

## 혼합용매계를 이용한 Theta-Condition에서 Poly(diphenylether sulfone)의 입체적 분자크기

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### Conformational Characteristics of Poly(diphenylether sulfone) Determined in Mixed Solvents under Theta-Condition

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**요 약 :** 혼합 용매계를 이용하여 poly(diphenylether sulfone)의 입체적인 분자형태를 규명하였다. ICI사 제품인 시료를 구입하여 정제 및 연속식 재침전법으로 분별하였고 각 분별 시료에 대하여 GPC와 용액 점성도 측정으로 분자특성을 결정하였다. Cloud point 적정법을 이용하여 DMF-MeOH(25°C) 및 DMF-toluene(30°C) 혼합용매계의 theta 조성을 결정하였다. 각 theta 조건 하에서 얻은  $K_{\theta}$  값은 DMF-toluene계에서  $0.112 \pm 0.002 \text{ ml mol}^{1/2} \text{ g}^{-3/2}$ , DMF-MeOH계에서  $0.124 \pm 0.0023 \text{ ml mol}^{1/2} \text{ g}^{-3/2}$ 이었다. DMF-MeOH계에서 얻은  $K_{\theta}$  값이 여러 종류의 간접방법에 의하여 구한  $K_{\theta}$ . 평균값과 잘 일치하였으므로, 이 값으로 부터 다음과 같은 비섭동분자 크기와 분자량과의 관계식을 얻었다.  $\langle R^2 \rangle_0^{1/2} = 0.0792 \times \bar{M}_w^{1/2}$  (nm). 여기서 얻은 값 0.0792는 isotactic polystyrene이나 isotactic PMMA보다는 큰 값을 나타내었고, cellulose trinitrate와는 유사한 경향을 보였다. 간소화한 rotational isomeric state 분석 및 화학구조 model을 이용한 계산 결과는 시료 중합체 연쇄의 기하학적 형태가 주로 trans-trans 구조이며, trans-gauche 및 gauche-gauche 형태가 간헐적으로 섞여 있을 가능성이 큰 것으로 해석되었다. 모든 실험적 결과 및 이론적 계산 결과는 주어진 중합체 시료의 입체적인 분자 형태가 크게 확장된 coil 형태인 것으로 해석하게 하였다.

**Abstract :** The conformational characteristics of the polymeric chain under unperturbed state is studied for the poly(diphenylether sulfone)-mixed solvent system. The polymer, supplied by the ICI, was purified and fractionated by the successive reprecipitational fractionation. Each fraction of the polymer sample was molecular characterized by GPC and viscometry. Two systems of theta-mixture, DMF-MeOH at 25°C and DMF-toluene at 30°C, were determined by the cloud point titration method. The values of  $K_{\theta}$  obtained from the DMF-toluene and DMF-MeOH systems under theta conditions were  $0.112 \pm 0.002$  and  $0.124 \pm 0.0023 \text{ ml mol}^{1/2} \text{ g}^{-3/2}$ , respectively. Since the latter was found to confirm best with the average value deduced from various graphical procedures, the value  $0.124 \pm 0.0023$  was used for the establishment of the relationship between the unperturbed chain dimension

of the polymer and molar mass, and it results as:  $\langle R^2 \rangle_0^{1/2} = 0.0792 \times \overline{M}_w^{1/2} (\text{nm})$ . The value 0.0792 was appeared as larger than isotactic polystyrene and PMMA, and comparable with cellulose trinitrate. A simplified rotational isomeric state approach and a model calculation revealed that the major contributor to the overall geometrical feature is trans-trans which separated intermittently with trans-gauche and gauche-gauche conformer. All the experimental results and theoretical calculations prove conclusively that the shape of the chain molecule under consideration is the type of highly extended coil.

## INTRODUCTION

The poly(diphenylether sulfone), (PDES), is one of the polyarylethers containing long bonds in their main chain. The long bonds are not single interatomic bonds but groups of atoms rigidly connected together.

In case of PDES, the constitutional repeating unit contains two rigid and planar p-phenylene groups. Since each phenylene group has a large molecular size, there may be a hindrance to rotation around the two neighboring phenylene groups which are separated by an ether or a sulfone linkage with fixed valence angle, and hence, it seems natural to expect that the molecular model of this type of polymer under unperturbed state may hardly be the one like freely rotating chain!

Contrary to this expectation, however, it has once been reported by Allen et. al.<sup>2</sup> that the value of the chain stiffness parameter  $\sigma = \langle R^2 \rangle_0^{1/2} / \langle R^2 \rangle_{of}^{1/2}$ , where  $\langle R^2 \rangle_{of}^{1/2}$  means the hypothetical chain dimension for a freely rotating chain, is  $0.96 \pm 0.10$  and has concluded that the experimentally determined dimension would be the same as those predicted by assuming non-hindered internal rotation about the main chain links. So then, the backbone chain of the real PDES should be the one that is more flexible than the hypothetical freely rotating chain. Furthermore, this result may lead to an erroneous conclusion that the unperturbed dimension of real PDES should be the small one.

However, the fact that the method they used for the evaluation of unperturbed dimension was not by the direct method using data obtained

from the theta-condition but by the indirect graphical procedure, left a problem of confidence. In addition, as Shah et. al.<sup>3</sup> asserted, the parameter  $\sigma$  is considered to be unsuitable for use with polymers containing cyclic structures in the main chain, because it has meaning only for chain molecules with flexibility imparted by rotation around valence bonds without distortion of valence angles.

The present study, therefore, is undertaken with an effort to estimate the molecular dimension of PDES more accurately by direct method using viscosity data obtained from the theta-condition. Since it was unable to find single theta-solvent, attempts were made to obtain the theta-condition by mixing good and poor-solvents at constant temperature. The intrinsic viscosity data at theta-condition are treated according to the theories of flexible chain polymer.<sup>1</sup>

## EXPERIMENTAL SECTION

### Polymer

The polymer sample used was commercially available polyether sulphone (grade 200 P) supplied by ICI. The unfractionated polymer was purified by several cycles of dissolution-precipitation procedures with DMF-MeOH system and finally dried under reduced pressure. The purified polymer was identified by IR spectrophotometry.

### Polymer Fractionation

The successive precipitation of polymer sample from the dilute solution by non-solvent addition was carried out with 1% DMF solution. The non-solvent used was 1% aqueous sodium chloride

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solution. Nine fractions were obtained, purified, and dried under reduced pressure.

**Cloud Point Titration**

The theta-composition was determined by modified Elias method.<sup>4,23</sup> Polymer solutions of different concentration at constant temperature were titrated with a non-solvent until the first sign of turbidity. The volume fraction  $\phi_3^1$  of non-solvent to give the first cloud point is then plotted against the logarithm of the volume fraction  $\phi_2^1$  of the polymer at the cloud point. An extrapolation of the straight line to the axis of 100% of polymer yielded the composition of solvent-precipitant theta-mixture at the temperature given. The solvent-precipitant systems used were DMF-MeOH at 25°C and DMF-toluene at 30°C, respectively.

**Viscosity**

Dilute solution viscosities were measured in an Ubbelohde type suspended level dilution viscometer for which kinetic energy corrections were negligible. The temperature control was  $\pm 0.02^\circ\text{C}$  at given temperature. The intrinsic viscosity  $[\eta]$  was determined by the usual extrapolation to zero concentration, and logarithmic viscosity number vs. concentration, respectively. The values of  $[\eta]$  estimated by these relations were well agreed.

**Gel Permeation Chromatography**

The average molar masses and polydispersity indices were determined by size exclusion chromatography. Measurements were carried out at 80°C with the instrument Waters Models 150 C,

and a combination of  $\mu$ -styrigel columns of  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6 \text{ \AA}$  was utilized. The flow rate of DMF as eluent was 1.0 ml/min.

**RESULTS AND DISCUSSION**

**Molecular Characteristics**

The molecular characteristics evaluated for the polymer fractions are summarized in Table 1. The highest and the lowest weight average molar masses found were  $1.40 \times 10^5$  and  $0.63 \times 10^5 \text{ g/mole}$ , respectively. This narrow span of molar masses for the sample fractions given is considered somewhat unsatisfactory for more correct estimation of overall conformation of the polymer, probably due to its failure to take into account the possible difference in molecular shape between oligomers and high molar mass homologues. But, this result is believed to be originated from the fact that the unfractionated polymer itself has originally a narrow width of molar mass distribution. And hence it seems appropriate to regard the conformational result obtained here as pertinent to the part encompassed within the limit of molar masses appeared in Table 1.

The values of polydispersity index obtained from GPC for each fractions are also listed in Table 1. As can be seen, each fraction shows moderately low values of polydispersity indices except for the case of first fraction (F 1). Some degree of criss-crossing or chain entanglement is believed to be occurred during the precipitation

**Table 1.** Molecular Characteristics and Intrinsic Viscosities Measured in DMF and Mixed Solvents for the Fractions of PDES.

Sample code	$\bar{M}_w \times 10^{-4}$ (g/mol)	$\bar{M}_w / \bar{M}_n$	$[\eta]$ , (mL/g) <sup>a</sup>				
			DMF	DMF-Tol (50:50)	DMF-Tol (45:55)	DMF-Tol (39:61)	DMF-MeOH (83:17)
F1	14.0	1.42	67.8	57.1	54.4	44.7	44.2
F2	11.6	1.36	58.7	49.8	47.9	41.2	41.3
F4	10.9	1.39	57.2	49.0	46.8	40.8	40.5
F5	9.1	1.37	49.6	41.8	39.6	36.8	37.0
F7	6.8	1.29	39.5	—	—	31.2	31.1
F8	6.3	1.39	38.5	33.8	32.8	30.2	30.5

a : Viscosity measurements were carried out at 30°C except for the system of DMF-MeOH at which was 25°C.

of the first fraction.

**Theta-Condition**

The determination of theta-composition of mixed solvent for the unbranched homopolymer via cloud point titration can successfully be accomplished by the use of following linear relationship between the volume fraction  $\phi_3^1$  of non-solvent at the cloud point and the logarithm of the volume fraction  $\phi_2^1$  of the solute,

$$\phi_3^1 = \phi_3^\theta - B_\phi \ln \phi_2^1 \quad (1)$$

where  $\phi_3^\theta$  is the theta-composition of the non-solvent in mixed solvent. And  $B_\phi$  is the constant for the ternary system of solvent-polymer-solvent with a given degree of polymerization of polymer and for a given temperature.

Fig. 1 shows the concentration dependences of toluene(non-solvent) at the cloud points on the logarithm of volume fraction  $\phi_2^1$  of PDES in DMF at 30°C. Extrapolations of the non-solvent concentrations to 100% of polymer intersected approximately at one point without regard to the size of molar masses, yielding  $\phi_3^\theta$  as 0.61 within the error range of  $\pm 0.5\%$ . The theta-composition thus found for the system of DMF-toluene at 30°C was 0.39 : 0.61 by volume fraction. Likewise, the ratio of theta-mixture for the system of DMF-MeOH at 25°C was 0.83 : 0.17, as is illustrated in Fig. 2.

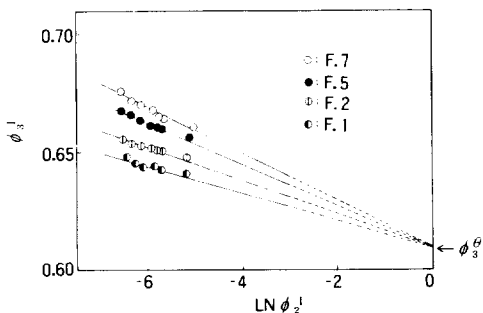


Fig. 1. Dependence of the volume fraction  $\phi_3^1$  of the precipitant toluene on the logarithm of the volume fraction  $\phi_2^1$  of poly(diphenyl ether sulfone) in DMF at 30°C.

On the other hand, in order to verify the identity of the theta-condition thus found for the respective solvent mixtures, values of intrinsic viscosity measured in each of the theta-mixtures are plotted against molar masses. The slopes, corresponding to the exponent of Mark-Houwink-Kuhn-Sakurata(MHKS) equation, of the straight lines shown in Fig. 3 came out as 0.507 for DMF-toluene and 0.498 for DMF-MeOH system. Although both values are slightly deviated from  $a=0.5$ , which is known as a characteristic for random

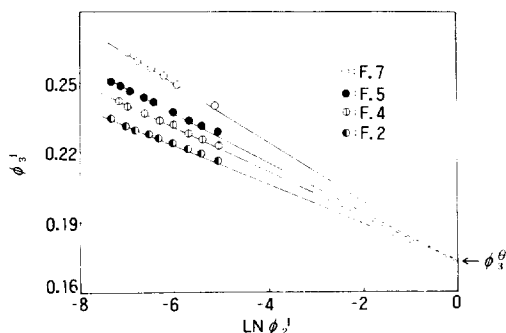


Fig. 2. Dependence of the volume fraction  $\phi_3^1$  of the precipitant methanol on the logarithm of the volume fraction  $\phi_2^1$  of poly(diphenyl ether sulfone) in DMF at 25°C.

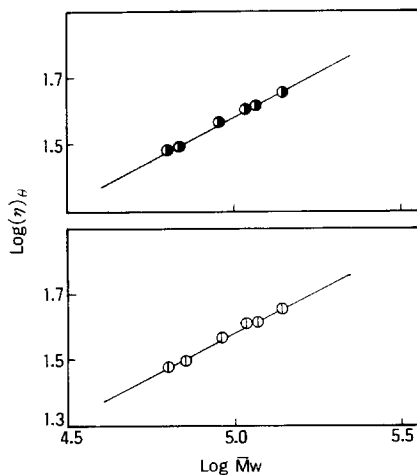


Fig. 3. Log-log plot of  $[\eta]$  vs.  $\bar{M}_w$  for poly(diphenyl ether sulfone) in  $\theta$ -condition, 83:17(v/v) DMF-methanol( $\bullet$ ) at 25°C and 39:61(v/v) DMF-toluene( $\circ$ ) at 30°C.

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coils in theta-solvents,<sup>4</sup> this does not necessarily mean a disproof of theta-conditions because there are examples<sup>4,5</sup> showing deviations of exponents determined in theta-mixture. This can be explained on the basis of the influence of preferential solvation of the polymer in mixed solvents: that is, the composition of the solvent mixture in the region of polymer coil is different from that in the space between coil because of the difference in their affinity to the polymer.

### The Parameter K and a of The MHKS Equation

Measurements of intrinsic viscosity for the sample fractions were done with solutions of DMF and various mixtures of DMF and non-solvents. The data of intrinsic viscosity and  $\bar{M}_w$  in Table 1 yielded straight lines, as depicted in Fig. 4, from which, together with the results obtained from Fig. 3, those semiempirical equations listed in Table 2 were able to be established.

An observation on the relation between a and K in respective equations shown in Table 2 makes it clear that a higher value of exponent is associated with lower value of parameter K, which is the decisive evidence that the excluded volume effect is progressively vanishing with the solvent becoming thermodynamically poorer. This is the usual trend that flexible chain polymers exhibit. Moreover, the fact that those values of exponent a found for the entire solvent systems employed lie between 0.5 and 0.8, allows us to conclude that the basic

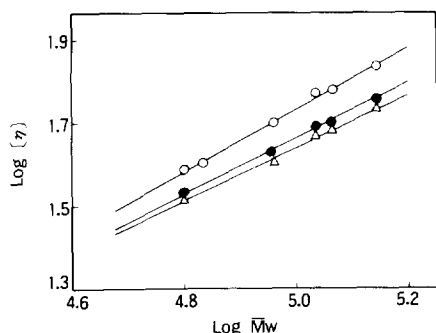


Fig. 4. Log-log plot of  $[\eta]$  vs.  $\bar{M}_w$  for poly(diphenylether sulfone) in DMF( $\circ$ ), 50:50(v/v) DMF-toluene( $\bullet$ ), 45:55(v/v) DMF-toluene( $\triangle$ ) at 30°C.

Table 2. MHKS Equations Established for the PDES in DMF and Various Mixed Solvents.

Solvent composition(v/v) (°C)	Temp. (°C)	MHKS eq <sup>a</sup> .
DMF	30	$[\eta]=0.012 \bar{M}_w^{0.726}$
DMF-Tol(50:50)	30	$[\eta]=0.022 \bar{M}_w^{0.662}$
DMF-Tol(45:55)	30	$[\eta]=0.027 \bar{M}_w^{0.643}$
DMF-Tol(39:61)	30	$[\eta]=0.112 \bar{M}_w^{0.507}$
DMF-MeOH(83:17)	25	$[\eta]=0.124 \bar{M}_w^{0.498}$

a : Mark-Houwink-Kuhn-Sakurada equation

\* :  $[\eta]$  is given in mL g<sup>-1</sup>

conformation of the polymer under consideration is clearly the coil-like one.

### Unperturbed Chain Dimension

For chains unperturbed by excluded volume effect, the intrinsic viscosity can be written in the following form:<sup>6</sup>

$$[\eta]_{\theta} = \Phi_0 \cdot (\langle R^2 \rangle_0 / \bar{M}_w)^{2/3} \bar{M}_w^{1/2} = K_{\theta} \bar{M}_w^{1/2} \quad (2)$$

where  $\langle R^2 \rangle_0$  represents the mean square unperturbed end-to-end distance,  $[\eta]_{\theta}$  is the intrinsic viscosity obtained under theta-condition, and  $\Phi_0 = 2.50 \times 10^{23} \text{ mol}^{-1}$  is the universal viscometric constant.<sup>1</sup> Thus, taking into account that

$$K_{\theta} = \Phi_0 \cdot (\langle R^2 \rangle_0 / \bar{M}_w)^{3/2} \quad (3)$$

it is possible to estimate the molar mass dependence of the unperturbed chain dimension if an accurate value of  $K_{\theta}$  is provided.

Values of  $K_{\theta}$  found directly from the  $[\eta]_{\theta} - \bar{M}_w^{1/2}$  relationship for the two systems of theta-mixture were  $0.112 \pm 0.002$  (DMF-toluene) and  $0.124 \pm 0.0023 \text{ ml mol}^{1/2} \text{ g}^{-3/2}$  (DMF-MeOH), respectively. This disagreement between  $K_{\theta}$ s, which is in contradiction to the theory<sup>7</sup> stating that the  $K_{\theta}$ s for the given polymer under theta-condition should be coincided without regard to what solvents are involved, suggests the possibility that the molecular dimension may not completely independent from the solvent systems used. There are ample experimental evidences showing the

same behavior that different theta-mixture leads to different unperturbed dimension even at the same theta-temperature<sup>20-22</sup> because of different preferential solvations.

For a confirmative purpose, eight kinds of graphical procedures so far known were tested. The Stockmayer-Fixman plot,<sup>9</sup> as an illustrative example, is shown in Fig. 5, which reveals the different values of ordinate intercept between theta- and nontheta-mixtures. Those straight lines drawn by the data obtained from the nontheta-conditions are not only showing discordance in  $K_\theta$  value but also yielding lower value of  $K_\theta$  than that of theta-condition. As a consequence, the estimation of  $K_\theta$  by indirect method is restricted to use only the data relevant to both the theta-mixtures.

The results thus estimated are summarized in Table 3, where a remarkable agreement of  $K_\theta$  values between different methods can be found for the case of DMF-MeOH system, except for only the I-S-K method. Also, the average value 0.125 of this system is quite close to the value obtained directly from the corresponding theta-mixture. This result allows us to establish a relationship between the unperturbed chain dimension of PDES and molar mass as equation (4):

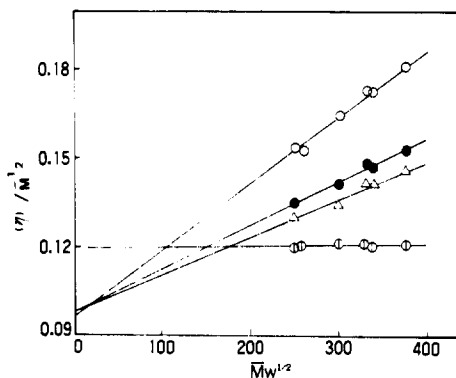


Fig. 5. Stockmayer-Fixman plot for poly(diphenyl ether sulfone) in DMF( $\circ$ ), 50:50(v/v) DMF-toluene( $\bullet$ ), 45:55(v/v) DMF-toluene( $\triangle$ ) and  $\theta$ -condition( $\square$ ) at 30°C.

$$\langle R^2 \rangle_0^{1/2} = 0.0792 \times \overline{M}_w^{1/2} \quad (\text{in nm}) \quad (4)$$

By comparing 0.0792 of this study with known values<sup>16</sup> of  $(\langle R^2 \rangle_0 / \overline{M}_w)^{1/2}$  for various polymers in Table 4, it appears that the chain dimension of PDES is found to be larger than those of PMMA, polystyrene, and PBLG in DCA, and comparable with those of isotactic poly(1-pentene) and cellulose trinitrate. In particular, the fact that the molecular dimension of PDES found is nearly the same level of cellulose trinitrate emphasizes strongly that the chain of PDES is highly extended.

Table 3. Values of  $K_\theta$  Deduced from the Various Indirect Procedures.

Procedures	$K_\theta$ , ml mol <sup>1/2</sup> g <sup>-3/2</sup>		Ref
	DMF-Toluene <sup>a</sup>	DMF-MeOH <sup>b</sup>	
F-F-S	0.121	0.125	8
S-F	0.119	0.124	9
Bohda	0.118	0.125	10
Cowie	0.119	0.124	11
I-S-K	0.160	0.169	12
U-K	0.119	0.124	13
Berry	0.121	0.125	14
D-B	0.119	0.126	15

a : Theta-mixture at 30°C b : Theta-mixture at 25°C

Table 4. Unperturbed Dimension of PDES and Various Linear Polymer Molecules (Ref. 16).

Polymers	Temp. (°C)	Solvents	$(\langle R^2 \rangle_0 / \overline{M})^{1/2} \times 10^4$ (nm)	$\sigma$
PMMA (isotactic)	27.6	Acetonitril	670	2.17
Polystyrene (isotactic)	30	Benzene	695 ± 25	2.30
PGLG <sup>a</sup>	25	DCA <sup>b</sup>	600 ± 20	2.32
Poly(1-pentene) (isotactic)	62.4	2-Propanol	790	2.14
Cellulose trinitrate	25	Acetone	810 ± 50	1.77 ± 0.11
PDES (this study)	25	DMF-MeOH	792	1.22

a : Poly( $\gamma$ -benzyl-L-glutamate)

b : Dichloroacetic acid

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An important simplification in the rotational isomeric state scheme is that the configuration of each bond is determined from the potential of interaction solely between near neighbors along the chain. In Fig.6 are illustrated the probable four-bond interactions encountered in PDES for purpose of conformational analysis in terms of pairwise rotations around the skeletal bonds, qualitatively. Interactions between elements that are farther apart are neglected in view of the fact that those interactions vanish rapidly as the interatomic spacing increases. Also the excluded volume effect is ignored in ideal chains.

First of all, simultaneous rotations of two consecutive bonds  $i$  and  $i+1$  in Fig. 6(a), are believed to be strongly forbidden, because the nonbonded hydrogen atoms attached to the ortho positions toward sulfur of both phenylene groups

should be sterically overlap if the bond angle  $\theta_2=100^\circ$ ,<sup>17</sup> and hence the most stable conformer to be attained by the O---S---O unit is the type of each benzene ring planes approximately perpendicular to O---S---O plane. Likewise, the rotations about the bond pair  $i$  and  $i-1$  flanking oxygen are also considered to be highly subjected to the steric obstruction. From a model calculation, it is cleared that the nonbonded hydrogen atom of both the phenylene groups, located near to the skeletal oxygen, should be in the state of steric overlapping under the conditions that the bond angle  $\theta_1=109.5^\circ$  and the benzene rings are parallel with S---O---S plane. If the  $\theta_1$  is  $123^\circ$ ,<sup>17</sup> however, the situation is a little different, ie, rotations about the bond pair  $i$  and  $i-1$  may possible, but, though permitted sterically in this case, the shortest distance between nonbonded hydrogen atoms, calculated roughly from a chemical model, is only 0.045 nm. Thus, taking into account that the van der Waals radius of hydrogen atom is 0.12 nm,<sup>18</sup> rotations about the S---O---S bond pair are also strongly be suppressed, which in turn suggests the favorable conformer should be analogous to the case of O---S---O bond pair.

Another conformers to be taken into consideration are those trans-gauche(T-C) and gauche-gauche(G-G) type of configuration. As for T-G type (Fig. 6b), which can be formed by  $120^\circ$  rotation of segment  $i+2$  against to the axis of  $i+1$ , not only the distance between those phenylene groups comprised in  $i$  and  $i+2$  segment is long enough (about 0.81 nm) not to occur any steric repulsion, but also less steric hindrance to rotation is available. This implies that the T-G form is also a conformer to be existed with relatively low energy state. On the same basis, G-G conformer, too, is the possible one that can contribute to the overall shape of PDES chain molecule. From a viewpoint of conformational potential energy,<sup>19</sup> however, the more preferable conformer should be the T-T type.

On the contrary, the cis type of conformer shown in Fig. 6d, may be the most unstable

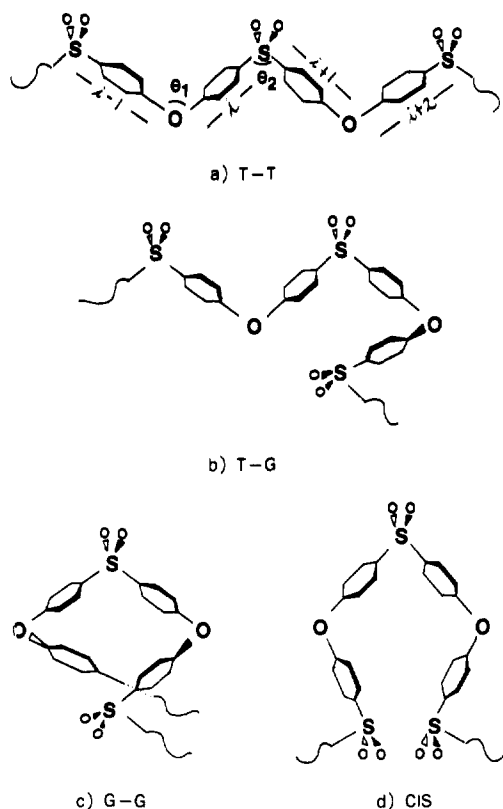


Fig. 6. Four probable conformational models of poly (diphenylether sulfone).

isomer to exist, owing principally to the severe steric hindrance being arised by the short distance (0.35 nm) between the end groups of segment  $i-1$  and  $i+2$ .

## CONCLUSION

All those experimental results and model calculations prove quite conclusively that the chain molecule of PDES can exist exclusively with T-T sequence separated intermittently with T-G and G-G conformers. This led us to postulate a model of PDES as a highly expanded coil. A severe hindrance to free rotation, due mainly to the planarity and bulkiness of aromatic ring in the skeletal bond, is believed to be the reason for the chain expansion. In particular, it seems appropriate to consider that an application of parameter like steric factor  $\sigma$  to characterize the molecular dimensions of polymer containing long skeletal bonds is quite impractical.

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