SYNTHESIS AND X-RAY STUDIES OF POLYDIPHENOXYPHOSPHAZENE

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Abstract Polydiphenoxyphosphazene was synthesised by nucleophilic substitution of chlorine atoms in polydichlorophosphazene by the phenyl groups in the reaction with sodium phenolate as the most of the poly(diorganoxyphosphazene)s. It was found full substitution of chlorine atoms in synthesised polymer. Poly(diorganophosphazene)s, synthesised in substitution reaction involving chlorine atom replacement in polydichlorophosphazene by a suitable group, have desirable properties (e.g. flexibility at low temperatures, fastness to oils, biodegradability). Poly(diorganophosphazene)s in defined temperature regions have liquid crystalline structures, characterised by two-dimensional hexagonal arrangement of the chain centres in an equatorial plane which is perpendicular to the chain axis.

For the high molecular mass fractions of polydiphenoxyphosphazene the X-ray analysis of crystal structure were carried out. The examination confirmed the crystalline structure of the synthesised polymer.

The increase of the intensity of X-ray reflections with increase of temperature was observed. This dependence and a number of X-ray reflections let determine the dimensions of the unit cell of the crystalline polymer.

INTRODUCTION

Polydichlorophosphazene, a starting material to preparation the poly(diorganophosphazene)s, is useless in itself, because of its strong hydrolytic instability. It can be reacted with suitable nucleophiles substituting the reactive chlorine with inert organic or organometallic residues, thus producing hydrolytically stable

poly(diorganophosphazene)s. The polydichlorophosphazene is reacted with aromatic or aliphatic alcohol, with primary aromatic amines or with primary or secondary aliphatic amines, to form different classes of very interesting, stable poly(organophosphazene)s.

It is known, that almost all polyphosphazenes have liquid crystalline structure in the definite range of temperatures. This structure is characterized by two-dimensional hexagonal arrangement of the chain centres in the equatorial plane, which is perpendicular to the chain axis. It was found, that below 160°C polydiphenoxyphosphazene has a crystalline structure, and above 160°C it undergoes into mesomorphic structure³. It is known that with increase of temperature the intensity of X-ray maximum decreases. For series of polymers with mesomorphic structure an unusual significant increase in reflection intensity with increase of temperature was observed. The increase in reflection intensity with increase of temperature can be explained by thermal expansion and is observed for polymers having big transverse diameters^{4,5}. The study of this phenomenon for different types of polymers is still very important.

EXPERIMENTAL PROCEDURE

Polydiphenoxyphosphazene was synthesised in a nucleophilic substitution reaction involving chlorine atom replacement in polydichlorophosphazene by phenyl groups in reaction with sodium phenolate in boiling diglyme. The reaction was performed during 8 hours with full substitution of chlorine atoms¹. Because the molecular weight of obtained polydiphenoxyphosphazene depends on molecular weight of initial polydichlorophosphazene, this polymer was synthesized according to original elaborated method^{1,2}. The obtained polymer was fractionated and it was found that it did not contain chlorine. The molecular weight of polymer, determined by light scattering, was 3000000. The glass transition temperature of the polydiphenoxyphosphazene was 265 K and melting point was 422 K (determined by DSC). X-ray radiography was used in order to determine the effect of temperature on changes of crystalline properties of polydiphenoxyphosphazene and to determine the unit cell parameters.

Polydiphenoxyphosphazene films of 1 mm thickness were obtained from a 20 % solution of the polymer in tetrahydrofuran and extended to 350 % at 343 K. X-ray texture diagrams of the oriented films were obtained at room temperature applying a collimator 0,15 mm to obtain the distinct diffraction lines. Diffraction spectra of isotropic films and powders of polydiphenoxyphosphazenes at various temperatures were obtained on X-ray diffractometer DRON-1 with high-temperature attachment.

RESULTS AND DISCUSSION

Elaboration of the original method of polydichlorophosphazene synthesis^{1,2} and study on influence of a substitution reaction condition of chlorine atom replacement by organic substituents¹ showed, that for full substitution of chlorine atoms by phenyl groups the reaction should be performed at temperature of boiling solvent during 8 hours. After this time the elemental analysis did not show existence of chlorine atom in polydiphenoxyphosphazene. The ³¹P NMR spectrum showed only singlet without any signals from defected fragments of polymer chain². In several syntheses the polydiphenoxyphosphazene of high number average molecular weight was obtained which was beneficial for film preparation for X-ray texture diagrams study.

On the ground of X-ray diagrams and diffraction spectra a position of 22 reflections on the base line, 15 reflection on the first line and reflection on 002 on the second one. Positions of 38 reflection were calculated by means of two methods ITO⁵ and Lipson⁶.

The results allowed for determination of the unit cell parameters of the monoclinic system:

$$a=16,92\ 0,2\text{\AA} ; b=14,04\ 0,2\text{\AA} ; c=4,92\ 0,2\text{\AA} ; \gamma=97$$

they differ from results obtained previously in other studies^{2,7}, where we can find the parameters:

$$a=16,06\text{\AA} ; b=13,69\text{\AA} ; c=4,91\text{\AA} ; \gamma=82,$$

counted for minor amounts of observed reflections.

The unit cell contains fragments of two macromolecules. Theoretical crystalline density $d = 1,32 \text{ g/cm}^3$ near to the experimental density $d = 1,30 \text{ g/cm}^3$ (determined by use of pycnometer) indicates that it is the high crystalline polymer.

Interplanar crystal spacing: d_h - calculated from the obtained parameters and measured values $-d_c$ is in good agreement.

The X-ray diagrams with increase of temperature show that bellow 130°C the polymer structure does not change. In the temperature range $130^\circ\text{C} - 169^\circ\text{C}$ polymer samples turn into mesomorphic state, and their cell approximates to the hexagonal form and the reflections 110 and 110 bring nearer each other.

Mesomorphic structure at 130°C is characterized by one reflection. Its position changes with thermal expansion when temperature rises (Table).

TABLE 1. Effect of temperature on values of d_c [$\text{\AA}$] of the three reflections for polydiphenoxyphosphazene.

	20°C	130°C	150°C	160°C	170°C
110	11.41	11.51	11.40	11.25	11.30
110	10.16	10.30	10.32		
200	8.45	8.48	8.48		

For mesomorphic hexagonal structures the value $d_c = 11.25 \text{ \AA}$ correspond with the average dimension of macromolecule $-13 \text{ \AA}$.

The measurements show that for both crystalline and mesomorphic states above room temperature reflection intensities 110 and 110 increase consecutively with temperature increase.

Calculation of the intensity after earlier described pattern [2] allows to the conclusions that for the thermal expansion $11.30/11.25 = 1.005$ the intensity should increase by about 10%.

The results confirm the suggestion that for the polymers with the transversal diameter above $10 \text{ \AA}$, the thermal expansion should lead to the rise of the roentgen reflection

intensity with increase of temperature. This takes place both in the mesomorphic and crystalline states.

More penetrating investigation of the unit cell parameters of polydiphenoxyphosphazene is necessary stage of the determination in the future coordinates of the atoms and a conformation of the polymer macromolecule.

SUMMARY

The synthesis of polydiphenoxyphosphazene of high molecular weight and without defected fragments was performed. For selected polymer the unit cell parameters were determined. It was found that for the polymers with the transversal diameter above 10 Å, the thermal expansion of polymer side groups lead to the rise of the roentgen reflection intensity and the unit cell at temp above 403K becomes hexagonal type.

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