

The Solubility Parameter of Polypropylene

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Synopsis

Solubility parameter values for polypropylene as reported in the literature cover a rather broad span, ranging from 7.9 to 9.4 (cal./cm.³)^{1/2}. This communication suggests the approximate value 8.2. This value is based on the swelling and dissolution characteristics of polypropylene films in various organic liquids. A calculated value of 8.1, obtained by Small's method, compares well with the experimentally determined value.

Introduction

The solubility parameter δ , defined as the square root of the cohesive-energy density,¹ represents a quantity that is useful in assessing the compatibilities of different chemical substances. It has served as an efficient guide in the selection of proper compounding ingredients² and solvents³ for polymers and paints. It is important to note, therefore, that for polypropylene, a polymer of growing commercial importance, the reported values of the solubility parameter cover a rather broad span, ranging from the value⁴ 7.9 (cal./cm.³)^{1/2} to the value⁵ 9.4 (cal./cm.³)^{1/2}. Moreover, making a selection of one of the literature values was difficult, since none had been experimentally determined.

Voeks's value⁵ of 9.4 was based on a method of estimating the intermolecular pair potential of polymers from density data alone. Voeks makes reference to an article by Hayes⁶ in quoting an empirically derived value of 9.2. Brydson⁴ reports a value of 7.9, but no apparent reference is made to the method of determining this value. In an earlier publication² he gives the value as 8.1. Finally, it is interesting to note that a recent compilation⁷ of the solubility parameters of several polymers does not give a value for polypropylene, yet it lists an experimental value for ethylene-propylene rubber as being 7.9.

It is the purpose of this communication to propose that the solubility parameter of semicrystalline isotactic polypropylene is close to 8.2 (cal./cm.³)^{1/2}. This value is primarily based on the determination of the solubilities of several organic fluids in polypropylene films.

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Experimental

The compatibility of various organic fluids with polypropylene films was determined by two procedures: measuring sorption levels of organic vapors in the polymer and observing the "dissolution temperature" of polypropylene in various solvents. Equilibrium sorptions of isooctane, methylcyclohexane, *p*-xylene, toluene, and *o*-xylene in the films were obtained by using a quartz spring balance enclosed in a constant-temperature air bath.⁸ This system allowed the detection of weight changes of the order of ± 0.03 mg. compared to a total sorption usually greater than 5 mg. in a 50 mg. film sample.

The dissolution temperatures were obtained by immersing a film sample in excess solvent, slowly increasing the temperature of the system, and noting the temperature at which the film disappears from view. This temperature provided a relative measure of the solvent power of toluene, *p*-xylene, cyclohexane, methylcyclohexane, and isooctane for polypropylene.

The polypropylene film used in this study, Profax-6520 F, was supplied by Hercules Incorporated. The material was reported to have a weight-average molecular weight of about 300,000 and to be 95% isotactic. The films employed were slot-cast and had a nominal thickness of 5 mils and a density of 0.9050 g./cm.³. Reagent-grade solvents were used in the course of the investigation.

Results and Discussion

The extent of polypropylene swelling in saturated organic vapors of different solubility parameters is shown in Figure 1. It is seen that a maximum in the sorption is indicated, near a solubility parameter of 8.2 (cal./cm.)^{1/2}. As shown by Gee⁹ and Small,¹⁰ the amount of polymer swelling will be greatest in the substance that has the same solubility parameter as that of the polymer. Thus, the swelling data indicate the solubility parameter of polypropylene to be nearly 8.2 (cal./cm.)^{1/2}.

The dissolution temperatures of polypropylene film samples in various solvents are given in Table I. That of a crystalline polymer, such as polypropylene, is dependent on the temperature at which crystallites, which act

TABLE I
Dissolution Temperatures of Polypropylene Films in Organic Solvents

Solvent	δ at 25°C., ^a (cal./cm.) ^{1/2}	$T_{\text{dissol.}}$, °C.
Toluene	8.90	105
<i>p</i> -Xylene	8.75	102
Cyclohexane	8.20	85
Methylcyclohexane	7.85	94
Isooctane	6.85	>100 ^b

^a Data of Hildebrand and Scott.¹

^b Solvent boils before dissolution occurs.

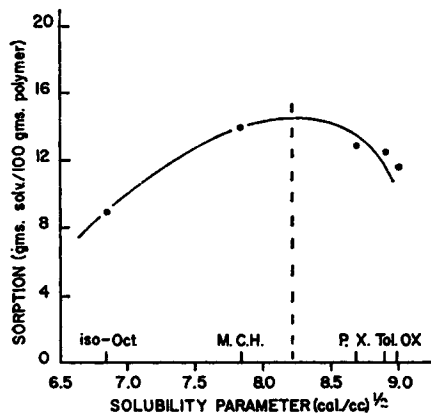


Fig. 1. Sorption in polypropylene as a function of solvent solubility parameter.

as "crosslinks" in the polymer, are melted. As shown by the Flory-Huggins equation,¹¹ the crystalline melting point is depressed in the presence of solvent, and a larger depression is expected with good solvents, i.e., when the solvent-polymer interaction parameter is small. Hildebrand and Scott¹ indicate that in the simplest case the solvent-polymer interaction parameter is proportional to the difference between the solubility parameters of the solvent and the polymer. Thus, the presence of a solvent with a solubility parameter close to that of polypropylene can contribute appreciably to the reduction of the polymer's crystalline melting point and its dissolution temperature. The data (Table I) indicate cyclohexane [$\delta = 8.2$ (cal./cm.³)^{1/2}] to be such a solvent, suggesting rather strongly that the solubility parameter of polypropylene is also close to this value.

It is possible to obtain another estimate of the solubility parameter of polypropylene from its structural formula and density by using Small's method.¹⁰ The method is based on "molar attraction constants" F , assigned to various atoms and molecular groups whose summation ΣF is related to the solubility parameter δ by the following formula:

$$\delta = \rho \Sigma F / (MW)$$

where ρ and MW are the density and molecular weight, respectively. In applying this relationship, which was derived for amorphous polymers, to polypropylene, a semicrystalline polymer, it is not clear which density value must be used. Since solvent sorption occurs primarily in the amorphous phase,⁸ it may be argued that the amorphous-phase density should be used. On the other hand, the crystalline regions of the polymer, acting as crosslinks, influence the sorption behavior; so the density of the sample may represent a better value for use in Small's relationship. Values of the solubility parameters calculated on the basis of these two density values ($\rho_a = 0.854^{12}$ and $\rho = 0.905$, g./cm.³) are 7.6 and 8.1 (cal./cm.³)^{1/2}.³ The second value is quite close to the experimentally determined solubility

parameter of polypropylene, suggesting that the degree of swelling of the noncrystalline regions is controlled by the tension of the intercrystalline tie segments, as found by Michaels and Hausslein¹³ in their work with polyethylene.

Conclusion

According to the swelling and dissolution characteristics of polypropylene films in several organic solvents, the solubility parameter of polypropylene is shown to be approximately $8.2 \text{ (cal./cm.}^3)^{1/2}$. This value compares with a calculated value of 8.1, obtained by Small's method, and the experimentally determined value for polyethylene, a chemically similar polymer, reported as 7.9.⁷

References

1. J. H. Hildebrand and R. L. Scott, *Solubility of Non-Electrolytes*, Dover, New York, 1964.
2. J. A. Brydson, *Plastics (London)*, **26**, 107 (1961).
3. H. Burrell, *Offic. Dig. Federation Paint Varnish Prod.*, **27**, 726 (1955).
4. J. A. Brydson, *Plastic Materials*, Van Nostrand, Princeton, N.J., 1966.
5. J. F. Voeks, *J. Polymer Sci. A*, **2**, 5319 (1964).
6. R. A. Hayes, *J. Appl. Polymer Sci.*, **5**, 318 (1961).
7. J. L. Gordon, *J. Paint Technol.*, **38**, (492) 43 (1966).
8. H. H. Alcalay, Ph.D. Thesis, Mass. Inst. Technol., Cambridge, Mass., 1966.
9. G. Gee, *Trans. Faraday Soc.*, **40**, 468 (1944).
10. P. A. Small, *J. Appl. Chem.*, **3**, 71 (1953).
11. P. J. Flory, *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, N.Y., 1953.
12. G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Morgaglio, *J. Am. Chem. Soc.*, **77**, 1708 (1955).
13. A. S. Michaels and R. W. Hausslein, in *Transport Phenomena in Polymeric Films (J. Polymer Sci. C, 10)*, Charles A. Kumins, Ed., Interscience, New York, 1965, p. 61.

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