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Forced crystallization of poly(1,5-di-oxapene-2-one)-Fe(III) chloride complex onto NaCl surface by polymerizing pyrrole

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SUMMARY

A novel polymer poly(1,5-di-oxepane-2-one) (PDXO) forms with iron(III) chloride a coordination complex,which is a highly viscous liquid.This complex initiates the vapour phase polymerization of pyrrole.The nucleation process of polypyrrole forces crystallization of the PDXO-$FeCl_3$ complex.This crystallization process occurs only on the surface of NaCl.

INTRODUCTION

We have found that poly(ethylene oxide)($-CH_2CH_2-O-$)(PEO),polyester (poly(β-propiolactone)($-CH_2CH_2-CO-O-$)(PPL) and a novel poly(etherester)(poly(1,5-di-oxepane-2-one)($-CH_2CH_2-O-CH_2CH_2-CO-O-$)(PDXO) form with iron(III)chloride coordination complexes (1).

The morphological structure of PEO-Fe(III)chloride complexes depends very much on the weight ratio polymer/Fe(III)chloride (2,3).Pure PEO crystallizes in the form of lamellae organized in spherulites.The PEO-Fe(III)chloride complexes with polymer/Fe(III)chloride weight ratios of 9:1 and 8:2 also crystallize as well developed one phase spherulites.However,PEO-Fe(III)chloride complexes with 7:3 or 5:5 weight ratio form single phase high viscous liquids.In a similar way PPL and PDXO form with Fe(III)chloride at weight 7:3 high viscous liquid complexes.These complexes initiate vapour phase polymerization of pyrrole (3).The electrical conductivity of polypyrroles obtained in this way depends very much on the type of polymer-Fe(III)chloride complexes used.In a series of experiments,we have observed that a liquid complex of PDXO-Fe(III)chloride at weight ratio 7:3 can crystallize when exposed to pyrrole vapour.This crystallization occurs only on the surface of NaCl but not on the glass plate.

EXPERIMENTAL

The poly(etherester)(poly(1,5-di-oxepane-2-one)(PDXO)(M_w=10 000-50 000) was synthesized by Dr T.Mathisen from our Department,by a ring-opening polymerization of the 1,5-dioxepane-2-one monomer at temperature 130°C in the presence of a transesterification catalyst such as Bu_2SnO_4 (5,5).This polymer is an amorphous highly viscous liquid,and do not crystallize in an ambient condition.

The complex PDXO-Fe(III)chloride at weight ratio 7:3 has been prepared by dissolving PDXO (5wt-%) and Fe(III)chloride (10 wt-%)in dry nitromethane,separately.These two solutions were mixed together and

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*To whom offprint request should be sent at his new address: Polymer Research Group, Department of Dental Materials and Technology, Karolinska Institutet, Box 4064, S-14104 Huddinge, Sweden shaken for 30 minutes,then cast on NaCl plate and dried under a dry-nitrogen blanket.

Polymerization of pyrrole on the PFXO-Fe(III)chloride complex has been carried out in a small exsiccator,the bottom of which has been covered with monomer (at ambient temperature and pressure).NaCl plates,coated with the PDXO-Fe(III)chloride complex film,were placed around the walls of the exsiccator above the pyrrole level and allowed to react with the monomer vapour in different required times.

Optical and SEM photomicrographs were made with the Leitz Ortholux II POL-BK and Super Mini SEM ISI microscope,respectively.Samples for SEM were shadow cast with palladium.

RESULTS AND DISCUSSION

A number of alkali halide (NaCl,KCl,KI) surfaces causes the epitaxial crystallization of polyethylene,polyoxymethylene and poly(ethylene oxide) from solution (6-11).The surface of alkali halides can be heterogenious with respect to epitaxial growth.The macromolecules are aligned in most of the epitaxy involving alkali halides along the directions of like charged ions.

The PDXO-Fe(III)chloride (7:3) complex initiates polymerization of vapour pyrrole.In the very early stage of this polymerization (first 60 seconds) the formation of assymetrical sheaf-like crystalline forms (Fig.1) was observed,which then grew to form open-branched spherulitic sheafs (Fig.2).As the polymerization process of pyrrole proceeds,the formed crystalline forms are then covered completely by a black thick polypyrrole film (50-200μm).

Fig.1 Photomicrographs of different forms of asymmetrical sheaf-like crystalline forms of the PDXO-Fe(III) chloride (7:3) complex observed after 30 seconds exposure to pyrrole vapour.Scale bar 50μm.

These crystalline complex shapes of fibrillar structure (fractals) can be characterized by a non-integer (fractal) dimentionality (12). The growing structures are self-similar in a statistical sense and scale-invariant objects.

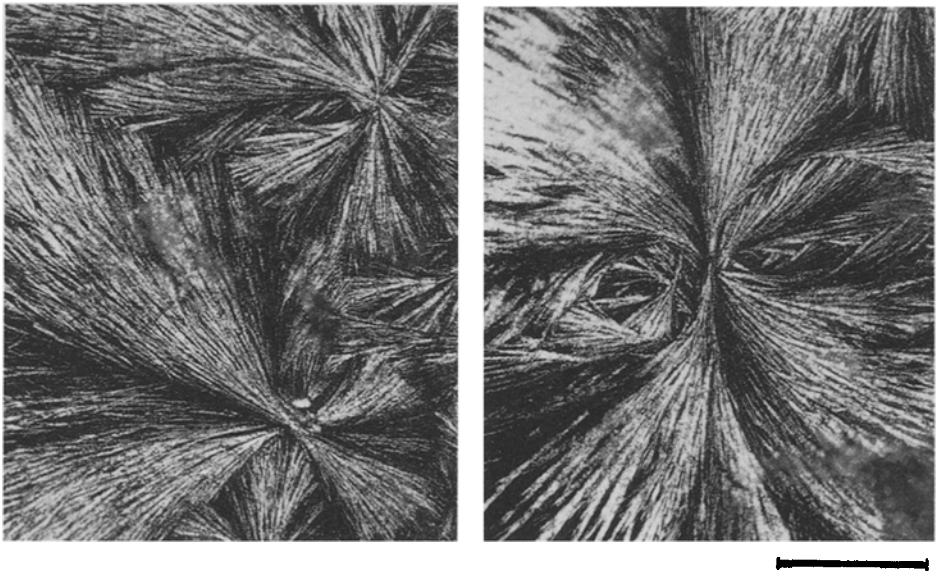

Fig.2 Photomicrographs of different forms of spherulites of the PDXO-Fe(III)chloride (7:3) complex observed after 60 seconds exposure to pyrrole vapour. Scale bar 50μm.

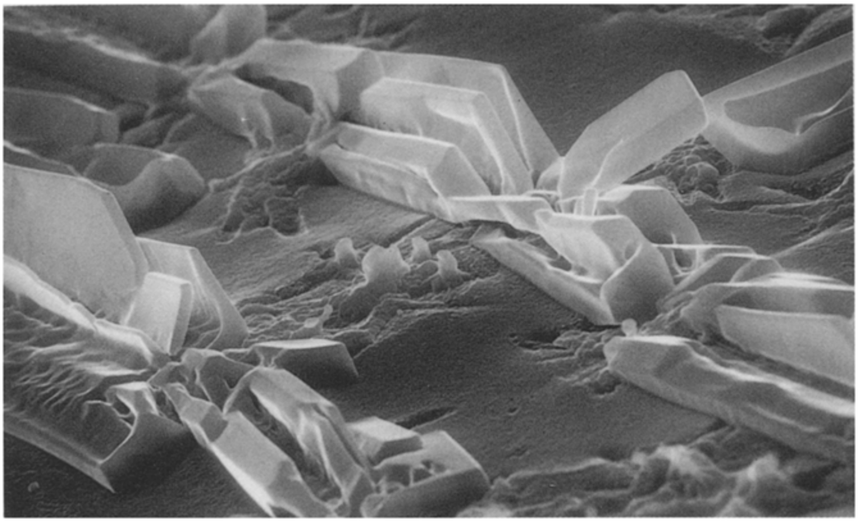

Fig.3 SEM photomicrograph of the crystalline forms as in Fig.1. Magnification x 1200.

The SEM photomicrograph (fig.3) shows that crystalline forms observed in Figs 1 and 2 are regular crystal blocks.However,they are broken probably because the parallel polymerized pyrrole on the PDXO-Fe(III) chloride complex surface,influences the crystallization of a complex.

The nucleation process of polypyrrole probably initiates the crystallization of PDXO-Fe(III)chloride complex.Tha leter occurs only on the NaCl surface and is probably due to the reduction in enthropy of partially adsorbed PDXO molecules onto the NaCl surface.

In conclusion,it is clear that the NaCl surface provides a strong inducement to the PDXO-Fe(III)chloride complex crystallization which is caused by polypyrrole nucleation. The pure PDXO does not crystallize in the same condictions.The interaction between the NaCl surface and the growing crystal seems to cause crystallization as far as several hundred angstroms.This effect may be caused by the relatively long range of the NaCl ionic forces.The PDXO-Fe(III)chloride (7:3) complex doesn´t crystallize in a smilar conditions on the glass plate.

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