

The DTA of Polymer—Solvent Systems. II. The Phase Diagrams of Transtactic Polybutadiene—Toluene, —Diethyl Ketone, and —Nitrobenzene Systems

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(Received May 4, 1971)

ABSTRACT: The phase diagrams of transtactic polybutadiene—toluene, —diethyl ketone, and —nitrobenzene systems were obtained by the DTA method. The solubility of transtactic polybutadiene in the toluene system increased monotonously on increase in temperature. In the case of the transtactic polybutadiene—diethyl ketone and —nitrobenzene systems, on the other hand, the dissolution curves were horizontal in the region of poor polymer content, indicating that diethyl ketone and nitrobenzene were poor solvents. From an analysis of DTA curves, it was found that the transition (solid—solid) peaks of transtactic polybutadiene were shifted to a higher temperature with a solvent content. This phenomenon is then discussed. The heat of fusion was estimated to be approximately 850 cal/unit mol on average from the equation for the melting point depression, and the heat of transition was estimated to be 1.0 kcal/unit mol from the area of the DTA curve.

KEY WORDS DTA / Phase Diagram / Transtactic Polybutadiene—Toluene / Transractic Polybutadiene—Diethyl Ketone / Transtactic Polybutadiene—Nitrobenzene / Transition /

In a previous paper,¹ we studied the dissolution process of a crystalline polymer, isotactic polypropylene, by differential thermal analysis (DTA).

In this paper, we will report on studies of the phase diagrams of transtactic polybutadiene—solvent systems from an analysis of DTA curves. In addition to the usual melting point at 146°C, transtactic polybutadiene has a solid—solid transition at 76°C (reported by Natta and his coworker²), which is considered to be a first-order type by many authors. It is interesting to study what kind of phase diagram can be obtained when the dissolution end point of a polymer approaches the transition point of a polymer with an increase in diluent.

EXPERIMENTAL

Apparatus

The DTA apparatus used was the same as

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that described in the previous paper¹ except for the removal of the stirring device (see Figure 1).

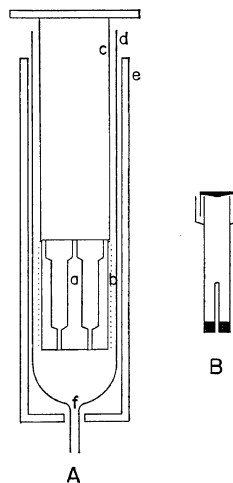


Figure 1. The DTA apparatus (A) and cell (B): a, cell holder; b, heater (nichrome wire); c, wire for suspending the cell holder; d, glass mantle; e, heater mantle; f, outlet for thermocouple.

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The heating rate of the sample was 0.5°C/min.

The emf of the thermocouple (copper—constantan) representing the temperature difference between the sample cell and the reference cell was amplified (Okura, AM1001B), and recorded on a time base chart recorder (YEW, ERI-30). The temperature was determined by measuring the potential difference of the thermocouple between the reference cell and the ice point by means of a potentiometer.

Materials

The polymer, transtactic polybutadiene supplied by Japan Synthetic Rubber Co., Ltd, was reprecipitated through toluene—methanol solution, from which the antioxidant had been removed. The precipitate was then washed several times with methanol and dried *in vacuo*. The molecular weight of the polymer was determined as 5×10^4 in number average by osmotic pressure measurements in toluene.

Toluene was purified by the usual method.³

Diethyl ketone (special grade) was purified by the following procedure in a vacuum system. The more volatile impurities in diethyl ketone were successively vaporized over phosphorus pentoxide in frozen and melted state, and the diethyl ketone was then fractionally distilled into

clean ampoules *in vacuo*. The middle fractions were used.

Nitrobenzene was purified twice in the same way as was diethyl ketone, apart from the use of phosphorus pentoxide.

Preparation of Sample

The sample cell containing the weighed polymer and solvent (total mass of sample was about 3.2 g) was heated until the polymer melted and was homogeneously mixed with the solvent, and then slowly cooled to room temperature.

RESULTS AND DISCUSSION

The DTA curve of pure transtactic polybutadiene shows two distinct endothermic peaks, as is shown in Figure 2. The sharp peak at the lower temperature corresponds to the solid—solid transition, and the other flatter one at the higher temperature corresponds to the fusion.

For the sharp peak, the transition temperature is readily taken as the temperature of the peak top. For the broad peak on the other hand, it is very difficult to determine the temperature in which the phase change takes place. In this experiment the peak top of the broad peak was assigned to the melting and the dissolution tem-

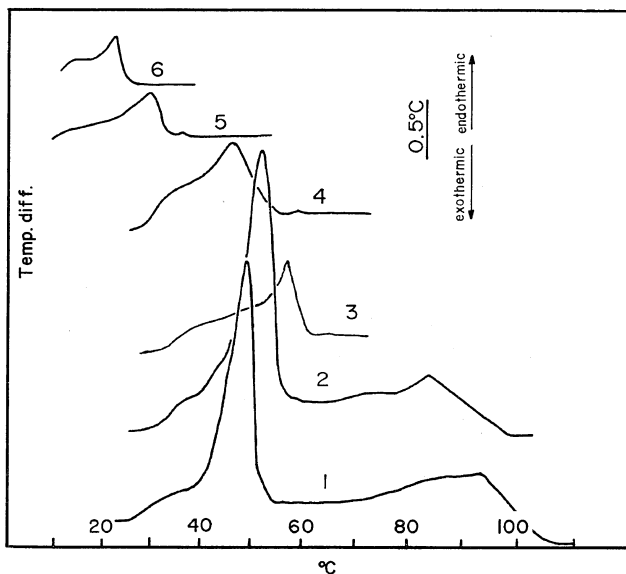


Figure 2. Typical DTA curves for transtactic polybutadiene—toluene system: polymer content, (1) pure; (2) 95.5%; (3) 84.5%; (4) 69.0%; (5) 37.9%; (6) 19.9%.

perature, in a manner similar to the previous paper.¹

When the sample is prepared by slowly cooling from the melt, these peak temperatures are 45°C and 92°C, respectively. These temperatures are reasonable in comparison with those reported by other authors: Natta and his co-worker² reported 76°C and 146°C as the temperatures at which transition and fusion take place, respectively, by means of X-ray diffraction and dilatometric measurements. Dainton and his coworkers⁴ obtained 44°C as the transition temperature from the measurement of heat capacity. Dannis⁵ reported 49°C and 97°C as the transition and fusion temperatures, respectively, using DTA measurements.

Transtactic Polybutadiene—Toluene System

The DTA curves obtained for the transtactic polybutadiene—toluene system with various proportions of polymer are shown in Figure 2. These curves are divided into two types, one appearing in polymer-rich mixtures with 85% or more polymer content, and the other appearing in polymer-poor mixtures. The former type, as is seen for the mixture of 95.2-% polymer contents, contains transition and dissolution peaks; the dissolution peak becomes broader and its temperature decreases with the solvent content, as is usually seen in polymer-diluent systems. The transition peak is similar to that of pure polymer in shape and its temperature increases from 45°C (for pure state) to 56.5°C (for the mixture of 85-% polymer content) with increasing solvent content, which is in remarkable contrast to the effect of solvent content on dissolution.

On the other hand, each DTA curve of the latter type, as may be seen for the sample with 69-% polymer content, shows only a sharp peak which is quite different in shape from the dissolution peak of the former type, and the temperature of this peak gradually decreases with solvent content. The sharp peak of the curves 4 or 5 in Figure 2 is followed by a small endothermic peak which does not appear in curve 6. It is very difficult to interpret the existence of this small peak. A plausible interpretation may be that on cooling the sample from the melted state, its small fraction is left on the wall of

the cell by volume contraction and dried to some extent. On heating this small fraction formed on the wall may show a different small peak from that of the bulk polymer-mixture. This small peak will depend on the polymer content left on the wall, and, therefore, on the concentration of polymer in the original mixture. Curve 6, representing the behavior of a more dilute polymer mixture, will not give this peak. Thus in the following discussion on the phase diagram, this peak will be ignored.

By plotting these peak temperatures against the polymer content in the mixture, the phase diagram is obtained, as is shown in Figure 3.

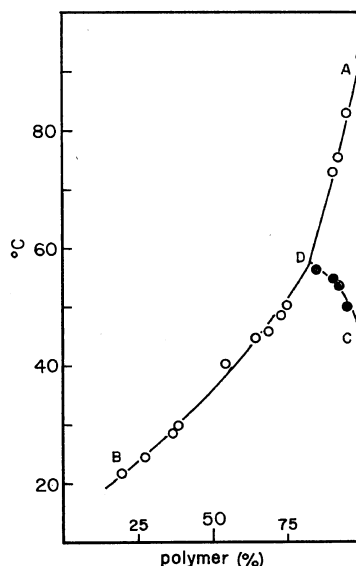


Figure 3. The phase diagram of the transtactic system: ○, dissolution temp; ●, polybutadiene—toluene transition temp.

We can see certain noteworthy points in the phase diagram of the transtactic polybutadiene and toluene system:

1. The solid (I)—solid (II) transition temperature curve CD intersects the dissolution curve AB at D, which corresponds to about 85 weight per cent in polymer content, indicating that AD is the dissolution curve (solubility curve) of the solid (II) and DB is that of the solid (I).

Since the slope of the solubility curve is inversely proportional to the heat of dissolution and the slope of AD is steeper than that of DB,

the heat of dissolution of solid (I) must be larger than that of solid (II), which may be reasonable, considering that the heat of dissolution of solid (I) will be nearly equal to the sum of the heat of dissolution of solid (II) and the heat of transition from solid (I) to solid (II).

2. The transition temperature increases with solvent content. This is rather odd, considering that the solid—solid transition in crystal is not usually affected by the solvent in the phase diagram containing low-molecular substances.

Two explanations for these phenomena are proposed as follows

(a) Stabilization of surface energy by surrounding solvent molecules;

(b) The thickening of the crystallites and a decrease in the crystalline defects in the crystallization process in solution, because the solvent makes polymer segments mobile and polymer segments easily orient.

Nagatani and his coworker^{6,7} reported the following fact favorable to the first explanation in the study of an ionic crystal, NH_4NO_3 . When the surface active reagents, octadecylamine, octadecylamine nitrate, and octadecylamine acetate, are adsorbed on the surface of the ammonium nitrate crystal, the solid—solid transition of ammonium nitrate from phase (III) to (II) is interfered with and the transition temperature increases. On the other hand, when the crystal of ammonium nitrate is exposed to water vapor, both the transition temperatures for phase (IV)→(III) and phase (III)→(II) decrease.

The second explanation would seem to be more reasonable from certain other information in spite of the above; Takayanagi and his coworkers⁸ reported from electron microscopic observations that the single crystal lamella of transtactic polybutadiene crystallized from a dilute solution is thickened and cave-like defects of crystal lamella appear on thermal annealing at 58°C (this phenomena cannot be observed below 58°C), and the transition temperature of the thickened lamella increases.

Moreover, we have found even on the crystal prepared from the melt that the transition and fusion temperatures of transtactic polybutadiene rise up to 60.5 and 105°C, respectively, on annealing at 90°C for 20 hr.⁹

The above data on pure polymers show at least that transition temperatures shift to higher ranges as the thickness of the lamella increases. If in the polymer—solvent system, the existence of solvent favours the thickening of the lamella in the crystallization process or for other reasons, the transition temperature will be expected to increase with an increase in solvent content.

Transtactic Polybutadiene—Diethyl Ketone System

The DTA curves obtained for the transtactic polybutadiene—diethylketone system with various proportions of polymer are seen in Figure 4.

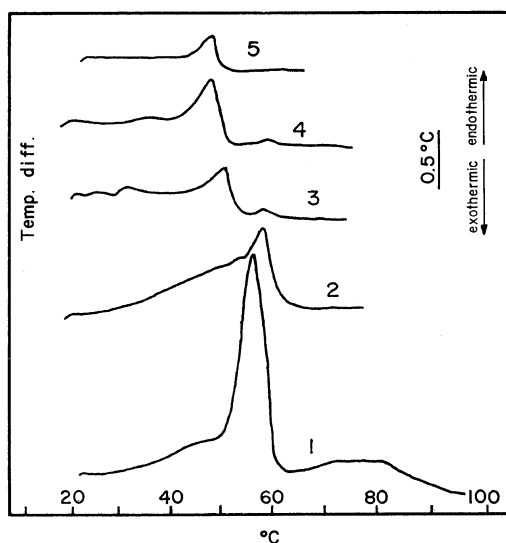


Figure 4. Typical DTA curves for transtactic polybutadiene—diethyl ketone system: polymer content, (1) 90.0%; (2) 79.2%; (3) 57.0%; (4) 43.4%; (5) 28.5%.

These curves are also divided into two types, one appearing in polymer-rich mixtures, and the other appearing in polymer-poor mixtures. The former type shows behavior similar to that appearing in polymer-rich mixtures in a toluene system, apart from extremely broad peaks of dissolution, as is seen for the mixture of 90% polymer content. Each curve of the latter type has a peak at almost the same temperature.

By plotting the peak temperatures against the polymer content in the mixture, a phase diagram as shown in Figure 5 is obtained.

The peak temperature curve assigned to the dissolution is similar to the melting curves of

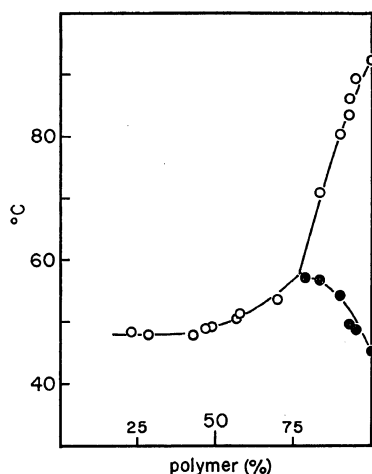


Figure 5. The phase diagram of transtactic polybutadiene—diethylketone system: ○, dissolution temp; ●, transition temp.

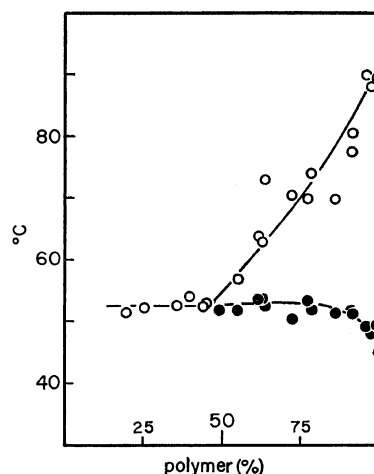


Figure 6. The phase diagram of transtactic polybutadiene—nitrobenzene system: ○, dissolution temp; ●, transition temp.

the isotactic polypropylene—nitrobenzene system, described in the previous paper,¹ and the polyethylene—*n*-butylphthalate and polyethylene—*o*-nitrotoluene systems obtained by Mandelkern and his coworker¹⁰ with dilatometric measurements. These curves show the characteristic features in that each curve contains a line with greater slope in the polymer-rich region and a horizontal line at a definite temperature in the polymer-poor region. This type of dissolution curve suggests, as described previously,¹ that diethylketone is a bad solvent for transtactic polybutadiene and consequently a phase separation curve should exist above the horizontal line of the dissolution curve.

In order to ascertain if the phase separation curve exists, 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. However we could not ascertain the existence of phase separation by this rough procedure because of the bubbling of solvent vapor before the opalescence disappeared.

Transtactic Polybutadiene—Nitrobenzene System

This system is similar to the diethylketone system. The phase diagram of the transtactic

polybutadiene—nitrobenzene system obtained is seen in Figure 6. A large difference in densities between solvent and polymer makes polymer crystallites rise to the surface of the solution and the viscous sol of the polymer does not smoothly dissolve into homogeneous solution when the mixture is heated. The dissolution peaks of DTA curves are, as a result, extremely broadened and their temperatures are scattered.

In this system we could not find the phase separation because the decomposition of polymer in nitrobenzene at high temperature and the coloration of solution made a direct observation impossible.

Heat of Fusion and Transition of Transtactic Polybutadiene

The heat of fusion, ΔH_u of transtactic polybutadiene is found by comparing the area under the DTA peak of the fusion of transtactic polybutadiene with that of a known heat change (*e.g.*, the heat of fusion of biphenyl) or by using Flory's equation for melting point depression;¹¹

$$1/T_m - 1/T_m^0 = (R/\Delta H_u)(V_{2u}/V_1)[v_1 - \chi v_1^2]$$

where T_m^0 is the melting temperature of a pure polymer; T_m , the melting temperature of a polymer with diluent; ΔH_u , the heat of fusion of the polymer per structural unit mole; χ , the interaction parameter; V_{2u} , the unit molar

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Table I. The values of the heat of fusion of transtactic polybutadiene

Method	Value of ΔH_u , cal/unit mol	Reference
Area of DTA	ca. 400	This work
Flory's equation		
in toluene	750 \pm 70	This work
in diethylketone	900 \pm 90	This work
in nitrobenzene	860 \pm 90	This work
Dilatometry		
in α -chloronaphthalene	1060	Natta, <i>et al.</i> ²
in benzophenone	1170	Natta, <i>et al.</i> ²
Area of DTA peak	1100	Danusso, <i>et al.</i> ¹¹

Table II. The values of the heat of transition of transtactic polybutadiene

Method	Value of ΔH_{tu} , cal/unit mol	Reference
Area of DTA peak	1000 \pm 100	This work
Heat capacity	820 \pm 80	Dainton, <i>et al.</i> ⁴
Dilatometry	2200	Natta, <i>et al.</i> ²

volume of the polymer; V_1 , the molar volume of the diluent; v_1 , the volume fraction of the diluent; and R , the gas constant. Values of heat of fusion obtained by these two methods are listed in Table I, together with those determined by other authors using various methods.

The value, 400 cal/unit mol, obtained by using the peak area is not particularly accurate, since the peak of fusion spreads over a wide temperature range and it is very difficult to estimate its area. This value is underestimated since we do not evaluate the degree of crystallinity and the observed values of the heats of fusion, and transition must be divided by the factor of the degree of crystallinity. On the other hand, the values which are obtained by performing the least-squares treatment according to Flory's equation for high concentration range of polymer ($v_1 < 0.1$), are 750 cal/unit mol in the toluene system; 900 cal/unit mol in the diethylketone system, and 860 cal/unit mol in the nitrobenzene system. They are a little smaller than those obtained by other authors.

The values of interaction parameters, χ , are estimated to be -0.10 for the toluene system; 0.68 for the diethylketone system, and about 0.2 for the nitrobenzene system, but the value of the nitrobenzene system is not usable in practice because of the poor accuracy ascribed

to the scattered dissolution temperatures.

The heat of transition, ΔH_{tu} , of transtactic polybutadiene is found by using the peak area of transition, and the value is listed in Table II together with those obtained by other authors. The value obtained in this study may be in close agreement with that reported by Dainton and his coworkers,⁴ but it is half the value obtained by Natta and his coworker.²

For the transtactic polybutadiene, the phase diagram and the values of interaction parameters show that toluene is a good solvent and both diethylketone and nitrobenzene are bad solvents.

The increments of the transition temperature with solvent content are 11, 12, and 7°C for toluene, diethylketone, and nitrobenzene, respectively. The amounts of increments should not be related to solvent power alone, as they seem to be affected rather by other factors such as viscosity and density.

Acknowledgement. The authors wish to express their deep appreciation to Mr. M. Fukuda for his assistance and to the Japan Synthetic Rubber Co. Ltd, for supplying the sample.

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