

## COHESIVE ENERGY DENSITIES OF POLYETHERS: POLY(HEXAMETHYLENE OXIDE)

C. MARCO, A. BELLO and J. G. FATOU

Sección de Fisicoquímica y Física de Polímeros, Instituto de Plásticos y Caucho, C.S.I.C., Juan de la Cierva,  
3 Madrid-6, Spain

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**Abstract**—The solubility parameter of poly(hexamethylene oxide) has been estimated by measuring solution viscosities and by turbidimetric titrations in a series of solvents. From both experimental methods, a value of  $\delta_p = 33.9 \text{ J}^{1/2} \text{ cm}^{-3/2}$  ( $8.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$ ) was obtained, whence the cohesive energy density is  $274.5 \text{ J cm}^{-3}$  ( $65.6 \text{ cal cm}^{-3}$ ). These experimental values are compared with those calculated by empirical methods.

### INTRODUCTION

The polyoxides, with the repeat unit  $[-(\text{CH}_2)_m-\text{O}-]$  are semi-crystalline polymers of simple and regular chemical structure. This series, with the limiting case of  $m \rightarrow \infty$  being polyethylene, is very suitable for a general analysis of properties in solution and in bulk related with the number of  $\text{CH}_2$  groups in the unit. Moreover, the values of intermolecular forces in these polymers are very important in describing the properties. Parameters, related to these intermolecular forces, are the cohesive energy density (CED) and the solubility parameter.

We have already investigated some related aspects, the synthesis [1-3], the dependence of the melting temperature on the crystallization conditions [4] and the influence of molecular weight on the crystallization kinetics [5] of poly(hexamethylene oxide) (PHO). Here, we present results on the solubility parameter of this polymer from viscosity and turbidimetric measurements and the experimental values are compared with those calculated by empirical methods.

### EXPERIMENTAL

#### Synthesis and fractionation

Poly(hexamethylene oxide) (PHO) was prepared by ring-opening polymerization of oxepane in bulk using as catalyst triethyloxonium antimonate [2]. The polymerization was done in vacuum at  $0^\circ\text{C}$  and killed with methanol. A fraction of  $\bar{M}_n = 25,000$  was isolated by fractionation in tetrahydrofuran-methanol at  $40^\circ\text{C}$ ; this fraction was used throughout this work.

#### Viscometry and turbidimetry

Viscosities were measured at  $25^\circ\text{C}$ , using an Ubbelohde viscometer; the flow efflux times for all the solvents listed in Table 1 exceeded 100 sec. The intrinsic viscosity  $[\eta]$  was determined as usual as a common intercept of  $|\eta_{sp}/c|$  vs  $c$  and  $(\ln \eta_r)/c$  vs  $c$  where  $\eta_r$  is the relative viscosity,  $\eta_{sp}$  is the specific viscosity and  $c$  is the solute concentration expressed in  $\text{g/cm}^3$ .

Turbidimetric measurements were carried out at  $25^\circ\text{C}$  on solutions of PHO in the solvents listed in Table 1 at concentrations of 0.3 g in 100 ml, in a Spekker apparatus using 15 ml of solution and slowly dropping a non-solvent

until a cloud point was reached. Two non-solvents, one of low (*n*-hexane) and other of high solubility parameter (methanol), were used for the titrations of the polymer solutions.

### RESULTS AND DISCUSSION

The intrinsic viscosities of polymer solutions are related to the expansion coefficient of the macromolecule. This parameter is influenced by the thermodynamic interaction between polymer elements and their environments.  $[\eta]$  is an indirect measure of the polymer-solvent interaction since increase of the thermodynamic quality of the solvent corresponds to higher values of the size of the polymer and, consequently, of  $[\eta]$ .

Analogy between swelling coefficients and intrinsic viscosity for evaluation of the solubility parameter of the polymer,  $\delta$ , was first pointed by Gee [6] who suggested that the solvent having the same cohesive energy density as the polymer corresponds to maximum value of  $\delta$ . The value of  $[\eta]$  for PHO are plotted in Fig. 1 against the solubility parameter,  $\delta_s$ , of the solvents, listed in Table 1. A smooth curve is drawn through the points and the maximum corresponds to a value of  $\delta_p = 8.0 \text{ cal}^{1/2} \text{ cm}^{-3/2}$  ( $33.5 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ).

A more precise assignment of  $\delta_p$  is obtained with the assumption [7] that  $[\eta]$  is a Gaussian function of  $V^{1/2}(\delta_s - \delta_p)$ , where  $V$  is the molar volume of the solvent, given by:

$$[\eta] = [\eta]_{\max} e^{V(\delta_s - \delta_p)^2} \quad (1)$$

The calculated values of  $1/V(\ln[\eta]_{\max}/[\eta])^{1/2}$  vs  $\delta_s$  are plotted in Fig. 2 and the point of intersection of the line with the abscissa gives  $\delta_p = 8.1 \text{ cal}^{1/2} \text{ cm}^{-3/2}$  ( $33.9 \text{ J}^{1/2} \text{ cm}^{-3/2}$ ).

The turbidimetric method, developed by Such and Clarke [8], was also used for evaluation of the solubility parameter of PHO. Turbidimetric titrations were done in several solvents, covering a wide range of solubility parameters and using two non-solvents, *n*-hexane and methanol, one of low and the other of high solubility parameter.

Table 1. Results of viscometric and turbidimetric measurements

	$\delta_1$ (cal cm <sup>-3</sup> ) <sup>1/2</sup>	$V_1$ (ml mol <sup>-1</sup> )	$[\eta]$ (10 <sup>-2</sup> g <sup>-1</sup> cm <sup>3</sup> ) K	$\delta_3$ (cal cm <sup>-3</sup> ) <sup>1/2</sup>
<i>Solvents</i>				
Isobutyl butyrate	7.8	167.0	0.56	0.356
Methyl cyclohexane	7.8	127.5	0.54	0.358
Secbutyl butyrate	8.0	165.0	0.60	0.342
Ethyl benzoate	8.2	144.4	0.59	0.354
n-Buthyl acetate	8.5	131.2	0.54	0.397
Tetrachloromethane	8.6	96.7	0.52	0.412
Toluene	8.9	107.1	0.47	0.438
Tetrahydrofuran	9.1	81.2	0.44	0.463
Benzene	9.15	88.9	0.43	0.459
Chloroform	9.3	81.2	—	—
Dichloromethane	9.7	63.6	—	—
Dioxane	10.0	85.0	—	—
<i>Non-solvents</i>				
Methanol	14.5	40.5	—	—
n-Hexane	7.3	130.6	—	—

If  $\delta_m$  is defined as the solubility parameter of solvent/non-solvent mixtures, at the cloud points the values of the interaction coefficients given by  $\chi = 1/Z + [V(\delta_s - \delta_p)^2/RT]$  are equal, and Such and Clarke[8] arrived at the following relationship for the solubility parameter of the polymer

$$\delta_3 = (V_{ml}^{1/2} \delta_{ml} + V_{mh}^{1/2} \delta_{mh}) / (V_{ml}^{1/2} + V_{mh}^{1/2}) \quad (2)$$

where subscripts mh and ml indicate mixtures of solvent with non-solvent of high or low solubility parameter and the values of  $\delta_m$  and  $V_m$  are calculated from:

$$\delta_m = \phi_1 \delta_1 + \phi_2 \delta_2 \quad (3)$$

$$V_m = V_1 V_2 / (\phi_1 V_2 + \phi_2 V_1) \quad (4)$$

where the subscripts 1 and 2 refer to the solvent and

non-solvent in the solution and  $\phi$  and  $V$  are volume fraction and molar volume, respectively.

As shown in Fig. 3, the values of  $\delta_3$  calculated according to Eqn (2) are almost constant i.e. yield almost a vertical line. The deviation from vertical probably is due to Eqn (3) not exactly describing the solubility parameter of the mixture solvent/non-solvent. The solubility parameter of PHO ( $\delta_p$ ) was determined as the point of intersection of the straight line expressing the dependence of  $\delta_1$  on  $\delta_3$  and from Eqn (2) with  $\delta_3 = \delta_1$  line (45° line). The value of  $\delta_p$  was found to be 8.0 cal<sup>1/2</sup> cm<sup>-3/2</sup> (33.4 J<sup>1/2</sup> cm<sup>-3/2</sup>).

The solubility parameter was also calculated from the tabulated group and bond attraction constants  $F$ . According to Small[9]

$$\delta_p = \frac{\rho \sum F}{M} \quad (5)$$

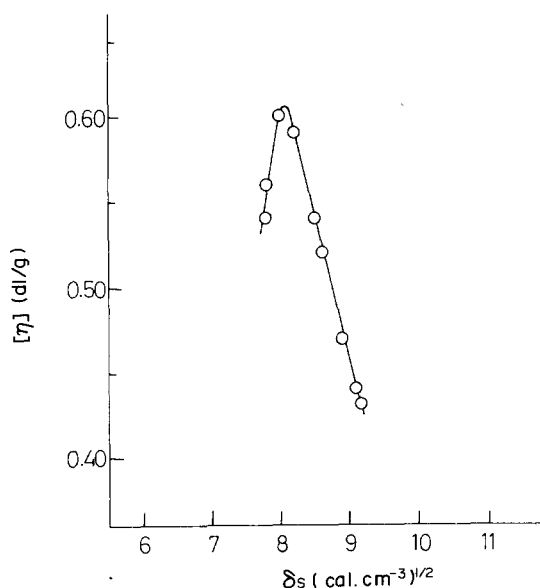


Fig. 1. Intrinsic viscosity vs solubility parameter of the solvents.

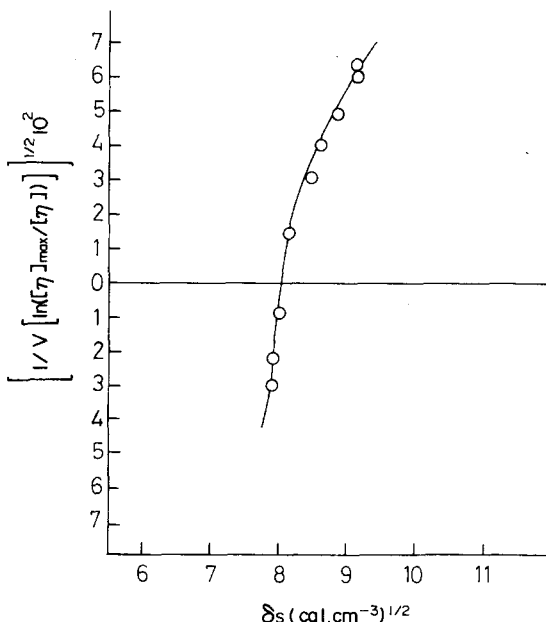


Fig. 2. Calculation of CED from viscosity by the intercept method.

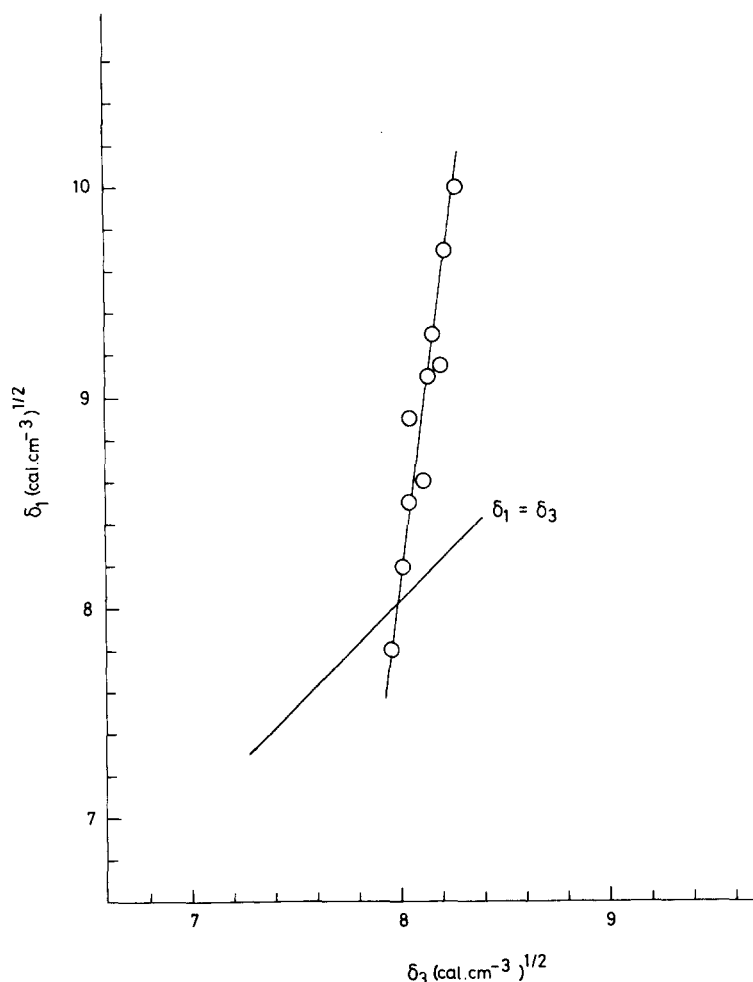


Fig. 3. Solubility parameter for poly(hexamethylene oxide) from turbidimetric titration with methanol and *n*-hexane.

where  $M$  is the molecular weight of the repeating unit and  $\rho$  the density of the polymer. As the polymer is semi-crystalline, the measured value of  $\rho$  at 25°C depends on the degree of crystallinity, and, for that reason, the value of the density of the amorphous polymer at 25°C was obtained by extrapolation of the density in the liquid state from well above the melting point, giving a value of  $\rho = 0.932 \text{ g cm}^{-3}$ .

For the  $\sum F$  values, there are two principal sets of tabulated data, one from Small[9] and more recently from Hoy[10]. Both values give almost the same molar attraction constants for the  $\text{CH}_2$  group, viz. 133 and 131.5  $\text{cal}^{1/2} \text{ cm}^{-3/2} \text{ mol}^{-1}$ , but they differ in the assigned value for the ether group,  $-\text{O}-$ , viz. 70 and 114.98  $\text{cal}^{1/2} \text{ cm}^{-3/2} \text{ mol}^{-1}$ . So the calculated values from Small's and Hoy's data are 8.09 and 8.42  $\text{cal}^{1/2} \text{ cm}^{-3/2}$  respectively, and the experimental evaluation of  $\delta_p$  for PHO agrees much better with the Small value. The value of the attraction molar constant assigned for the ether group in Hoy's table perhaps would represent better the solubility characteristic of the acetal group.

The solubility parameter of PHO, obtained by the present measurements, agree among themselves and

with the calculated value by Small's method. Assuming  $\text{CED} = (\delta_p)^2$ , the cohesive energy density of PHO is 65.6  $\text{cal cm}^{-3}$ , intermediate between values for polyethylene and poly(tetramethylene oxide) (Table 2). The value of CED decreases with increase in methylene chain length as would be expected.

Intermolecular forces are of fundamental importance in determining the physical properties of polymers. However, glass transition and melting temperatures for this series are not a linear function of CED. Thus, decrease in the intermolecular forces should give the corresponding gradual decrease of  $T_g$ . This is not the case for this series, meaning that other molecular factors such as flexibility (internal rotation) play important roles in determining this parameter.

Table 2. Cohesive energy densities of polyoxides

Polymer	CED ( $\text{cal cm}^{-3}$ )	Ref.
Poly(methylene oxide)	104	[11]
Poly(tetramethylene oxide)	69	[12]
Poly(hexamethylene oxide)	65.6	This work
Polyethylene	62.4	[13]

Moreover, focussing attention on the equilibrium melting temperature, the lower melting temperature of PHO (346.5 K) as compared with PE (417 K) is due to its lower enthalpy of fusion  $\Delta H_u$  [4]. Again, CED and  $\Delta H_u$  are not directly correlated. The lack of correlation between CED and  $T_m$  or  $\Delta H_u$  is not unexpected, noting that the CED is the difference of intermolecular forces between liquid and vapour and  $\Delta H_u$  between crystal and liquid states.

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