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Crystallization of Polymers in the Presence of Electric Fields

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ABSTRACT

The influence of the external constant and alternating electric field on the crystallization from melt has been studied for poly(ethylene oxide) and poly(vinylidene fluoride). No real effect has been found. The orientation of crystals due to the external constant electric field has been established in one of the two liquid crystal polymers studied. The results point out that the external electric field could only influence the crystallization of species having very large resultant dipole moment.

INTRODUCTION

The processes related to the influence of constant and alternating electric field on crystallization have received some attention in recent years. The literature dealing with this problem describes the results of electric field influence on crystallization of low molecular weight compounds. These studies concerned several inorganic salts, organic low molecular substances, metals, oxides and particularly water, e.g. GELLER et al.(1975), KOZLOWSKI et al. (1976), LATHAM, SAUNDERS (1964), TILMANS (1977). However, there has not been distinctly selected the case in which electric current is small enough to neglect the orientation effect due to the charge carrier motions. Such condition fulfilles a large group of nonionic and partly conducting solutions and melts. In many cases an immense influence of the electric field on the kinetics of the nucleation and crystal growth has been reported.

BAZYLEVICH (1928) has studied the influence of the constant electric field on the crystallization of azobenzene and diphenylamine. He has found that the temperature of the spontaneous crystallization can decrease or increase depending on the field intensity. FEDOROV (1973) has investigated the influence of the field on the crystallization of parafines in the raw oil in pipelines. He has noticed the lower rate of parafin crystal growth in the oil and on the pipe walls under the con-

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stant field while polar components were the nucleation centers. The influence of electric field on the rate of growth of molecular solids was studied by SZYMANSKI, LABES (1968). They have found the changes of growth rate of p-terphenyl and tetracene, however, their results were not confirmed.

The influence of the constant electric field on the crystallization of polar compounds could be expected if one compare the intensities of intramolecular electric fields (10^6 - 10^7 V/cm) and intermolecular electric fields (10^5 - 10^6 V/cm) with possible external electric field (10^5 V/cm).

Gorski GORSKI (1955), GORSKI, PRISCHEPA (1962) has treated the influence of the constant electric field on the basis of fluctuation theory of nucleation. In that case the rate of nucleation I (primary or secondary) is controlled by the temperature T and the activation energy U of the nucleus creation and is given by the following equation:

$$I = C \exp(-A/T\Delta T - U/RT)$$

where ΔT - supercooling and A - parameter dependent on the surface energy.

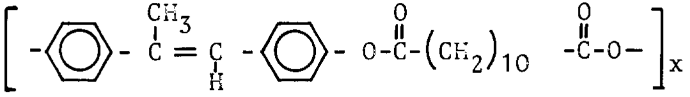
It was suggested that in the electric field an increase of A and U occurs. The increase of A may result from a rise of the surface energy and could be much higher than the increment of U. The character of these changes could be reflected in the crystallization process. Gorski and Prischepa have studied the influence of the electrical field on the nucleation of crystallization centers in betol and antipiryne and they confirmed the theoretical suggestion of Gorski.

NAEGELE, YOON (1978), NAEGELE et al. (1978) have found the evidence for another new crystal form of poly(vinylidene fluoride) which is formed upon subjecting the α -crystal form of poly(vinylidene fluoride) to high electric field.

We have undertaken the investigation of the electric field influence on the crystallization of low molecular poly(ethylene oxide) and poly(vinylidene fluoride) expecting the changes in the crystallization kinetics and morphology, especially for the chain folding is engaged. We used also for experiments some liquid crystal polymers expecting the effect of orientation under electric field.

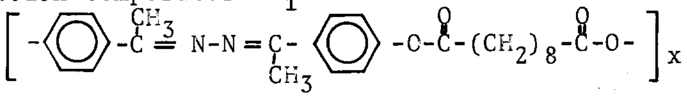
EXPERIMENTAL

For experiments we used poly(ethylene oxide) with molecular weight 20000 made by Fluka. The crystallization measurements were carried out on microscopic thin slides (0.15 μm) between two flat molibdenium electrodes (30 μm thick) on the temperature controlled microscopic stage (0.02°C) the relative humidity of the environment was kept below 3%. The polymer in a sandwich sample was at first melted at 85°C and then quickly shifted to crystallization stage having different temperature in the range 40-65°C. Before the crystallization starts the constant voltage was applied from 0 to 4.5 x 10^4 V/cm. The spherulite growth was observed by means of polarizing microscopy. The lamella morphology was examined using the electron microscopy. The possible increase of the crystallization temperature during crystallization due to the electric current was estimated to be less than 0.03°C/s at the moment of field application. Final change of temperature due to electric current was measured by means of colour transition of liquid crystals (mixture of cholesteric propionate and cholesteric nonanoate) and it was for example of order 1.0°C at 3 kV. The alternating field of 0-3 kHz was also applied for the studies of the electric field influence on the crystallization of poly (ethylene oxide). Poly(vinylidene fluoride) (PFVD) of Polysciences Co. (M_W = 130000) was dissolved in dimethylformamide and then purified by selective precipitation. The samples were crystallized from melt at 153°C without and with applied electric field up to 100 kV/cm. All PFVD samples contained spherulites. Small dimensions of spherulites did not allow to carry out the direct measurements of their growth rate. For the estimation of possible orientation and anisotropy the small angle light scattering and X-ray wide angle diffraction were applied. Two liquid crystal polymers:



(C_{12} α MS)

having the melting temperature T_m = 183°C and isotropization temperature T_i = 217°C and



($C_{10}F_3$) having T_m=211°C

and T_i= 245°C were used for further studies of the influence of the electric field on the crystallization. The samples were melted above the isotropization temperature, the electric field of 10kV/cm was applied and then the samples were cooled slowly to 150°C or 185°C, respectively. The X-ray wide angle diffraction patterns were taken to estimate the induced orientation.

RESULTS

Spherulites arising in the samples of poly(ethylene oxide) under the influence of the constant electric field do not show any anisotropy of the growth. From optical microscopic examination it results that the birefringences of spherulites of all samples are the same. Electron microscope investigation does not indicate any changes of their lamellar structure of spherulites due to the electric field application. X-ray diffraction pattern shows a polycrystalline structure of the samples without any orientation,

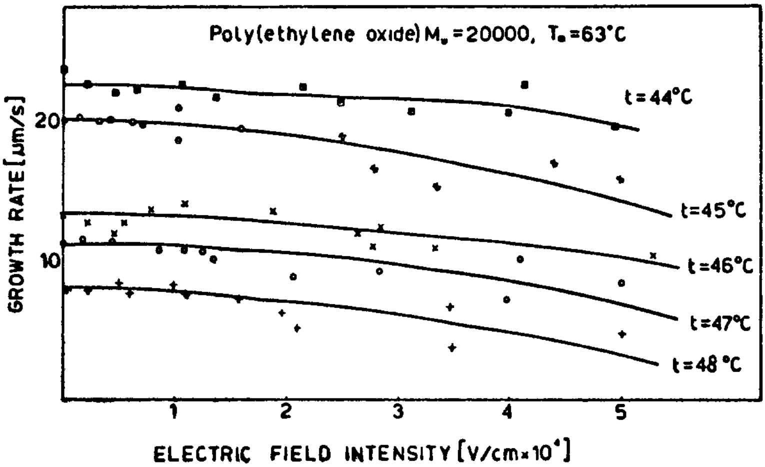


Fig.1. Poly(ethylene oxide) spherulite growth rate plotted against the constant electric field intensity applied to the melted samples. The crystallization temperatures indicated on the graph.

In Fig.1 there are presented the plots of poly(ethylene oxide) spherulite growth rate drawn against the electric field intensity for various temperatures of crystallization. One can see the region up to 20kV/cm in which the spherulite growth rate does not depend on the field intensity whereas above this region the growth rate decreases. If the increase of the temperature, due to some electric current, was responsible for the decrease of the growth rate then the temperature rise would be of the order of 2-3°C. Direct measurements of the temperature rise using liquid crystals show the smaller increase of the temperature. The plots of spherulite growth rate drawn against temperature of crystallization for various field intensities do not change the shape. They are only shifted due to the temperature rise

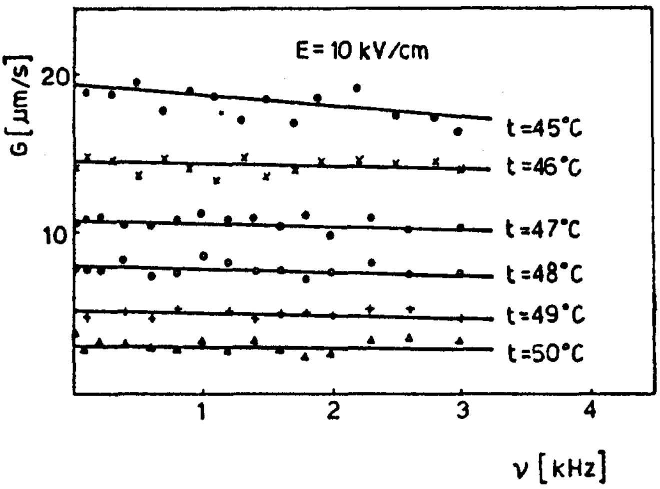


Fig.2. Poly(ethylene oxide) spherulite growth rate plotted against the frequency of the external electric field applied to the melted samples. The crystallization temperatures indicated on the graph.

In the case of the alternating field application the dependences of the spherulite growth rate plotted against frequency are presented in Fig.2. A small decrease of the spherulite growth rate are seen for higher frequences (approx. 2.5-3.0 kHz) of the electric field. At that range of frequency the relaxation of polymer melt occur which may result in some temperature rise due to energy loss. It follows that any changes are due to the indirect effect such as additional heating or electrode polarization rather than the direct influence of the electric field on the crystallization process. In the case of poly(vinylidene fluoride) all samples contained spherulites of a size of a few micrometers. Angular distributions of small angle light scattering intensities do not indicate any directional distortion of the spherulites due to the constant electric field influence. Any distortion of the fine crystalline phase was not concluded on that basis as well. X-ray diffraction patterns for PFVD samples crystallized without and under the 100 kV/cm electric field at 153^{o}C are not different. No formation of any new crystalline phase was observed in the case of PFVD. Stronger, observable effects of the electric field on the crystallization process can be expected for polymeric substances having larger dipole moments than poly(ethylene oxide) and poly(vinylidene fluoride). We chose for our further studies two liquid crystal polymers.

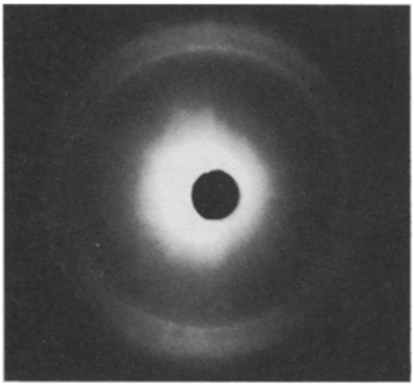


Fig.3. X-ray diffraction pattern of liquid crystal polymer asigned as $C_{10}F_3$ crystallized by slow quenching from 255°C to 185°C while the 10 kV/cm external constant electric field was applied to the sample.

Polymer indicated as C_{12} MS does not show any orientation while being crystallized under the electric field influence whereas polymer asigned as $C_{10}F_3$ undergoes the orientation during crystallization due to the external electric field as it is seen from the X-ray diffraction pattern shown in Fig.3.

CONCLUSIONS

It was shown that the external constant electric field up to 100 kV/cm and the alternating electric field up to 4 kHz do not apparently influence the crystallization of polar polymers from melt. In the temperature range between the isotropization point and the melt point the domain structure of liquid crystal polymers is formed. If the chain arrangement in the domains is such that the dipole moments of chain segments are summarized then the total dipole moment of the domain is large.In the case of liquid crystal polymer signed as $C_{10}F_3$ the domain can be oriented in the external electric field and the crystallization occuring below 211°C freezes the orientation. The results point out that the interaction energy of the external electric field with the dipole moments of polar polymers (such as poly(ethylene oxide) or poly(vinylidene fluoride)) is too small comparing with the energy of thermal motions of polymer chains in melt unless the chains are specially arranged in order to give large resultant dipole moment.

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