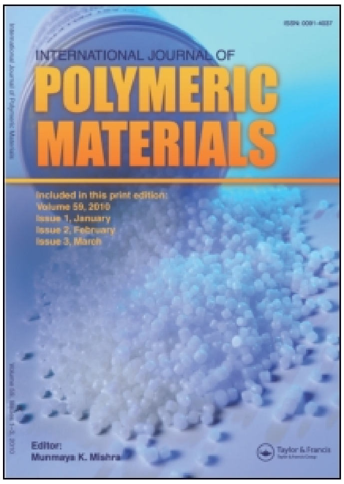

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Orientational Phenomena in Poly[Bis-(2,2,3,3,3-Pentafluoropropoxy)-Phosphazene] Mesophase

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The thermotropic behavior and morphology of poly[bis-(2,2,3,3,3-pentafluoropropoxy)phosphazene] (PPPh) have been investigated by various methods such as: differential scanning calorimetry, scanning electron microscopy and X-ray diffraction. It was shown that a polymer is able to exist in a four phases. A wide-angle X-ray temperature analysis indicates a monoclinic crystalline form for the first (low temperature) phase, the orthorhombic crystalline modification for the second one and the two-dimensional pseudohexagonal mesophase lattice for the mesomorphic state followed by the isotropic melt. Transition from the crystalline into the mesophase state in the range 85–100°C is observed. PPPh macromolecules in the mesomorphic state are found to be oriented in the extrusion direction.

KEY WORDS Mesophase, X-ray diffraction, polymer extrudates, fluoroalkoxy side chain, phase transitions, crystalline forms.

INTRODUCTION

Polyorganophosphazenes (PPh) are an important class of polymers with an inorganic main chain and organic side chains. A remarkable peculiarity of these compounds is their ability to form a mesophase state. Previous studies have revealed the influence of length of alkoxy side chains on the temperature interval of the PPh mesophase existence.[1,2] However, the structure of the PPh with fluoroalkoxy side groups is described only for poly[bis-(2,2,2-trifluoroethoxy)phosphazene] (PTPh).[3,4] The aim of this work is to study phase transitions and the structure of the linear PPPh with longer fluoroalkoxy side chains.

EXPERIMENTAL

Materials

Poly[bis-(2,2,3,3,3-pentafluoropropoxy)phosphazene] (PPPh) was prepared by polymerizing of poly(dichlorophosphazene) with 2,2,3,3,3-pentafluoropropylatesodium in the mixture of toluene and tetrahydrofuran at room temperature in accordance with the method previously used for PTPh synthesis.[6] The polymer synthesized had the intrinsic viscosity $[\eta] = 5.05$ dl g^{-1} (in hexafluorobenzene at 25°C) and the content of residual chlorine less than 0.07 mol%. The study was made of polymer samples after reprecipitation as well of the extrudates obtained in the mesomorphic state.

Equipment

DSC measurements were performed using a Mettler TC-11 calorimeter. The samples were heated and cooled in the temperature range from -80°C to $+280$°C at the rate 20°C min^{-1}. X-ray diagrams were obtained with a Ni-filtered CuK_α radiation in IRIS-3,0 camera. High temperature X-ray diffraction patterns were taken with Ni-filtered CuK_α radiation in a diffractometer Rigaku Dmax-RC equipped with a heating camera wherein the temperature was automatically controlled within 0.5°C. The low temperature X-ray experiments were carried out with a ADP2-01 apparatus (CuK_α, curved quartz crystallmonochromator) by means of a commercial low-temperature attachment URNT-180, with automatically regulated temperature (±1°C). The morphological investigations were carried out with a scanning electron microscope Tesla BS-301 (9 kV, magnification was up to 12 000).

RESULTS AND DISCUSSION

In contrast to PTPh (Figure 1, curve A), the DSC curve reveals one exothermic and three endothermic peaks (curve B) on heating a reprecipitated PPPh sample. The stepwise change of the DSC curve usually corresponding to the glass transition is observed at -55°C. Judging by its nature the exothermic peak (T_r) may be assigned to recrystallization process on heating. As will be shown below by the analysis of the X-ray diffraction data, the endothermic peaks at T_c and $T(1)$ are associated with the crystal-crystal and mesomorphic transitions, respectively. Besides, it is found that PPPh occurs in the mesomorphic state up to 310°C. In the DSC trace at T_m a wide and not very-pronounced peak corresponds to isotropic melting of the polymer.

The X-ray pattern of PPPh after reprecipitation (Figure 2a) shows several isotropic well pronounced rings. The crystallinity of the initial sample is low. If the sample is heated above the transition temperature T_m and then cooled, its crystallinity increases (Figure 2b).

On second heating the maximum of the exothermic peak in the DSC curve shifts to higher temperatures and is observed at -20°C (Figure 1, curve C). The thermal effect exhibits a twice as low decrease in comparison with the first heating run. Simultaneously the heat values corresponding to the endothermic peaks at T_c and $T(1)$ increase about twice and their maxima shift to higher temperatures. This enables a suggestion that a more regular structure develops on heating, as was concluded from the X-ray data. When cooled, the two exothermic peaks become well-pronounced in the DSC traces (Figure 1, curve D). It is to be noted that the difference between the values $T(1)$ on heating and cooling is about

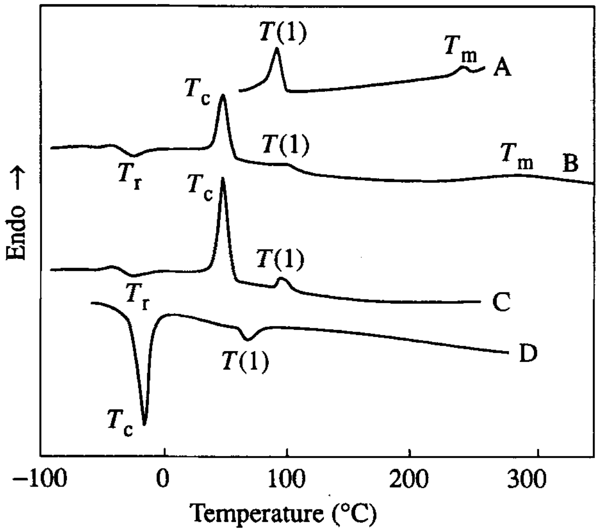

FIGURE 1 DSC curves for PTPh (curve A) and for PPPh: the first heating run (curve B), the second heating run (curve C) and cooling (curve D).

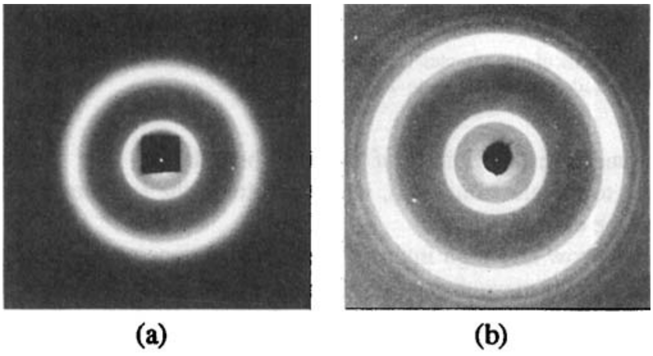

FIGURE 2 X-ray patterns of the samples reprecipitated (a) and annealed (b).

20°C, as for T_c, the shift reaches about 65°C. In the first case, it results from hysteresis which is typical of the flexible chain polymers at the high scanning rate. In the second case, such a shift can be due to the significant conformational changes of the macromolecule backbones.

We have recently demonstrated that under extrusion PTPh exhibits a considerable ability for macromolecule orientation.[7] To identify the PPPh structure the extrudates were obtained in a mesomorphic state.

An electron microscopic study of the extrudates cleaved at low temperature shows a well developed supermolecular structure (Figure 3a). Apart from fibrils with the average diameters of about 50–800 nm, bands and ribbons with the width above several hundreds nanometers and more can be observed (Figure 3b). These morphological elements overlap and bend, generating a three-dimensional network. Micro- and macrovoids stretched along the direction of the extrusion with the small axis of about tens nanometers and more are

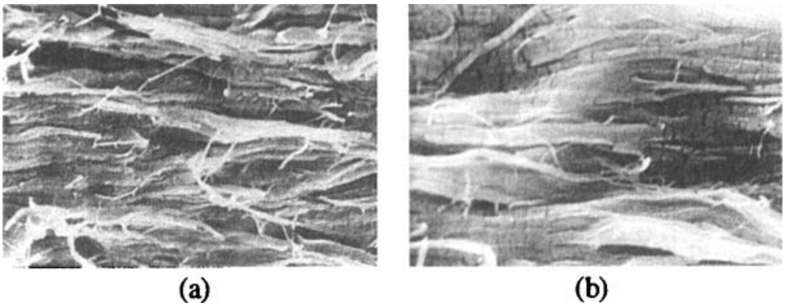

FIGURE 3 The morphology of PPPh extrudates at the magnification (a) ×10 000 and (b) ×12 000.

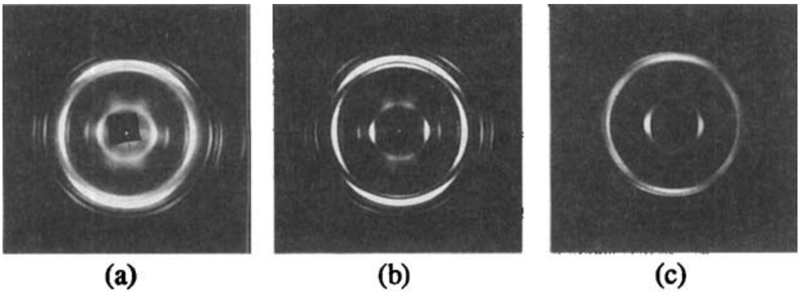

FIGURE 4 X-ray patterns of the samples (a) extruded and cooled at room temperature, (b) extruded and supercooled, and (c) extruded and heated up to $T(1)$.

very well pronounced in the vicinity of the fibril boundaries. The specimens appear to be very sensitive to the electron beam, which results in the surface microvoids oriented perpendicular to the extrusion axis.

A number of narrow and high intensity Bragg reflections of the X-ray pattern of the specimen extruded in the mesophase state (Figure 4a) indicates a high level of crystallinity. A relatively high degree of the macromolecule orientation is obvious for such systems.

DSC measurements of these samples show that the crystal-crystal transition temperature (T_c) and the corresponding endothermic heat are greater (Figure 5, curve A) than presented in Figure 1 (curve A). This indicates the higher level of crystallinity in a strongly oriented sample, than that in the isotropic one.

On the contrary, the coincidence of the heats and positions of the phase transitions of both reprecipitated and extruded samples at the $T(1)$ implies independence of these transitions on the degree of crystallinity. The disappearance of the exothermic peak in the DSC traces of the extrudates is a clear evidence of the more completed phase transitions. Under cooling two exothermic peaks are observed in the DSC curve of the extrudate (Figure 5, curve B). The difference of the value T_c on heating and cooling is again as great as in the case of the reprecipitated sample.

Figure 4b shows the X-ray pattern of the extrudates previously cooled below T_c (Figure 5, curve B) and heated thereafter up to room temperature. The angle positions and the intensities of the Bragg maxima agree with the reflections presented in Figure 4a. The equatorial and meridional diffractograms obtained at −75 °C display a high degree of crystallinity (Figure 6, curve A). A very high reflection intensity at the angle position

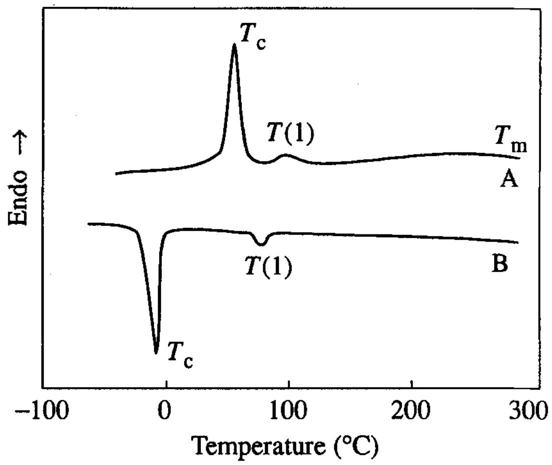

FIGURE 5 DSC curves for samples extruded in the mesophase state in heating (curve A) and in cooling (curve B).

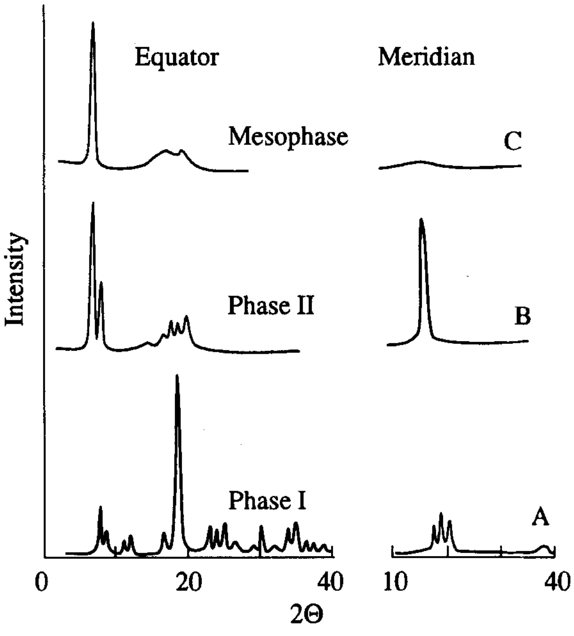

FIGURE 6 Equatorial and meridional X-ray diffraction patterns of phase I (curve A), the phase II (curve B), and mesophase (curve C).

$2\Theta = 18.8°$ can be caused by more regular packing of the side chains containing five atoms of the phosphorus with a relatively high atomic factor. In Figure 4b high intensity reflections of the four-point pattern arise, obviously, from the scattering of the side chains inclined to the polymer backbone. The meridional reflections at the angle positions $2\Theta = 18.8°$ and 37.6° indicate the conformational order within macromolecular backbone with spacing of 4.74 Å. This value comes close to the data obtained for polyorganophosphazenes with other side groups.[8,9]

TABLE I
The spacings calculated and determined from X-ray patterns for monoclinic form of the phase I

N	hkl	d_{calc} (Å)	d (Å)	N	hkl	d_{calc} (Å)	d (Å)
1	010	10.69	10.69	10	130	4.22	4.23
2	210	10.37	10.37	11	530	4.10	4.14
3	220	7.61	7.59	12	440	3.80	3.82
4	200	7.28	7.28	13	400	3.64	3.61
5	420	5.18	5.16	14	630	3.46	3.45
6	430	4.74	4.74	15	240	3.41	3.38
7	001	4.74	4.74	16	640	3.33	3.34
8	101	4.51	4.44	17	620	3.25	3.27
9	011	4.33	4.31	18	450	3.00	2.98

TABLE II
The spacings calculated and determined from X-ray patterns
for orthorhombic form of the phase II

N	hkl	d_{calc} (Å)	d (Å)
1	200	11.98	11.97
2	010	10.77	10.77
3	400	5.99	5.91
4	020	5.39	5.32
5	220	4.91	4.90
6	320	4.46	4.42

The identification of phase state I at −75°C exhibits a monoclinic crystalline structure with unit cell $a = 20.75$ Å, $b = 15.22$ Å, $c = 4.74$ Å, and $\gamma = 44.6°$ (Table I). According to Reference 8, there are two chains with the opposite directions per a unit cell. The density calculated from the crystallographic data is 2140 kg m^{-3}. This value is approximately the same as that obtained for polyorganophosphazene containing hydrogen atoms instead of the fluorine ones in side chains.[10]

Heating of the sample above $T(1)$ (Figure 5, curve A) and the subsequent cooling to room temperature leads to a change in the crystalline structure (phase II). Its X-ray pattern is characterized by the equatorial reflections of high intensity (Figure 6, curve B) and two series of the arcs located at an equal distance from the center, which generate the four-point and six-point patterns, respectively (Figure 4c). The low intensity reflections of the four-point pattern correspond to scattering of the side chains of macromolecules in phase I inclined to the backbone. The arcs of the six-point picture are the scattering of side chains of the macromolecules in phase II which are perpendicular to the backbone and form hexagonal lattice. It is noteworthy that the intensity of the meridional reflections on the six-point picture exceeds the intensity of the other reflections. This may be explained by supplementary scattering of the conformation-ordered main chains.

The analysis of X-ray diagram obtained at the temperature above 60°C leads to a conclusion that the polymer in phase II crystallizes in an orthorhombic modification with the unit cell parameters $a = 23.96$ Å, $b = 10.77$ Å, $c = 4.64$ Å (Table II). The calculated density (two chains per unit cell) is 1900 kg m^{-3}.

Above $T(1)$ PPPh transforms into a mesophase state characterized by a strong narrow equatorial reflection at the angle position $2\Theta \cong 8°$ and the amorphous halo in the angle region 15–25°. Besides, a weak but well-pronounced crystalline peak takes place on the right flank of the amorphous halo (Figure 6, curve C). The Bragg spots on the equator in the X-ray pattern from the polymer mesophase indicate a two-dimensional long-range order in the basal plane and only short-range ordering along the *c*-axis.

CONCLUSION

A high ability to molecular orientation under shear flow of the mesophase PPPh has been found. It is established that PPPh can exist in four phase states. Crystalline phase I has a monoclinic lattice with spacing 4.74 Å, the side chains being inclined toward the backbone. The polymorphic transition which occurred at 40–50°C is due to the transformation of the crystalline monoclinic modification into the orthorhombic structure (phase II), spacing 4.64 Å with side chains being orthogonal to the backbone. In the mesomorphic state the polymer exists in the range 100–310°C and transforms to the isotropic melt at higher temperatures.

References

1. I. B. Sokolskaya, Ya. S. Freidzon, V. V. Kochervinskii, and V. P. Shibayev, *Polym. Sci. USSR,* **28,** 329 (1986).
2. D. R. Tur, N. P. Provotorova, S. V. Vinogradova, V. I. Bachmutov, M. V. Galakhov, V. P. Zhukov, I. I. Dubovik, D. Ya. Zvankin, and V. S. Papkov, *Makromol. Chem.* **192,** 1905 (1991).
3. T. P. Russel, D. P. Anderson, R. S. Stein, C. A. Desper, J. J. Beres, and N. S. Schneider, *Macromolecules,* **17,** 95 (1984).
4. M. Kojima and J. H. Magill, *Polymer,* **26,** 1971 (1985).
5. A. N. Zadorin, E. M. Antipov, V. G. Kulichichkin, N. P. Tsukanova, D. R. Tur, and N. A. Plate, *Polym. Sci. USSR,* **35,** 000 (1993).
6. V. V. Korshak, S. V. Vinogradova, D. R. Tur, N. N. Kazarova, L. I. Komarova, and N. N. Gilman, *Acta Polymerica,* **30,** 245 (1979).
7. E. M. Antipov S. A. Kuptsov, V. G. Kulichikhin, D. R. Tur, and N. A. Plate, *Makromol. Chem., Macromol. Symp.,* **26,** 69 (1989).
8. N. S. Schneider, C. R. Desper, and J. J. Beres, *Liquid Crystalline Order in Polymer,* Ed. A. Blumstein (Academic Press, New York, 1978) Chap. 9, p. 300.
9. R. E. Singler, R. A. Willingham, C. Noel, C. Friedrich, L. Bosio, and E. Atkins, *Macromolecules,* **24,** 510 (1991).
10. D. Ya. Tsvankin, M. V. Gerasimov, V. P. Zhukov, I. I. Dubovik, D. R. Tur, and V. S. Papkov, *J. Polym. Sci.,* **B30,** 851 (1992).