The effect of compaction pressure on the conductivity and structure in undoped poly(1,4-phenylene) (PPP)

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Poly(paraphenylene) has been prepared according to two different procedures. The d.c. conductivity measurements, obtained under compaction pressure, were correlated to the structural modifications undergone in the same pressure range. X-ray diffraction line profile analysis has been applied to determine the variations in the microstructural parameters.

INTRODUCTION

Conducting polymers have been the subject of much experimental and theoretical work since it was discovered that these materials dramatically increase their conductivity upon appropriate doping with both electron acceptors and donors. Much effort has been devoted to the clarification of the conductivity mechanism in such polymers.

Recently two different models of charge transport and doping[1] have been proposed and partly substantiated for interpreting several available experimental data.

The soliton theory of Su et al.[2] which was proposed specifically for polyenic systems such as *trans* polyacetylene (PA) cannot fully account for the conductivity of polyaromatic systems such as poly(1,4-phenylene) (PPP), which does not possess a degenerate electronic ground state. For the latter polymer a different model[1] has been put forward which implies the formation of charged paraquinoidic and localized structures (bipolarons) which prevent good charge transport along the chains. Hence the mechanism of conduction is mainly due to the interchain hopping.

On the basis of the conduction model proposed for PPP[1] and of the observation of the band gap reduction on increasing the pressure[3], we have undertaken a study of the influence of the compaction pressure on the conductivity in undoped PPP. This paper reports the results of such a study with particular reference to the structural modification undergone by PPP upon pressing.

EXPERIMENTAL

Poly(1,4-phenylene), (PPP) was prepared according to the methods developed by Yamamoto[4] and Kovacic[5] (hereafter indicated Y and K respectively).

Both the polymers were submitted to repeated purifications and annealing at 400°C under an inert atmosphere to eliminate both oligomers and impurities. The polymer was reduced into pellets by pressing the powder in a hydraulic press. The average degree of polymerization was determined using the infra-red spectroscopy method suggested by Kovacic[5].

The X-ray diffraction spectra and data were collected on a computer controlled diffractometer Siemens D-500 for unoriented specimens, using both continuum and step scan techniques in the reflection and transmission modes. The steps and time of scans were of $0.05°$ (2θ) and 100 s, respectively. Narrow slits ($1°$ for divergence and $0.05°$ for receiving, respectively), and CuKα (Ni filtered) radiation were used. The instrumental broadening was not taken into account, as it was found to be less than $0.08°$ (2θ) when measured.

Line profile analysis was performed on a Univac 1100/80 computer using a series of programs written by these authors.

D.c. resistivity measurements were carried out by the two electrode method at room temperature under nitrogen using a Keithley 602 electrometer.

RESULTS AND DISCUSSION

In *Table 1* the values of conductivity at increasing compaction pressure are given for two differently prepared PPP samples, K and Y (see Experimental section). These values reveal that both K and Y samples are slightly doped by catalytic residuals[6]. No detectable variation in conductivity values was found for samples examined under pressure and after releasing pressure. Moreover, somewhat differently to that observed by Moses et al.[3] in polyacetylene and by Pohl et al.[7] in a series of semiconducting organic polymers, no appreciable variation of d.c. conductivity could be detected for both K and Y samples in the pressure range considered. In order to account for the conductivity invariance on varying the compaction pressure we have carried out a structural study on the influence of this parameter by means of X-ray diffraction line profile analysis of PPP according to the single line method proposed by Zocchi[8]. In *Figure 1* the X-ray diffraction spectra of unpressed PPP are shown with K and Y

Table 1 D.c. conductivity values of PPP samples at different pressures

	K		Y	
P (bar)	5	12000	5	12000
σ (Ω^{-1} cm^{-1})	2.2×10^{-11}	2.0×10^{-11}	2.7×10^{-10}	2.5×10^{-10}
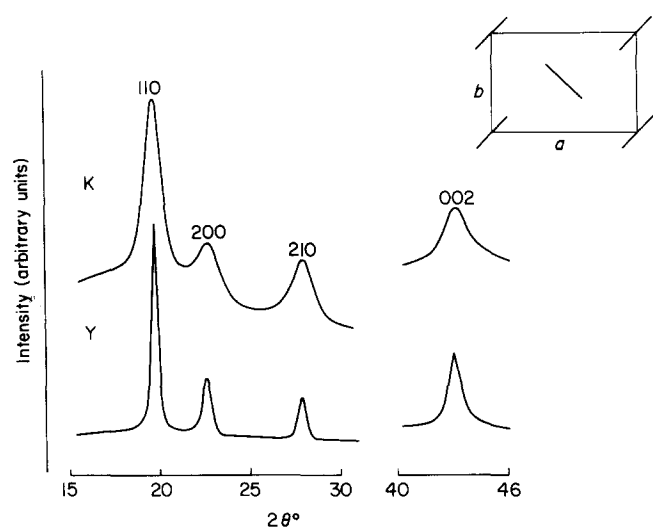
Figure 1 X-ray diffraction spectra of PPP (K and Y) indexed according to the cell parameters derived in ref. 9. In the inset is represented the projection along chain axes of the same cell

.respectively indexed on the basis of the monoclinic unit cell proposed by Stamm[9]. In the inset the unit cell projection is drawn along the chain axes. In *Table 2* we report the results of the profile analysis of the K and Y samples for five increasing pressure values in terms of the interplanar spacing (d), paracrystalline distortion parameter (g), paracrystal dimension (T), referring to the different detectable crystallographic directions[8], that is along the chain axes (001 reflections) and along interchain directions ($hk0$ reflections).

The unit cell average number (M) derived from this study, along the chain direction, indicates the average degree of polymerization (X_N). This value for sample K, obtained by infra-red spectroscopy[5], is close to the corresponding M value (ca. 11). However, in the case of Y the i.r. X_N value is about one half of the corresponding M value.

In order to explain this apparent discrepancy we propose that the thermal treatment undertaken on samples Y makes an exact end chain match of adjacent chains possible, with such a head-to-tail facing simulating a paracrystal whose dimensions average out to a value of about 17.

Figure 2a shows the idealized Y paracrystal exhibiting the above suggested chain facing. Indeed even high molecular weight polymers (synthetic or natural) are known to exhibit crystalline regions, whose sizes exceed their molecular lengths[10].

Table 2 and *Figure 2b* show that for K and Y, on increasing the pressure, the d values decrease for the interchain directions, i.e. the PPP chains approach each other by progressive displacing of their centres of gravity in the ab plane. In addition the interchain diffraction
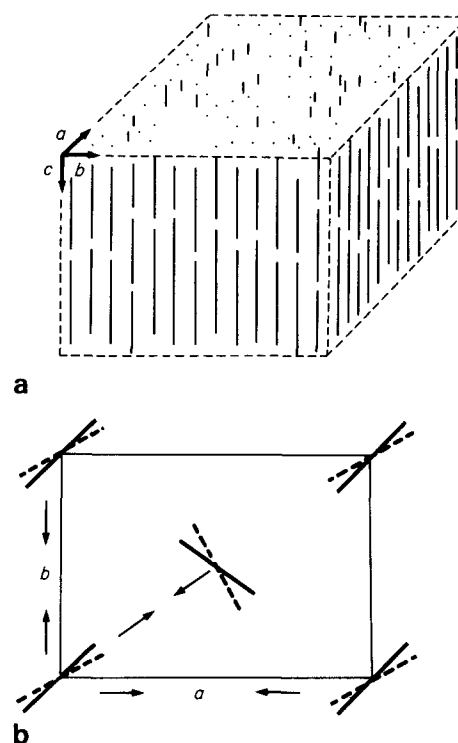

Figure 2 (a) Approximate sketch of idealized PPP paracrystal exhibiting the supposed facing of adjacent chains. (b) The pressure effect on the structure of PPP

Table 2 Microstructural parameters of PPP (K and Y samples) as a function of the pressure applied on pellets[a]

Crystallographic direction	P (bar)	K					Y				
		1	5	10	50	12000	1	5	10	50	12000
110	d (Å)	4.55	4.53	4.52	4.52	4.51	4.53	4.52	4.51	4.51	4.50
	g	0.039	0.040	0.040	0.041	0.041	0.024	0.029	0.030	0.032	0.033
	t (Å)	55	53	51	48	48	145	142	130	105	105
100	d (Å)	7.85	7.81	7.78	7.77	7.78	7.91	7.88	7.85	7.84	7.83
	g	0.026	0.026	0.027	0.028	0.028	0.019	0.020	0.021	0.021	0.022
	t (Å)	47	46	42	38.4	39	102	92	84	75	74
001	d (Å)	4.19	4.19	4.18	4.18	4.18	4.23	4.23	4.23	4.23	4.23
	g	0.021	0.021	0.020	0.021	0.020	0.017	0.017	0.017	0.017	0.017
	t (Å)	43	44	44	42	42	73	75	75	75	75

[a] d is the interplanar spacing obtained by Bragg law for the first order reflections
  g is the relative standard deviation within a family of netplanes defined according to Hosemann[14]
  t represents the paracrystal mean dimension along the crystallographic directions considered ($t = M \cdot d$ where M is the average number of cells)
  The average standard deviations are 0.02 Å, 0.002, 2 Å for d, g and t, respectively

peaks broaden, that is the g values increase and the T values decrease. Moreover, no appreciable effect on the microstructural parameters is observed along the chain direction in the pressure range studied. The non-zero g value may be related to a librational motion of the phenyl rings as already found, to a different extent, in the series of oligomers of PPP (biphenyl, terphenyl, quaterphenyl), and as already theoretically predicted[11,12].

As PPP is a low molecular weight, very crystalline rigid polymer, exhibiting no endothermal phenomenon attributable to a glass transition up to its partial decomposition (above 500°C), at room temperature only single chain motion through the paracrystal is allowed, without severe packing variation. Its behaviour closely resembles that expected for a glass. Therefore, on increasing the pressure the paracrystals progressively break along the interchain directions (ab plane), while along the chain axes no break can take place, requiring a single C–C bond rupture or severe packing rearrangement in the case of Y (*Figure 2a*).

As a result of the above considerations, the X-ray spectra of PPP pressed powder annealed above 350°C for a day are close to those of the unpressed material.

The observed microstructural variation undergone in PPP by compaction pressure shows no effect on the conductivity. Nevertheless Enkelmann et al.[13], studying the conducting phase of doped PPP using an oligomer model concluded that the lateral phenyl facing (see *Figure 1*) plays an important role in the chain hopping conductivity mechanism and they inferred a lateral anisotropy.

In conclusion we expect that for slightly doped PPP the chain hopping largely contributes to the conductivity. The pressure could have a double effect on the chain hopping: on the one hand it may favour the phenomenon by approaching the chains, or on the other hand it could oppose such hopping by increasing the interchain paracrystalline disorder. The balance of these two competing effects leads to a nearly equivalent situation, so that the conductivity does not appreciably change.

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