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The DTA of Polymer-Solvent Systems. The Solubility Curves of Isotactic Polypropylene-Decalin and Isotactic Polypropylene-Nitrobenzene Systems

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A DTA apparatus for a polymer solution has been constructed. The heating rate was adjusted to approximately 0.50 or 0.42°C/min., a favorable rate for a polymer solution. From the DTA curves obtained by the use of this apparatus, the temperatures of the end points of the melting or dissolution have been determined; their plots give the solubility curves. The solubility of the isotactic polypropylene in decalin system increases monotonously with the increase in the temperature, except for the abnormality in the region from 30 to 50 wt.% in polymer content. In the case of the isotactic polypropylene-nitrobenzene system, on the other hand, the melting curve has a horizontal part in the region with a polymer content of less than 50 wt.%; above this point lies the phase separation curve, which touches the melting curve at the point with a polymer content of approximately 50 wt.%. The double peaks which appear in the DTA curve of the melting of pure isotactic polypropylene, may be due to the paracrystalline smectic modification of isotactic polypropylene, as has been suggested by Natta *(Makromol. Chem.,* **35,** 93 (1960)). The heat of fusion for isotactic polypropylene has been estimated to be approximately 1000 cal./unit mol. by measuring the area under the melting peak of the DTA curve and the equation for the melting point depression.

It is known that differential thermal analysis (DTA) is very useful in investigating such a thermal change as the phase transition. The applications of the DTA method to polymeric materials, however, have been restricted mainly to the thermal change in a pure polymer or in one with only a small amount of diluents. In this paper we shall use this DTA method in studying the dissolution behavior of isotactic polypropylene-decahydronaphthalene (decalin) and isotactic polypropylene-nitrobenzene mixtures, over the whole concentration range. Decalin and nitrobenzene will be used as a typically good and a typically bad solvent respectively for isotactic polypropylene. Further, the analysis of DTA curves on pure isotactic polypropylene will also be carried out under some pretreatment conditions.

Experimental

Apparatus.—We constructed the DTA apparatus, equipped with a stirrer to secure the smooth dissolution of polymer during heating, illustrated in Fig. 1. A sample cell and a reference cell made of stainless steel were put into the cell holder and fitted with copper-constantan thermocouples at their bottoms.

The e. m. f. representing the temperature difference between the sample cell and the reference cell was amplified by the Okura AM101B amplifier, and the signals for the temperature difference were recorded on a time-base chart recorder (YEW ER1-30). The temperature was determined by measuring the potential difference between the reference substance and the ice point with the potentiometer.

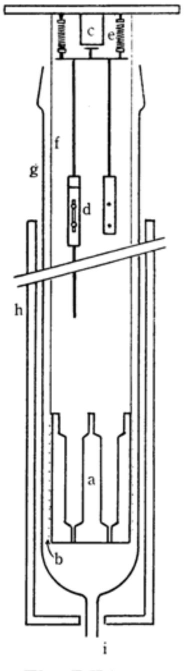

Fig. 1. The DTA apparatus.

(a) Cell holder
(b) Heater (nichrome wire)
(c) Magnetic vibrator for stirrers
(d) Joint of stirrer and vibrator
(e) Spring
(f) Wires for suspending the cell holder
(g) Glass mantle
(h) Heater mantle
(i) Outlet of thermocouples

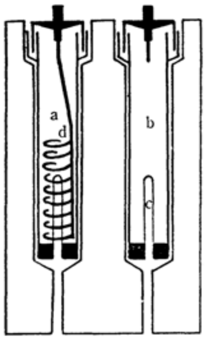

Fig. 2. The cell holder.

(a) Sample cell
(b) Reference cell
(c) Bored capillary for thermocouples
(d) Stirrer

The rate of heating was manually controlled.

Material.—Isotactic polypropylene, Avisun 101117-Q84, was reprecipitated through decalin-methanol, in which the antioxydant had been removed; the precipitate was then washed several times with methanol and dried in a vacuum. The mean molecular weight of the polymer was determined to be 3.7×10^5 by viscometric measurements in decalin.(1)

Decalin was purified by the ordinary method;(2) the ratio of *cis*- to *trans*-decalin was about 3 to 2, as determined by observing the density and the viscosity.

Nitrobenzene was distilled twice in a vacuum.

The urea to be used in calibrating the apparatus for calorimetry was reprecipitated from a methanol solution and dried in a vacuum.

The Pre-treatment of the Sample.—The sample was prepared by putting the weighed solvent and isotactic polypropylene into the sample cell; it was then melted so that the stirrer could be inserted. After the sample cell had been set at the apparatus, the sample was melted once more and then slowly cooled to room temperature at the rate of 0.3—0.5°C/min.; thus a definite condition was given to all samples.

Results and Discussion

The Effect of the Heating Rate.—A sample with an approximately 15% polymer content in a decalin solution was repeatedly run, at the heating rates of approximately 1.25, 0.83, 0.63, 0.50, 0.42 and 0.31°C/min., in order to check the effect of the heating rate on the peak temperature of the dissolution in a highly viscous solution.

We found that the heating rate is not very effective on the dissolution temperature at these rates, while the cooling rate in the pre-treatment is rather effective, as will be discussed later. Therefore, we took the heating rate of 0.50 or 0.42°C/min., in which the reproducibilities of DTA curves seem favorable.

The Isotactic Polypropylene-Decalin System.—The DTA curves obtained for the isotactic polypropylene-decalin system with various proportions of polymer are shown in Fig. 3. The dissolution of a polymer into a solvent is accompanied by each curve reaching a peak which represents the absorption of heat in this experiment. Each curve increases gradually in the low-temperature region,

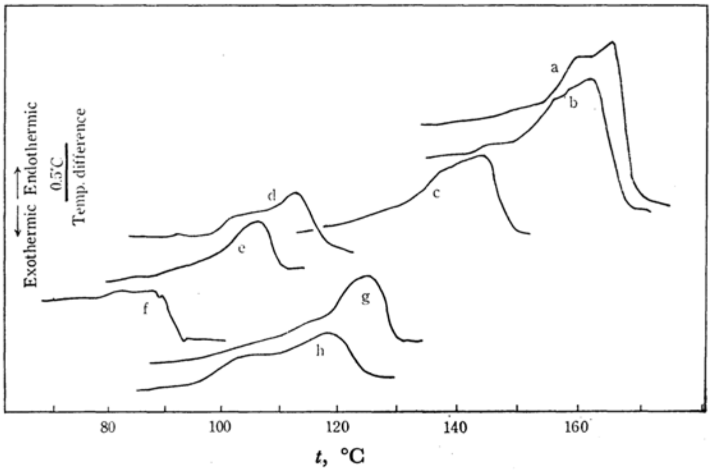

Fig. 3. The DTA curves of isotactic polypropylene-decalin system.

(a) 98% polymer content
(b) 95% polymer content
(c) 64.7% polymer content; stirred
(d) 24.9% polymer content; stirred
(e) 15% polymer content; stirred
(f) 1.05% polymer content; stirred
(g) 34.8% polymer content; annealed; stirre
(h) 34.8% polymer content; rapidly cooled; stirred

The heating rate is 0.5°C/min. except (d) and (f), that of (d) 0.43°C/min., and that of (f) 0.83°C/min.

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1) F. Danusso and G. Moraglio, *Makromol. Chem.*, **28**‘ 250 (1958).

2) A. Weissberger and E. S. Proshauen, "Organic Solvent," Interscience Publisher Inc., New York (1955).

particularly for the mixture with a small polymer content, reaches the top of the peak, and then rapidly descends. The gradual increase in the low-temperature region suggests that the dissolution may begin at a fairly low temperature. Since the dissolution process is completed at the top of the peak, the corresponding temperature will be assigned to the end point of dissolution.

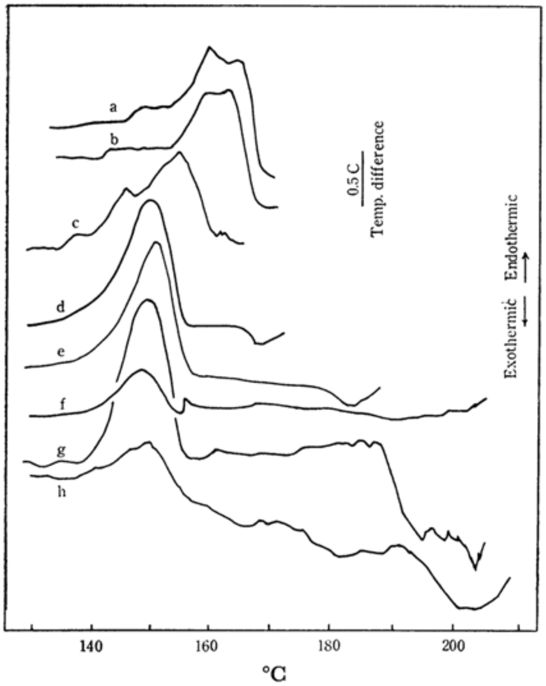


Fig. 4. The DTA curves of isotactic polypropylene-nitrobenzene system.

(a) 98% polymer content
(b) 95% polymer content
(c) 65% polymer content
(d) 41.4% polymer content
(e) 37.5% polymer content
(f) 21.5% polymer content
(g) 25.4% polymer content; stirred
(h) 15.0% polymer content; stirred
The heating rate is 0.5°C/min. for all samples.

By plotting the end points of the dissolution against the polymer content in the mixture, the solubility curve is obtained, as is shown in Fig. 6. Except for the region from 30 to 50% in polymer content, the curve increases smoothly with the polymer content, indicating that decalin is a good solvent for isotactic polypropylene. In the region of the polymer content of from 30 to 50%, the DTA curves are not so reproducible [see Fig. 3. (g) and (h)] and, hence, the end points determined from them are considerably scattered, suggesting that some anomalous states exist in this region. If we connect the curve of a lower polymer content with the other one of a higher content, we must draw the discontinuous curve with a flection in this region shown by the dotted line in Fig. 6. We can not give a full explanation of this anomalous behavior, but it may be due to the existence of two crystal modifications, such as the usual one crystallized from the melt (or from the concentrated solution) and the other either the one from the dilute solution, as confirmed in polyethylene by Flory,[3] or the metastable paracrystalline smectic one.[4]

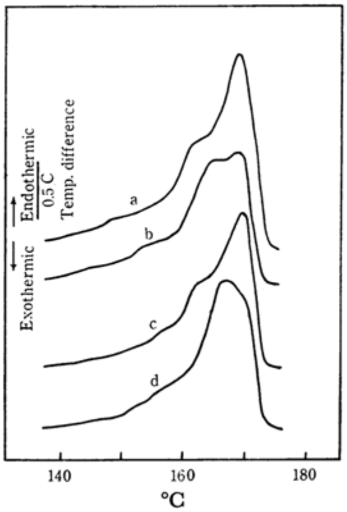
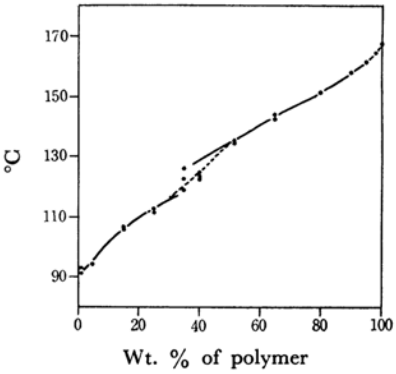


Fig. 5. The DTA curves of isotactic polypropylene.

(a) The sample crystallized by rapid cooling (3—5°C/min.) from the melt
(b) The sample crystallized by slow cooling (0.3—0.5°C/min.) from the melt
(c) The sample crystallized by rapid cooling from the melt with antioxidant
(d) The sample crystallized by slow cooling from the melt with antioxidant



Fie. 6. The solubility curve of isotactic polypropylene-decalin system.

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[3] J. B. Jackson, P. J. Flory and R. Chiang, *Trans. Faraday Soc.*, **59**, 1906 (1963).

[4] G. Natta, *Makromol. Chem.*, **35**, 93 (1960).

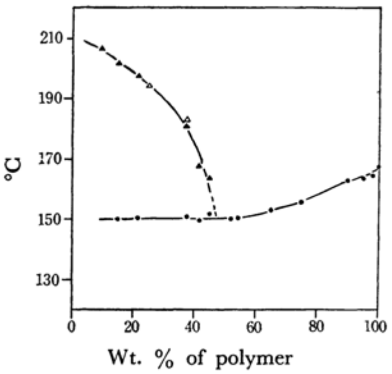

Fig. 7. The solubility curve of isotactic polypropylene-nitrobenzene system.
—●— dissolution point
—▲— phase separation point

The Isotactic Polypropylene-Nitrobenzene System.—The DTA curves obtained for the isotactic polypropylene-nitrobenzene system are shown in Fig. 4. These curves are divided into two types, one appearing in polymer-rich mixtures, and the other in polymer-poor mixtures. The former type contains a main peak the temperature of which decreases with the solvent content, indicating that these peaks may be due to the dissolution of the polymer into nitrobenzene, as in the cases of the decalin system. On the other hand, each curve of the latter type has a peak at almost the same temperature; then it gradually falls until it suddenly shows a small bend at the high-temperature region according to the solvent content, followed by another sharp, upward bend, a bend which is probably due to the beginning of the vaporization of the solvent. In the dilute solutions, the curve after the peak, as a whole, is curved in the endothermic direction as a result of the vaporization of the solvent. When the solution is stirred, as may be seen in Figs. 4. (g) and (h), the curve makes a sharp descent just before the first bend (the cause of this we can not find), and the curve, as a whole, becomes rugged.

By plotting the temperatures of the tops of the peaks and those of the first bends against the polymer contents in the mixtures, the solubility curve shown in Fig. 7 is obtained. "The first bend point-polymer content" curve closely resembles the phase separation curve in the polymer solution, suggesting that two liquid phases may coexist, because nitrobenzene is a bad solvent for isotactic polypropylene.

In order to ascertain if this curve is due to the phase separation, we tried to observe directly the temperature at which the mixture becomes homogeneous or at which the homogeneous solution separates into two phases; we attempted to do this by heating or cooling the polymer-solvent mixture in a test tube immersed in an oil bath. The temperatures obtained by this rough procedure are shown by open triangles in Fig. 7; they are close to the bend point curve, indicating that this curve may be the phase separation curve.

The peak temperature curve is very analogous to the melting curves of the polyethylene - *n*-butyl phthalate and polyethylene - *o*-nitrotoluene systems obtained by Mandelkern and his co-worker[5] with the dilatometric method. These curves show the characteristic feature that each curve contains a slope in the polymer-rich region and a horizontal line at a definite temperature in the polymer-poor region.

In Fig. 7, the extrapolation of the phase separation curve leads to an intersection with the peak temperature curve at an approximately 50% polymer content; this seems to correspond to the furthermost right end of the horizontal part of the peak temperature curve.

When a polymer-poor mixture with a polymer content of less than 50% is heated, the crystallites of the polymer may dissolve into nitrobenzene, forming two polymer solutions in equilibrium with each other at a definite temperature of 150°C, as is indicated by the horizontal line of the dissolution curve. This abrupt dissolution of the polymer shows as a sharp peak in the DTA curves.

The Melting of Pure Isotactic Polypropylene.—The DTA curves of pure isotactic polypropylene show a broad peak, accompanied by a small peak in the low temperature region, and have approximately a 9°C spread, as is illustrated in Fig. 5. The temperature of the top of the main peak, corresponding to the completion of melting, is in the range of 167.7 ± 0.3°C for the samples pre-treated under various conditions.

As may be seen in Fig. 5, the cooling rate in the pre-treatment has a slight effect on the location of the small peak on the low-temperature side. The slower the cooling rate, the more the small peak seems to approach the main peak. The presence of an antioxidant may not produce any effect, showing that the existence of the earlier peak is not due to the thermal degradation and the oxidation of samples.

The double peaks of the melting of isotactic polypropylene have been reported by several authors.[6–8] Ke,[7] one of them, suggests that the double peaks are associated with structural differences, probably different stereospecificities (atactic or syndiotactic) in isotactic polypropylene. Atactic polypropylene has two transitions at 70

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[5] F. A. Quinn, Jr., and L. Mandelkern, *J. Am. Chem. Soc.*, **77**, 781 (1955).

[6] I. M. Tolchinski, N. A. Nechitailo, and A. V. Topchiev, *Plasticheskie Massy*, **1960**, (No. 7) 3 (1960).

[7] B. Ke, "Newer Methods of Polymer Characterization," Polymer Review, No. 6, Interscience Publisher Inc., New York (1964).

[8] R. F. Schwenker, Jr., and R. K. Zuccarello, *J. Polymer Sci., Part C*, (No. 6) 1 (1964).

and 155°C,[9] but the heats of these transitions, 2.1 and 0.30 cal./g.[9] respectively, are too small in comparison with the heat of the fusion of isotactic polypropylene, 20 cal./g.,[9] to enable one to assign the earlier peak to the two transitions of atactic polypropylene. Syndiotactic polypropylene has been reported to melt at 183°C; this seems inadequate to explain the earlier peak.

Schwenker and his co-worker[8] have observed that the DTA curve of drawn polypropylene shows the double peaks at 158 and 174°C; they also observed that if the melt from the drawn fiber is cooled and rerun, the earlier peak disappears. They have concluded that the earlier peak may be ascribed to the disorientation of the crystallites, as has been confirmed in nylon 66 by White.[10] According to them, our samples crystallized by slow cooling and those crystallized by rapid cooling from the melt consist of disoriented and orientated crystallites respectively; this seems curious, though we can not deny the disorientation of crystallites because we have not carried out measurements of the drawn samples.

As may be seen in Figs. 3 (a), (b) and 4 (a), (b), the earlier peak seems to be enlarged by the addition of solvents; this may confirm that it is not due to disorientation, since, the addition of solvents makes it impossible for the disorientation of crystallites (perhaps perfectly at random in solvents) to occur.

On the other hand, on the bases of the X-ray and infrared spectra of samples rapidly cooled and annealed from the melted isotactic polypropylene, though there has been no information obtained by the thermal method, Natta[4] has reported that a rapid cooling of the melted isotactic polypropylene produces a metastable paracrystalline smectic modification in which right- and left-helices of polymers are placed at random in a psuedo-hexagonal cell, while in the usual samples, produced by slow cooling and annealing, they are regularly disposed facing one another, two by two. Though we can not give an explicit conclusion for the earlier peak, since we have not examined the sample by X-ray, it may be suggested that the earlier peak, produced by rapid cooling, is due to the melting of the metastable paracrystalline smectic modification, and that the location and magnitude of the earlier peak varies with the degree of randomness and with the amount of modification.

The Heat of the Fusion of Isotactic Polypropylene.—The heat of the fusion, ΔH_u, of isotactic polypropylene is easily found by the ratio of the area under the DTA peak of the fusion of isotactic polypropylene to that of a known heat change (e. g., the heat of the fusion of urea), or by Flory's equation of melting point depression:[11]

$$1/T_m - 1/T^\circ_m = (\boldsymbol{R}/\Delta H_u)[(V_{2u}/V_1)v_1 - \chi v_1^2] \qquad (1)$$

where T°_m is the melting temperature of a pure polymer; T_m, the melting temperature of a polymer with a diluent; ΔH_u, the heat of the fusion of the polymer per structural-unit mole; χ, the interaction parameter; V_{2u}, the unit molar volume of the polymer; V_1, the molar volume of the diluent, and v_1, the volume fraction of the diluent. The former method gives a value of 1070±100 cal./unit mol. for the heat of fusion, while the latter method gives values of 870±50 cal./unit mol. for a decalin system and 920±50 cal./unit mol. for a nitrobenzene system. These values are in good agreement with each other. The values of the interaction parameter, χ, are estimated to be 0.88 and 2.93 for decalin and nitrobenzene respectively by the above equation. These values may, however, be considered to be a little large.

TABLE I. THE VALUES OF THE HEAT OF FUSION OF ISOTACTIC POLYPROPYLENE

Method	Value of ΔH_u cal./unit mole	Reference
Area of DTA curve	1070±100	This work
Eq. 1		
in decalin	870±50	This work
in nitrobenzene	920±50	This work
Dilatometry	1700	12
Dilatometry	2500	13
Area of DTA curve	650	14
Specific heat	870 (1500)*	9
$dP/dT=\Delta H/T\Delta V$	630	15
$dP/dT=\Delta H/T\Delta V$	2370	16

* Calculated for 100% crystallized.

The above values of the heat of fusion are listed in Table I, together with the values[9,12–16] determined by other authors by using various methods; our values are reasonable, especially considering that Wilkinson and his co-worker,[9] by specific heat measurement, calculated the value to be 1500 cal./unit mol. for the heat of the fusion of the 100% crystallized isotactic polypropylene.

Summary

A DTA apparatus for a polymer solution has been constructed. By using this apparatus, we have investigated the solubility curves of isotactic polypropylene-decalin and isotactic polypropylene-nitrobenzene systems; we have then discussed the DTA curves obtained for these systems, and also

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[9] R. W. Wilkinson and M. Dole, *J. Polymer Sci.*, **58**, 1089 (1962).

[10] T. R. White, *Nature*, **175**, 895 (1955).

[11] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

[12] O. Ishizuka, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 244 (1962).

[13] F. Danusso, G. Moraglio and E. Flores, *Atti accad. nazl. Lincei. Rend., classe sci. fis., mat. e nat.*, **25**, 420 (1958).

[14] B. Ke., *J. Polymer Sci.*, **42**, 15 (1960).

[15] G. Gee, *Proc. Chem. Soc.*, **1957**, 111.

[16] J. R. Schaefgen, *J. Polymer Sci.*, **38**, 549 (1959).

the double peaks which appear in the melting of pure isotactic polypropylene, peaks which may be due to the paracrystalline smectic modification of isotactic polypropylene. The heat of the fusion of isotactic polypropylene has been estimated to be approximately 1000 cal./unit mol. by the methods of measuring the area under the melting peak and of the equation of the melting point depression.

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