Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

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Version of record first published: 13 Dec 2006.

To cite this article: J. Mügge & P. Zugenmaier (1988): X-Ray Investigations on Poly(Methylsiloxanes) with Mesogenic Side Groups at the Isotropic-Nematic-Smectic-Crystalline Phase Transitions, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 155:1, 409-431

To link to this article: http://dx.doi.org/10.1080/00268948808070382

Mol. Cryst. Liq. Cryst., 1988, Vol. 155, pp. 409-431
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Printed in the United States of America

X-RAY INVESTIGATIONS ON POLY(METHYLSILOXANES) WITH MESOGENIC SIDE GROUPS AT THE ISOTROPIC-NEMATIC-SMECTIC-CRYSTALLINE PHASE TRANSITIONS

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Abstract:

X-ray investigations have been carried out on Poly(methylsiloxanes) with mesogenic side groups which are attached to the main chain by a flexible spacer of 5 or 6 methylene groups, respectively. The diffraction patterns have been taken on samples placed in a magnetic field between two permanent magnets in the isotropic, nematic, smectic and crystalline state at respective temperatures. In particular, the smectic-crystalline phase transition was studied very carefully. The X-ray diagrams reveal an almost continuous transition from the smectic to the crystalline state. The present investigations support the schematical structural models of the smectic and crystalline state for the same polymers.

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INTRODUCTION

Liquid crystalline (lc) polymers have attracted much attention in academic and industrial research in recent years since they combine special properties of polymers and liquid crystalline phases [1-7]. Besides the main chain lc polymers which in the past have gained an essential interest in an application as high modulus fibers, the lc polymers with mesogenic side groups have now also come into focus with the goal of applying them as optical storage materials. Therefore, the electrooptical behaviour and structural details of these side group polymers in lc phases, in particular in the smectic phase, are of considerable interest. Structural studies are mostly carried out by scattering techniques as e.g. neutron and X-ray scattering for detection of long range order and by spectroscopic measurements as e.g. NMR which are powerfull methods to investigate local order. An overview on X-ray diffraction studies on lc polymeric materials has been published recently [8].

Most structural models for lc side group polymers have been derived from a conception of Liebert and Strzelecki [9], especially those for smectic phases. They have drawn models for lc polymeric phases very similar to those in use for low molar mass liquid crystals. The side groups in a smectic structure e.g. are involved in a

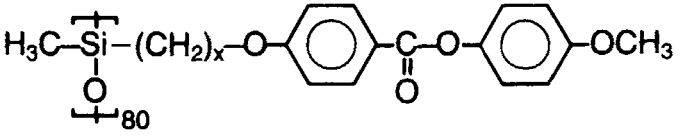
lamellar type of packing with the main chains running in a preferentially two dimensional coil or bundle like structure between the layers. This model does not contain further information about the conformation of the main chains. Generally the mesogenic side groups are placed on both sides of the main chain which may lead to a single or double layered structure depending on packing of the layers. In a recent study, a structural model of a lc poly(methacrylate) with cyanobiphenyl side groups was proposed with the mesogenic side chains all placed on one side of the main chain [10,11].

In this paper, results concerning structural changes will be presented at phase transitions occuring at cooling from the isotropic melt to the crystalline state. In particular, the smectic-(semi)crystalline transition will be monitored on magnetic field oriented samples. Structural models are available for the crystalline and smectic phases of the same lc poly(methylsiloxane) side group compounds and have been published in previous papers [12-15]. It was found that this type of lc polymer exhibit a chain conformation with the mesogenic groups on both sides of the main chains.

EXPERIMENTAL PART

All investigations in this study were performed with poly(methylsiloxanes) *) whose mesogenic side groups are attached to the main chains by an alkyl spacer of 5 or 6 methylene groups, respectively. The preparation of the samples was achieved by an addition of the side groups with terminal

TABLE I. Chemical constitution, abbreviations and phase transition temperatures for the polymers used in this study



x	Polymer (abbrev.)	Phase Transition Temperature in K	Crystallization
5	C-5	c 360 n 388 i (c 337 s 350 n 386 i)[1]	fast
6	C-6	g 278 s 319 n 385 i (c 330 n)[2]	slow

1) at cooling; 2) annealed sample

*) The polymers were kindly supplied by Prof.H.Finkelmann

double bonds to a poly(hydrogenmethylsiloxane) [16]. The degree of polymerization lies between 50 and 100. The tacticity of the polymer was not determined but it can be assumed that the polymer should contain mostly atactic sequences. The phase transition temperatures were measured in a polarisation microscope equipped with a hot stage and are listed in Table I [16].

X-ray diffraction experiments were carried out with Ni-filtered CuK_{α} -radiation in a vacuum flat film camera. The sample to film distance was kept between 4-5 cm. CaF_2 was dusted onto the samples and served for distance calibration purpose.

The orientation of the samples was obtained by an external magnetic field. The sample was brought between two pole-pieces of two permanent magnets of sizes of a penny which have been placed into a special heating holder (Fig. 1). The sample was solely fixed by adhesion. The temperature can be kept in this device at ±3 K. The magnetic flux was approximately 0.7 T in the 1 mm gap between the pole pieces. The irradiated sample thickness was estimated to 0.3 - 0.5 mm.

A magnetic field parallel to the incident X-ray beam was achieved by a facing of identical poles of the permanent magnets. The resultant inhomogeneity may cause some artefacts.

The X-ray patterns were taken with the X-ray beam parallel and perpendicular to the magnetic field direction. If orientation of the polymers occurs as in the nematic, smectic and crystalline

phase for C-5 and C-6, a uniaxial axis is observed which lies along the magnetic field direction and is placed horizontally in the respective figures.

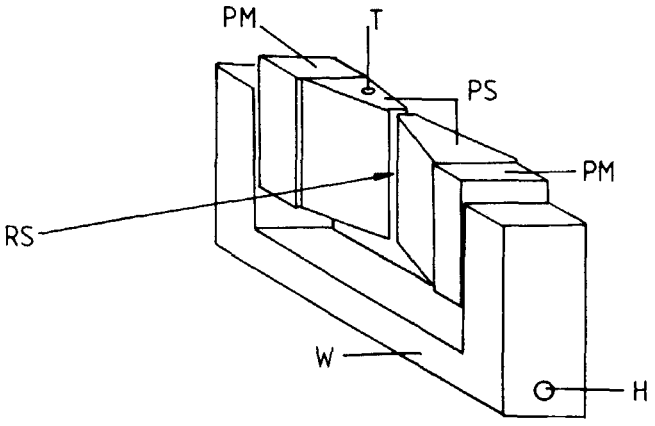


FIGURE 1. Schematic drawing for a device of orienting lc polymers at elevated temperatures (PM: permanent magnet; RS: incident X-ray beam; PS: pole pieces; W: iron with a U-profile; T: temperature gauge; H: hole for heating probe).

The exposure time for an X-ray pattern was about 4-5 hours which might cause annealing effects in the sample, especially if a metastable phase is present. A metastable smectic A phase e.g. for C-5 polymer under certain annealing conditions causes transformations into a probable smectic C or higher ordered smectic phases and

leads to a large number of peaks in a DSC thermogram [17].

RESULTS AND DISCUSSION

The X-ray patterns for the C-5 polymer in the isotropic, nematic, smectic and crystalline phase are represented in Figs. 2-6 with the X-ray beam perpendicular and in Figs. 7 and 8 with the beam parallel to the magnetic field direction. Only the sample in the isotropic state can not be oriented with the magnitude of the available magnetic field. All other phases show amazingly well oriented fiber X-ray patterns with an uniaxial axis serving as director for the orientation correlation of the mesogenic side groups. A random distribution of the scattering moieties or domains is encountered in a plane perpendicular to the fiber axis as shown by the diffraction rings in Figs. 7 and 8.

The X-ray diffraction pattern of the isotropic melt of C-5 is shown in Fig. 2. It is a pattern of a randomly oriented material. Two very broad reflection rings are observed comparable in width with ones obtained from scattering of an amorphous or liquid like material. They correspond to Bragg d-spacings of 4.2 - 4.7 and 10 - 15 Å, respectively. The two reflection rings in the isotropic melt are confined onto the equator with different intensity ratios and

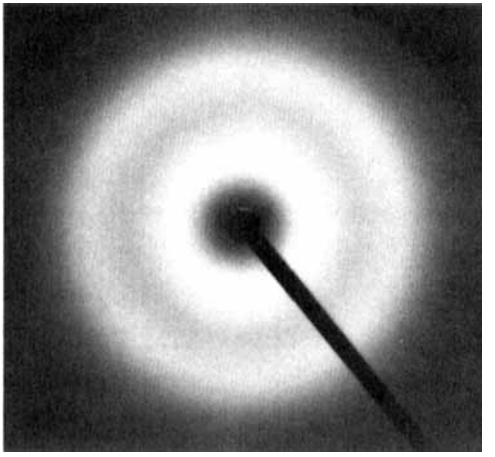


FIGURE 2. X-ray pattern of an isotropic C-5 polymer in a magnetic field (0.7 T) at 125°C. Magnetic field perpendicular to X-ray beam.

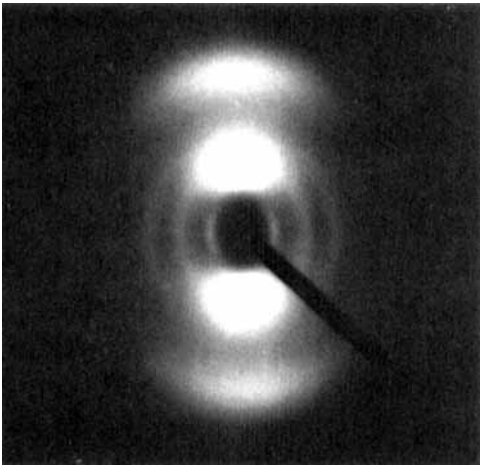


FIGURE 3. X-ray pattern of a nematic C-5 polymer in a magnetic field (0.7 T) at 100°C. Magnetic field perpendicular to X-ray beam. Fiber axis horizontal.

sharpness on all oriented X-ray fiber patterns of C-5 (Figs. 3-6), that is in the nematic, smectic and crystalline state. The reflection at ca. 4,5 Å can be attributed to the van der Waals distances of atoms belonging to the side groups since the direction of these contact vectors are perpendicular to the uniaxial axis or side group direction. The reflection at 10 - 15 Å, also observed on the equator for the oriented samples, might be caused by a disordered packing of side groups or weakly ordered structures perpendicular to the side group direction. Such long range distances are not commonly found in amorphous or liquid materials.

The X-ray diagram of an aligned nematic sample (Fig. 3) exhibits a fiber diagram with equatorial reflections discussed above and some meridional reflections with large arcing. The d-spacings of the meridional reflections compare well with multiples of the length of the side groups or the size of a smectic layer in the smectic phase (cf. Fig. 4). However, the intensity distribution of the meridional reflections is different from that of a smectic phase with a much lesser intense innermost reflection. It is evident from this diffraction pattern, that small layered domains or clusters with smectic layer spacings are preformed in this nematic phase. No conclusions can be drawn on the stability of the preformed clusters with the performed X-ray experiments. Higher order in nematic phases besides a

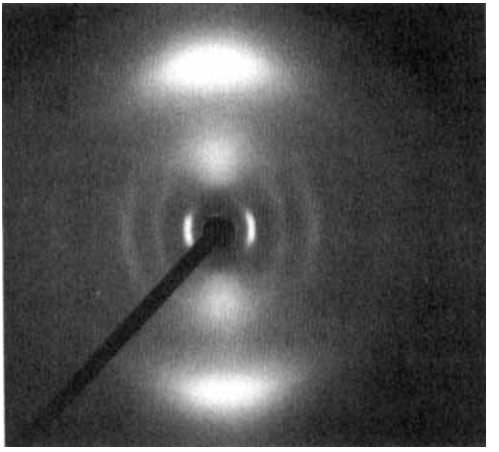


FIGURE 4. X-ray pattern of a smectic C-5 polymer with crystalline parts in a magnetic field (0.7 T) at 83°C. Magnetic field perpendicular to X-ray beam. Fiber axis horizontal.

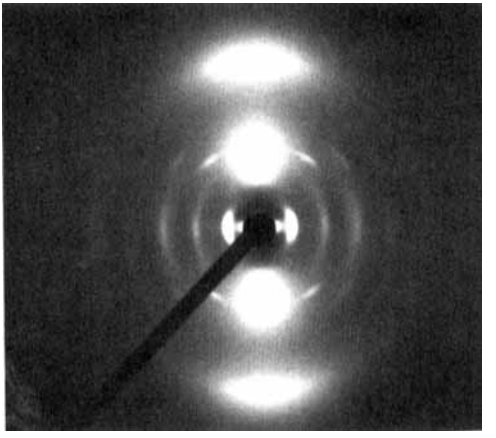


FIGURE 5. X-ray pattern of a slightly annealed C-5 polymer in a magnetic field (0.7 T) at 75°C. Magnetic field perpendicular to X-ray beam. Fiber axis horizontal.

directional correlation has also proposed by other authors [18,19].

The X-ray diagramm of the smectic phase is represented in Fig. 4. It contains some scattering from a crystalline part which cannot be avoided. Rapid crystallization in conjunction with the long exposure time for the X-ray diagram hinders the detection of a pure smectic phase. A very few sharp reflections appear on a horizontal layer line, the sharpness of which clearly indicates the scattering from the crystalline portion of the sample.

The X-ray pattern of the smectic phase seems to be transient by appearance between the pattern of the nematic and crystalline phase. The reflections on the equator and meridian have the same d-spacings but are sharper than the ones in the nematic pattern and broader than for the crystalline pattern. The d-spacing of the innermost reflection represents the layer thickness of a smectic layer and compares well with the side group length.

A pronounced change in the X-ray pattern occurs at the smectic-crystalline phase transition (Fig. 5). A sharp horizontal layer line can be easily recognized and sharp higher order meridional reflections, all multiples of the innermost reflection representing the thickness of layers, are observed. The d-spacing of the innermost meridional reflection compares well with the one obtained from the smectic pattern. However, the

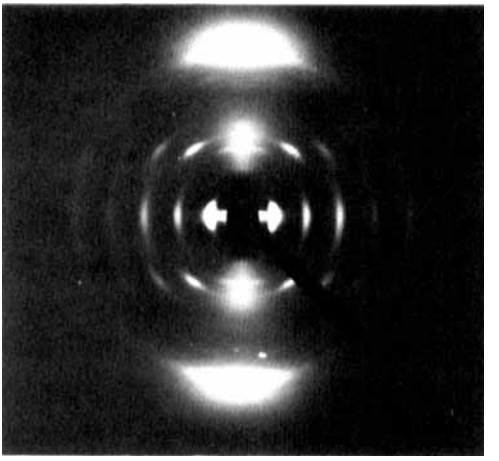


FIGURE 6. X-ray pattern of an annealed C-5 polymer in a magnetic field (0.7 T) at 45°C. Magnetic field perpendicular to X-ray beam. Fiber axis horizontal.

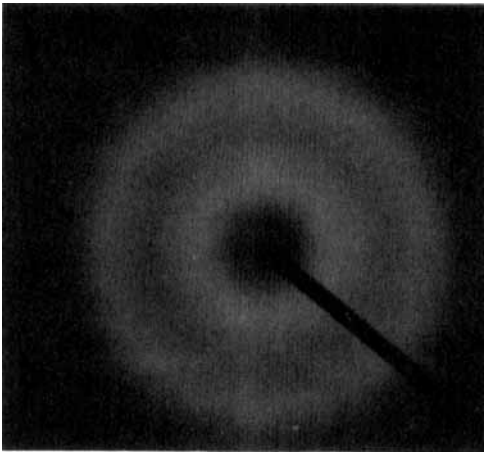


FIGURE 7. X-ray pattern of the nematic C-5 polymer taken parallel to the magnetic field at 100°C (cp. Fig. 3).

layer thickness derived from the innermost reflection on the horizontal layer line is twice the size derived from the reflection on the meridian and indicates that the side groups are placed on both sides of the main chain.

A further drop in temperature and some annealing at 45°C leads to the diagram of Fig. 6 which has the appearance of a normal fiber diagram of a crystalline polymer. The liquid like reflections on the X-ray pattern in Figs. 3-5 have almost disappeared especially the strong 10-15 Å reflection of Fig. 5 has lost considerably in intensity. It should be noticed that the reflection at ca. 4,5 Å is an overlap of two reflections and also appears broad because of some overexposure of the pattern. A second horizontal layer line having half the d-spacing of the first layer line is now visible. A discussion of the X-ray data and proposed structural models for the crystalline and smectic phases of the C-5 polymer is published elsewhere [12-15].

It should be pointed out, however, that the fiber axis lies along the side group direction in magnetic field aligned samples in contrast to the fiber axis of stretched samples which is found along the drawing direction or the main chain direction. The equator of the pattern in Fig. 6 becomes the meridian in a pattern of a stretched sample but both patterns of the differently aligned material exhibit the same overall appearance, and the d-spacings of the reflections maintain their values.

The isotropic X-ray patterns of Figs. 7 and 8 have been taken with the incident beam parallel to the magnetic field direction for a nematic (Fig. 7), and with little change in the appearance, for a smectic and crystalline (Fig. 8) phase. The reflections from the layers of the structures, the meridional reflections in Figs. 3-6, are missing as expected for this exposure techniques for a smectic A or comparably aligned phases. The other reflections of Figs. 3-6 are present which confirms the realization of a parallel magnetic field with respect to the incident X-ray beam.

The changes in the X-ray diffraction diagramms have been persued for the C-6 polymer in the following figures at the phase transitions nematic-smectic-crystalline and evaluated as for the C-5 polymer.

Fig. 9 shows the diffraction diagram of an oriented nematic phase which is well comparable to the pattern for the C-5 polymer. The arcs of the reflections on the equator are longer, the degree of orientation lower for C-6 polymer which is due to the fact that the pattern was taken a few degrees below the equilibrium temperature at which an alignment of the side groups occurs in the magnetic field. Above this temperature, the thermal motion overcomes the applied directional forces, and an isotropic scattering pattern is observed. Disordered packing of side groups is

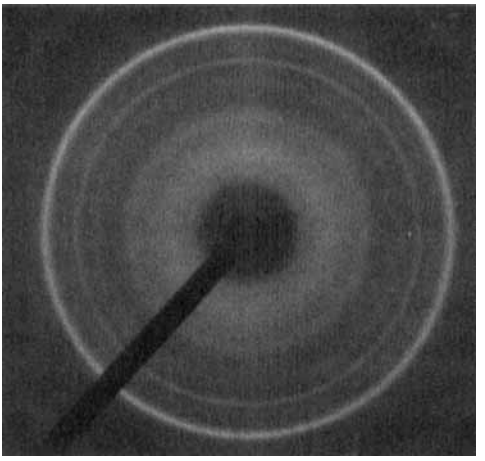


FIGURE 8. X-ray pattern of the annealed crystalline C-5 polymer taken parallel to the magnetic field at 45°C (cp. Fig. 6).

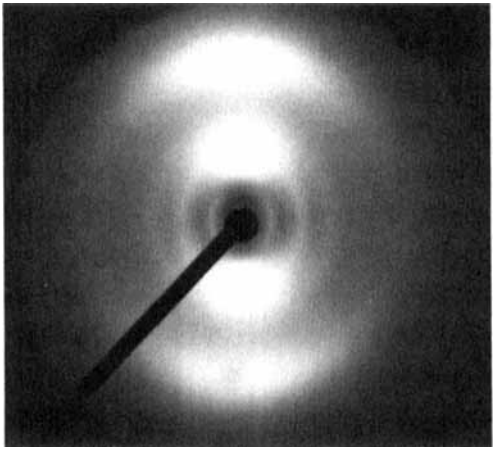


FIGURE 9. X-ray pattern of a nematic C-6 polymer taken perpendicular to the magnetic field at 92°C. Fiber axis horizontal.

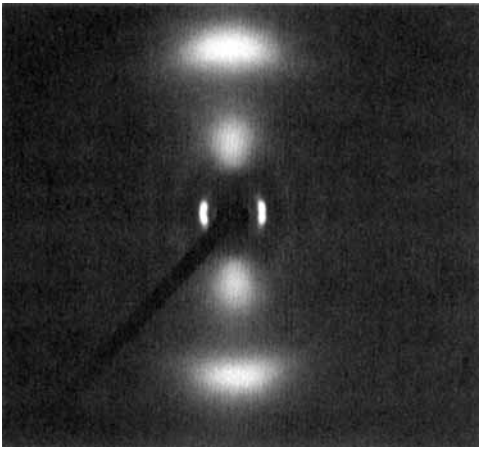


FIGURE 10. X-ray pattern of a smectic C-6 polymer taken perpendicular to the magnetic field at 40°C. Fiber axis horizontal.

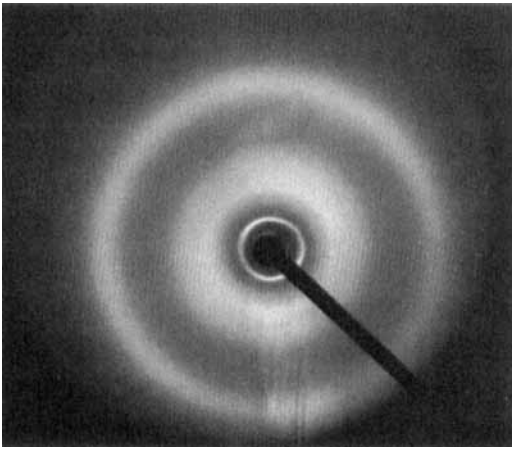


FIGURE 11. X-ray pattern of the smectic C-6 polymer taken parallel to the magnetic field at 40°C (cp. Fig. 10).

observed according to a broad 10-15 Å reflection on the equator. The meridional reflections point towards the formation of clusters of a layered structure of smaller domain sizes than in the smectic phase concluded from the broader reflections in the nematic phase. The d-spacing of the layers is increased by the size of a methylene group as compared with the C-5 polymer.

Figs. 10 and 11 represent X-ray diagrams of the smectic phase with the incident X-ray beam perpendicular and parallel to the magnetic field direction, respectively. The strong innermost reflection is caused by the formation of smectic layers. A clear x-shaped form of these reflections is visible in Fig. 10 which in conjunction with the appearance of a reflection of the same d-spacing in Fig. 11 indicates the presence of a smectic C phase for C-6 which is in agreement with recently published results[20]. The slightly anisotropic innermost ring originates from the tilted arrangement of the side groups. Inhomogeneities of the magnetic field in Fig. 11 can almost be ruled out since a similar reflection for C-5 cannot be detected (cf. Fig. 8).

If a smectic order is quenched at 20°C, a frozen in smectic phase is obtained whose X-ray patterns are represented for the two different X-ray beam directions in Figs. 12 and 13. The intensity ratio of the two equatorial reflections (Fig. 12) at ca. 4.5 and 10-15 Å is different compared with the one for the smectic C phase.

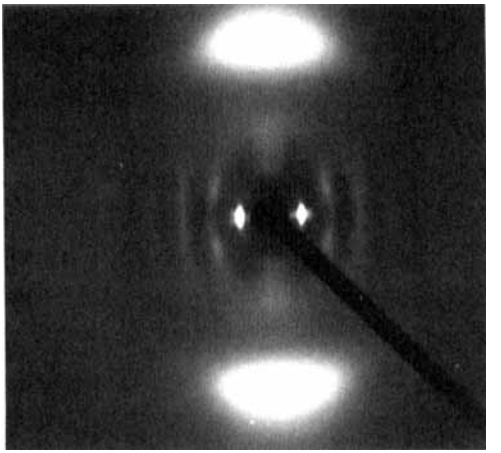


FIGURE 12. X-ray pattern of a frozen in smectic order of the C-6 polymer taken perpendicular to the magnetic field at room temperature. Fiber axis horizontal.

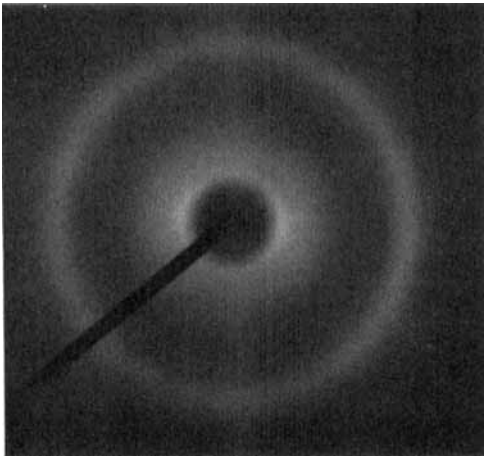


FIGURE 13. X-ray pattern of the frozen in smectic order of the C-6 polymer taken parallel to the magnetic field at room temperature (cp. Fig. 12).

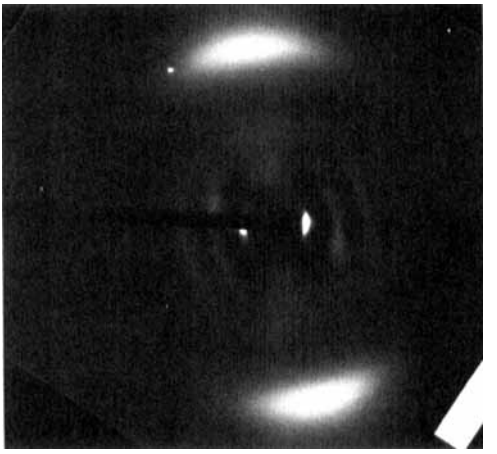


FIGURE 14. X-ray pattern of a slightly annealed C-6 polymer taken perpendicular to the magnetic field at the smectic-crystalline phase transition. Fiber axis horizontal.

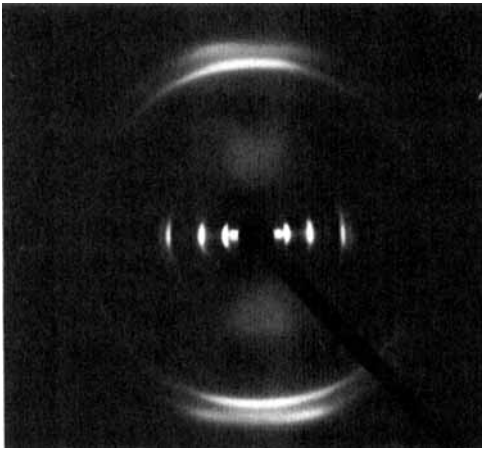


FIGURE 15. X-ray pattern of an annealed crystalline C-6 polymer taken perpendicular to the magnetic field at room temperature. Fiber axis horizontal.

The very intense innermost reflection lies now on the meridian and does not appear as a ring in Fig. 13. A four point pattern is found for the next reflections which again is not mirrored in the isotropic diagram (Fig. 13). It only shows the two broad equatorial reflections of Fig. 12 as halos.

The X-ray diagram of Fig. 14 resulted when the smectic C-6 polymer glass was annealed for about 3-4 days at room temperature. An asymmetric pattern is now observed with two of the innermost reflections of an x-shaped formation (cf. Fig. 10) missing. This pattern indicates the presence of a smectic C phase. It can be explained by assuming that the director or uniaxial axis of the side groups is not placed perpendicular on the layer surface of the tilted mesogens.

Further annealing of the C-6 polymer glass at room temperature leads to the X-ray pattern of Fig. 15. The meridional reflections are well resolved as for a crystalline diffraction pattern but only few sharp equatorial and near equatorial reflections are visible. Layer lines as for the crystalline C-5 pattern are not present. A schematic structural model of the crystalline and smectic phase of the C-6 polymer on X-ray evidence has been proposed and reported elsewhere [12-15].

CONCLUSIONS

Temperature dependent X-ray diffraction experiments on C-5 and C-6 poly(methylsiloxanes) represent the structural changes which occur at successive transitions from the isotropic melt to the crystalline state through liquid crystalline phases. It was found that only gradual differences are present for the various phases. In the nematic phase, small sized clusters are formed with the same layer spacing as observed for the layers in the smectic and crystalline phases. However, the sharpmess of reflections and intensity of the innermost reflection as well as their total number increases from the nematic to the smectic and crystalline state. The existence of a smectic A phase for C-5 and smectic C for C-6 polymer can be concluded from the X-ray diffraction patterns.

The smectic phase represents a less ordered state as compared with the crystalline state but with the same overall type of packing. This means a model for the smectic phase can be proposed with the information available from the crystalline phase with generally more reflections and layer lines in the X-ray diagram then normally found in smectic phases. For the crystalline C-5 polymer, a model with the side groups on both sides of the main chain was found. It also has to be assumed for the smectic C-5 polymer and the

crystalline and smectic C-6 polymer because of similar spacings of the layers for all structures.

The orientational behaviour of the crystalline and smectic domains by different alignment procedures as drawing by a mechanical force or an application of a force field are difficult to describe by the model of Liebert and Strzelecki for a smectic phase. A model with more or less ordered main chains and a packing of the chains commonly accepted in polymeric crystallites can describe the structural behaviour found in X-ray experiments. This model is also supported by a conformational analysis of polymeric polysiloxane model compounds [17].

ACKNOWLEDGEMENT: This work was supported by a grant from Deutsche Forschungsgemeinschaft

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