

Solubility Parameters in Polyoxetanes: Poly(oxetane), Poly(3,3-Dimethyl Oxetane), and Poly(3,3-Diethyloxetane)

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Synopsis

The solubility parameter of poly(oxetane), poly(3,3-dimethyloxetane) and poly(3,3-diethyl oxetane) has been estimated by measuring solution viscosities. Values of $\delta = 9.4, 7.9,$ and $7.9 \text{ cal}^{1/2}\cdot\text{cm}^{-3/2}$ for each polymer were obtained and compared with those calculated from empirical methods. The 3-dimensional solubility parameter approach has been also applied in order to get additional information on the effect of structural modifications on the main chain in the solubility behavior.

INTRODUCTION

In this work we report the results on the study of the solubility parameter of three polymers, polyoxetane (PTO), poly(3,3-dimethyl oxetane) (PDMO), and poly(3,3-diethyloxetane) (PDEO). These polymers form a series, with the repeat unit $-\text{CH}_2-\text{C R}_1\text{R}_1-\text{CH}_2-\text{O}$, in which, by simple change of the substituent R_1 , in this case the length of the paraffinic lateral group, the volume of the structural unit and the conformational energies of the skeletal bonds of the main chain can be changed. Therefore, important differences on the properties are expected on increasing the length of the lateral chain. In poly(3,3-dialkyl oxetane) the lateral groups of two consecutive structural units are separated by four bonds, and for this reason its steric interaction and its influence on the properties is small, when compared with polymers derived from disubstituted vinyl monomers.

A property easily accessible, which depends on the structure of the polymer, is the solubility. In order to analyze it, the solubility parameter δ has proven to be a valuable concept in obtaining information of solubility behavior of a polymer, specially in nonpolar solvents. Moreover, this parameter is closely related to the cohesive energy density (CED) that, in turn, gives useful information above the value of intermolecular forces, the molecular cohesion, which plays an important role in determining the physical properties.

The solubility parameter of the three polyoxetanes can be obtained by solution viscosity measurements,¹ and in this way a single solubility parameter δ that is based on the theory developed for mixing of nonpolar substances² is obtained. However, many of the solvents in common use are polar, and these polyoxetanes contain dipolar C—O bonds; moreover, the ether group gives to these polymers capabilities for hydrogen bonding. It is clear that these factors should be taken into account for a better understanding of the factors that play important roles in the solution process. For this reason we have used with these polymers the

3-dimensional solubility parameter approach as developed by Hansen,³ in which the solubility parameter is divided in three contributions, dispersion, δ_d , polar, δ_p , and hydrogen bonding, δ_h , and we tried to explain the relative importance of these contributions as a function of the structure of the polyoxetanes.

EXPERIMENTAL

Materials

Oxetane, 3,3-dimethyl oxetane and 3,3-diethyloxetane were synthesized from the corresponding 1,3-diols as described by Schmoyer and Case.⁴ The monomers, after being dried over calcium hydride, were distilled in a vacuum line several times from Na-mirror, and stored in tubes equipped with teflon stop-cocks.

Triethyloxonium hexafluoroantimoniate synthesized from benzoyl fluoride, antimony pentafluoride, and ethyl ether,⁵ was used as initiator of the polymerization, which was carried out in methylene chloride at 0°C. The polymers were isolated by precipitation into methanol. The samples were filtered and dried in vacuum.

Viscometry

Viscosities were measured at 25°C using an Ubbelohde viscometer. The flux time of the used solvents were higher than 100 s. The intrinsic viscosity $[\eta]$ was determined as a common intercept of η_{sp}/c vs. c and $(\ln \eta_r)/c$ vs. c , where η_r is the relative viscosity, η_{sp} is the specific viscosity, and c is the solute concentration expressed in g/dL.

RESULTS AND DISCUSSION

The solubility parameter concept is defined from the Hildebrand-Scatchard solution theory² as the square root of the energy of vaporization by unit of volume that usually is equated with the square root of the ratio of the potential energy to the volume. The usual methods of measuring the solubility parameter of polymers are based on the study of some properties related to the value of the polymers-solvent interaction. Gee⁶ studied the swelling of crosslinked polymers and found that swelling is greatest in solvents having the same cohesive density as that of the polymer. Moreover, Gee pointed out the analogy between swelling coefficients and intrinsic viscosities for evaluation of the solubility parameter. The intrinsic viscosities of polymer solutions are related to the expansion coefficient of the macromolecule. This parameter is influenced by the thermodynamic interaction between elements and their environments. The intrinsic viscosity is an indirect measure of the polymer-solvent interaction since an increase of the thermodynamic quality of the solvent corresponds to higher values of the size of the polymer and, consequently, of intrinsic viscosities.

The intrinsic viscosity data for PTO, PDMO and PDEO in several solvents are presented in Table I. Plots of $[\eta]$ vs. δ_s were obtained for each polymer and are shown in Figures 1-3. Smooth curves are drawn through the points and the values at the maximum correspond to the maximum polymer-solvent interaction

TABLE I
 Solubility of PTO, PDMO, and PDEO

Solvent	δ (cal ^{1/2} ·cm ^{-3/2})	PTO	$[\eta]$ (dL·g ⁻¹)	PDMO	$[\eta]$ (dL·g ⁻¹)	PDEO	$[\eta]$ (dL·g ⁻¹)
Isooctane	6.9	—		+	1.42	+	
Hexane	7.3	—		+		+	
Heptane	7.5	—		+	1.57	+	0.12
Octane	7.6	—		+		+	0.22
Decane	7.8	—		+		+	0.31
Dodecane	7.8	—		+		+	
Methylcyclohexane	7.9	+		+	1.62	+	0.33
Cyclohexane	8.2	— ^a		+	1.60	+	0.29
Benzene	9.2	+		+	1.15	+	
Toluene	8.9	+		+		+	
Tetralin	9.5	+		+		+	
Carbon tetrachloride	8.6	+	1.65	+	1.45	+	
1,2-Dichloroethylene	9.0	+	1.76	+		+	
Chloroform	9.3	+	2.37	+		+	
Trichloroethylene	9.2	+	1.93	+		+	
Methylene chloride	9.9	+		—		—	
tetrachloroethane	9.7	+	2.01	+		+	
Chlorobenzene	9.6	+		+		+	
<i>o</i> -Dichlorobenzene	10.0	+	1.75	+		+	
Acetone	9.8	+		—		—	
Methyl ethyl ketone	9.3	+		+		—	
Acetonitrile	11.9	—		—		—	
Nitromethane	12.3	—		—		—	
Nitrobenzene	10.7	+		—		—	
Triethyl phosphate	10.9	—		—		—	
Dioxane	10.0	+		+		+	
Methylal	8.5	+		+		+	
Ethyl acetate	9.1	+		+		—	
<i>n</i> -Butyl acetate	8.5	+		+		+	
Ethanol	12.9	—		—		—	
Cyclohexanol	11.0	—		—		—	

^a θ at 27°C.

and, hence, to the solubility parameter of the polyoxides. An assignment of δ is also obtained with the assumption⁷ that the intrinsic viscosity is a Gaussian function of $V^{1/2}(\delta_s - \delta)$, where V is the molar volume of the solvent, given by

$$[\eta] = [\eta]_{\max} \cdot e^{V(\delta_s - \delta)^2}$$

The calculated values of $V^{-1}(\ln[\eta]_{\max}/[\eta])^{1/2}$ are plotted against δ_s in Figures 1–3, and approximate straight lines are drawn covering most points; the δ values of polyoxetanes were established from the points of intersection of the lines with the abscissa. The values are included in Table II.

The solubility parameter was also calculated from the tabulated groups and bond attraction constants F . According to Small,⁸ $\delta = \rho \Sigma F/M$, where M is the molecular weight of the repeating unit and ρ the density of the amorphous polymer. As the three polyoxetanes are semicrystalline polymers and melt above room temperature, the measured value of the density at 25°C was obtained by extrapolation of the density in the liquid state from well above their melting temperatures, giving values of ρ listed in Table III. For the ΣF values, there

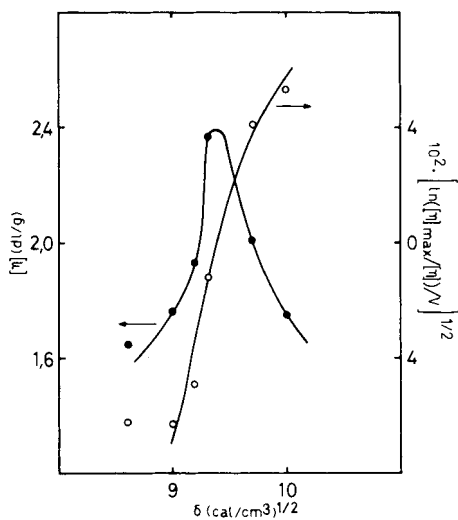


Fig. 1. Determination of solubility parameter of PTO.

TABLE II
Solubility Parameters of Poly(oxetanes)

Polymer	δ_{expl} ($\text{cal}^{1/2} \cdot \text{cm}^{-3/2}$)	δ_{Small} ($\text{cal}^{1/2} \cdot \text{cm}^{-3/2}$)	δ_{Hoy} ($\text{cal}^{1/2} \cdot \text{cm}^{-3/2}$)
PTO	9.4	8.5	9.2
PDMO	7.9	7.2	7.5
PDEO	7.9	7.9	8.1

are two sets of tabulated data, one from Small⁸ and the other from Hoy.⁹ Both values give almost the same molar attraction constants for the CH_3 and CH_2 groups, but they differ in the assigned value for the tetrasubstituted carbon and the ether group. The calculated values with both sets of data are shown in Table II. The experimental values agree better with the calculated from Hoy data.

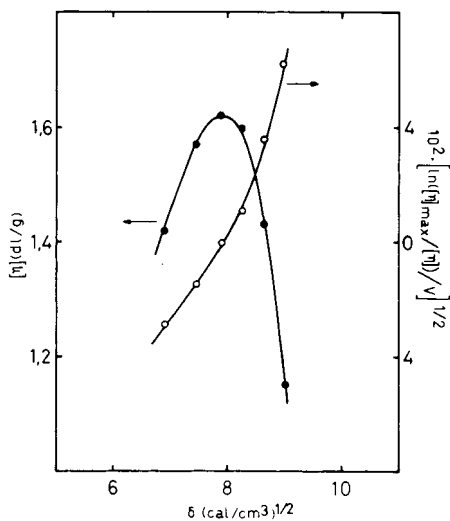


Fig. 2. Determination of solubility parameter of PDMO.

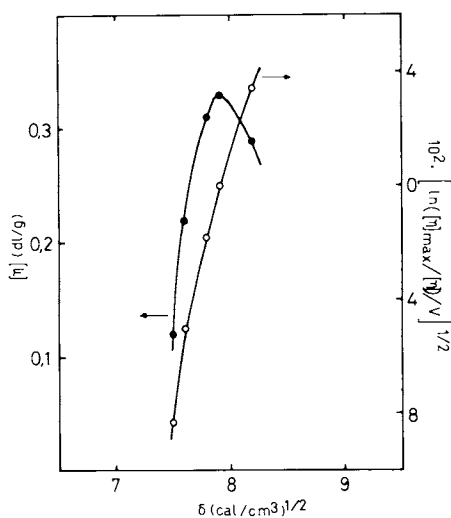


Fig. 3. Determination of solubility parameter of PDEO.

The solubility parameter or the related cohesive energy density must be a measure of the interaction forces in these polyoxetanes. However, using the single parameter approach, neither the nature of these interactions nor the factors which are modified on passing from polyoxetane to the diethyl derivatives are taken into account. The nature of the intermolecular forces in these polyoxetanes are shown throughout the type of liquids in which they are miscible, and, therefore, it is possible to get some insight about the kind of intermolecular forces which are present in these polymers from their solubilities in solvents of different polarities.

For interpreting interaction data throughout the solubility parameter, different methods have been derived, and one of the most practical methods has been the 3-dimensional approach,¹⁰ which has been used to correlate different systems, and it represents a useful method of comparing the solubility properties. The basis of the 3-dimensional solubility parameter system is that the total cohesive energy can be divided into contributions from dispersion forces, dipole forces, and hydrogen-bonding forces.

With the purpose of analyzing the contribution of intermolecular forces to the solubility parameter in these polyoxetanes, the 3-dimensional approach, as developed by Hansen¹⁰⁻¹² has been used. If these interactions are the result of dispersion (δ_d), dipole (δ_p), and hydrogen bonding (δ_h) forces, the original Hildebrand solubility parameter is related to these parameters by the relationship

TABLE III
Three-Dimensional Solubility Parameters

Polymer	δ_d	δ_p	δ_h	Refractive index	Density ^a
PTO	8.7	2.5	2.5	1.46	1.05
PDMO	7.5	1.2	2.0	1.44	0.92
PDEO	7.6	1.0	1.7	1.48	0.95

^a Density of the amorphous polymer at 25°C.

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$$

where $\delta = (E/V)^{1/2}$, $\delta_d = (E_d/V)^{1/2}$, $\delta_p = (E_p/V)^{1/2}$, and $\delta_h = (E_h/V)^{1/2}$, V being the molar volume and E the energy of vaporization.

This means that in a 3-dimensional space, each polymer is represented by a point that is placed into the center of a sphere which encloses all the solvents of the polymer. In order to find this central point for the three polyoxetanes, a test of solubility with several liquids was done. The results are given in Table I. For instance, cyclohexane is a bad solvent (Θ at 27°C),¹³ and methylene chloride is a good solvent for the first member of this series, PTO, while the reverse situation occurs with the diethyl derivative. These facts are reflected in the values for the three components of the solubility parameter (Table III).

The biggest differences in the three parts of the solubility parameter are found between PTO and the other two derivatives, while between the PDMO and PDEO the differences are very small. The dispersion component of the solubility parameter follows an irregular pattern along these three polymers, and, first, it decreases on passing from PTO to PDMO and, then, practically levels off to a constant value for the PDMO and PDEO. The interaction energy manifested in this parameter is dependent on the polarizability, which can be calculated from the Lorentz-Lorentz equation

$$\alpha = 3V(n_D^2 - 1)/(n_D^2 + 2)(4\pi N_A)$$

where the polarizability is related to the index of refraction, n_D , and the molar volume V . As these two parameters do not follow the same trend along this series, the dispersive component does not change linearly with either of these two parameters. However, on increasing the molar volume, the proportional participation of the dispersive component δ_d^2/δ^2 into the solubility parameter is raised. There are in the literature semiempirical relationships between the dispersion component and some physical properties of the polymer. It has been suggested¹⁴ the dependence of δ_d on $V^{1/6}$ (V molar volume), and so δ_d would be related with the ratio $n_D/V^{1/6}$. For the three analyzed polyoxetanes, we have found that the relation corresponds to

$$\delta_d = 11.4n_D V^{-1/6}$$

With this equation, the δ_d values are 8.53 for PTO, 7.70 for PDMO, and 7.60 for PDEO, which agree quite well with the experimental ones (Table III).

The dipole component of the solubility parameter δ_p , decreases to the half of its value on passing from PTO to PDMO, but from this one to the diethyl derivative almost remains constant. The contribution of permanent dipoles to the cohesive energy density can be seen, at least qualitatively, from the equations which relate the dipole moment to the polar component of the solubility parameter. Thus Hansen,¹² calculated this component from the following equation proposed by Böttcher¹⁵:

$$\delta_p^2 = \frac{12,108}{V_m^2} \frac{\epsilon - 1}{2\epsilon + n_D^2} (n_D^2 + 2)\mu^2$$

where ϵ = dielectric constant, μ = dipole moment, and n_D = refraction index.

In the method outlined by Gardon,¹⁶ the fractional polarity is defined as the fraction of the total interactions that are due to dipole-dipole attractions: $\delta_p^2/\delta^2 = (2/3)kT\mu^4/\epsilon$, where ϵ represents all the interactions energies that contribute

to the cohesive energy density. So a direct relation exists between δ_p and μ , which, in turn, is related to the number of dipoles which are in the structure of the polymer. In these three polyoxetanes, the number of dipoles O—C—O in each structural unit is the same, but, in spite of it, there are important differences in the dipole moment, at least between the PTO and PDMO. The dipole moment of PTO is not very high,¹⁷ but substituting two hydrogen atoms for two methyl groups in the 3 position results in a decrease of the dipole moment.¹⁸ The reason for this difference has been reported as due to the fact that the addition of two pendent methyl groups in the chain of polyoxetane, favors $g^\pm g^\pm$ conformations in pairs of bonds which place pairs of bond dipoles in antiparallel orientation,¹⁸ with the result that the dipole moment of PDMO is lower than PTO. The decrease of the dipole moment leads to the diminution, in the same way, of the polar component of the solubility parameter. Dielectric properties of PDEO have still not been reported; but from this solubility study it is deduced that the polarity of this polymer has very small differences with the dimethyl derivative, and it is probable that the conformational changes on the main chain which affect the polarity on passing from the PDMO to PDEO must be very small.

Concerning the hydrogen-bonding component, δ_h , its value, as can be seen in Table III, decreases slightly on passing from PTO to PDEO. This component represents the donor-acceptor character of the polymer. It seems fairly well established that donor-acceptor interactions (either though hydrogen bonding or charge transfer) of ethers are quite sensitive to both steric and electronic effects.¹⁹ As far as we know, for these polyethers values of these interactions have not been reported so that there is no experimental proof about the trend that this parameter must follow along this series. Nevertheless, the above results clearly hint some steric influences on the basicity of these polymers. It is not an unexpected result that to the least crowded molecular, PTO, corresponds the biggest value of the basicity, while the smallest one corresponds to the highly crowded, more heavy substituted PDEO.

In summary, solubility parameters of these three polyoxetanes are a very helpful instrument to estimate their solubilities; also, when the components of the 3-dimensional solubility parameter are taken into account, an explanation is found for the modification on solubility which is introduced by increasing the size of the substituent in the skeletal chain.

We acknowledge the financial support of the Comisión Asesora de Investigación Científica y Técnica, Spain.

References

1. C. Marco, A. Bello, and J. G. Fatou, *Eur. Polym. J.*, **17**, 41 (1981).
2. J. Hildebrand and R. Scott, *Solubility of Non-Electrolytes*, Reinhold, New York, 1949.
3. C. M. Hansen, *J. Paint Technol.*, **39**, 104 (1967).
4. L. F. Schmoyer and L. C. Case, *Nature*, **187**, 592 (1960).
5. R. Szymanski, H. Wiczorek, P. Kubisa, and S. Penczek, *J. Chem. Soc. Chem. Commun.*, **33** (1976).
6. G. Gee, *Ann. Rep. Prof. Chem.*, **39**, 7 (1942).
7. D. Mangaraj, S. Bhatuagar, and B. Rath, *Makromol. Chem.*, **67**, 75 (1963).
8. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
9. K. L. Hoy, *J. Paint Technol.*, **42**, 76 (1970).
10. C. M. Hansen, *Ind. Eng. Chem., Prod. Res. Dev.*, **8**, 2 (1969).
11. C. M. Hansen, *J. Paint Technol.*, **39**, 505 (1967).
12. C. M. Hansen and K. Skaarup, *J. Paint Technol.*, **39**, 511 (1967).

13. D. S. Chiu, J. Takahashi, and J. E. Mark, *Polymer*, **17**, 670 (1976).
14. D. M. Koenhen and C. A. Smolders, *J. Appl. Polym. Sci.*, **19**, 1163 (1965).
15. C. F. Böttcher, *The Theory of Electric Polarisation*, Elsevier, Amsterdam, 1952.
16. J. L. Gardon, in *Encyclopedia of Polymer Science and Technology*, H. F. Mark, N. G. Gaylors, and N. M. Bikales, Eds., Wiley-Interscience, New York, 1968, Vol. III, p. 843.
17. J. E. Mark and D. S. Chiu, *J. Chem. Phys.*, **66**, 1901 (1977).
18. E. Saiz, E. Riande, J. Guzmán, and J. de Abajo, *J. Chem. Phys.*, **73**, 958 (1980).
19. E. M. Arnett, *Progress in Physical Organic Chemistry*, Wiley, New York, 1963, Vol. I, p. 223.

Received March 1, 1982

Accepted March 25, 1982