Effect of Differences in the Backbone Chemical Environment of Carbonyl and Ether Groups in Poly(aryl ether ketones) on Crystallographic Parameters

Xiang Ling Ji,*,†,§ Wan Jin Zhang,‡ Hui Na,‡ Xue Peng Qiu,† Jun Zuo Wang,‡ Zhong Wen Wu,‡ Zhi Shen Mo,† and Hong Fang Zhang†

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China, and Polymer Laboratory, Department of Chemistry, Jilin University, Changchun 130023, P. R. China

Received March 11, 1997
Revised Manuscript Received May 27, 1997

Poly(aryl ether ketone) high performance engineering plastics and matrix resins have attracted considerable interest in the recent decade because of their high yield stress, ductile behavior, other mechanical properties, and stability at high temperature.[1,2] Many authors have investigated their crystal structure and lattice parameters.[3−18] Dawson and Blundell[3] first reported X-ray data of PEK and PEEK, and found that PEK and PEEK have a unit cell and chain conformation similar to that of poly(phenylene oxide), which suggested that the crystal structure of poly(phenylene oxide) was also a good model for aryl ether ketone polymers. From then on, almost all researchers have accepted the conclusions that poly(aryl ether ketones) have an orthorhombic unit cell and ether and ketone linkages can be interchanged with only a minimum of distortion.

For para-substituted poly(aryl ether ketones), the para-linked phenyls are torsionally rotated out from the *bc* plane as in PEEK,[9] but the *m*-phenyl ring remains parallel to the *bc* plane. In this note, we only discuss the para-substituted ether ketone polymers whose unit cell parameters are influenced by the different chemical environment of carbonyl and ether groups. Rueda and co-workers studied the X-ray diffraction from oriented PEEK rods obtained by die drawing,[4] and they explained a slight increase in the c-axis length resulting from the difference between the length of 1.47 Å of the C−C bond in the phenyl ketone group and the length of 1.36 Å of the C−O bond in the phenyl ether group. For unoriented crystalline PEEK dimensions of the *a* and *b* axes agree well with those reported previously,[3,4] but the length of the *c*-axis was different from that reported previously.[5] Many researchers reported the c-axis dimension of PEEK to be 10 Å. Wakelyn calculated six aryl units as a *c*-axis length.[6] A schematic representation is shown in Figure 1. The average of the three parts (1, 2, and 3) is about 10 Å, while their sum is about 30 Å.

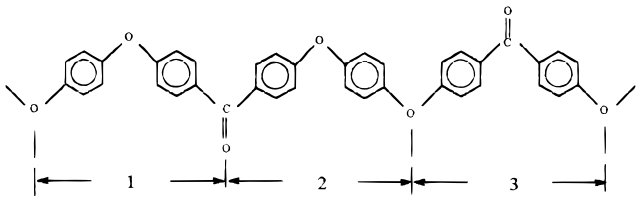


Figure 1. Two repeat units of PEEK.

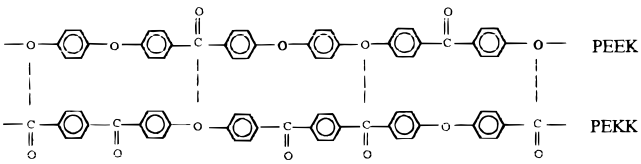


Figure 2. Two repeat units of PEEK and PEKK.

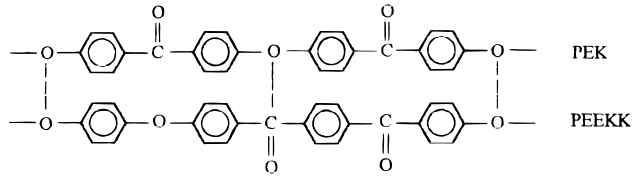


Figure 3. Chemical structures of PEK and PEEKK.

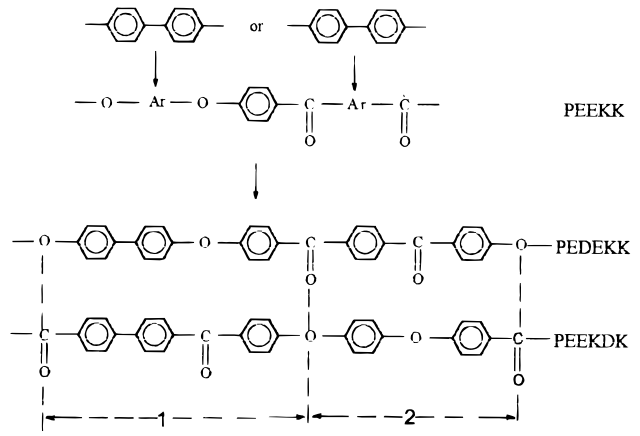


Figure 4. Chemical structures of PEDEKK and PEEKDK.

I. Phenyl Rings Linked by Both Ether (Ketones, Ether Ketone) Groups

Poly(aryl ether ketones) members, such as PEK, PEEK, PEEKK, PEKK, etc., vary in their proportion of ketone and ether linkages ([CO]/[O]) in a repeat unit from 0.5 to 2. Table 1 lists the crystallographic parameters for poly(aryl ether ketones). Considering the effect of difference in the backbone chemical environment of ether and ketone groups on cell parameters, we must distinguish between two cases, [CO]/[O] ≠ 1 and [CO]/[O] = 1.

a. [CO]/[O] ≠ 1. An exchange between ether and ketone groups are means all the ketone groups substituted by the ether groups and all the ether linkages are substituted by the ketone linkages in a repeat unit. Many authors concluded that the ketone and ether linkages can be interchanged with only a minimum of distortion. But it must be noted that the interchange between ether and ketone groups may produce two different poly(aryl ether ketones) as in PEEK, which changes into PEKK (shown in Figure 2). Their cell parameters are very different, PEEK (a = 7.75 Å, b = 5.86 Å, c = 10.0 Å)[3] and PEKK (a = 4.17 Å, b = 11.34 Å, c = 10.08 Å).[17] The exchange between ether and ketone groups evidently influences the *a*- and *b*-axis dimensions, which implies that this exchange resulted in the changes in chain packing and arrangement of neighboring chains in a unit cell. Under the circumstances, equivalence between ether and ketone linkages is untenable.

b. [CO]/[O] = 1. As shown in Table 1, PEK and PEEKK have an equal number of ketone and ether linkages in a repeat unit. The exchange between CO

* To whom correspondence should be addressed.
† Chinese Academy of Sciences.
‡ Jilin University.
§ E-mail: jiangbz@ns.ciac.ac.cn.

S0024-9297(97)00340-9 CCC: $14.00

Table 1. Crystallographic Parameters for Poly(aryl ether ketones)

sample	[CO]/[O]	*a* (Å)	*b* (Å)	c (Å)	crystal density (g cm^{-3})	refs
PEEK	0.5	7.75	5.86	10.0	1.400	3
	0.5	7.75 ± 0.01	5.89 ± 0.01	9.883 ± 0.005	1.415	4
	0.5	7.781 ± 0.009	5.922 ± 0.010	10.056 ± 0.014	1.378 ± 0.005	5
	0.5	7.88	5.94	30.50	1.341	6
	0.5	7.83 ± 0.02	5.94 ± 0.01	9.86 ± 0.04	1.392	7
PEK	1	7.65 ± 0.01	5.97 ± 0.01	10.09 ± 0.02	1.412	1
	1	7.63	5.96	10.0	1.430	3
PEKEKK	1.5	7.71	6.07	10.27	1.384	8
PEEKK	1	7.747	6.003	10.100	1.385	8
PEKK	2	4.17 ± 0.02	11.34 ± 0.04	10.08 ± 0.01		17
PEEKmK	1	7.71	6.05	39.9		9
PEDEK	0.5	7.72	5.94	37.5		10

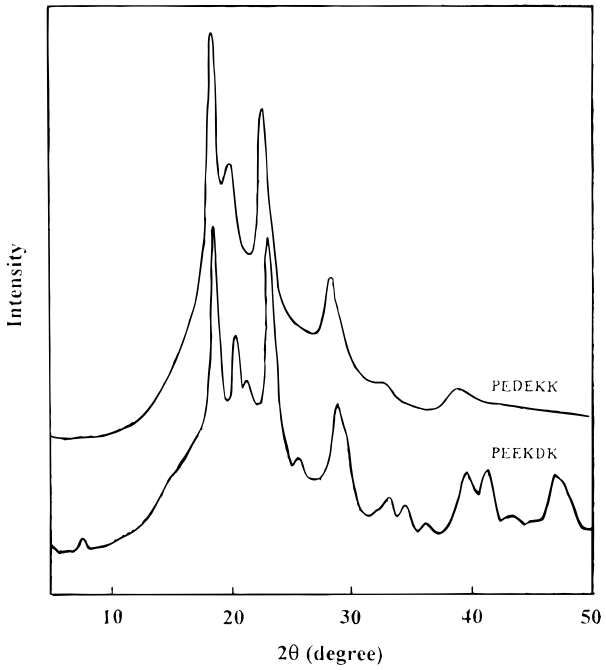
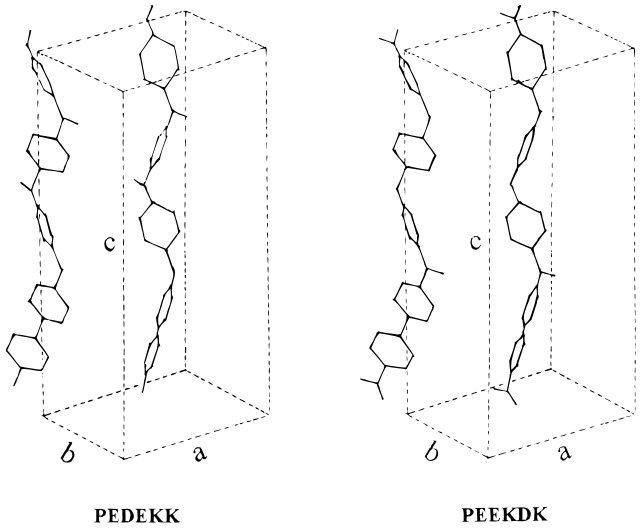


Figure 5. Wide-angle X-ray diffractograms of PEDEKK and PEEKDK.



PEDEKK **PEEKDK**

Figure 6. Crystal structures for PEDEKK and PEEKDK.

and O groups does not cause any change in the structure and does not affect cell dimensions.

PEK has unit cell dimensions similar to those of PEEKK. In Figure 3, the exchange of CO → O or O → CO has an equivalent frequency at least in two pseudo-repeat units, so that PEK and PEEKK have similar cell parameters. In addition, Table 1 shows an increasing trend in *c*-axis with an increasing ratio of ketone and ether groups in a repeat unit.

Table 2. Unit Cell Parameters of PEDEKK and PEEKDK

sample	*a* (Å)	*b* (Å)	*c* (Å)
PEDEKK	7.57	5.98	24.04
PEEKDK	7.60	5.98	22.88

Table 3. X-ray Data

a. PEEKDK

reflection					
h	*k*	*l*	*d*(calcd) (Å)	*d*(obsd) (Å)	I/I_{max} (%)
1	1	0	4.70	4.70	100
1	1	2	4.35	4.31	45
2	0	0	3.80	3.80	100
2	1	2	3.09	3.08	25
0	2	0	2.99	3.01	14
1	2	2	2.70	2.70	4
0	2	4	2.65	2.60	3
2	0	8	2.29	2.28	13
3	1	2	2.29	2.28	13
2	2	4	2.17	2.19	13
1	3	0	1.93	1.94	11

b. PEDEKK

reflection					
h	*k*	*l*	*d*(calcd) (Å)	*d*(obsd) (Å)	I/I_{max} (%)
1	1	0	4.69	4.68	100
1	1	2	4.37	4.32	67
2	0	0	3.79	3.80	81
2	1	2	3.09	3.08	38
1	2	2	2.71	2.70	13
2	2	2	2.30	2.29	12
3	1	2	2.28	2.29	12

II. Polymer Containing an Equal Number of Ketone and Ether Groups But with a Repeat Unit Including a Diphenyl Group Which Joins Two Ethers or Two Ketones

We want to know whether two such poly(aryl ether ketones) exhibit similar cell parameters. Figure 4 shows two poly(aryl ether ketones) synthesized through the nucleophilic substitution route.

If a phenyl between two ethers is substituted by a diphenyl, PEEKK becomes poly(ether diphenyl ether ketone ketone) (PEDEKK); if a phenyl between two ketones is substituted by a diphenyl, PEEKK becomes poly(ether ether ketone diphenyl ketone) (PEEKDK). Their wide-angle X-ray diffraction is shown in Figure 5. The unit cell parameters (listed in Table 2) are calculated by least-squares methods to fit the observed and calculated spacings (shown in Table 3). These two polymers have similar *a* and *b* dimensions but exhibit an obvious difference in the *c* dimension, 24.04 Å for PEDEKK and 22.88 Å for PEEKDK. *c*(PEEKDK) < *c*(PEDEKK), and their chain packing is shown in Figure

6. Here, *c*-axis length is equal to the chemical repeat unit. Researchers often use the *c*-axis length and standard bond length to calculate the bridge bond angle although the actual bond length is a little different from the standard bond length.[13] Evidently a diphenyl group inserted into two ketone linkages causes the bridge bond angle to be smaller than in a diphenyl inserted into two ether linkages. Colquhoun[13] studied two ether ketone oligomers, oligomer **2** with the chemical structure ArOArCOArArCOArOAr, similar to PEEKDK, and its bridge bond angles 121.7°(C−O−C) and 121.3°(C−CO−C) which were lower than the values calculated from the standard bond lengths. PEEKDK's bridge bond angle is about 118°.

Acknowledgment. We thank the Chinese "863" high technology funds for their financial support.

References and Notes

(1) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, A. I. M. *Polym. Commun.* **1985**, *26*, 283.
(2) Jones, D. P.; Leach, D. C.; Moore, D. R. *Polymer* **1985**, *26*, 1385.
(3) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.
(4) Rueda, D. R.; Ania, F.; Richardson, A.; Ward, I. M.; Balta Calleja, F. J. *Polym. Commun.* **1983**, *24*, 258.
(5) Hay, J. N.; Kemmish, D. J.; Langford, J. I.; Rae, I. M. *Polym. Commun.* **1984**, *25*, 175.
(6) Wakelyn, N. T. *Polym. Commun.* **1984**, *25*, 306.
(7) Fratini, A. V.; Cross, E. M.; Whitaker, R. B.; Adams, W. W. *Polymer* **1986**, *27*, 861.
(8) Zimmermann, H. J.; Könnecke, K. *Polymer* **1991**, *32*, 3162.
(9) Blundell, D. J. *Polymer* **1992**, *33*, 3773.
(10) Blundell, D. J.; Bayon, V. *Polymer* **1993**, *34*, 1354.
(11) Hay, J. N.; Langford, J. I.; Lloyd, S. R. *Polymer* **1989**, *30*, 489.
(12) Abraham, R. J.; Haworth, I. S. *Polymer* **1991**, *32*, 121.
(13) Colquhoun, H. M.; O'Mahoney, C. A.; Williams, D. J. *Polymer* **1993**, *34*, 218.
(14) Blundell, D. J.; Liggat, J. J.; Flory, A. *Polymer* **1992**, *33*, 2475.
(15) Wakelyn, N. T. *J. Polym. Sci., Part C: Polym. Lett.* **1987**, *25*, 25.
(16) Blundell, D. J.; D'Mello, J. *Polymer* **1991**, *32*, 304.
(17) Blundell, D. J.; Newton, A. B. *Polymer* **1991**, *32*, 308.
(18) Gardner, K. H.; Hsiao, B. S.; Matheson, R. R. Jr.; Wood, B. A. *Polymer* **1992**, *33*, 2483.
(19) Na, Hui Ph.D. dissertation, Department of Chemistry, Jilin University, 1994.

MA970340D