3706 *Macromolecules* **1991**, *24*, 3706-3708

Theoretical Young's Moduli of Poly(*p*-phenylenebenzobisthiazole) and Poly(*p*-phenylenebenzobisoxazole)

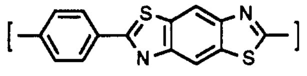
KOHJI TASHIRO* AND MASAMICHI KOBAYASHI

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

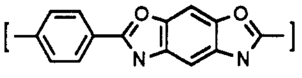
Received October 12, 1990;
Revised Manuscript Received January 24, 1991

Introduction

Among the many synthetic polymers reported so far, poly(*p*-phenylenebenzobisthiazole) (PBT) and poly(*p*-phenylenebenzobisoxazole) (PBO) show the highest bulk Young's moduli along the fiber axis.[1] What is the limiting moduli for these polymers? In order to solve this problem, the X-ray diffraction measurements were performed under tensile stress.[2] The crystallite moduli evaluated under the assumption of the homogeneous stress distribution within the sample were as follows:



PBT (trans form)



PBO (cis form)

PBT, 395 GPa; PBO, 477 GPa

The crystalline modulus of PBO is much higher than that of PBT. The reason must be clarified from the molecular level. Wierschke calculated the theoretical moduli of PBT and PBO on the basis of the molecular orbital method to give quite high values compared with the observed data.[3] His method seems reasonable, but the obtained values are, as a whole, too high even in the cases of the most simple polyethylene chain and graphite. In a series of papers we calculated the elastic constants of polymer crystals based on the lattice dynamical equations.[4,5] The obtained results are, as a whole, in good correspondence with the observed values. Then we will try to estimate the theoretical moduli of PBT and PBO chains on the basis of this lattice dynamical method, which has been proven to give relatively good results as stated above. In the previous paper[5] we have already reported the calculated result on the Young's modulus of PBT, the value of which will be modified only a little because of a slight improvement of the used force constants. In the present paper, we will compare the calculated results of the limiting Young's moduli between these two polymers and discuss the mechanical behaviors of them from the molecular theoretical point of view.

Calculation Procedures

The equations used in the calculation are the so-called lattice dynamical theory:[4] the Young's modulus of the single chain (or the three-dimensional crystal) is calculated by using the parameters of the Cartesian coordinates of the constituent atoms and the force constants representing the interactions acting between the atoms. The X-ray structure analyses were carried out for both the polymers,[6,7] the structural parameters of which will be utilized here. In Figure 1 are shown the molecular parameters actually used in the calculation. As illustrated, PBT takes the trans-type structure concerning the relative position of the N atoms of the benzobisthiazole ring, while for PBO the benzobisoxazole ring is of the cis type. In order to clarify the difference in the effect of the trans and cis structures on the Young's modulus, we calculated the modulus of PBO for both the trans and cis structures. (For the PBT only the trans structure was employed.) The actual PBT chain takes a twisted conformation with the internal rotation angle of 23° around the bond connecting the two rings. For PBO the torsional angle is about 13°. In order to clarify the effect of the internal torsion upon the modulus, a completely planar model was also employed in the calculation. As to the intramolecular interactions, the force constants of valence force field type were used, the numerical values of which were quoted with some modifications from those reported for the related low molecular weight model compounds.[3,8,9] Reasonableness of the force constants was checked by comparing the calculated vibrational frequencies with those actually observed for these two polymers. The detailed results will be described in a separate paper. The force constants are listed in Table I.

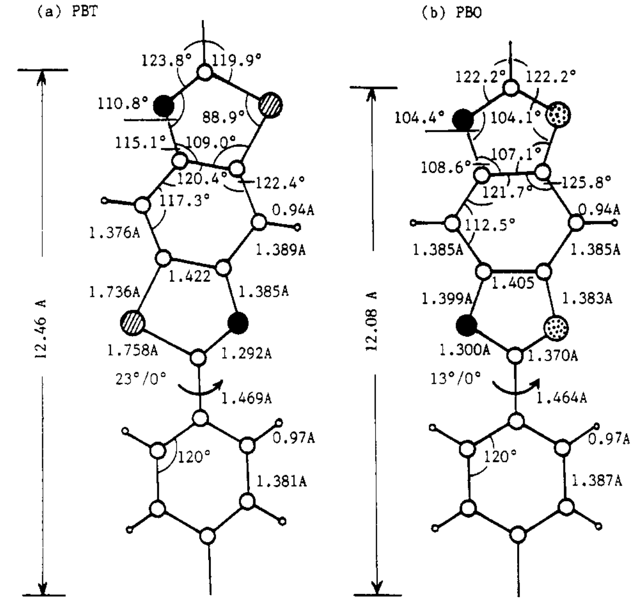


Figure 1. Molecular parameters of PBT and PBO used in the calculation: (○) C, (●) N, (◍) S, (◎) O.

Results and Discussion

The calculated Young's moduli of PBT and PBO are listed below, where the effective cross-sectional area of the chain S was assumed as $S = 20.81$ Å^2 for PBT and 19.44 Å^2 for PBO:[6]

PBT (trans form)	twisted structure, 405.2 GPa
PBO (trans form)	twisted structure, 458.0 GPa
	planar structure, 458.1 GPa
PBO (cis form)	twisted structure, 459.9 GPa
	planar structure, 459.9 GPa

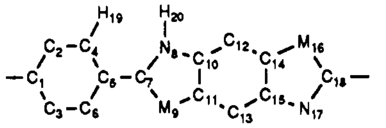
The calculated modulus of PBT is in good agreement with the actually observed X-ray value of 395 GPa.[2] The PBO sample used in the X-ray experiment is of the cis type of the benzobisoxazole ring. The theoretical value of 460 GPa is also in good agreement with the experimental value of 477 GPa.[2] (Although the theoretical value is a little lower than the observed data, however, it must be reminded

0024-9297/91/2224-3706$02.50/0

Table I
Intramolecular Force Constants of PBT and PBO Chains[a]

coordinates involved	values PBT	values PBO	coordinates involved	values PBT	values PBO
1. Stretching (mdyn/Å)					
1-2	6.433	6.433	4-19	5.055	5.055
12-20	5.055	5.055	10-12	6.03	6.03
5-7	5.50	5.50	9-11	4.65	5.22
8-10	6.4	6.4			
2. Bending (mdyn·Å/rad²)					
1-2-4	0.934	0.934			
4-5-7	0.75	0.75	7-9-11	1.95	1.14
7-8-10	1.34	1.96	8-7-9	1.41	1.41
9-11-10	1.41	1.96	8-10-11	1.34	1.72
11-10-12	0.907	0.907	10-12-14	0.937	0.937
9-11-13	0.727	0.727	19-4-5	0.511	0.511
20-12-10	0.511	0.511	C-H (out-of-plane)	0.2	0.2
3. Skeletal Torsion (mdyn·Å/rad²) 0.1 for all the skeletal bonds					
4. Stretch-Stretch (mdyn/Å)					
1-2,2-4	0.75	0.75	1-2,4-5	−0.32	−0.32
1-2,5-6	0.31	0.31	4-5,5-7	0.49	0.49
7-9,9-11	0.30	0.56	10-12,12-14	0.758	0.758
9-11,11-13	0.614	0.614	8-10,10-12	0.614	0.614
7-8,7-9	0.478	0.478	5-7,7-9	0.70	0.70
9-11,10-11	0.70	0.70	7-8,8-10	0.70	0.70
8-10,10-11	1.05	1.05	5-7,7-8	1.05	1.05
7-8,9-11	−0.20	−0.20	10-11,10-12	0.758	0.758
7-9,10-11	−0.20	−0.2	10-12,11-13	−0.242	−0.242
10-11,15-17	−0.169	−0.169	10-12,13-15	0.3	0.3
10-11,14-15	−0.069	−0.069	8-10,14-15	−0.069	−0.069
9-11,13-15	−0.122	−0.122	9-11,10-12	0.146	0.146
8-10,11-13	0.146	0.146	9-11,10-12	0.146	0.146
7-9,12-14	0.03	0.03			
5. Stretch-Bend (mdyn/rad)					
1-2,1-2-4	0.3	0.3	5-4,5-4-19	0.14	0.14
7-9,7-9-11	0.80	0.80	7-8,7-8-10	0.85	0.85
10-11,11-10-12	0.85	0.85	8-10,8-10-11	0.85	0.85
10-12,10-12-14	0.414	0.414			

[a] *i*–*j* and *i*–*j*–*k* denote the bond and angle, respectively, where *i*, *j*, and *k* are atomic numbers. The numbering of the atoms are referred to in the following figure (M = S or O).



that the experimental error in estimating the slight shift of the X-ray reflecional peak position is about 10%, and therefore the observed value seems located in the range of 429–525 GPa.)

As indicated above, the Young's modulus is not affected much by the difference in the polymer conformation: the twisted and the planar structures give almost the same values. A similar situation can also be seen for the influence of the chemical structure of the benzobisoxazole ring; the trans and cis types give essentially the same modulus with each other. The reason is easily extracted from the calculation of the atomic displacements and strain distribution for the tensioned polymer chains. In Figure 2 are shown the calculated results, where the chains are assumed to be tensioned by a hypothetically large strain of 10%. The essential features of the strain energy distribution are almost in common with the PBT and PBO (for both the trans and cis types). The strain energy distributes to the internal deformation of the phenylene and complex rings as well as to the stretching of the linkages connecting these two rings. The energy of the torsional coordinates around these linkages is zero, indicating no contribution of such torsional modes to the Young's modulus. A more detailed search of the energy distribution indicates that the distribution to the bond angles of C(p)–C(b)–N(b) [p = phenylene and b = benzobisthia(oxa)zole] is different between PBT and PBO; a higher percentage is in the PBT. The benzobisthiazole ring of PBT tilts to some extent from the main-chain axis, and the tensile deformation induces the rotation of this ring so that the long axis becomes parallel to the chain axis. Such a structural change is not seen in the case of PBO because the benzobisoxazole ring already stands almost vertically along the chain axis even when tension free. This may come from the similarity in the length (and angle) between the C–N and C–O bonds compared with the large difference between the C–N and C–S bonds in PBT. Therefore, the large difference in the Young's modulus between PBT and PBO is considered to originate mainly from the geometrical factor. In order to confirm it and to clarify the contributions of the geometrical and interaction factors, the Young's modulus was calculated for the following chain models: (a) the structure of PBO with the force constants used for PBT, and (b) the structure of PBT (twisted) with the force constants of PBO. The results are (a) E = 455.7 GPa and (b) E = 403.6 GPa. The value of b is almost coincident with that calculated originally for the PBT chain (405.2 GPa). The value of a is also in agreement with the original value of PBO (458.0 GPa for trans structure). That is to say, the difference in the Young's modulus between the PBT and PBO is considered to come mainly from the difference in the geometry of the molecular chain (the symmetrical structure of PBO and asymmetrical structure of PBT) and not to be affected much by a slight change of the utilized force constants. In other words, the difference in the stereochemical bulkiness between oxygen and sulfur atoms may be the most plausible origin for the difference in the modulus.

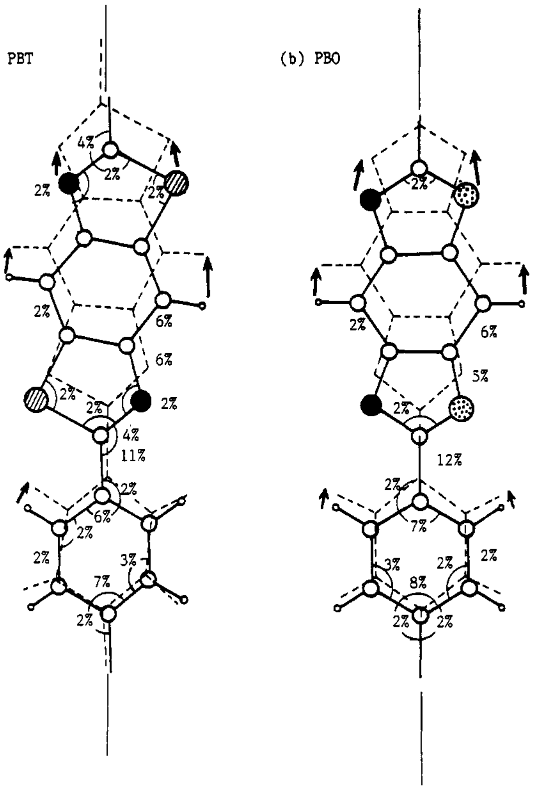


Figure 2. Calculated atomic displacements and strain energy distribution for the chains of PBT and PBO subjected under a tensile strain of 10%.

Acknowledgment. This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Areas, New Functionality Materials—Design, Preparation and Control, the Ministry of Education, Science and Culture, Japan.

References and Notes

(1) The Materials Science and Engineering of Rigid-Rod Polymers. *Mat. Res. Soc. Symp. Proc.* **1989**, *134*.

(2) Lenhart, P. G.; Adams, W. W. *Mat. Res. Soc. Symp. Proc.* **1989**, *134*, 329.

(3) Wierschke, S. G. *Mater. Res. Soc. Symp. Proc.* **1989**, *134*, 313.

(4) Tashiro, K.; Kobayashi, M.; Tadokoro, H. *Macromolecules* **1978**, *11*, 908, 911.

(5) Tashiro, K.; Kobayashi, M. *Sen-i Gakkaishi* **1987**, *43*, T78.

(6) Minter, J. R. University Microfilms International, Ann Arbor, MI, 1982, 8219829.

(7) Fratini, A. V.; Lenhert, P. G.; Resch, T. J.; Adams, W. W. *Mat. Res. Soc. Symp. Proc.* **1989**, *134*, 431.

(8) Pouchan, C.; Seuez, S.; Raymond, J.; Sauvaitre, H. *J. Chim. Phys. Phys.-Chim. Biol.* **1974**, *71*, 525.

(9) Mille, G.; Pouchan, C.; Sauvaitre, H.; Chouteau, J. *J. Chim. Phys. Phys.-Chim. Biol.* **1975**, *72*, 37.

Registry No. PBT (SRU), 69794-31-6; PBO (SRU), 60871-72-9.