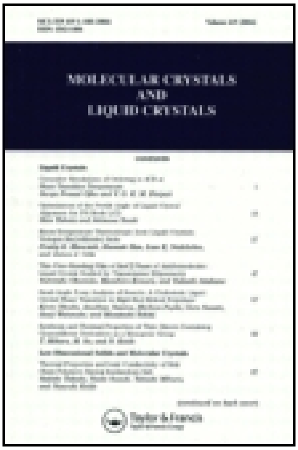

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Structure of Polymers With Phenyl Benzoate Side Groups By X-Ray Evidence

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STRUCTURE OF POLYMERS WITH PHENYL BENZOATE SIDE GROUPS BY X-RAY EVIDENCE

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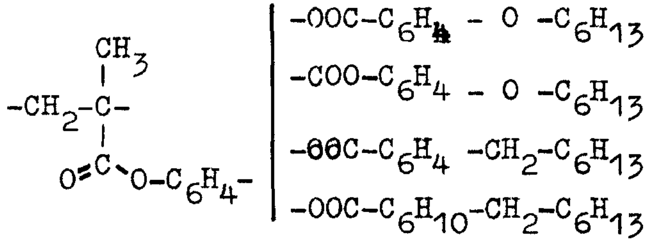
Structure of four polymers were studied: poly-p-methacryloyloxy phenyl esters of p-n-hexyloxy benzoic acid (PMB-6), p-n-heptyl benzoic acid (PMH-7) and p-n-heptyl - trans-cyclohexane carboxylyc acid (PMC-7) and poly-p-n-hexyloxy phenyl ester of p-methacryloyloxy benzoic acid (PM-O6). Diffractions parameters and polymer organization were discussed in terms of both crystallinity and paracrystal. The structural organization of PMB-6, PMH-7 and PM-O6 was interpreted on the basis of block model. Structure of PMC-7 assumed to be organized similar to cybotactic nematics.

A manner of structural organization of polymers with mesogenic side groups depends on a number of factors - the nature of mesogenic side groups, the length of a spacer group, the nature of the main chain and so on[1,2]. The formation of mesomorphic structure is influenced by both the method of polymer preparation[3] and the method of macroscopic ordering of samples.[4,5] These problems, however, are not clear enough and need further careful research.

The present paper concerns the structural investigation of four polymers consisting of the following monomer units:



$-CH_2-C(CH_3)(C(=O)O-C_6H_4-)-$

$-OOC-C_6H_4-O-C_6H_{13}$ PMB-6

$-COO-C_6H_4-O-C_6H_{13}$ PM-06

$-OOC-C_6H_4-CH_2-C_6H_{13}$ PMH-7

$-OOC-C_6H_{10}-CH_2-C_6H_{13}$ PMC-7

X-ray diffraction data were obtained with a Ruscher camera and Debye camera (model DS-114) with Ni-filtered CuKα radiation at room temperature. Samples of the polymers were oriented by stretching above T_g.

X-ray diagrams and polymer organization were discussed in terms of Tsvankin's concept of crystallinity[6] and Hoseman's concept of paracrystal[7]. It has also been suggested that the use of Tsvankin's model will enable to calculate the size of "well" and "poorly" ordered regions (l and a resp.) related to the different parts of the side groups, whereas Hoseman's model permits to determine the parameters of the distortions of the second kind such as g_1 - the degree of the paracrystalline distortions, L - an average size of coherent scattering regions.

PMB-6. X-ray texture diagram from the polymer shows four spots on the first layer line, two reflections on the meridian, a diffuse ref - lections on the equator and a marked diffuse background within the region of the third layer line (Fig. 1). The degree of diffusion ($k=I/\Delta 2\Theta$) of the spots is by an order of magnitude greater than that of the meridian reflections and comparable to that of the equator reflections (Table).

The presence of two or more reflections on the layer line may be explained by the lattice structure of the object, but in this case the the lattice is formed by the correlation of bigger structural units than the mesogenic groups.

Such structural unit may be a block which is formed by the macromolecule or by its part. The main chain of the macromolecule is coiled within a plane containing two layers of the me - sogenic groups.

The meridian reflectins are on even layer lines only. It may be explained either by the presence of glide-reflection plane in the macrolattice or by the fact that the lattice is cen - tered. Then the reflections on uneven layer li - nes would disappear.

Thus, according to x-ray diffraction pattern the structural model will be as follows. The blocks are lined in rows along Z so that they form layer packs. In this case, the shifts along Z in the adjacent rows (along X) are correlated and equal to half a height of the block, i.e.

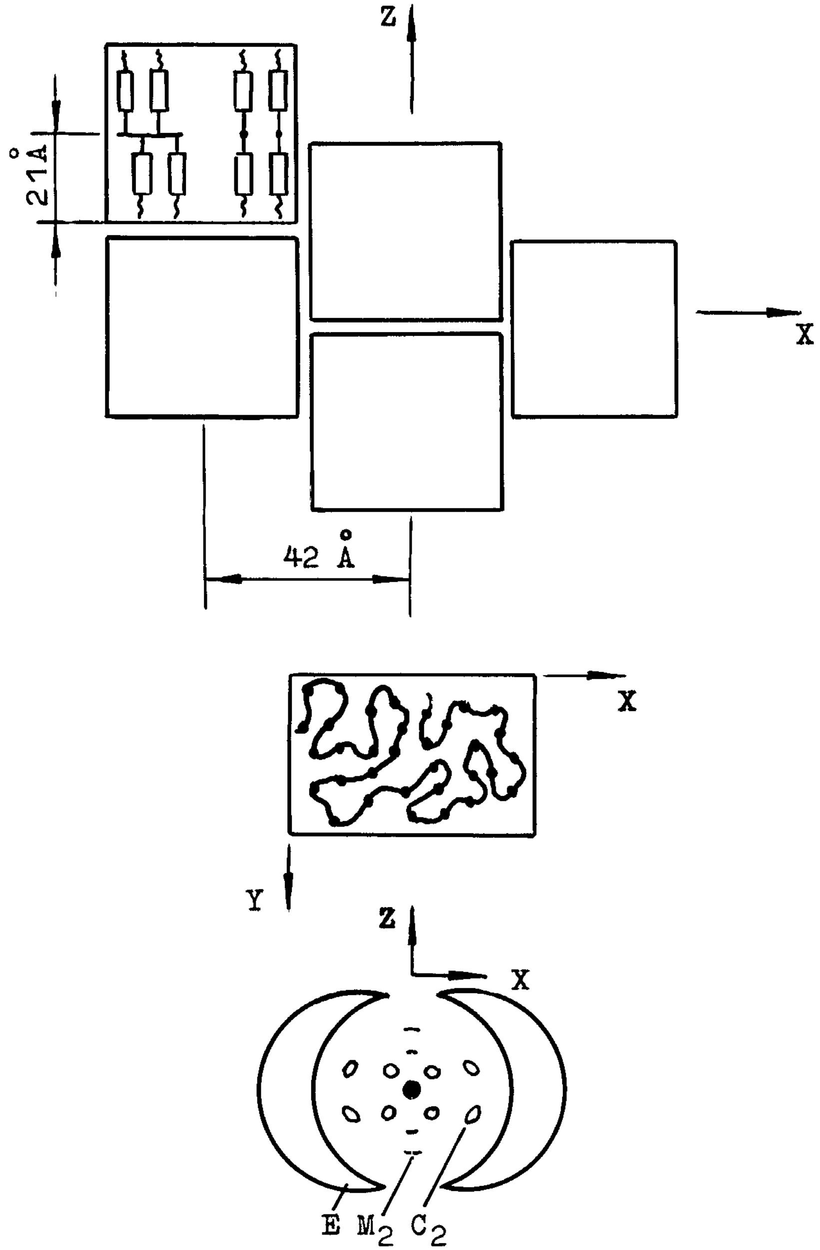


FIGURE 1 Scheme of x-ray texture diagram and block model for PMB-6

TABLE 1 Diffraction and structural parameters of the polymers

Polymer	Refl.	θ grad.	I a.u.	$\Delta 2\theta \cdot 10^{3}$ radn	$k \cdot 10^{-3}$	d Å	g_1 %	$\mathcal{H}$ %	c Å	l Å	a Å
1	2	3	4	5	6	7	8	9	10	11	12
PMB-6 orient.	M_1	2.11	42	2.65	15.9	20.99	4.5	96	20.3	19.5	0.8
	M_2	4.23	14	10.86	10.5	10.46					
	C_{1Z}	1.13	10	8.21	1.2	39.11	16.5				
	C_{1X}	1.05	10	6.57	1.5	42.10	13.0				
	C_{2X}	3.17	10	11.33	1.0	13.92					
	E	9.68	96	92.76	1.0	4.59	18.8				
PMB-6 unorien	1	1.46	82	18.41	4.2	30.17	25.0				
	2	2.07				21.34					
	3	4.05				10.92					
	4	9.52	66	98.46	0.8	4.63	21.0				
PMC-7	M	1.29	48	10.86	4.4	34.19	18.0	64	37.4	23.8	13.6
	E	9.87	46	62.20	7.4	4.50	15.0				

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11	12
PMH-7	M_1	1.49		16.55		29.62					
	M_2	2,03	54	5.19	10.4	21.73	8.9	88	21.9	19.3	2.6
	M_3	3.40				12.99					
	M_4	4.92		21.03		8.99					
	M_5	7.45				5.94					
	E	9.65	77	47.15	1,6	4,60					
	C_{1X}	1.09	54	7.02	7.7	40.54					
	C_{1Z}	0.99	54	5.17	10.4	44.53					
PM-06	1	1.31	82	19.38	4.2	33.67	28				
unorien̄ted	2	2.33				19.00					
	3	3.57				12.39					
	4	9.57	26	101.61	0.3	4.63	21				

c - long period by Tsvankin,

$\varkappa$ - the degree of packing perfection,

$\Delta 2\theta$ - diffraction half-width of the reflection.

the thickness of a layer. The diffuse character of the reflections from the block structure suggests a limited number of correlating structural units.

The analysis of the block, layer and intralayer structure parameters obtained by the calculation of corresponding reflections (C_1 and C_2 - block structure, M_1 and M_2 - layer structure, E - mesogenic side group packing) using Hoseman's model gave the following results. The macrolattice is less in size along X (L_x = 230 Å) than along Z (L_z = 580 Å) and has large distortions in this direction caused possibly by different block sizes (average size along X is 42 Å). The size of block along Z is twice the length of two mesogenic groups, i.e. the groups are perpendicular to the plane of the layer.

As follows from Table distortions of the second kind in the layer packing are insignificant and comparable to those of low molecular mass smectics. On the other hand, the distortion in lateral packing of mesogenic groups exceed those in low molecular mass smectics and are comparable with those in nematics[8].

It is necessary to note that our data on both diffraction pattern and the proposed model for PMB-6 considerably differ from the data given in[5]. Here, the difference in the way of orientation of the sample may have played the leading role.

The results obtained by Tsvankin's model for the layer system make it possible to suggest that the mesogenic groups are packed "well" along the whole legth of the layer, i.e.there is no difference in perfection of aromatic and aliphatic parts packing and the zone of "poor" ordering is rather limited and it possibly located in the joint of the adjacent layers (in the region of a limited interpenetration of the alkoxy chains from different layers).

X-ray diffraction pattern from unoriented PMB-6 shows three inner rings and the outer halo Their parameters correspond to the block, layer and intralayer structures, but all these structures have more essential distortions than in the oriented sample.

PMH-7. X-ray texture diagram from the polymer has some small angle reflections. Their spacings are not the multiplicity of higher orders. The presence of two spots symmetrically shifted about the meridian on the first layer line may be explained by means of chevron model[9]. In this case blocks formed by regularly shifted fragments of macromolecules (skewed angle 48°) are lined in rows along Z without any correlation (Fig. 2). Reflection M_1 (the second layer line) appears at the rotation of the block system around Z by 90°. This is confirmed by that interplanar spacings of M_1 and C_{1Z} give the same angle of skew as do C_{1X} and C_{1Z}. Reflection M_2 is related to the layer packing. Weak diffuse streaks on 4th, 5th and 6th layer lines are the

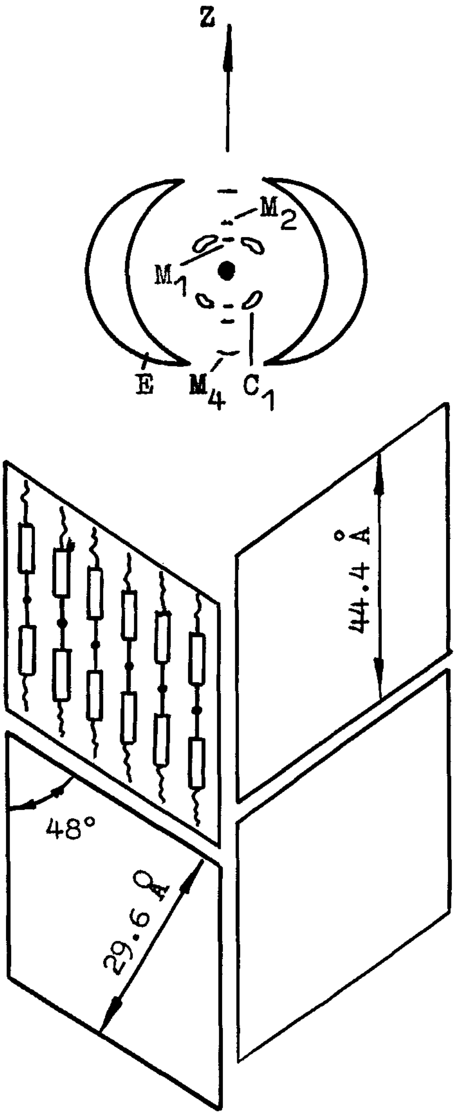


FIGURE 2 Scheme of x-ray texture diagram and block model for PMH-7

multiplicity of higher orders of diffraction from both block and layer structures. The structure with a tilted arrangement of mesogenic groups in the layer is similar to that of low molecular mass smectic C. The structure is characterized by bigger distortions in the layer packing and by larger zone of "poorly" packed parts of mesogenic groups as compared to PMB-6.

PMC-7. X-ray texture diagram from the polymer has an order of meridian reflections only (Fig. 3). There are no indications of large scale ordering. Distortions of longitudinal packing of mesogenic groups exceed those of lateral one that is peculiar to classic nematics.[8] The intensity of the meridian reflection, however, speaks in favour of structure of cybotactic nematics. The greater azimuthal half-width of wide angle reflection (82°) as compared to that of small angle reflection (50°) may be explained by either a tilted arrangement of mesogenic groups in pseudo-layers or interpenetration of mesogenic groups in adjacent layers (Fig. 3).

The calculation of diffraction parameters in terms of Tsvankin's model provides a long period (c), which to some extent exceeds the double lenth of a mesogenic group, and a wide zone of "poorly" ordered regions (a). The formation of the structure is likely to be greatly influenced by cyclohexane fragments which hinder the close packing of mesogenic groups within a layer. In this case, quickly accu -

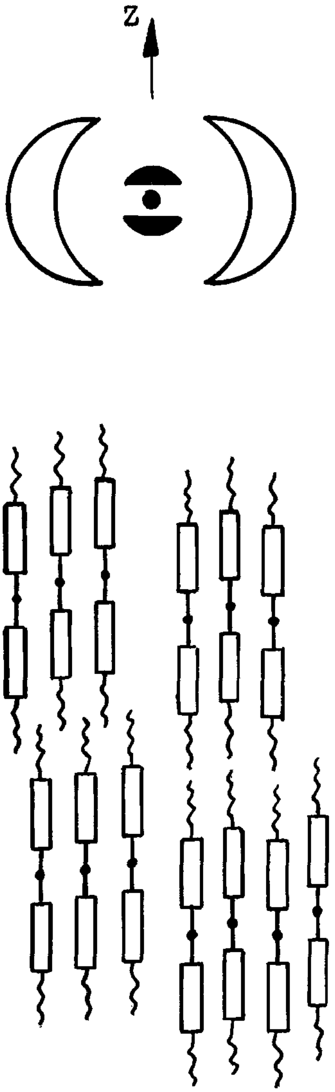


FIGURE 3 Scheme of x-ray texture diagram and arrangement of mesogenic groups for PMC-7

mulated lateral shift defects give rise to "breake" in layer.

PM-06. X-ray diagram of an unoriented sample shows three small angle rings and the outer halo. As follows from the Table, lateral packing distortions here are the same as for unoriented PMB-6.

Owing to the absence of orientation it is impossible to establish a structural model. There may be both a double-layer packing with interpenetration of aliphatic groups and a structure with mesogenic groups being at an angle to planes. The latter may appears as a result of correlated shift of planar fragments with the formation of a chevron structure.

Thus, the polymers under study are characterized by a layer packing of mesogenic groups. The peculiarities of chemical constitution of mesogenic groups lead to a variety in lateral and longitudinal packing as well as in a large-scale ordering.

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