this problem. In our studies we investigated thermal oxidation of isotactic PP films of constant thickness, crystallized from the melt at different temperatures. The samples obtained in this way differed in the initial degree of crystallinity X_0 and morphological structure (Refs. 41,42). Films of isotactic PP ($\bar{M}_v = 168,000$) of constant thickness (100 μm) were obtained by melt-pressing at 190° C. The samples were crystallized from the melt under isothermal conditions at different temperatures for a period of time which was equal to twice the crystallization half-time $t_{1/2}$ (the $t_{1/2}$ values are known from the literature (Ref. 43)). These samples, crystallized in the temperature range from -75° C to +120° C, have a crystallization degree X_0 varying from 0.35 to 0.62. The samples crystallized at low temperatures contained very small and defective spherulites; their diameters d_1 varied from 5 μm to 300 μm , and d_2 values were from 10 μm to 270 μm (d_1 and d_2 correspond to the so-called α and β forms of spherulites respectively). These are the upper values of spherulite sizes, while in reality they are distributed over a fairly wide range. Studies of thermooxidative degradation were conducted in air in the temperature range from 80 to 145° C. Physical and chemical changes in PP during its oxidation were determined by investigating the changes in density, intrinsic viscosity in p-xylene at 85° C, IR absorption, T_g values, X-ray diffraction patterns, the DSC method, and by optical microscopy in order to obtain a body of information on the reaction course and morphological structure changes. The degree of chain scission S was calculated from the values of intrinsic viscosity $(\eta)_0$ and $(\eta)_t$ before and after thermooxidative degradation at appropriate temperatures (cf. Ref. 44). The micrographs of morphological structures that arose during crystallization at different temperatures show that samples with higher initial crystallinity degree X_0 contain larger spherulites with crystallites of the α and β form. Spherulites of the β form are larger because of the higher rate of this type of crystal growth (Ref. 45) in that form. The thermooxidative degradation of these films carried out in air at 130° C for 10 hrs did not influence the morphology of PP films to any high degree. This is due to the fact that chain scission occurs mainly in the amorphous phase. Only the crystal surfaces are changed and the overall degree of crystallinity X increases as was found by density measurements of samples degraded at temperatures $T_d = 85^\circ\text{C}$, 115°C and 145°C for different time periods t_d . It was found that the degree of crystallinity rises sharply in the first step of heat treatment in air following which it is almost constant. The rate of crystallinity increase depends on T_d and the initial crystallinity X_0 . The results concerning the changes in the X values were confirmed by investigations of IR absorption at 995 cm^{-1} which

corresponds to the crystalline phase (the increase of absorption related to the formation of C=O groups during degradation was small). The dependence of the number of chain scissions (S values) on degradation time at temperatures ranging from 100° C to 145° C exhibit a faster increase in the first steps of thermal oxidation than in the later ones (see Fig. 9). This increase depends on the temperature and initial sample morphology. The time

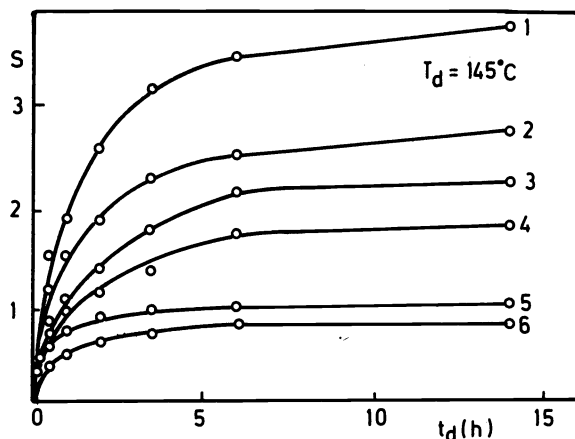


Fig. 9. Dependence of the number of chain scissions S on degradation time t_d at $T_d=145^\circ\text{C}$ (curves 1-6 correspond to samples with crystallinity degree $X_0 = 0.35, 0.45, 0.50, 0.58, 0.60$ and 0.67 respectively, and spherulite diameters $d_1 = 5\ \mu\text{m}, 10\ \mu\text{m}, 10 - 20\ \mu\text{m}, 18 - 40\ \mu\text{m}, 120 - 270\ \mu\text{m},$ and $150 - 300\ \mu\text{m}$ respectively).

dependence of the S values in the first stages of thermooxidative degradation can be correlated with the consumption of oxygen absorbed in the sample. In that time interval the change in the number of chain scissions is a linear function of time: $S = P_0 K_S t_d$ where P_0 is the initial degree of polymerization, K_S is the chain scission rate constant, and t_d is degradation time. Thus, K_S can be calculated from the initial slope of the tangent to curve $S = f(t_d)$ for $t_d \rightarrow 0$. Using this procedure for samples degraded at different temperatures one can calculate the dependence of K_S on $1/T$, as well as the corresponding activation energy value E_g . Using this procedure we obtained $E_g = 17$ Kcal/mole. The K_S value depends on the degree of sample crystallinity X . Because the thermooxidative degradation occurs first of all in the amorphous phase, we expected the expression $\lg dS/dt = f(\lg(1-X))$ to be valid (see Fig. 10). The plots obtained are straight lines with different slopes (at various temperatures), the exponent n being in each case in the 2.0 - 2.3 range (see Fig. 10). The difference from the $n=1$ value shows that not only crystallinity but also the morphology of the sample affects PP degradation in air (otherwise n would be equal to 1).

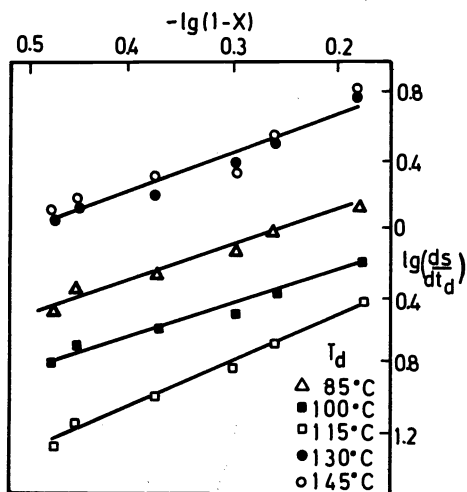


Fig. 10. Plots of $\lg(ds/dt_d)$ vs. $\lg(1-X)$ for different degradation temperatures T_d .

Thermooxidative degradation of solid polymers is diffusion controlled. The oxygen molecules may diffuse into the film and undergo attachment to the radicals that arise there (Refs. 46-49). If O_2 consumption is an irreversible first order chemical reaction, the investigated process can be discussed from the point of view of one-dimensional diffusion. The solution of the diffusion equation for steady state conditions and appropriate boundary conditions can be obtained for two particular cases when $1/\sqrt{K/D}$ is large or small (1 being film thickness, K - the rate constant of first order oxygen attachment reaction, and D - the O_2 diffusion constant). It was also shown in Ref. 42 that the

assumption that $\sqrt{lK/D}$ is small is valid; thus, introducing the value of chain scission efficiency E and the determined value of the rate of chain scission q one can correlate the activation energy E_g of thermooxidative degradation with the activation energy E_d of thermooxidative degradation with the activation energy of oxygen diffusion E_d and activation energy of oxidation E_o in the following way: $E_g = (E_d + E_o) / 2$. The value of E_d is known from the literature (Ref. 49) ($E_g = 11.4$ Kcal/mole), so with known E_g one obtains $E_o = 22.6$ Kcal/mole which is in good agreement with the literature data (cf. Ref. 50). This result shows that the process under discussion is controlled by oxygen diffusion. Further evidence to support the effect of X -values and of morphology on thermooxidative degradation comes from an analysis of the factors describing the rate of chain scission q on S and D . If chain scission efficiency E and sample thickness l are constant, then one can take into account the dependence of D and solubility S' on the degree of crystallinity. The diffusion constant D in partially crystalline polymers is $D = D_o \Psi / B$ (Ref. 51), where D_o is diffusion constant in amorphous polymers, Ψ is impedance factor which depends on the degree of crystallinity and spherulite size, and B is the blocking factor. For spherulitic PE it was found that $\Psi = (1-X)^n$, where $n = 1.25 - 1.50$ (Refs. 52, 53). Assuming the same values of n for PP one can obtain the relation between D and X taking into consideration that the solubility S' depends on the free volume ϕ and diffusant concentration C . When $\phi \approx (1-X)^{0.5}$, then $K_S \approx (1-X)^n$. We have found that in the first step of the reaction n is equal to the predicted value. This confirms the previous suggestions that the content and the kind of morphological structures affect the thermooxidative degradation even though it takes place predominantly in the amorphous phase.

The lowering of the chain scission rate in the thermooxidative degradation observed in the later phases is due to the increased packing and decrease of free volume. The detailed analysis of the dependence X on the S values given in Ref. 42 shows that in the first stage the ΔX values increase relatively fast with a change in S , especially for samples crystallized at low temperatures (small X_o values). Crystallization during thermal annealing and degradation leads to an increase of crystallinity or ordering of the earlier formed paracrystalline phase or imperfect crystals. In the latter stages of the discussed oxidation reaction the chain scission makes it possible for the recrystallization process to occur in all samples, and the $\Delta S / \Delta X$ values for them are similar. This shows that the initial crystallinity and morphology during oxidation at higher temperatures have an important role in PP thermooxidation.

CONCLUSIONS

The results discussed briefly in this paper of studies aimed at establishing the relations between morphological structure and the mechanical and electrical properties of semicrystalline polymers as well as the thermooxidative processes occurring in these substances do not exhaust the problem; the discussion has only concentrated on those aspects of the problem which were investigated at our laboratory and in other centres working in similar fields. It seems, however, that we have been able to show that some progress has been made in the attempts to establish correlations between the different processing conditions, which result in various morphologies arising in partially crystalline materials, and their various properties. It appears that physical modification of the structure of high molecular weight materials that can undergo crystallization may lead to controlled changes of their properties and that studies in this area are topical problem in polymer science with important consequences for practical applications.

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