Molecular packing in alkylated and chlorinated poly-*p*-xylylenes*

N. Sanjeeva Murthy
Allied Corporation, Corporate Technology, Morristown, NJ 07960, USA

and Hyo-gun Kim
Laboratory for Laser Energetics, University of Rochester, Rochester, NY 14623, USA
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The changes in the structure of poly-*p*-xylylene (PPX) films when substituted with chlorine (Cl), ethyl (Et), and isopropyl (iP) groups were investigated by X-ray diffraction methods. As-polymerized films exist in the α crystalline form. The reflections from these films could be indexed with a monoclinic unit cell. The cell dimensions in the plane of these films do not change with the substituents: $a = 5.9$ Å, the chain axis $c = 6.55$ Å, and $\beta = 135°$. However, the cell dimension *b*, normal to the plane of the film, varies with the groups attached to the benzene ring: PPX, 10.64 Å; PPX–Cl, 12.8 Å; PPX–Et, 13.4 Å; and PPX–iP, 14.1 Å. The molecular packing in these polymers is discussed.

(Keywords: alkylated and chlorinated poly-*para*-xylylenes; X-ray diffraction; unit cell changes; molecular packing)

INTRODUCTION

Poly-*para*-xylylene (PPX) is a unique polymer which can be polymerized by vacuum deposition of the monomeric material on a substrate kept at temperatures below 30°C[1]. The resulting coating is pin-hole free and conformal to the substrate topography with thicknesses ranging from several hundred angstroms to several tens of microns. Because of these unique properties, PPX is extensively used in coating and encapsulating processes. One novel application of this process is the fabrication of inertial fusion targets[2]. An ablatively driven inertial fusion experiment requires a precise, layered target consisting of concentric spherical shells with the outermost layer called the ablation layer. The ablation layer consists of materials of low atomic number, most commonly polymeric hydrocarbons. Vapour phase pyrolysis of di-*para*-xylylene (DPX) is the method extensively employed for fabricating the ablation layer of the inertial fusion targets.

The PPX film produced by vacuum deposition is highly crystalline and this crystalline texture introduces small-scale density fluctuations in the coating and introduces a coarse surface finish. To achieve uniform implosion of the inertial fusion target, it is essential that the density fluctuation be less than 5% and the surface roughness be less than 1 μm[3]. It has been shown that modification of the symmetrical molecular structure of PPX with the addition of alkyl pendant groups onto the phenylene ring decreases the crystallinity and improves the surface finish[2]. Alkylation of the starting PPX also introduces significant changes in the properties and the structure, such as in crystallinity, glass transition, and melting temperatures, and the rate of deposition[4]. In order to elucidate these changes, we have embarked on the study of modified PPX by X-ray diffraction, and i.r. and n.m.r. spectroscopies. This report describes the results of the X-ray diffraction measurements, and those of spectroscopic studies will be published elsewhere[5].

In the present study, PPX was alkylated with ethyl and isopropyl groups, chlorinated PPX was obtained from Union Carbide, and their crystal structures are compared with that of unsubstituted PPX. The structure of PPX has been refined through several stages by Niegesh[6-8] and Wunderlich and co-workers[9-13]. It has been known that PPX exists in two crystalline forms α and β. As-polymerized PPX usually exists in the α form, and the β form can be obtained either by heating[14] or by stretching[3]. In this paper we compare the α polymorphs of the unsubstituted and modified PPX's.

EXPERIMENTAL PROCEDURE

Di-*para*-xylylene (DPX) was alkyl substituted via a Friedel–Crafts electrophilic substitution using aluminium trichloride as the Lewis acid[15]. DPX was reacted with alkyl halide in the presence of aluminium chloride and the catalyst decomposed by hydrolysis. The resulting alkylated DPX was purified by recrystallization. The molecular structure of the resulting ethyl and isopropyl DPX was extensively studied by ^{1}H n.m.r. and i.r. spectroscopies. The results[5] indicate that the ethyl DPX is 96% monosubstituted at phenylene and isopropyl DPX is 100% monosubstituted.

From these alkylated DPX's, semicrystalline films of ethyl and isopropyl poly-*para*-xylenes (PPX–Et and PPX–iP, respectively) were prepared by vacuum deposition according to the method of Gorham[16]. I.r. spectra of PPX–Et are consistent with the structure:

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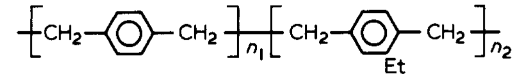

but the exact sequential distribution and the grouping of the blocks are not known. Although when averaged over large chain segments, the values of n_1 and n_2 are equal, it is probable that n_1 varies over a wide range; therefore, as our X-ray diffraction results suggest, unsubstituted PPX may not crystallize into a separate phase but might remain amorphous. Chlorinated PPX (PPX–Cl), which is commercially available, has a molecular structure similar to PPX–Et and PPX–iP, except that PPX–Cl has every phenylene mono-chlorinated.

Small pieces (2 mm × 10 mm) were cut from these transparent films of 20 to 50 μm thickness. X-ray diffraction (XRD) patterns of these specimens showed that they were disordered and had very low crystallinity. Well defined XRD patterns were obtained by annealing the films in a vacuum oven for ~8 h at elevated temperatures (PPX ~200°C; PPX–Cl ~150°C; PPX–Et ~120°C; PPX–iP ~70°C). This heat treatment did not induce any β form except in PPX, in which some β form was produced.

X-ray diffraction (XRD) photographs were obtained on a flat-plate camera with CuKα radiation and a sample to film distance of 4 cm. Precession photographs were also obtained, especially from stretched films, with a sample to film distance of 6 cm. As-polymerized specimens were randomly oriented in the plane of the film and hence most of the photographs were taken with the beam parallel to the surface.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) phorographs of representative samples of PPX and the modified PPX's are shown in *Figure 1.* Although the resolution of our photographs is not adequate to lend themselves to a detailed analysis, as has been done for PPX by Wunderlich and co-workers[13], it is sufficient to see how the substituent molecules affect the lattice parameters. The data can also offer insight into the packing of the substituent groups among the benzene rings.

Figures 1a, b, c and *d* are the XRD patterns of the annealed samples of as-polymerized films. The pattern of PPX (*Figure 1a*) is similar to that published elsewhere[10]. This is usually identified as the α crystalline form. The pattern from PPX–Cl, PPX–Et and PPX–iP (*Figure 1 b, c* and *d*) closely resemble that of PPX and hence can be regarded as being due to the α forms of these substituted

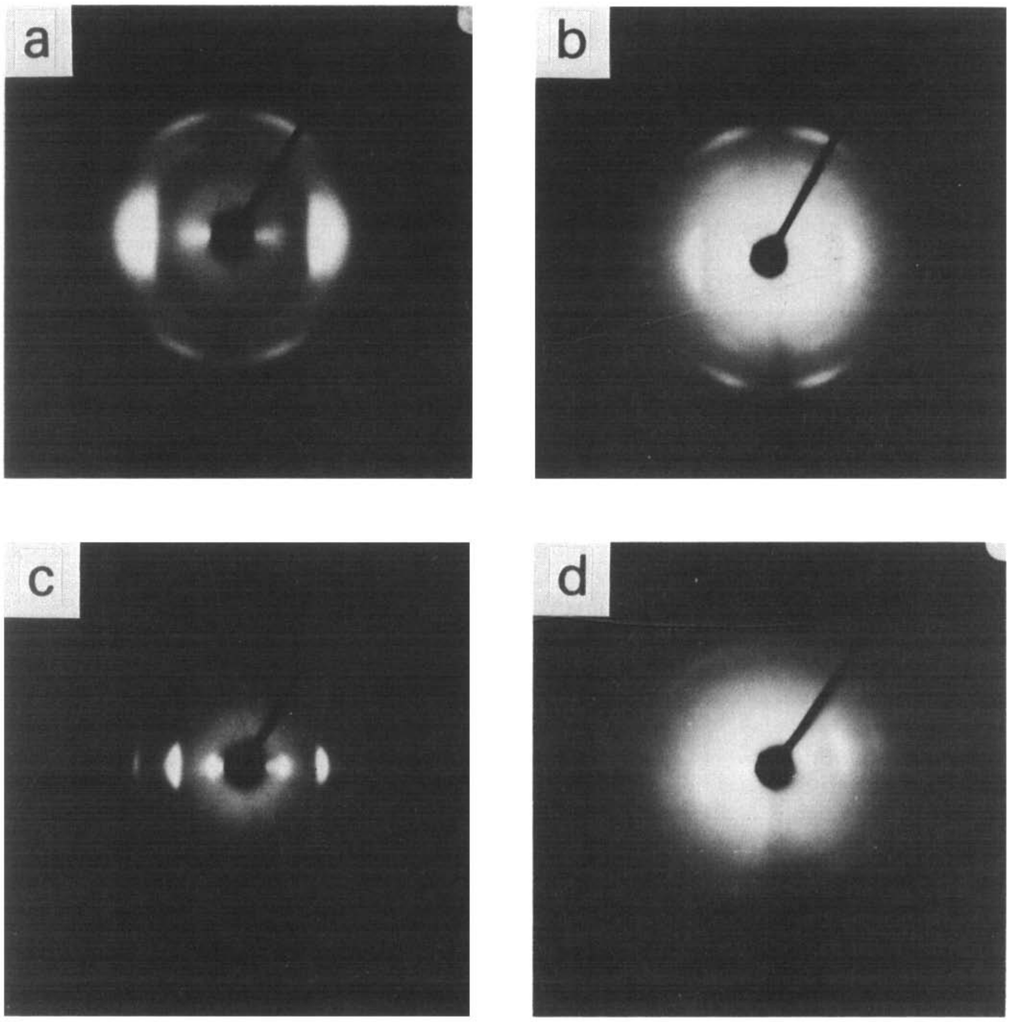

Figure 1 X-ray diffraction photographs of the α forms of substituted and unsubstituted poly-*p*-xylylene obtained on a flat-plate camera with the X-ray beam parallel to the plane of the film. (a) PPX; (b) PPX–Cl; (c) PPX–Et; and (d) PPX–iP

polymers. The patterns of these polymers, *viz.*, PPX–Cl, PPX–Et and PPX–iP were indexed using a monoclinic unit cell following the scheme of Iwamato and Wunderlich[13]. *Table 1* gives the lattice parameters for the α forms of PPX and the modified PPX's based on a monoclinic lattice. The cell is chosen so that the c axis coincides with the chain axis. In as-polymerized specimens the a–c plane, which is parallel to the substrate, is randomly oriented in the plane of the film. The b axis, which is the unique two-fold axis, is normal to the substrate as well as to the plane of the film. All the specimens, PPX, PPX–Cl, PPX–Et and PPX–iP show this planar orientation. As can be seen from the data in *Table 1*, the cell dimensions in the plane of the film does not change with the substituents: a, c and β remain the same in PPX and the modified PPX's. The cell dimension along the unique b axis normal to the substrate, however, increases from 10.64 Å for PPX to 12.8 Å in PPX–Cl, 13.4 Å in PPX–Et and 14.1 Å in PPX–iP. This suggests that adding the side groups to the benzene ring does not change the packing of the molecules in the plane of the substrate but they extend the unit cell dimensions normal to the substrate. This is schematically shown in *Figure 2* which is based on the crystal structure derived for PPX by Iwamoto and Wunderlich[13]. The benzene rings are parallel in different levels and are preferentially oriented perpendicular to the substrate. The side groups in the modified PPX's possibly lie along the normal to the a–c plane. Such an arrangement will clearly increase the b axis dimension without changing the a–c plane dimension.

Since very few reflections were observed for the substituted forms of PPX, it is not possible to discuss in detail the packing of the modified PPX's in the lattice. However, based on symmetry requirements, we can suggest possible arrangement of the molecules. The space group of PPX has been reported as $C2/m$ and the packing shown in *Figure 3a* has been derived[13]. Just as in PPX, $(0k0)$ reflections only with k even were observed for PPX–Cl. However, PPX–Cl lacks the inherent symmetry of the PPX molecule and hence cannot be located on special positions at $x=0, y=0$ and $x=1/2, y=1/2$ as proposed by Iwamoto and Wunderlich for PPX[13]. However, if a $P2_1$ space group is chosen and the molecule located as shown in *Figure 3b*, one can account for the systematic absences as well as the increase in the lattice dimension only along b. Since Cl lies in the plane of the benzene ring, it is not surprising that addition of Cl results only in an increase in the b axis dimension. Since no systematic absences could be observed for PPX–Et and PPX–iP in their $(0k0)$ reflections, it is difficult to deduce the space group of PPX–Et and PPX–iP. Because the cell dimension along a and c remain unchanged from PPX, the arrangement shown in *Figure 3b* for PPX–Cl is probably valid for PPX–Et and PPX–iP as well. Since all $0k0$ reflections

Table 1 Unit cell parameters of substituted and unsubstituted poly-*para*-xylylenes) (PPX)

	a (Å)	b (Å)	c (Å)	β
PPX	5.9	10.6	6.55	135°
PPX–C1	5.9	12.8	6.55	135°
PPX–Et	5.9	13.4	6.55	135°
PPX–iP	5.9	14.1	6.55	135°

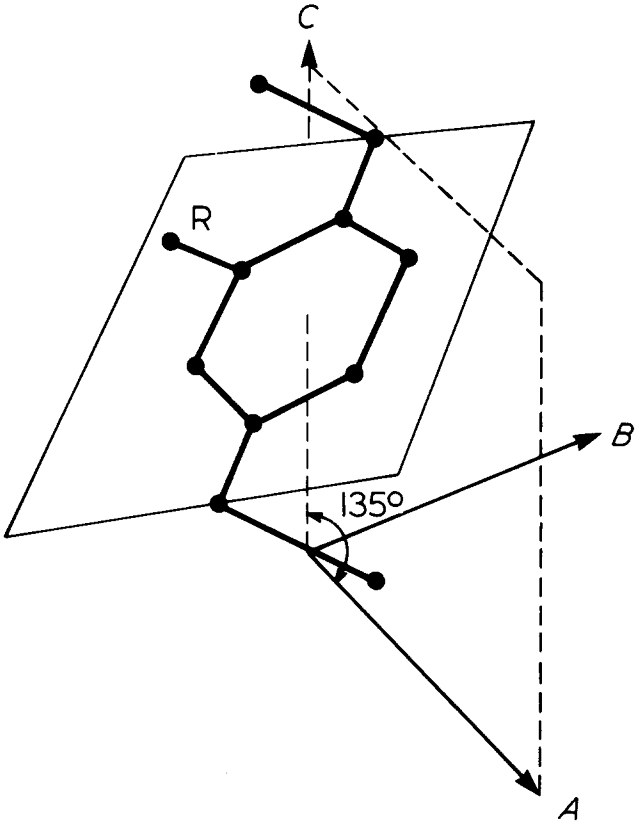

Figure 2 Molecular arrangement in PPX and the possible disposition of the side groups in substituted PPX

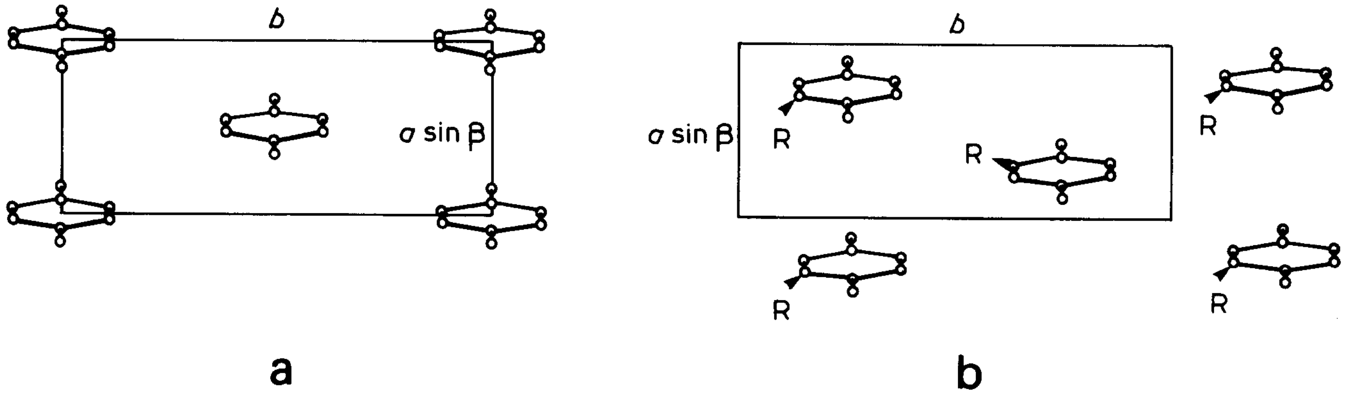

Figure 3 (a) PPX molecules in the unit cell (Ref. 13). (b) Possible molecular packing of the modified PPX's molecules in the unit cell. These are projections along the c-axis

were observed for PPX–Et and PPX–iP, it is possible that these two unit cells possess a lower symmetry, probably *P*2, with two molecules in the asymmetric unit. Space-filling models of PPX, PPX–Cl, PPX–Et and PPX–iP show that the molecular packing suggested here is not unreasonable, and that the addition of Cl, Et and iP can indeed increase the separation of the benzene rings along the *b*-axis.

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