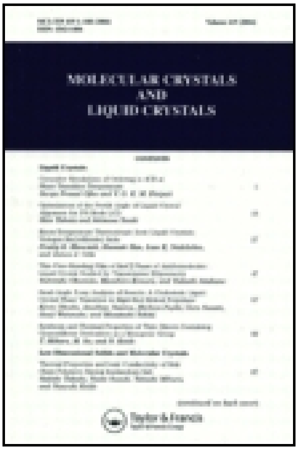

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Electron Diffraction Study on the Structure of Some Comb-Like Polymers in Glassy State

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ELECTRON DIFFRACTION STUDY ON THE STRUCTURE OF SOME COMB-LIKE POLYMERS IN GLASSY STATE

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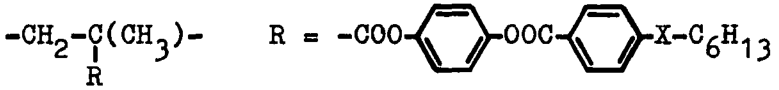
Abstract Electron diffraction from liquid crystalline polymers with direct connection of mesogenic side groups to main chain has been investigated. The polymers exhibit crystalline phase as local inclusions which form by crystallization of macromolecule fragments. The content of the crystalline phase is about 2%.

INTRODUCTION

Liquid crystalline polymers with mesogenic side groups connected to main chain via flexible spacers are crystallizable. The content of crystalline phase may be high enough to be detected by x-ray method.[1] In the case of polymers with direct connection of mesogenic groups to main chain, the ability for crystallization is largely suppressed. In such polymers the crystalline phase may be present as slight heterophase inclusions which can be recognized by electron diffraction only.

EXPERIMENTAL

In the present work the structure of poly-p-methacryloyloxy phenyl esters of p-n-heptyl benzoic acid (PMH-7) and p-n-hexyloxy benzoic acid (PMB-6)



$-CH_2-\underset{R}{C}(CH_3)-$

X = $-CH_2-$ (PMH-7) or -O- (PMB-6)

were studied by electron diffraction.

According to the x-ray data[2] PMH-7 and PMB-6 exhibit smectic structure of C and A type respectively.

Electron diffraction patterns were obtained from an electron microscope operating at a voltage of 75 kV. The investigations were carried out under microdiffraction conditions, covering exposed regions about of 1 μm. For calibration of diffraction pattern TlCl was used. Sample preparation was carried out in the following manner. The sample plates were heated up to T_g+ 30°C in a press and then were cooled. The plates were sectioned at room temperature by means of an ultramicrotome equipped with a glass knife. The thin sections were 200-300 Å in thickness. The sections were immersed in acetone for 40 hours to remove possible residual monomer.

RESULTS AND DISCUSSION

The both polymers have two kinds of electron diffraction patterns. The first contains two broad rings (Figure 1a), the second exhibits diffrac -

tion pattern typical of crystalline phase (Figure 1b and c).

The broad rings are 2 order of diffraction corresponding to spacings of 4.6 Å and 2.3 Å both for PMH-7 and PMB-6. Spacing of 4.6 Å is in a good agreement with that calculated from x-ray data[2] (4.6 Å for PMH-7 and 4.59 Å for PMB-6). It indicates that the first kind of electron diffraction pattern is from smectic structure, spacings corresponds to lateral packing of the mesogenic groups.

The absence of layer spacings on the patterns appears to be due to microtoming along smectic layers mostly. In this case the layer planes are in "unreflecting" positions.

The long period diffractions are also absent on the second kind of the patterns, indicating a specific incorporation of crystalline structure into that of mesomorphous matrix.

The degree of crystallinity of the polymers estimated by scanning over the effective area of a specimen (0.5×0.5 mm) is about 2%.

Patterns of various Laue zones from the single-crystal inclusions of the both polymers carried out with different angles of incidence were obtained. The values of the angles between the zone axes were subjected to refinement at assignment of indices.

Because of quick destruction of single-crystal inclusions under electron beam (a diffraction

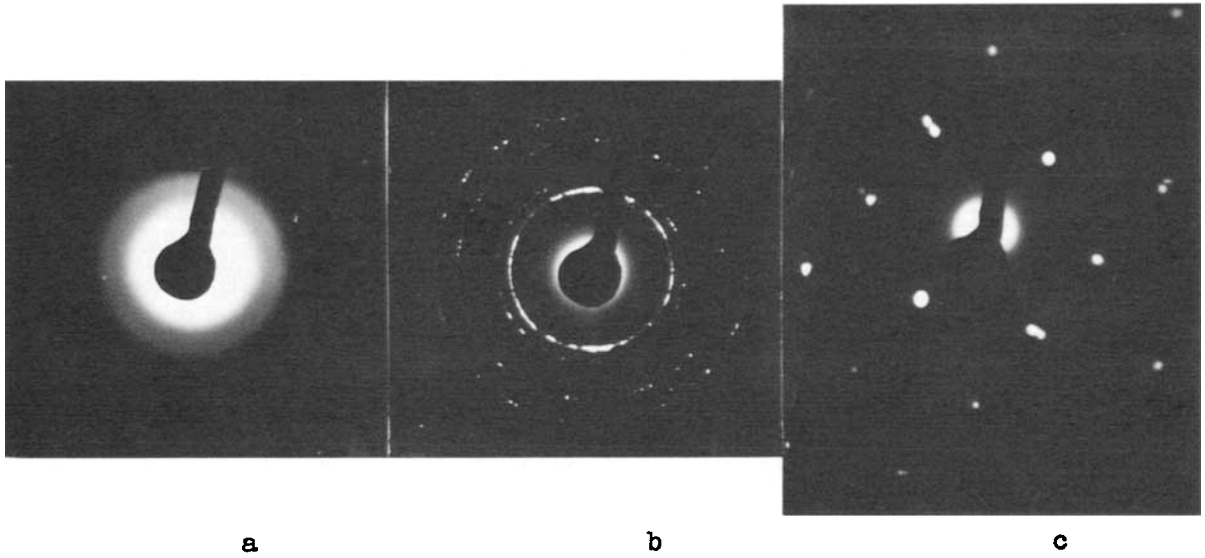


FIGURE 1. Electron diffraction patterns of PMH-7:
(a) mesophase, (b) polycrystal, (c) single crystal.

pattern of mesophase appears) and a narrow range of tilt angle of the object (up to 10°) we did not succeed in obtaining any sections through the reciprocal lattice to construct the spatial structure and reveal the lattice constants of the crystals.

Therefore, in order to be indicated the reflections and determine the unit cell of the lattice the following assumptions were introduced.

i) The crystalline phases observed are those of the polymers since the monomers, as will be seen below, crystallize in other forms.

ii) There must exist a correlation between the arrangement of the mesogenic groups with respect to basal planes of the mesophase and the crystal. The reflections on the single-crystal diagram of PMH-7 can be easely indicated (Table 1) if we assume monoclinic lattice with angle of 132° determined from the tilt of the mesogenic groups in smectic C structure.[2] As for PMB-6 we can suggest hexagonal lattice and an arrangement of the mesogenic groups perpendicular to basal plane as with smectic A phase (Table 2).

Figure 2 illustrates the arrangements of mesogenic groups in crystal. PMH-7 has monoclinic lattice with a = 44.4 Å, b = 14.0 Å, c = 5.0 Å and γ = 132° containing four mesogenic groups. PMB-6 has monoclinic (pseudohexagonal) lattice with a = b = 5.7 Å, c = 43.2 Å and γ = 120° containing two mesogenic groups. In the both cases

TABLE I Electron diffraction data for single crystal of PMH-7

hkl				d_{calc} (Å)	d_{exp} (Å)	hkl		d_{calc} (Å)	d_{exp} (Å)
zone axis [110]						zone axis [164]			
111	$\bar{1}\bar{1}\bar{1}$	$\bar{1}\bar{1}1$	$11\bar{1}$	4.36	4.36	$\bar{2}\bar{1}1$	$21\bar{1}$	4.14	4.14
222	$\bar{2}\bar{2}\bar{2}$	$\bar{2}\bar{2}2$	$22\bar{2}$	2.18	2.18	$\bar{4}\bar{2}2$	$42\bar{2}$	2.07	2.11
333	$\bar{3}\bar{3}\bar{3}$	$\bar{3}\bar{3}3$	$33\bar{3}$	1.45	1.40	$\bar{6}\bar{3}3$	$63\bar{3}$	1.38	1.40
444	$\bar{4}\bar{4}\bar{4}$	$\bar{4}\bar{4}4$	$44\bar{4}$	1.09	1.09	401	$\bar{4}0\bar{1}$	4.29	4.30
220	$\bar{2}\bar{2}0$			4.37	4.36	802	$\bar{8}0\bar{2}$	2.15	2.18
440	$\bar{4}\bar{4}0$			2.19	2.15	610	$\bar{6}\bar{1}0$	4.09	4.11
660	$\bar{6}\bar{6}0$			1.46	1.40	1220	$\overline{12}\,\bar{2}0$	2.05	2.04
331	$\bar{3}\bar{3}\bar{1}$	$\bar{3}\bar{3}1$	$33\bar{1}$	2.52	2.47	821	$\bar{8}\bar{2}\bar{1}$	2.35	2.40
442	$\bar{4}\bar{4}2$			1.65	1.60	$2\bar{1}2$	$\bar{2}1\bar{2}$	2.46	2.45
$\bar{4}\bar{4}2$	$44\bar{2}$			1.65	1.59	$4\bar{2}4$	$\bar{4}2\bar{4}$	1.23	1.23
551	$\bar{5}\bar{5}\bar{1}$	$\bar{5}\bar{5}1$	$55\bar{1}$	1.65	1.59	$0\bar{2}3$	$02\bar{3}$	1.60	1.62
002	$00\bar{2}$			2.52	2.54	$\bar{6}1\bar{3}$	$6\bar{1}3$	1.62	1.62
004	$00\bar{4}$			1.26	1.27				

TABLE II Electron diffraction data for single crystal of PMB-6

hkl		d_{calc} (Å)	d_{exp} (Å)	hkl		d_{calc} (Å)	d_{exp} (Å)
	ZONE AXIS	[111]			ZONE AXIS	[221]	
101	$\bar{1}0\bar{1}$	4.89	4.92	102	$\bar{1}0\bar{2}$	4.80	4.80
202	$\bar{2}0\bar{2}$	2.46	2.46	204	$\bar{2}0\bar{4}$	2.40	2.40
303	$\bar{3}0\bar{3}$	1.64	1.64	306	$\bar{3}0\bar{6}$	1.60	1.60
011	$0\bar{1}\bar{1}$	4.89	4.91	012	$0\bar{1}\bar{2}$	4.80	4.83
022	$0\bar{2}\bar{2}$	2.46	2.46	024	$0\bar{2}\bar{4}$	2.40	2.42
033	$0\bar{3}\bar{3}$	1.64	1.64	036	$0\bar{3}\bar{6}$	1.60	1.62
123	$\bar{1}\bar{2}\bar{3}$	1.84	1.84	114	$\bar{1}\bar{1}\bar{4}$	2.83	2.80
112	$\bar{1}\bar{1}\bar{2}$	2.82	2.83	228	$\bar{2}\bar{2}\bar{8}$	1.42	1.40
224	$\bar{2}\bar{2}\bar{4}$	1.41	1.42	216	$\bar{2}\bar{1}\bar{6}$	1.82	1.82
231	$\bar{2}\bar{3}\bar{1}$	1.84	1.83	318	$\bar{3}\bar{1}\bar{8}$	1.32	1.33
314	$\bar{3}\bar{1}\bar{4}$	1.35	1.35	126	$\bar{1}\bar{2}\bar{6}$	1.82	1.82
134	$\bar{1}\bar{3}\bar{4}$	1.35	1.35	138	$\bar{1}\bar{3}\bar{8}$	1.32	1.32
$\bar{1}10$	$1\bar{1}0$	4.92	4.90	$\bar{1}10$	$1\bar{1}0$	4.92	4.90

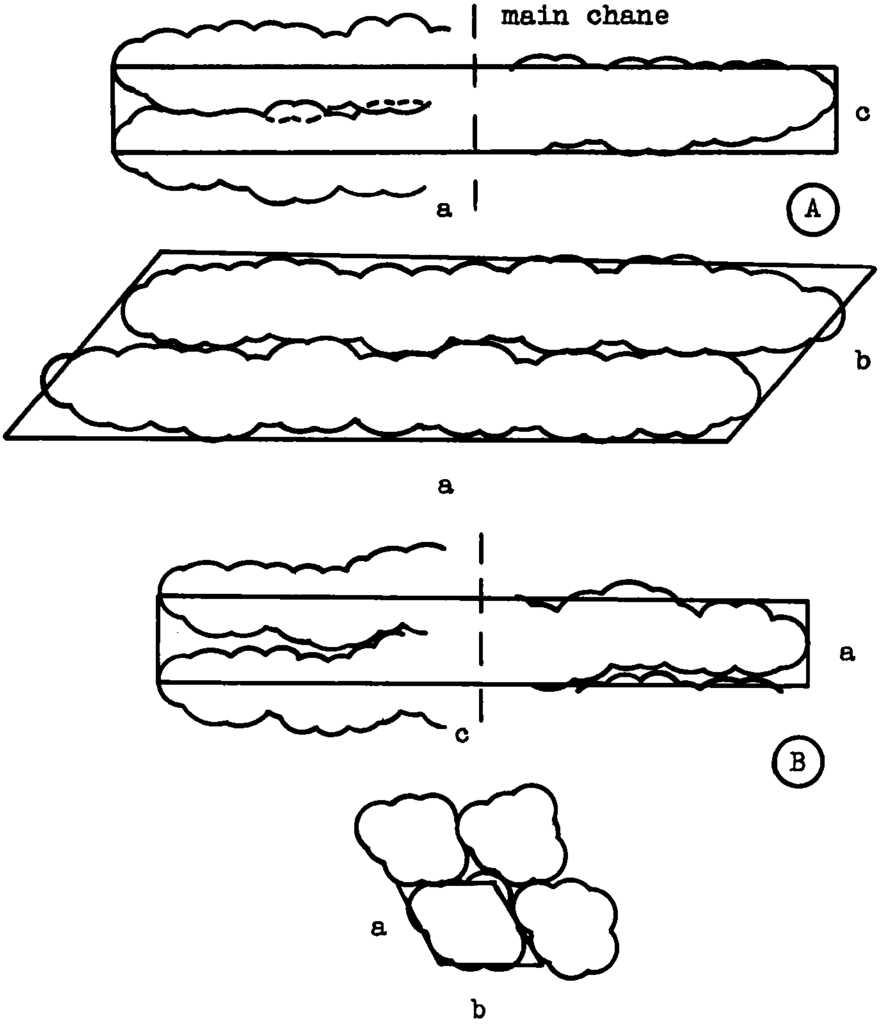


FIGURE 2. Approximate arrangement of mesogenic groups in unit cell of PMH-7 (A) and PMB-6 (B).

the computational error (0.06 Å) is less than the experimental one (0.07 Å).

The validity of the assumption are confirmed by a coincidence of the values of spacings obtained from polycrystal diffraction patterns with those calculated from above data as it is seen in Table 3 by an example of PMH-7.

The monomers, previously mentioned, crystallize in different crystal lattices. Interplanar distances calculated from x-ray data do not agree with electron diffraction data of the polymers. X-ray reflections have been indicated by Ito method[3] with subsequent matching unit cells by Delone method.[4] Table 4 lists the spacings of the monomers crystals and Figure 3 shows the arrangement of MH-7 molecules in crystal lattice with $a = 5.74$ Å, $b = 8.92$ Å, $c = 20.2$ Å, $\alpha = 111.8°$, $\beta = 96.3°$ and $\gamma = 92°$.

Taking into consideration these results the crystalline phase of the polymers can be believed to be formed by crystallization of macromolecule fragments. However, steric hindrances in the couplings of the mesogenic groups to the main chain lead to quick accumulation of defects. Therefore, the crystalline phase in the polymers under study is of most local nature, making it impossible to be recognized by other, less sensitive methods.

TABLE III Observed and Calculated Spacings of polycrystals of PMH-7

hkl					d_{exp} (Å)	d_{calc} (Å)
$\bar{1}32$	422	$4\bar{4}0$	330	032	2.94	2.94
032	$\bar{2}52$	150	$1\bar{3}4$	442	2.03	2.03
264	844	$8\bar{8}0$	164	426	1.47	1.47
056	$\bar{1}56$	464			1.31	1.31
066	028	$\bar{1}66$	288		1.21	1.21
158	386	$4\bar{8}6$	376		1.07	1.07
0610	$3\bar{9}8$	198	588		0.87	0.87
1710	$2\overline{10}8$	398	888		0.82	0.82
1108	0810	4710	598		0.80	0.80
4128	1286	$12\overline{12}0$	$2\overline{10}10$	3910	0.74	0.74
31010	8910	0812			0.70	0.70
01210	2614	8126			0.66	0.66
01211	0814	01112	1814		0.63	0.63

TABLE IV Spacings of monomer crystals

MB-6	MH-7									
d_{exp} (Å)	d_{exp} (Å)	hkl				d_{exp} (Å)	hkl			
21.90	18.41	001				3.18	113	120		
8.47	9.00	002	$01\bar{1}$			3.01	$\bar{1}22$	121		
7.41	8.00	010	012			2.90	$20\bar{1}$	$20\bar{2}$		
6.14	6.40	011				2.75	122	$\bar{1}23$	$2\bar{1}0$	201
5.76	5.67	100	$10\bar{1}$			2.67	$21\bar{1}$	$21\bar{3}$	$1\bar{3}2$	
5.20	5.20	101	012	$10\bar{2}$		2.61	$\bar{2}12$	$2\bar{1}2$	$1\bar{3}1$	$13\bar{2}$
4.89	4.86	$1\bar{1}0$	$1\bar{1}1$			2.49	$21\bar{2}$	$13\bar{1}$	123	$\bar{2}13$
4.67	4.70	$11\bar{1}$	$11\bar{2}$			2.43	$2\bar{2}1$	$1\bar{3}1$	$2\bar{2}0$	$2\bar{2}2$
4.20	4.56	$\bar{1}11$	102	$1\bar{1}2$	022	2.37	$\bar{2}21$	$22\bar{2}$	$22\bar{4}$	
3.69	4.40	110	024	$02\bar{1}$		2.24	131	213	220	$\bar{2}22$
3.46	4.33	$11\bar{3}$				2.15	221	132		
3.41	4.13	$\bar{1}12$	020			2.10	$2\bar{1}1$			
3.13	4.00	$1\bar{1}3$				1.97	$\bar{2}31$	$23\bar{1}$		

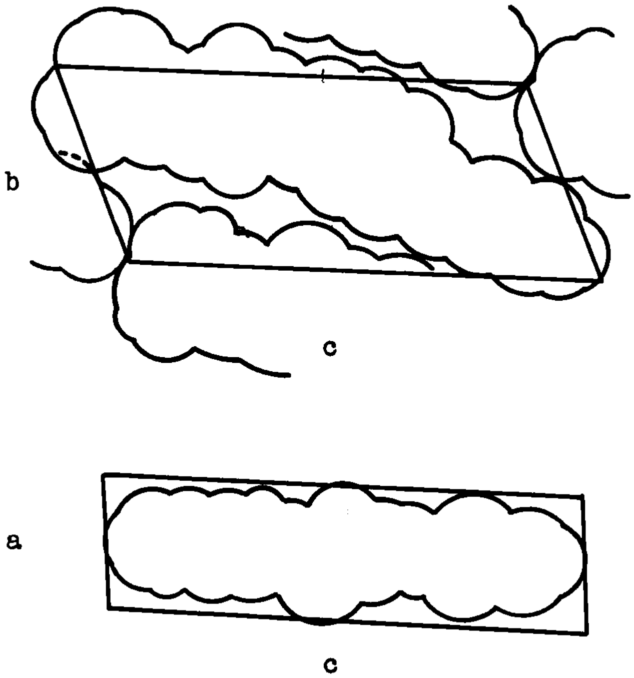


FIGURE 3. Approximate arrangement of MH-7 molecules in unit cell.

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