

Polymerization of Aromatic Nuclei. XIII. X-Ray Analysis and Properties of Poly(*p*-phenylene) Pellets

PETER KOVACIC,* MICHAEL B. FELDMAN, *Department of Chemistry*, and JAN P. KOVACIC, and JEROME B. LANDO, *Division of Polymer Science, Case Western Reserve University, Cleveland, Ohio 44106*

Synopsis

X-ray diffraction experiments with poly(*p*-phenylene) pellets demonstrated an increase in crystallinity with increase in molding temperature or annealing temperature. The increase in crystallinity may be attributed to annealing effects and loss of chlorine under severe conditions. Lattice constants for the crystalline polymer are presented, and the crystallographic data are compared with those of the lower oligomers. Poly(*p*-phenylene) was investigated also in relation to oxidative thermal stability, chemical and solvent resistance, and the effect of temperature and variation in molding conditions on fracture strength. The decrease in strength at elevated temperatures appears to be related to the increase in crystallinity.

INTRODUCTION

The interesting properties and easy preparation^{1,2} of poly(*p*-phenylene) have led to its commercial availability.³ Although the material has the practical disadvantages of infusibility and extreme insolubility, it can be molded⁴⁻⁶ under pressure and subsequently machined.³ Prior investigations have dealt with thermal and oxidative stability,⁷⁻¹⁰ electrical properties,⁴ solvent, chemical, and radiation resistance,^{3,4,8,10} and conversion to various derivatives.⁹⁻¹¹ This report provides the results of an x-ray diffraction study of the polymer. In addition, the pellet form was investigated in relation to oxidative thermal stability, chemical and solvent resistance, and the effect of temperature and variation in molding conditions on fracture strength.

X-RAY DIFFRACTION

Figure 1 presents x-ray flat-plate photographs of poly(*p*-phenylene) samples pressed at room temperature and at 200°C. with subsequent annealing at 400°C. for 24 hr. Table I contains x-ray diffractometer data on the strongest crystalline reflection of the polymer as a function of sample treatment, together with the results from elemental analysis. The x-ray

* Present address: Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201.

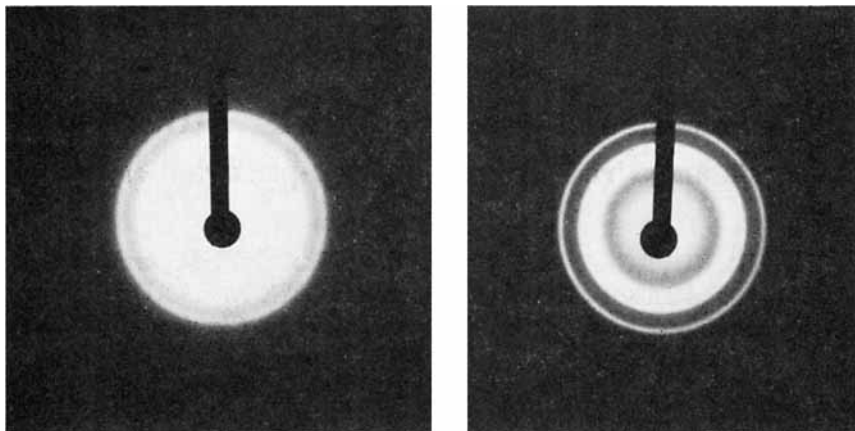


Fig. 1. X-ray flat-plate photographs of poly(*p*-phenylene): (a) sample pressed at room temperature; (b) sample pressed at 200°C. and then annealed at 400°C. for 24 hr. under vacuum.

findings indicate a marked increase in crystallinity as a result of pressing the powder, increasing the molding temperature, and subsequent annealing at 400 and 500°C. It should be noted that the major change in the elemental analysis during exposure to high temperatures was the loss of chlorine. Along with the increase in crystallinity the half-width of the strongest crystalline reflection decreased, indicating an increase in crystallite size. Furthermore, the d spacing of this reflection decreased systematically as the crystallinity increased. Annealing at 600°C., which resulted in an appreciable decrease in hydrogen content, produced a complete loss of crystallinity.

The observed increase in crystallinity and crystallite size and the decrease in the d spacing of the most intense reflection may be attributed to both annealing effects and loss of chlorine at 400–500°C. Thermal treatment, by enhancing the mobility of chains in the amorphous portion of the sample, would be expected to induce additional crystallization. The relatively large chlorine atom present in the ratio of 1 per 20–25 phenylene groups would act to decrease crystallinity and crystallite size to some extent. The loss of chlorine should lead, therefore, to an increase in crystallinity and crystallite size as well as to more efficient lateral packing of the chains, as was observed. The lesser decrease in oxygen content should not have much effect on crystallinity, especially since oxygen is smaller than chlorine.

We wish to emphasize that the most intense reflection cannot be related to the repeat distance along the chain, as previously reported.⁷ The repeat of one *p*-phenylene unit should be 4.20–4.30 Å., not 4.53 Å. In addition, any reasonable chain conformation would be expected to result in a very weak 001 reflection (chain repeat distance), since the carbon atoms should scatter almost completely out of phase for this reflection.

TABLE I
X-Ray Analysis of Poly(*p*-phenylene) Pellets

Sample treatment	Wt. loss, %	Data on strongest crystalline reflection			Elemental analysis, wt.-%			
		<i>d</i> Spacing, A.	Uncorr. intensity (relative)	Half- width, °2θ	C	H	Cl	O
1. None, powder form	—	4.638	130	2.9	—	—	—	—
2. Pressed, 10,000 psi at room temp., 5 min.	—	4.537	185	2.8	91.10	5.17	1.85	1.20
3. Pressed, 10,000 psi at 200°C., 5 min.	—	4.530	255	2.2	93.57	5.04	0.48	1.06
4. As in 3, then an- nealed under vac- uum, 24 hr., at 400°C.	4.0	4.525	400	1.3	93.88	5.06	0.04	1.04
5. As in 3, then an- nealed under vac- uum, 24 hr., at 500°C.	7.7	4.525	400	1.3	93.96	5.02	none	0.89
6. As in 3, then an- nealed under vac- uum, 24 hr., at 600°C.	13.1	—	no crystall.	—	95.58	3.10	none	0.88

The reflection at 4.53 Å. is most probably related to the lateral packing of the poly(*p*-phenylene) chains. Furthermore, the reflection at 2.10 Å. can be indexed as 002.

Given the number of observed x-ray reflections, it is not feasible to determine unequivocally the unit cell constants. However, it is possible to index the observed reflections in an orthorhombic unit cell with $a = 7.81$ Å., $b = 5.53$ Å., and c (chain axis) = 4.20 Å., which would contain one phenylene unit from each of two chains passing through the unit cell, with a resulting x-ray density of 1.39 g./cm.³. A comparison of the calculated and observed values of $(1/d)^2$, together with the appropriate Miller indices based on this assumed unit cell is given in Table II. The broad, amorphous band observed with all samples at approximately 12 Å. may be caused by the presence of low molecular weight oligomers.

A comparison of the proposed unit cell constants of poly(*p*-phenylene) with those of the lower oligomers (Table III) reveals the similarity in

TABLE II
X-Ray Diffractometry Data for Poly(*p*-phenylene)^a

2θ	d , Å.	$(1/d)^2$ (obsd.)	$(1/d)^2$ (calcd.)	Miller indices
7.5 ^b	12			
19.60	4.525	0.04883	0.04909	110
22.75	3.910	0.06543	0.06557	200
27.95	3.190	0.09766	0.09827	210
34.4°	2.60	0.1474	0.1472	120
38.20	2.354	0.1795	0.1802	310
43.12	2.096	0.2278	0.2268	002
48.0°	1.89	0.2800	0.2783	320
49.9°	1.83	0.2985	0.2950	410
58.0°	1.59	0.3922	0.3931	420

^a Samples 4 and 5, Table I.

^b Broad, amorphous peak.

^c Very weak, position difficult to measure.

TABLE III
Unit Cell Constants^a for $p\text{-C}_6\text{H}_5\text{-(C}_6\text{H}_4\text{)}_n\text{C}_6\text{H}_5$

n	a , Å.	b , Å.	c , Å.	Mono- clinic angle β	No. of molecules in unit cell	Space group	$c_n - c_{n-1}$, Å.
0	8.04	5.51	9.39	94.5	2	P_{21}/a	
1	8.08	5.60	13.59	91.9	2	P_{21}/a	4.20
2	8.05	5.55	17.81	95.8	2	P_{21}/a	4.22
3	8.04	5.485	21.99	92.0	2	P_{21}/a	4.18
4	8.09	5.60	26.23	91.8	2	P_{21}/a	4.24
(poly- mer)	7.81	5.53	4.20	90?	2	?	

^a See Toussaint.¹²

lattice constants. With the data available for the polymer it is not possible to distinguish between an orthorhombic and a monoclinic unit cell.

The proposed polymer chain repeat of 4.20 Å. is in reasonable agreement with the difference between the magnitudes of the c axis of the oligomers. However, one should bear in mind that the value of 4.20 Å. for the length of a p -phenylene unit is close to the lowest possible value. If the unit cell of the polymer is monoclinic with a β angle of 100° , then the length of the phenylene unit (c axis) would be 4.26 Å., and the length of the a axis would be 7.93 Å. Since the space group of the oligomers is P_{21}/a , it is likely that the polymer would also be in the same space group, provided that the unit cell is monoclinic.

We should point out that this represents a more restricted x-ray investigation than is normally carried out with polymers. If oriented samples could be obtained, then a more detailed study would be possible. However, limitations are imposed by the infusibility and insolubility of poly(p -phenylene).

POLYMER PROPERTIES

Results

In an investigation of molding variables temperature was altered over a 275° range (Table IV). Resistance to disk fracture was greatest at 0 – 100°C . Decreased chain mobility may be an important factor at very low temperatures. At the lowest temperatures an increase in time proved beneficial, whereas the reverse situation prevailed at high temperatures.

Using the same amount of polymer, we noted that more drastic conditions for pellet formation resulted in somewhat thinner specimens, e.g., for a time of 60 min., 0.154 in. at 200°C . versus 0.168 in. at 28°C . Therefore this variable should be taken into consideration in an interpretation of results.

TABLE IV
Effect of Molding Conditions on Pellet Strength*

Temp., $^\circ\text{C}$.	Time, min.	Thickness, in.	Pellet fracture load, lb.
-75	60	0.179	23
0	60	0.173	35
28	3	0.174	34
28	60	0.168	39
100	3	0.159	32
100	60	0.159	35
150	3	0.156	30
150	60	0.155	31
200	3	0.157	16
200	60	0.154	12

* See under "Experimental."

No appreciable change in fracture strength was noted when pellets were allowed to stand at room temperature for 1 wk. The pressed polymer was reduced to 50-mesh material only with some difficulty. This powder, when remolded, possessed a strength one-tenth that of the original pellet and was easily pulverized.

In keeping with earlier observations of the powder form the pellets exhibited good stability toward oxidative thermal degradation in air (Table V). For example, only a 2% loss in weight and a relatively small

TABLE V
Oxidative Thermal Stability^a

Temp., °C.	Wt. loss, %		Pellet fracture load, lb.	
	I	II	I	II
28			31	28
400	2.1	3.3	24	16
450	19.6		16	
500	^b		^b	

^a Time, 16 hr.; see under "Experimental."

^b Disintegrated.

decline in pellet strength were observed at 400°C. for 16 hr. Even at 450°C., the poly(*p*-phenylene) maintained its integrity reasonably well during this period of time. However, at 500°C. gross deterioration occurred.

A study of the effect of temperature on pellet strength was carried out (Table VI). The greatest resistance to fracture was observed at room

TABLE VI
Effect of Temperature on Pellet Strength^a

Pellet temp., °C.	Pellet fracture load, lb.
-195	7
-78	11
28	31
150	16 ^b
225	15

^a See under "Experimental."

^b A similar result in comparison with the control was obtained when the pellets were allowed to cool to room temperature before testing.

temperature with weakening at higher and lower temperatures over a 420° range.

In general the material possessed outstanding resistance to solvent and chemical attack on prolonged exposure at elevated temperatures (Table VII). Only a 10% increase in weight resulted in chloronaphthalene, with little or no change in concentrated caustic and nitric acid. Concentrated

TABLE VII
 Chemical and Solvent Resistance^a

Reagent or solvent	Pellet wt., g. (av.)		Pellet fracture load, lb.
	Before	After	
^b	2.5070	—	41
1-C ₁₀ H ₇ Cl	2.4871	2.7550	12
NaOH (50%)	2.5100	2.5103	15
H ₂ SO ₄ (96%)	2.5030	2.4928 ^c	11
HNO ₃ (70%)	2.4740	2.5735	20

^a See under "Experimental."

^b No heat treatment.

^c Approximate.

sulfuric acid produced the greatest effect, in the form of surface erosion. Although a decline in pellet fracture load was observed in all cases, in no instance was it catastrophic.

Discussion

A decrease in pellet strength occurred at elevated temperatures, as evidenced by the data in Tables IV and VI. Although the wafers fractured more readily after contact with solvents and chemical reagents, analysis of the data suggests that a temperature effect is contributing in an adverse manner (Table VII, entry 3). We surmise that the decrease in disc strength with increase in temperature is related to the increase in crystallinity observed in the x-ray studies. An increase in crystallinity would be expected to increase the brittleness, since the amorphous polymer, although glassy, can respond to stress more readily than the crystalline material. It is unlikely that oxidative thermal degradation is involved to any significant extent except at temperatures above 400°C.

EXPERIMENTAL

Polymer Source

Poly(*p*-phenylene) was obtained either from a commercial source³ (Eimac 221) or by the reported method^{1,2} (a small part was obtained from an 8:1:1 ratio of benzene to aluminum chloride to cupric chloride).

With 1 in. Mold. An adaptation of a published procedure⁴ was followed with 2.5 g. of polymer. Standard conditions comprised a molding time of 3 min. at 150°C. Sometimes two pellets were formed during the same operation. Polishing the surfaces of the metal inserts facilitated removal of the samples.

For pressing at 0°C. the mold was cooled in an ice bath, charged with the powder, and then placed in a container filled with ice for the pelletizing operation. A similar technique was used in the -75°C. (Dry Ice-acetone) experiment.

With 2.25 in. Mold. This technique was used to prepare specimens for x-ray diffraction studies. The molding apparatus, surrounded by an asbestos jacket, was placed between the heated platens of a Pasadena hydraulic press and taken to the desired temperature during about 1 hr. The poly(*p*-phenylene) powder, 2 g., 50 mesh, was then spread between Teflon discs, the apparatus was heated to temperature during 5 min., and then 10,000 psi of pressure was applied (usually for 5 min.). For the x-ray exposure 1 × 2 in. samples were cut out with scissors.

Pellet Testing

The test rig and method were described previously.⁴ Part of the way through our work the wooden bars of the rig were replaced with metal ones. In the temperature studies with preformed pellets the apparatus was placed in an oven, in Dry Ice-acetone ($-80^{\circ}\text{C}.$), or liquid nitrogen ($-195^{\circ}\text{C}.$) for 0.5–1 hr. After the pellet was kept at the desired temperature for 5–10 min., testing was immediately carried out. In the experiments on oxidative thermal stability the pellets were heated in a muffle furnace and then allowed to cool before being tested.

In the various experiments two or three samples in each category were tested, yielding results that were in satisfactory agreement. Average values are reported in the tables.

X-Ray Diffraction Studies

A General Electric XR66 diffractometer was used for scanning the polymer pellets with CuK_{α} radiation at a rate of $0.4^{\circ} 2\theta$ per minute. Uncorrected relative intensities of the observed reflections were obtained by measuring peak heights; the half-widths of the reflections, by determining the width at half the peak height. Flat-plate photographs were taken at a film to sample distance of 3 cm.

Pellet annealing was performed under vacuum in a quartz furnace. The elemental analyses were done by Galbraith Laboratories, Knoxville, Tenn.

Chemical and Solvent Treatment

The pellets were placed in a large excess of the reagent or solvent, which was then heated at reflux for 8 hr. At the end the appearance of the pellets was noted: (a) 1-chloronaphthalene, surface slightly cracked and pitted; (b) NaOH (50%), no change; (c) H_2SO_4 (96%), surface deterioration but firm beneath (acid became highly colored); (d) HNO_3 (70%), darkened, rough surface. After treatment the pellets exposed to the inorganic reagents were washed with water, blotted, and weighed immediately. In the case of the organic solvent the samples were simply blotted.

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under contract NAS7-100. We wish to thank David D. Lawson, Jet Propulsion Laboratory, for helpful discussions and generous quantities of Eimac 221, and Vincent M. Miskowski for assistance with the experimental work.

References

1. P. Kovacic and J. Oziomek, *J. Org. Chem.*, **29**, 100 (1964).
2. P. Kovacic and J. Oziomek, *Macromol. Syntheses*, **2**, 23 (1966).
3. Eimac 221 Bulletin, Eimac, 301 Industrial Way, San Carlos, Calif. 94070.
4. P. Kovacic, V. J. Marchionna, and J. P. Kovacic, *J. Polymer Sci. A*, **3**, 4297 (1965).
5. G. K. Ostrum, D. D. Lawson, and J. D. Ingham, *Abstr. Papers*, Am. Chem. Soc., 152nd Meeting, Sept. 1966, New York, p. W74.
6. H. Naarmann, F. Beck, and E. G. Kastning, Ger. Pat. 1,178,529 (1964); *Chem. Abstr.*, **62**, 3522 (1965).
7. C. S. Marvel and G. E. Hartzell, *J. Am. Chem. Soc.*, **81**, 448 (1959).
8. P. Kovacic and A. Kyriakis, *J. Am. Chem. Soc.*, **85**, 454 (1963).
9. P. Kovacic, V. J. Marchionna, F. W. Koch, and J. Oziomek, *J. Org. Chem.*, **31**, 2467 (1966).
10. D. A. Frey, M. Hasegawa, and C. S. Marvel, *J. Polymer Sci. A*, **1**, 2057 (1963).
11. P. E. Cassidy, C. S. Marvel, and S. Ray, *J. Polymer Sci. A*, **3**, 1553 (1965).
12. C. Toussaint, *Acta Cryst.*, **21**, 1002 (1966).

Received December 22, 1967

Revised December 30, 1967