

# The Effect of Solid Surfaces on the Structure and Orientation of Poly-4-oxybenzoate

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## SYNOPSIS

Polymerization–crystallization of poly-4-oxybenzoate (P-4-OB) by various techniques on different solid substrates results in different crystal structures and orientation types. Confined thin film melt or solution polymerization of P-4-OB between glass slides or mica sheets resulted in various lamellar single crystal formations of phase I or II with crystal orientations of the  $hk0$  or  $Ok1$  type on the substrate surface. In some cases, different structures were formed in the polymerization–crystallization on the free surface of the solid substrate. © 1996 John Wiley & Sons, Inc.

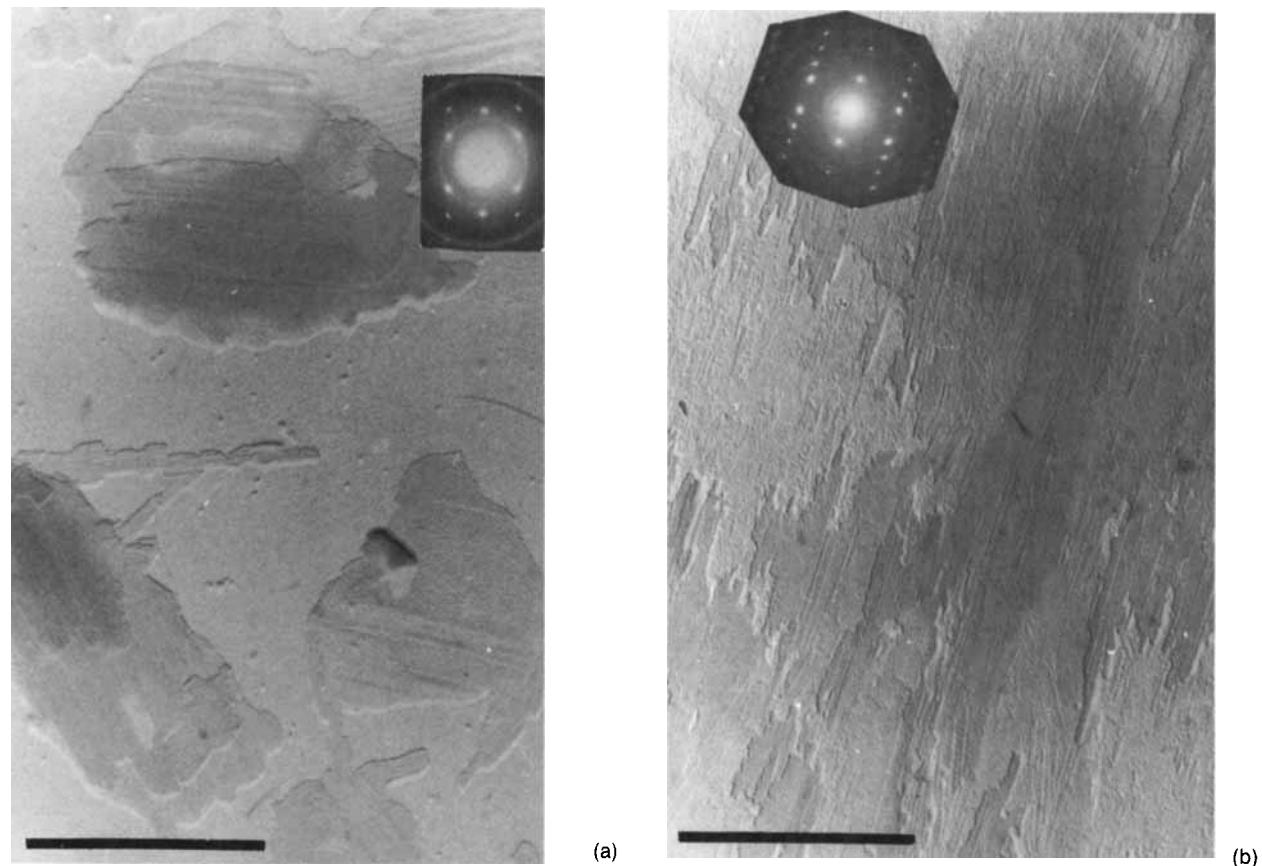
## INTRODUCTION

The polymerization and crystallization of polymers often takes place in contact with solid surfaces. Such surfaces are usually materials of polymerization and crystallization vessels, such as glass or metals. Frequently, one does not pay any particular attention to a possible effect of the substrate on the polymer structure. Only in studies of epitaxial crystallization and nucleation is the substrate chosen to attain a certain polymer structure and orientation. For this, mostly ionic crystals are used, such as alkali halides, quartz, talc, mica, calcite, or other inorganic and organic crystals. In previous reports, we have described a new technique for simultaneous polymerization–crystallization as constrained thin films between glass slides from the melt or solution of various liquid crystal polymers and copolymers.<sup>1–8</sup> This technique has enabled the preparation of thin single crystals suitable for electron microscopy (EM) and electron diffraction (ED) examination of the morphology and crystal structure. We have shown that the glass surface exerted a strong catalytic effect on the polymerization of aromatic polyesters but also on the orientation of molecular chains of the lamellar single crystals. In such lamellar single crystals, the molecular chains (crystal  $c$ -axes) were ori-

ented perpendicular to the glass surface irrespective of the polymer crystal modification, e.g., phase I, phase II, or pseudohexagonal (P-H) modification. This specific substrate orientation type prompted the investigation of orientation on solid substrates other than glass. In another report,<sup>9</sup> we have shown the results concerning the morphology, crystal structure, and orientation of poly-4-oxybenzoate (P-4-OB) samples formed by polymerization–crystallization and recrystallization in a thin layer between mica sheets. There, we have found a markedly different structure and orientation of P-4-OB on the mica surface, namely, the molecular axes were parallel to the surface. Here, we report results of the effect of several solid surfaces on the P-4-OB structure and orientation. The main attention was paid to the effect of the substrate and to the method of sample polymerization, either in a thin layer between two surfaces or on one free surface.

## Experimental

The measurements were done with P-4-OB samples prepared by polymerization–crystallization of 4-acetoxybenzoic acid (4-ABA), a product of Aldrich Co., on the pertinent substrate. Glass cover slips and freshly cleaved mica (muscovite) sheets were used as solid substrates on which 50–100 Å of Au, C, and Al were vacuum-evaporated in some cases. The melt thin polymerization was performed in a



**Figure 1** Phase I (a) and II (b) lamellar single crystals of P-4-OB with  $hk0$  orientation. Sample G/G type, polymerized 5 h at  $190^{\circ}\text{C}$ . Insets show the pertinent ED patterns. The rings in diffraction patterns are due to Au. Bar marks equal  $1\ \mu\text{m}$ .

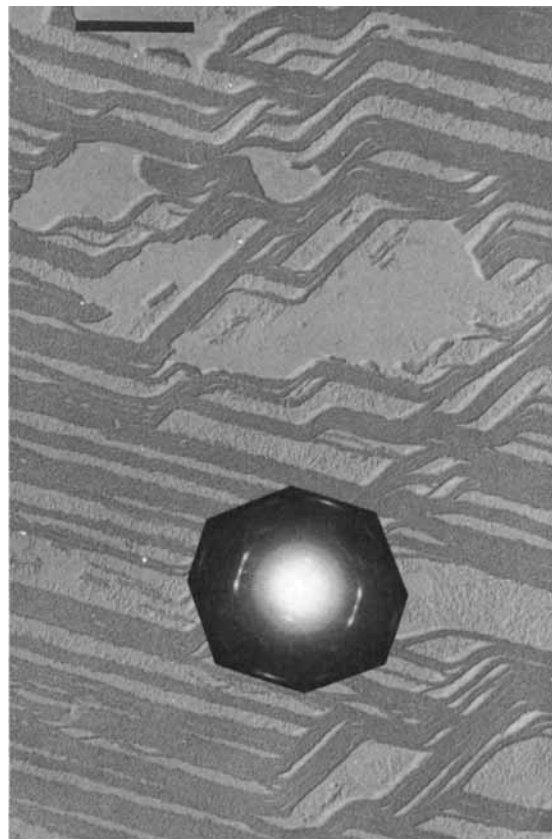
wide polymerization temperature ( $T_p$ ) range from  $160\text{--}400 \pm 0.5^{\circ}\text{C}$ . Two drops of a 0.5% acetone solution of 4-ABA were put on the tested surface; after solvent evaporation, two such slides were combined with the monomer layers facing each other, the sandwich was wrapped in a thin Al foil, and then it was placed on a hot stage heated to the chosen  $T_p$ . In the case of melt thin film polymerization on one free surface, the glass or mica sheets covered with monomer were separated by a 1 mm diameter wire. The solution polymerization was done in 1% solution of 4-ABA in mineral oil or biphenyl. The glass or mica sheets, joined by paper clips, were placed in the solution. After polymerization, the sandwiches were split apart and washed with hexane and acetone to get rid of the solvent and soluble fractions (monomer and oligomers). In the case of thin film polymerization between two equal surfaces, the samples are marked (e.g., M/M or G/G) as mica or glass. The marking *M/G* means that the sample was polymerized in a thin layer

between mica and glass. The marking —M or —G means that the sample was polymerized with free surface of mica or glass, with the other sample surface in contact with the air or solution. We have also investigated the surfaces of glass or mica on which a thin layer of carbon, Al, Au, or Pt was vacuum-evaporated. Such surfaces are labelled MC, MAI, GC, etc.

The sample morphology and crystal structure was investigated at room temperature using EM and ED at 80 kV on the Tesla BS 613 electron microscope. The polymer samples for electron microscopy examination were Au-shadowed and C-reinforced and released from the substrate by flotation on 1% HF water solution.

## RESULTS AND DISCUSSION

Using melt thin film polymerization–crystallization between glass or mica sheets the P-4-OB samples



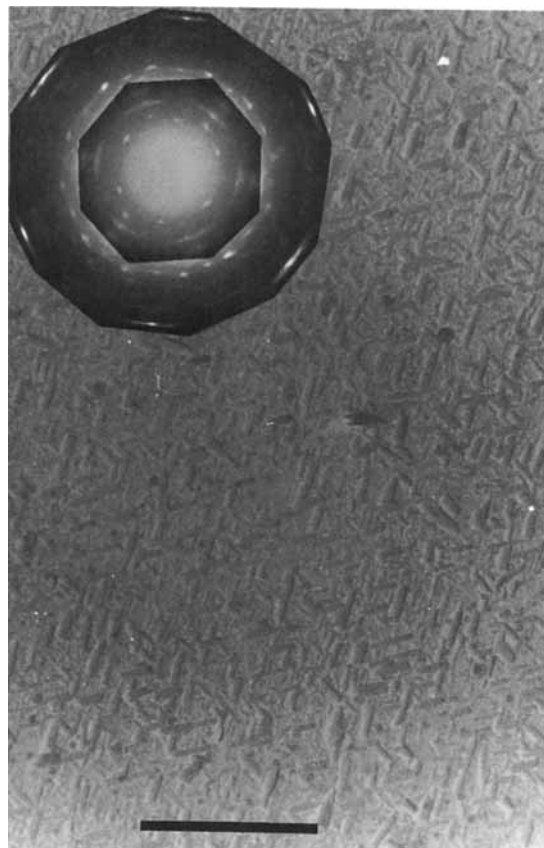
**Figure 2** Epitaxial structure (E) of the P-4-OB M/M sample polymerized/crystallized 2 h at 190°C. Bar marks equal 1  $\mu\text{m}$ . Inset shows the pertinent electron diffraction pattern.

formed in a wide  $T_p$  range, from 160–400°C. It is an interesting fact that the polymerization also takes place both above and below the monomer melting point ( $T_m$  of 4-ABA = 196°C). As it was referred to in another article,<sup>10</sup> this points not only to a complicated polymerization mechanism of 4-ABA but also to an important catalytic effect of glass or mica on 4-ABA polymerization rate.

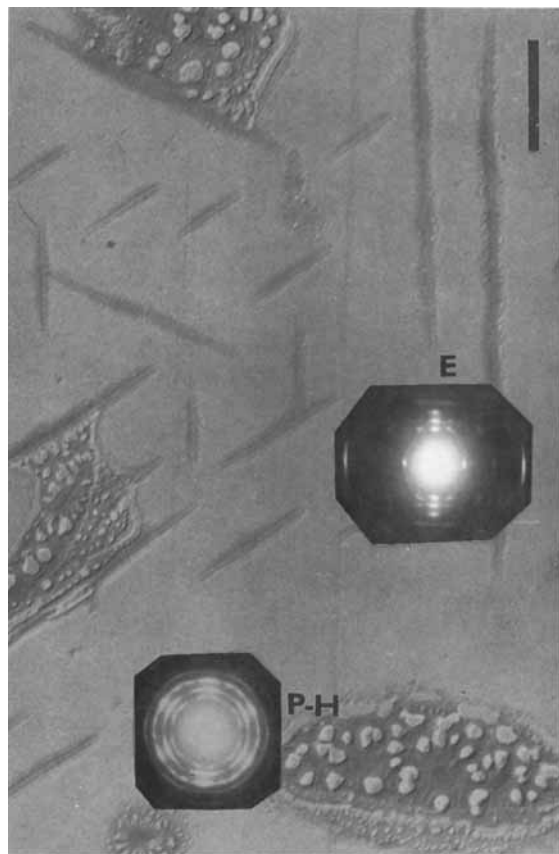
The results of melt polymerized-crystallized samples are summarized in Table I and of solution polymerized in Table II. The crystal structure, derived from ED patterns, is characterized by orthorhombic unit cell of the phase I or II or a pseudo-hexagonal phase (P-H), which is, in fact, built by a regular superposition of phase I and II crystals. In all such cases, the crystal orientation is of the  $hk0$  type; that is, the molecular chains ( $c$ -axes of the crystal cell) are oriented perpendicular to the substrate. In cases labelled  $E$ , the epitaxial crystallization took place, and axes  $c$  and  $a$  of the phase I or

II crystal cell lie on the substrate (mica) surface.<sup>9</sup> Generally, the morphology could be characterized as lamellar (L), which are single or multilayered single crystals and their aggregates or polycrystalline formations, or “foams” (F) of recrystallized lamellar formations, with holes and empty spots. In such cases, the crystal structure was that of P-H type. The epitaxial morphology (E) was characterized by sets of ribbons differing in length and width, oriented in one to three substrate directions rotated by 60°, as it was described in another publication.<sup>9</sup> Some typical examples of such structures and morphologies are shown in Figures 1–7.

The results shown in Table I for samples of the G/G type agree with previously published facts.<sup>1</sup> P-4-OB forms on the glass surface monolamellar and multilamellar systems, with the thickness of the individual lamellae being approximately 100 Å and the molecular chains oriented perpendicular to the glass surface. No other preferred crystal orientation (e.g., orientation of  $a$  or  $b$  axes) on the glass surface



**Figure 3** Epitaxial structure (E) of the P-4-OB M/M sample polymerized/crystallized 22 h at 280°C in a 0.5% mineral oil solution. Inset shows the pertinent ED pattern.



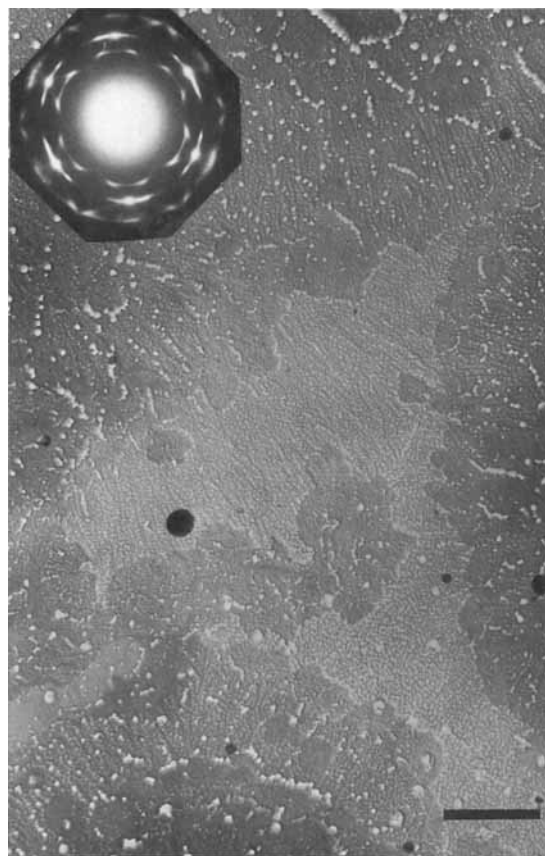
**Figure 4** Epitaxial structure of the P-4-OB M/M sample polymerized/crystallized 1 h at 400°C. Inset shows ED patterns of the one-dimensionally oriented E structure and the recrystallized P-H structure.

was observed. At lower  $T_p$ , both phases I and II are present in a roughly equal amount; at  $T_p$  above 200°C, phases II and P-H prevail. Glass covered with a thin layer of amorphous carbon (samples GC/CG) behaves similarly, as does polymerization on a free glass surface (-G). Using glass covered with a thin metal layer, e.g., GAu/AuG at 250°C only, phase II forms. At 400°C only, phase I forms if the glass surface is covered by Au or Al. In case of Pt cover, both phases I and II were observed at 400°C. Both phases I and II also appear in polymerization at the glass free surface or on glass in samples G/M where sheets of glass and mica were combined.

As far as the polymerization of 4-ABA in a thin layer on mica is concerned, the situation is more complicated. At  $T_p$  below 200°C, the situation is the same as in the case of glass. Again, one can see both phases I and II with  $hk0$  orientation. At higher  $T_p$ , the epitaxial structure with  $Ok1$  orientation appears accompanied by phases I and P-H with  $hk0$  orien-

tation, with phase II being completely missing. At 400°C, only E and P-H structures form. The samples prepared on the free surface (-M) or using a combined sandwich (M/G) have the same structure as samples prepared on the glass surface, that is, phase I and II. In such cases, the epitaxial overgrowth on mica appears only scarcely in a less perfect form, although it is common in M/M type samples prepared at similar conditions. A thin C layer on mica does not basically affect the character of the structure formed. Namely, with the MC/CM sample, the phases I, P-H, and a less perfect E structure is observed. As in the case of glass and also in the case of mica, a thin metal layer exerts a marked influence on the P-4-OB structure. Again, mainly phase I or phase II and P-H forms, with the exemption being a thin Al layer on mica where a small amount of E structure also appears at 400°C.

The results obtained with solution polymerized samples (Table II) basically agree with those of melt polymerized samples.



**Figure 5** P-4-OB sample polymerized/crystallized 1 h at 350°C (G/G) characterized by the P-H structure.



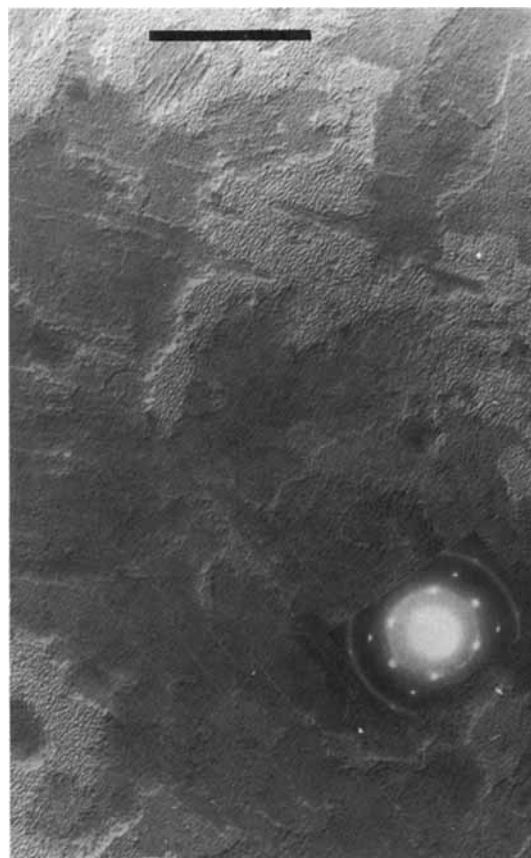
**Figure 6** P-4-OB sample polymerized/crystallized 23 h at 270°C in a 1% biphenyl solution between glass (G/G). Inset shows the phase II  $hk0$  orientation.

## CONCLUSIONS

Our results show that different substrates influence the polymerization–crystallization of P-4-OB in different ways. We have shown, using the example of an amorphous glass and crystalline mica, which are chemically related silicates, how such substrates influence the structure and orientation of P-4-OB. The principal difference consists in that on glass, where the P-4-OB molecular chains are oriented perpendicular to the glass surface; whereas on mica, the molecules tend to lie parallel to mica cleavage surface, ordered regularly in an epitaxial overgrowth. Glass and mica also influence the type of the P-4-OB crystal structure. Below 200°C on both substrates, lamellar single crystals and polycrystalline formations of the phase I and II form in approximately equal amounts. At higher  $T_p$ , the glass surface favors phase II of P-4-OB; whereas it favors phase I in mica. At  $T_p$  above 250°C on both substrates, the P-H phase forms, which represents a

regular superposition of phase I and II crystals in the ratio of 1 : 1. In this connection, one question arises: Where does the second type of crystal structure, necessary for the formation of the P-H structure, come from when both substrates favor the formation of only one type of crystal structure (I or II)? One possibility could be a relatively easy transformation of phase I into II and vice versa. Another possibility might be liquid crystal formation followed by crystallization and space saving reorganization during cooling down to room temperature.

The investigation of the limited space effect (between two substrates) has shown that basically it has no influence on orientation and P-4-OB crystal structure, namely in case of glass. In the case of mica, the limited space favors the epitaxial overgrowth but it is not essential. Namely, the epitaxial overgrowth is observed also in samples -M, though into lesser extent. This is due to the fact that on the mica-free surface (mainly in solution polymerization) a substantially thicker polymer layer builds



**Figure 7** P-4-OB sample polymerized/crystallized 20 h at 250°C (GA1/AIG). Inset shows the phase I  $hk0$  orientation.

**Table I** The Effect of Various Substrate Types on the Structure, Orientation, and Morphology of Melt Polymerized P-4-OB Samples

$T_p$ (°C/h)	Substrate	Crystal Structure	Orientation Type	Morphology
160/23	M/M	I, II	hk0	L
160/23	G/G	I, II	hk0	L
180/20	M/M	I, II, E	hk0, 0kl	L, E
180/20	G/G	I, II	hk0	L
200/72	M/M	<u>I</u> , P-H, E(a)	hk0, 0kl	L, F, E
200/72	G/G	<u>I</u> , <u>II</u> , P-H	hk0	L, F
220/95	M/M	I, E	hk0, 0kl	L, E
250/22	M/M	I, E	hk0, 0kl	L, E
250/20	G/G	<u>II</u> , I	hk0,	L
250/20	-M	<u>I</u> , <u>II</u> , <u>P-H</u> , E	hk0, 0kl	L, F, E
250/20	-G	I, II	hk0	L
250/20	<u>M</u> /G (b)	I, II	hk0	L
250/20	<u>G</u> /M (b)	I, II	hk0	L
250/4	MC/CM	<u>I</u> , <u>P-H</u> , E	hk0, 0kl	L, F, E
250/4	GC/CG	II, I	hk0	L
250/20	MAI/AlM	I, P-H	hk0	L, F
250/20	GAl/AlG	I, P-H	hk0	L
250/21	MAu/AuM	I	hk0	L
250/21	GAu/AuM	II	hk0	L
350/1	M/M	<u>E</u> , I, P-H	hk0, 0kl	L, F, E
350/1	G/G	P-H	hk0	F
390/24	M/M	E, P-H	hk0, 0kl	E, E
400/1	M/M	E, P-H	hk0, 0kl	E, F
400/1	MAI/AlM	<u>I</u> , <u>P-H</u> , E	hk0, 0kl	L, F, E
400/1	MAu/AuM	I	hk0	L
400/1	GAu/AuG	I	hk0	L
400/1	MPt/PtM	I	hk0	L
400/1	GPt/PtG	<u>II</u> , I	hk0	L

<sup>a</sup> The prevailing structure is underlined.

<sup>b</sup> The substrate examined is underlined.

than in case of limited space. A thin surface epitaxial layer is then covered by a thick layer of P-4-OB crystals with hk0 orientation. A thin carbon layer on glass or mica did not change the original substrate influence; only in case of mica was the extent of the

epitaxial overgrowth of P-4-OB lower than compared to mica alone. In cases where glass or mica were covered by a thin metal layer, a tendency to form lamellar type I P-4-OB crystals with hk0 orientation was noticed. Two exemptions were found:

**Table II** The Effect of Various Substrate Types on the Structure, Orientation, and Morphology of Solution Polymerized P-4-OB Samples

$T_p$ (°C/h)	Solvent	Substrate	Crystal Structure	Orientation Type	Morphology
250/23	Min. oil	M/M	I, II, P-H, E	hk0, 0kl	L, F, E
255/23	Biphenyl	M/M	I, II, P-H, E	hk0, 0kl	L, F, E
255/23	Biphenyl	-M	I, E	hk0, 0kl	L, E
255/23	Biphenyl	G/G	II	hk0	L
270/7	Min. oil	M/M	I, II, P-H, E	hk0, 0kl	L, F, E
270/7	Min. oil	-M	I, E	hk0, 0kl	L, E
270/7	Min. oil	G/G	II	hk0	L
270/7	Min. oil	-G	II, I	hk0	L

sample GAu/AuG at 250°C had the phase II structure; and in sample GPt/PtG at 400°C, the phase II structure prevailed over phase I. Also of some interest is the fact that in the MAI/AlM sample at 400°C, in addition to phase I and P-H, a small amount of epitaxial crystallization still appears.

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