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Gaseous Polymer Solutions: Solubilities of Polydimethylsiloxane
and Polypropylene in Carbon Dioxide and
Viscosities of Polydimethylsiloxane in Carbon Dioxide

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fraction PDMS ~ 0.026 to ~ 0.33, pressure ~ 80 to ~ 450 atm, and
35° to 80°C temperature region. Polypropylene is soluble in
carbon dioxide in the weight fraction PP ~ 0.062 to ~ 0.33,
pressure ~ 440 to ~ 950 atm, and 165° to 190°C temperature
region. Solutions of PDMS (M ~ 17.$_5\cdot$10³, viscosity 168
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Polydimethylsiloxane is soluble in carbon dioxide in the weight fraction PDMS ~ 0.026 to ~ 0.33, pressure ~ 80 to ~ 450 atm, and 35° to 80°C temperature region. Polypropylene is soluble in carbon dioxide in the weight fraction PP ~ 0.062 to ~0.33, pressure ~ 440 to ~ 950 atm, and 165° to 190°C temperature region. Solutions of PDMS ($M \sim 17._5 \cdot 10^3$, viscosity 168 centipoises) at 0.26 weight fraction in CO_2 have viscosities in the 3.8 to 7.4 centipoise range.

Supercritical polymer solutions should be attractive
possibilities as media for the fabrication and transport of
polymers. Measurements of the appreciable solubilities of
polydimethylsiloxane, PDMS, and polypropylene, PP, in carbon
dioxide, CO_2, and the relatively low viscosities of PDMS in CO_2
support this hypothesis.

I.   Solubility Measurements

   A.   Experimental Methods

      Solubilities were determined by observing visually the
onset of critical opalescence while very slowly decreasing or
increasing gas pressure in a pressure system (Fig 1.). A weighed
charge of polymer was placed in pressure vessel c. with 6 to 12
steel balls (0.794 cm diameter). The system was outgassed at
room temperature. Carbon dioxide at pressure ~100 atm was
admitted to the system, and the system was heated to temperature
of measurement. During the heating, the pressure increased; this
was controlled easily by admitting CO_2 as necessary from the
heated storage vessel s.v. (in which CO_2 had been condensed
before start of the experiment) or by bleeding to the atmosphere.
Gas pressures were adjusted so as to dissolve polymers at the
temperatures of the experiments. The pressure vessel was rocked
slowly about its axis through an angle of about 120°. Steel
balls in the vessel provided some stirring. The 0.6328 μ laser
beam passing through the cell and projected on a screen permitted
easy observation of dissolution of polymer in gas and
precipitation of polymer from gas. Pressures were observed by a
diaphragm strain gage pressure transducer t. which was calibrated

1

at elevated temperatures using free piston gages. Pressures were adjusted, usually by slowly bleeding the system, to observe the onsets and disappearances of critical miscibility, usually seen as complete absorption (or interruption) or undiminished transmission of the laser beam. Pressures between onset and ending of critical opalescence usually differed by less than one atmosphere; maximum differences were a few atmospheres.

Solubilities were observed repeatedly by raising and lowering gas pressures. Care was exercised in observing as carefully as possible to minimize the failure to observe any condensed phase in "blind spots" in the pressure cell. A volume reducing cylinder with inside diameter equal to the unobstructed diameters of the cell windows was used to eliminate "blind spots" in a few runs. A light scattering cell (1), which had no "blind spots" when viewed from a variety of angles, was used to check for failures to observe condensed phases.

The solvent gas, carbon dioxide, CO_2, 99.99+percent pure (Matheson) was used as received. Polydimethylsiloxanes (PDMS) used in solubility studies were:

Supplier	Designation	Nominal Molecular Weight
General Electric Co.	SF-96-350	$17.5 \cdot 10^3$
	CF1215	$40 \cdot 10^3$
	Viscasil 300,000	$300 \cdot 10^3$
	(AM009)	$1.0 \cdot 10^6$

Polypropylene solubility studies were made using Hercules, Inc., Profax 6301 polypropylene.

B.   Data Analyses

Concentrations of polymers in gas were estimated from weights of polymers charged to the pressure vessel and the weight of CO_2 in the pressure vessel calculated from the observed pressure, p, and temperature, T, and the net volume of the pressure cell using a real gas equation:

$$\text{Weight of gas} = M_{gas} \cdot \frac{P \cdot (V_{cell} - V_{polymer} - V_{balls})}{Z(p,T) \cdot R \cdot T}$$

where $V_{polymer} = \dfrac{\text{weight of polymer}}{\text{crystal density}}$

$Z(p,T)$ = compressibility factor of pure gas.

Using literature values of the compressibility factor of pure CO_2(2) rather than the unknown compressibilities of the solutions probably overestimated the compressibility factors slightly resulting in overestimates of solubilities. Using crystal densities (3) to estimate the volumes occupied by polymer molecules in solution may have underestimated these volumes slightly leading to underestimates of solubilities.

C.   Results of Solubility Studies

PDMS and PP are quite soluble in dense CO_2. Concentrations in excess of 33 percent by weight PDMS in CO_2 and 20 percent PP were measured in this study. In earlier work solubilities up to 37 percent PP in CO_2 were observed (4).

The pressure-concentration isotherms for PDMS-CO_2 and PP-CO_2 solutions are given in Figures 2 and 3. PDMS ($M \sim 17._5 \cdot 10^3$) is quite readily soluble in CO_2 in the 90 to 140 atmosphere region at 35°C and ~300 atmospheres at 80°C. PDMS of molecular weight

about $17._5 \cdot 10^3$ is a viscous oil at room temperature; it dissolves readily in dense CO_2 if densities are sufficiently great. PP ($\overline{M}_w \sim 40 \cdot 10^3$ to $50 \cdot 10^3$) dissolves in CO_2 at temperatures above its melting point. Because fiber grade PP melts between $150°$ and $160°C$, solubility measurements were made from $165°$ to $190°C$. In this temperature range, pressures of CO_2 dissolving PP increase from ~ 440 atm to ~ 950 atm. At these higher temperatures, higher pressures are necessary to produce CO_2 densities high enough to dissolve molten polymer. Pressure-temperature-concentration measurements of critical immiscibility are shown as isobars in Figures 4 and 5. The almost closed loops of temperature-concentration plots for PDMS in CO_2 (Figure 4) suggest that the one phase, PDMS soluble in CO_2 region may enclose a two phase volume in pressure-temperature-concentration space as shown in Figure 6. The solubility data for PP in CO_2 measured to date indicate that the region of miscibility in pressure-temperature-concentration space lies above a surface shaped such that miscibility temperatures increase with concentration of PP at constant pressure and decrease with increasing pressure at constant concentration (Figure 5 and 7).

Temperature dependence of the solubilities of PDMS and PP in CO_2 are quite different (Figures 4 and 7) in that temperature-concentration plots at constant pressure for PP in CO_2 appear to be only the upper left hand portions of any almost closed loops like those for PDMS in CO_2. That the lower portions of solubility curves like those for PDMS in CO_2 probability cannot

4

be observed for PP in CO_2 is not surprising because the PP is partially crystalline, m.p.~160°C, precluding solubility at temperatures much below the melting temperature. The solubility of PP in CO_2 increases with increasing temperature at constant pressure (Figure 5). The solubility of PDMS in CO_2 decreases with increasing temperature at constant pressure at most concentrations (Figure 4). At lower concentrations of polymer and at higher temperatures, solubilities increase with increasing temperatures as they must if the p-T-concentration space encloses a two phase region (Figure 6).

Pressures necessary to dissolve PDMS in carbon dioxide increase with increasing molecular weight as shown in Figure 8 for concentrations approximately 15 weight percent. Pressure increases were about 30 percent from ~300 to ~390 atm as molecular weight increases from $17._5 \cdot 10^3$ to $40 \cdot 10^3$ and about 15 percent to ~440 atm as molecular weight increases from $40 \cdot 10^3$ to $1.0 \cdot 10^6$.

D.   Solution Thermodynamics

For any multicomponent system the Helmholtz and Gibbs partial molal free energies are related by the equations.

$$\Delta \overline{A}_1 = \left(\frac{\partial \Delta A}{\partial n_1} \right)_{v_1 T} = \Delta \overline{G}_1 = \left(\frac{\partial \Delta G}{\partial n_1} \right)_{p_1 T} = RT \; \ln \left(\frac{f_1}{f_1^o} \right) \tag{1}$$

where

$$\Delta \overline{A}_1 = \Delta \overline{E}_1 - T \; \Delta \overline{S}_1 \qquad\qquad\qquad (\text{Helmholtz})$$
$$\Delta \overline{G}_1 = \Delta \overline{H}_1 - T \; \Delta \overline{S}_1 = \Delta \overline{E}_1 + p \; \Delta \overline{V}_1 - T \Delta \overline{S}_1 \quad (\text{Gibbs})$$

f_1 = fugacity of gas at equilibrium pressure,
f_1^o = fugacity of gas in standard state at temperature T (taken as $f_1^o = 1$ atm)

and

$$RT \; \ln f = \frac{RT}{p} \; \ln p - \int_o^p \alpha(p,T) \, dp \tag{2}$$

where
$$V = \frac{RT}{p} - \alpha(p,T) \qquad 3$$

is the equation of state of the real gas. The temperature derivatives of the partial molal free energies may be used to calculate changes in partial molal energies and entropies of dilution:

$$\left(\frac{\partial \Delta \overline{A}_1}{\partial T}\right)_1 = -\Delta \overline{S}_1 \qquad 4$$

and,

$$\left[\frac{\partial (\Delta \overline{A}_1/T)}{\partial T}\right]_V = -\frac{\Delta \overline{A}_1}{T^2} + \frac{1}{T}\left(\frac{\partial \Delta \overline{A}_1}{\partial T}\right)_1 = -\frac{\Delta \overline{E}_1}{T^2} = R\left(\frac{\partial \ln f_1}{\partial T}\right)_V \qquad 5$$

Because the pressure system has essentially constant volume, partial molal energies of dilution are calculated and reported rather than the usual partial molal enthalpies (heats) of dilution which can be calculated only for systems maintained at constant external pressure.

Partial molal energies, $\Delta \overline{E}_1$, and entropies, $\Delta \overline{S}_1$, of dilution are given in Table I. These are $\Delta \overline{E}_1 \sim -0.6_6$ to -1.1_4 kcal/mol and $\Delta \overline{S}_1 \sim -13._9$ cal/mol $^\circ K$ for CO_2 in the PDMS-CO_2 system in which solubility decreases with increasing temperature at constant pressure. For CO_2 in the PP-CO_2 solutions, $\Delta \overline{E}_1 \sim 5._0$ to 1.5_3 kcal and $\Delta \overline{S}_1 \sim -2._1$ to $-8._8$ cal/mol-$^\circ K$ as weight fraction decreases from 0.20 to 0.06_9 PP.

The partial molal energies and entropies of dilution of CO_2 in gaseous solutions of PDMS in CO_2 are quite different. The interactions of the nonpolar but strongly quadripolar and quite polarizable CO_2 molecules with the quite polarizable polydimethylsiloxane and the much less polarizable polypropylene

6

should be quite different. These differences in interactions should be manifest in differences in solution thermodynamics at comparable pressures and temperatures.

II Viscosity Measurements

Viscosities of PDMS (MW ~ $17._5 \cdot 10^3$) - CO_2 solutions were measured using a rolling ball viscosimeter, Ruska Instrument Corp., Model 1602. The viscosimeter was calibrated using silicone oils of known viscosities, i.e. Dow-Corning 200-5 silicone fluid.

The viscosities of solutions of 0.26 weight fraction PDMS in CO_2 are relatively low from 0.038 to 0.074 poise decreasing with increasing temperature and pressure. Results are given in Table II. The viscosity of the pure silicone oil (MW ~ $17._5 \cdot 10^3$) is about 1.64 poise; thus the 0.26 weight fraction PDMS solutions have viscosities only two to five percent as great as the pure silicone polymer. The solution viscosities are about 100 times the viscosities of pure carbon dioxide in the pressure-temperature region of the solutions.

Conclusions

Polydimethylsiloxanes and ploypropylene are easily dissolved and sufficiently soluble in carbon dioxide at easily accessible pressures (p < 450 atm for PDMS and p < 900 atm for PP) that these solutions can be useful as media in processing these

7

polymers.   Further, the viscosities of polydimethylsiloxane $(M \cdot 17._5 \cdot 10^3)$ at useful concentrations (weight fraction PDMS $\cdot$ 0.26) are low (3.8 to 7.4 centipoises) suggesting that gaseous solutions of polymers may be attractive alternatives to melts, liquid solutions, and suspensions in transporting and fabricating polymers.

Table I

Partial Molal Energies and Entropies of Dilution of Carbon Dioxide in Gaseous Solutions of Polydimethylsiloxane and Polypropylene in Carbon Dioxide

Polymer	Concentration Weight Percent	Temperature °C	Partial Molal Energy of Dilution ΔE_1 kcal/mol	Partial Molal Entropy of Dilution ΔS_1 cal/mol
PDMS	2.6	80	-0.8_1	$-13._6$
Polydimethyl-siloxane	$17._5$	35 and 80	-1.1_4	$-11._7$
$\overline{M} \sim 17._5 \cdot 10^3$	$33._2$	35 and 80	-0.6_6	$-13._2$
PP	$6._8$	175	1.5_3	$-8._5$
polypropylene	10	186	1.7_9	$-8._3$
$\overline{M}_w \sim (40 \text{ to } 50) \cdot 10^3$	12	187	2.9_5	$-6._0$
	16	183	3.6_0	$-4._9$
	$20._4$	180	$5._0$	$-2._1$

Table II

Viscosities of Gaseous Solutions of Polydimethylsiloxane in
Carbon Dioxide and of Pure Components

		Viscosity-centipoises	$\frac{g}{cm \cdot sec} \cdot 10^-$	
	Temperature--> Pressure	35°C	50°C	80°C
PDMS - CO_2 (0.26 wt.fraction polydimethylsiloxane M~17.5·10³)	82 atm 114 132 148 211	7.4 4.3	5.4 3.3	4.1
PDMS polydimethylsiloxane (pure)		164		
CO_2 (pure)	82 114 132 148 211	0.040* 0.061*	0.050* 0.057*	0.050*

* Viscosity data for CO_2 are estimated by interpolation of published
data cited in reference 5.

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4. Unpublished data.

5. E. L. Quinn & C. L. Jones, _Carbon Dioxide_ (Reinhold, 1936) p.44; M. P. Vukalovich & V. V. Altunin, _Thermophysical Properties of Carbon Dioxide_, translated by D. S. Gaunt (Collet's, Ltd, 1968), p. 387; A. Michels, A. Botzen & W. Schurman, _Physica_, _23,_ 95 (1957); J. Kestin, J. H. Whitelaw & T. F. Zien, _Physica_, _30_, 161 (1964).
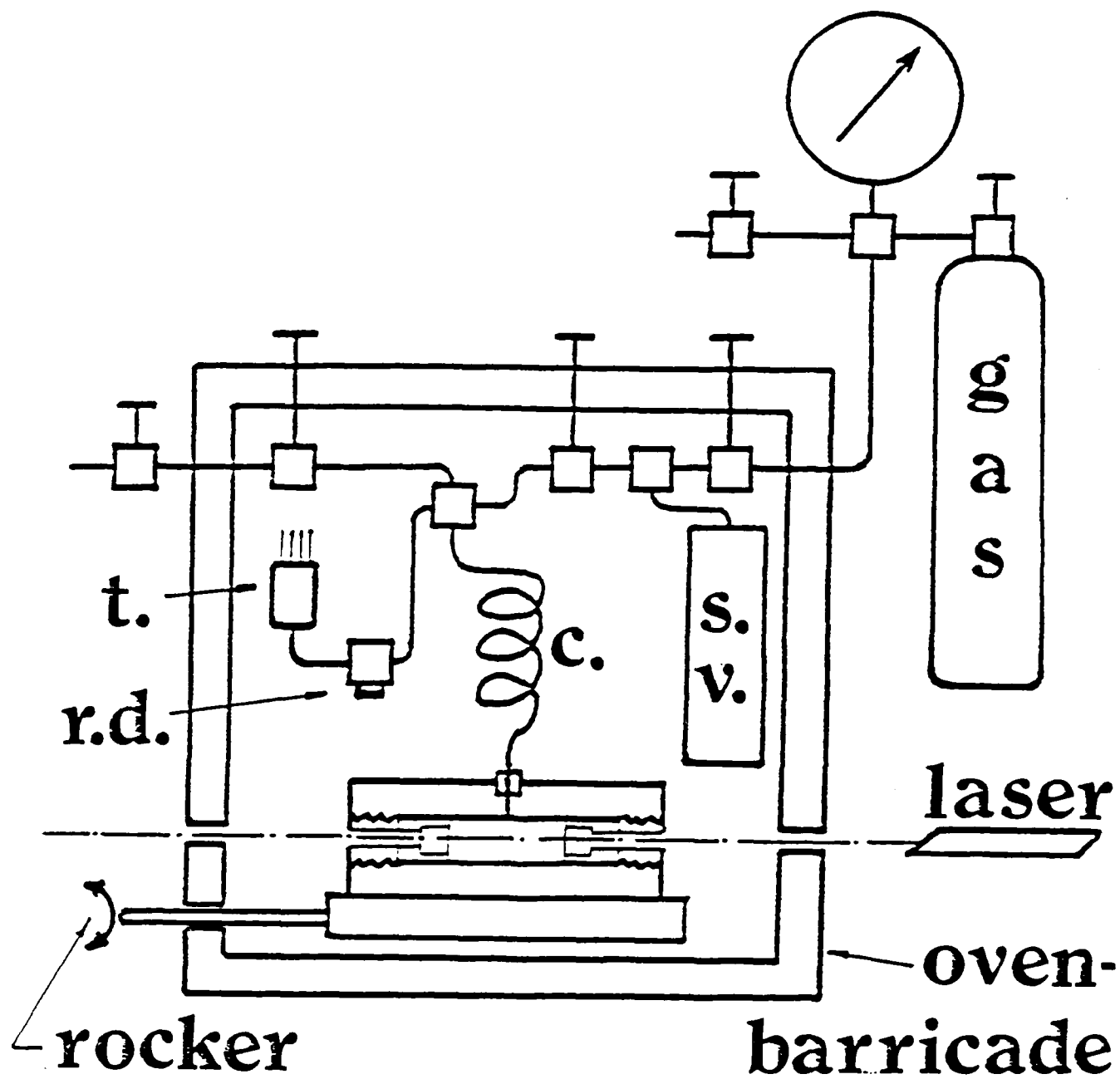
Captions for Figures

Figure 1 - Polymer in Gas Solubility Apparatus. (Components: t.: pressure transducer, r.d.: rupture disc, c.: pressure cell, s.v.: storange vessel for gas at high pressure.)

Figure 2 - Solubility Isotherms for Polydimethylsiloxane in Carbon Dioxide, Plots of CO_2 Pressures versus Weight Fractions Polydimethylsiloxane at Constant Temperatures.

Figure 3 - Solubility Isotherms for Polypropylene in Carbon Dioxide, Plots of CO_2 Pressures versus Weight Fractions Polypropylene at Constant Temperatures.

Figure 4 - Solubility Isobars for Polydimethylsiloxane in Carbon Dioxide, Plots of Temperatures versus Weight Fractions Polydimethylsiloxane at Constant Pressures (CO_2).

Figure 5 - Solubility Isobars for Polypropylene in Carbon Dioxide, Plots of Temperatures versus Weight Fractions Polypropylene at Constant Pressures (CO_2).

Figure 6 - Plot of Pressure – Temperature – Concentration (X) Behavior of Solubility of Polydimethylsiloxane in Carbon Dioxide.

Figure 7 - Plot of Pressure – Temperature – Concentration (X) Behavior of Solubility of Polypropylene in Carbon Dioxide.

Figure 8 - Effects of Molecular Weight on Solubility of Polydimethylsiloxane in Carbon Dioxide, Plot of CO_2 Pressures versus Temperatures for Solutions of Polydimethylsiloxane of Various Molecular Weights at 0.18 Weight Fraction PDMS.

CO_2 PRESSURE - ATM

POLYPROPYLENE CONCENTRATION - WEIGHT FRACTION

TEMPERATURE - °C

POLYPROPYLENE CONCENTRATION - WEIGHT FRACTION

CO_2 PRESSURE - ATM

WT
FRACT
PP

TEMPERATURE - °C

CO_2 PRESSURE - ATM

TEMPERATURE - °C

Figure 1 - Polymer in Gas Solubility Apparatus. (Components: t.: pressure transducer, r.d.: rupture disc, c.: pressure cell, s.v.: storange vessel for gas at high pressure.)
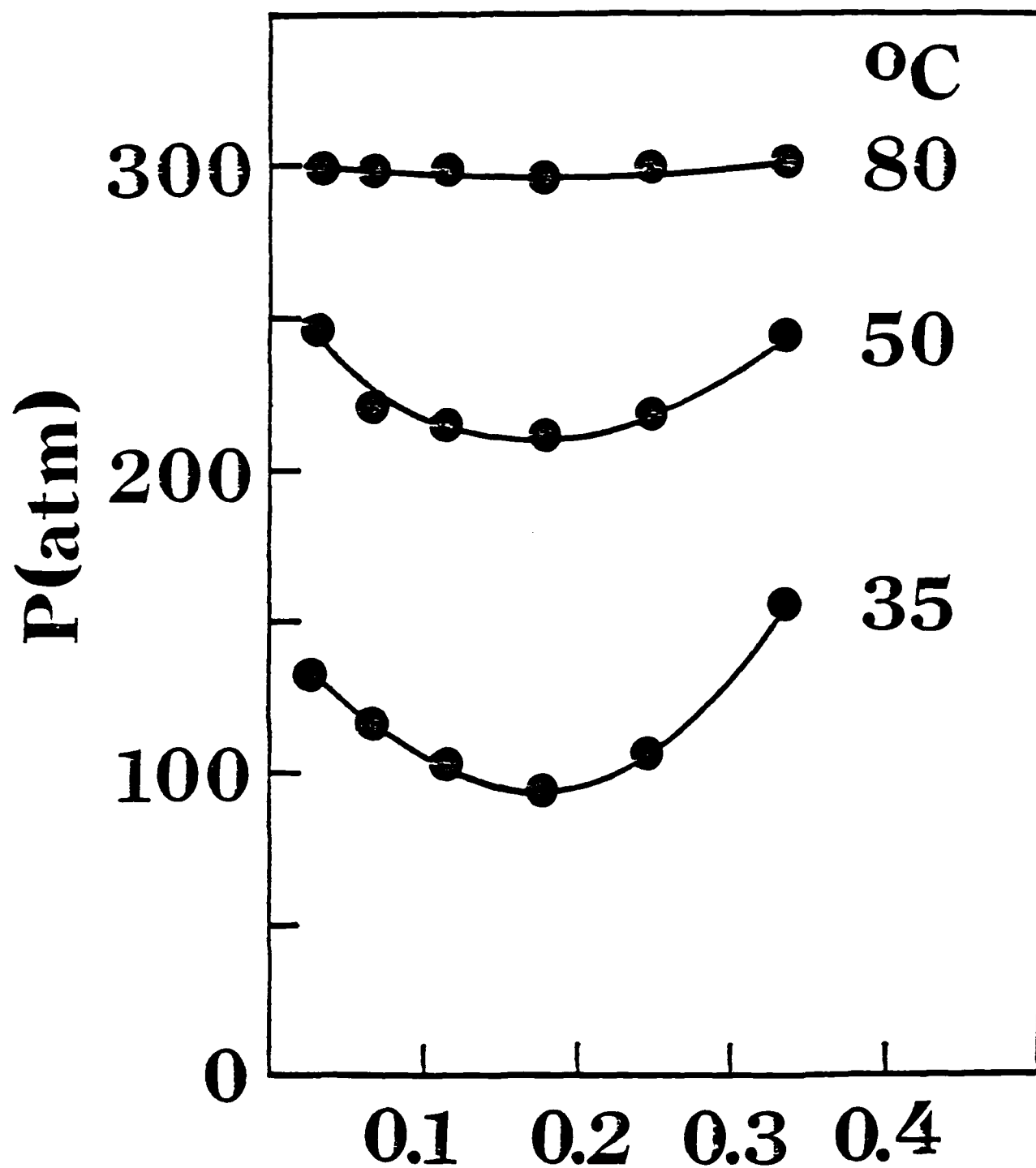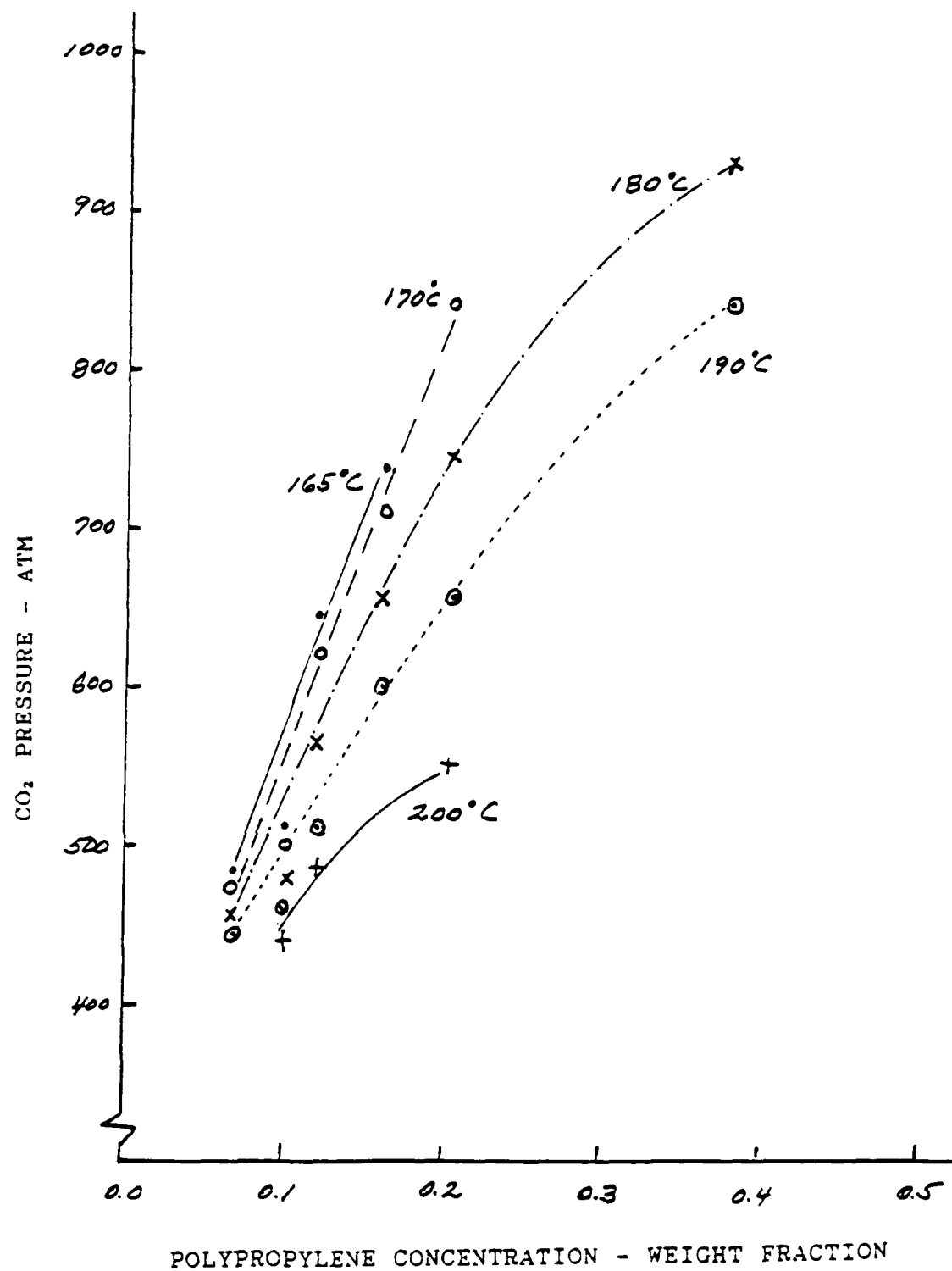
Figure 2 –   Solubility Isotherms for Polydimethylsiloxane in
                Carbon Dioxide, Plots of CO_2 Pressures versus
                Weight Fractions Polydimethylsiloxane at Constant
                Temperatures.

Figure 3 -   Solubility Isotherms for Polypropylene in Carbon
              Dioxide, Plots of CO_2 Pressures versus Weight
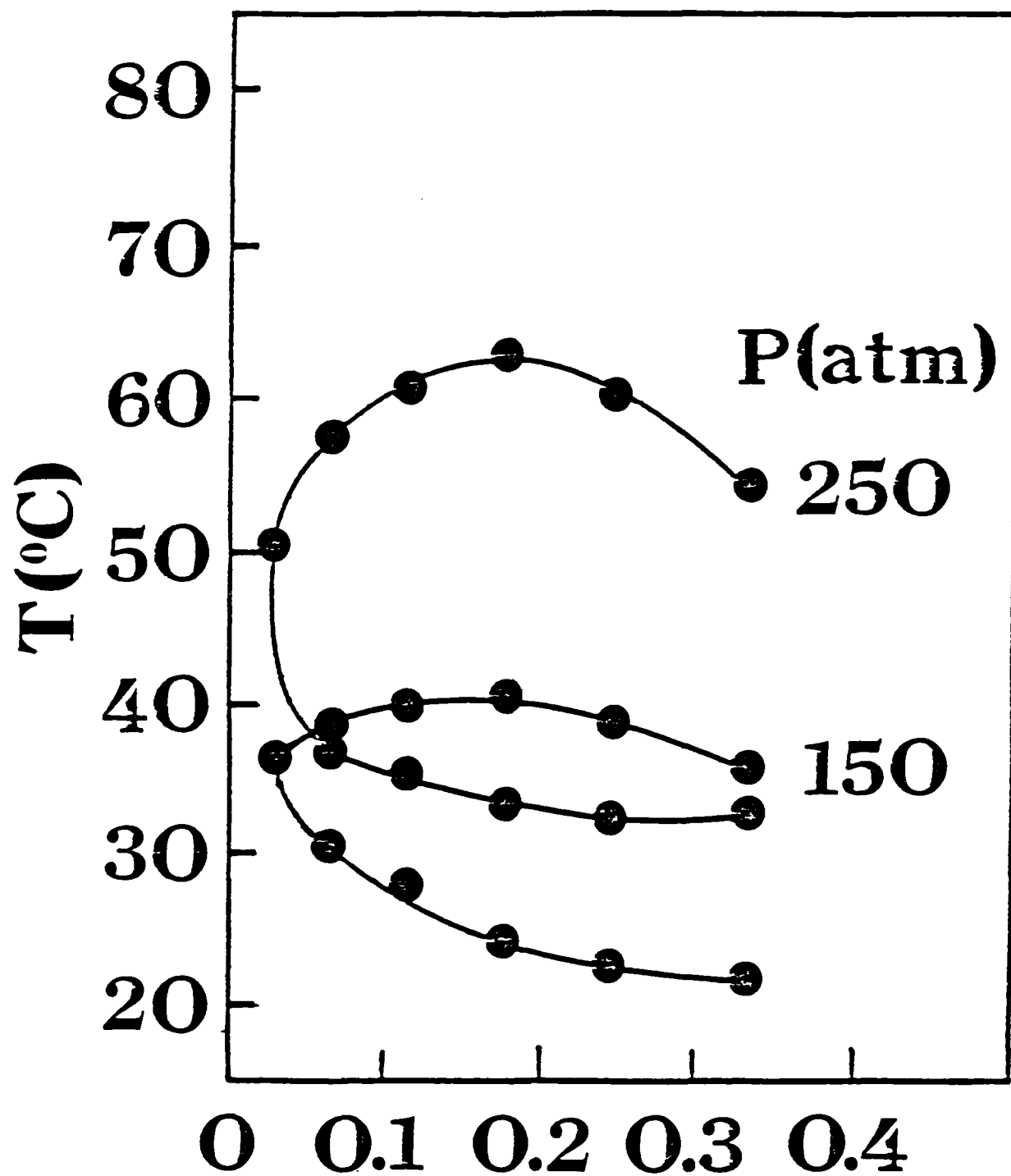   Fractions Polypropylene at Constant Temperatures.

Figure 4 - Solubility Isobars for Polydimethylsiloxane in Carbon Dioxide, Plots of Temperatures versus Weight Fractions Polydimethylsiloxane at Constant Pressures (CO_2).
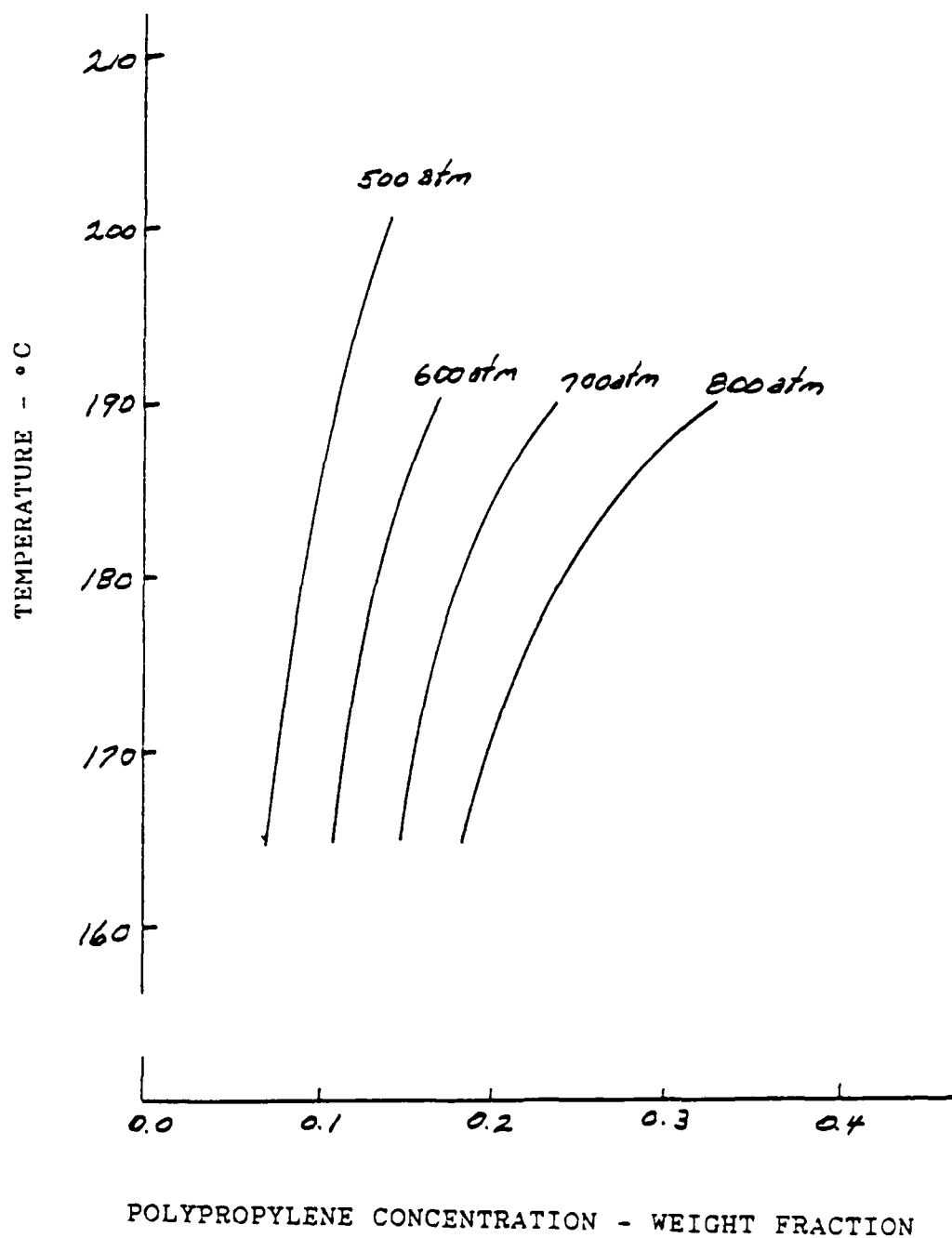
TEMPERATURE - °C

210
200
190
180
170
160

500 atm
600 atm 700 atm 800 atm

0.0   0.1   0.2   0.3   0.4

POLYPROPYLENE CONCENTRATION - WEIGHT FRACTION

Figure 5 -   Solubility Isobars for Polypropylene in Carbon
Dioxide, Plots of Temperatures versus Weight
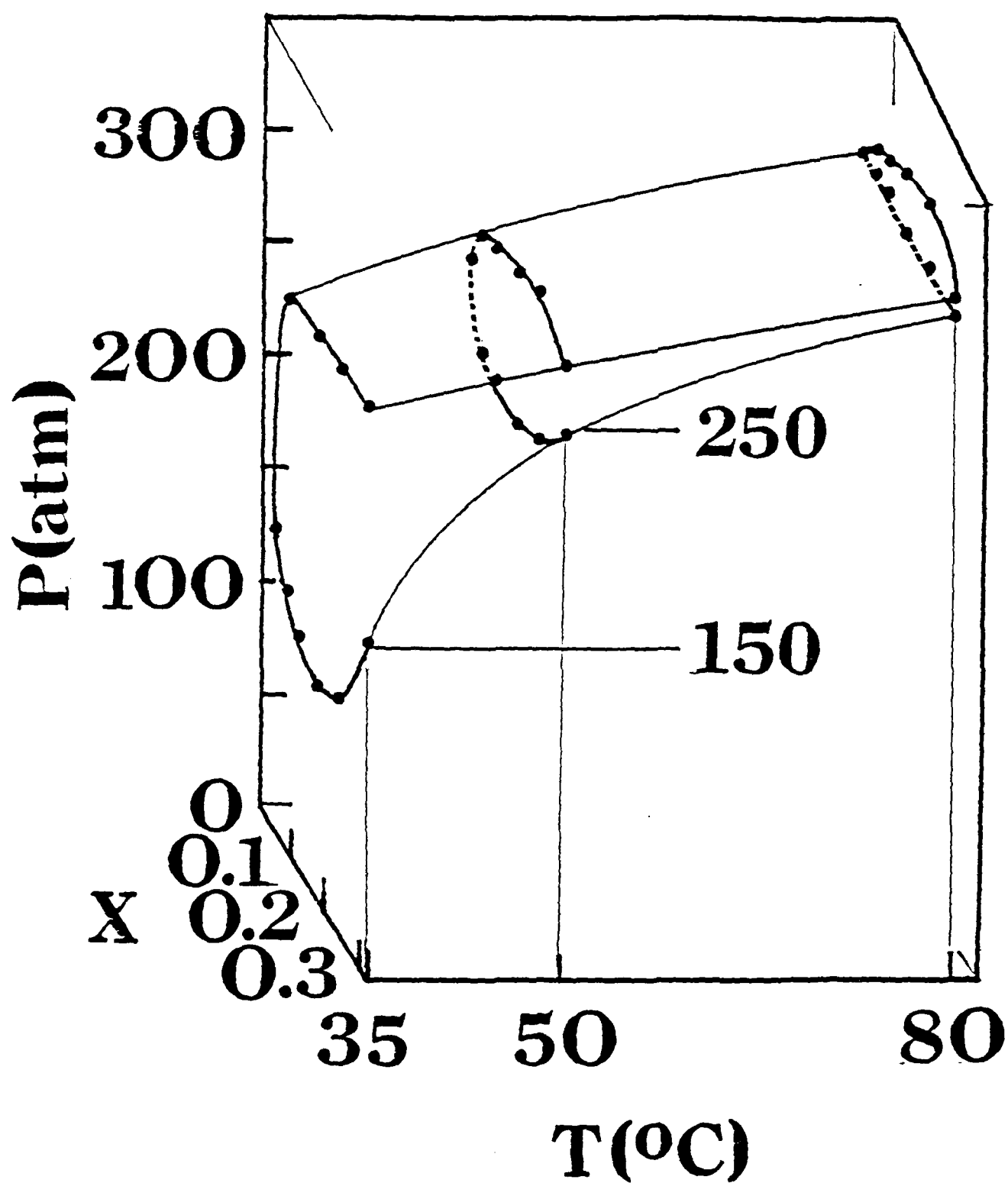Fractions Polypropylene at Constant Pressures
(CO_2).

Figure 6 – Plot of Pressure – Temperature – Concentration (X) Behavior of Solubility of Polydimethylsiloxane in Carbon Dioxide.
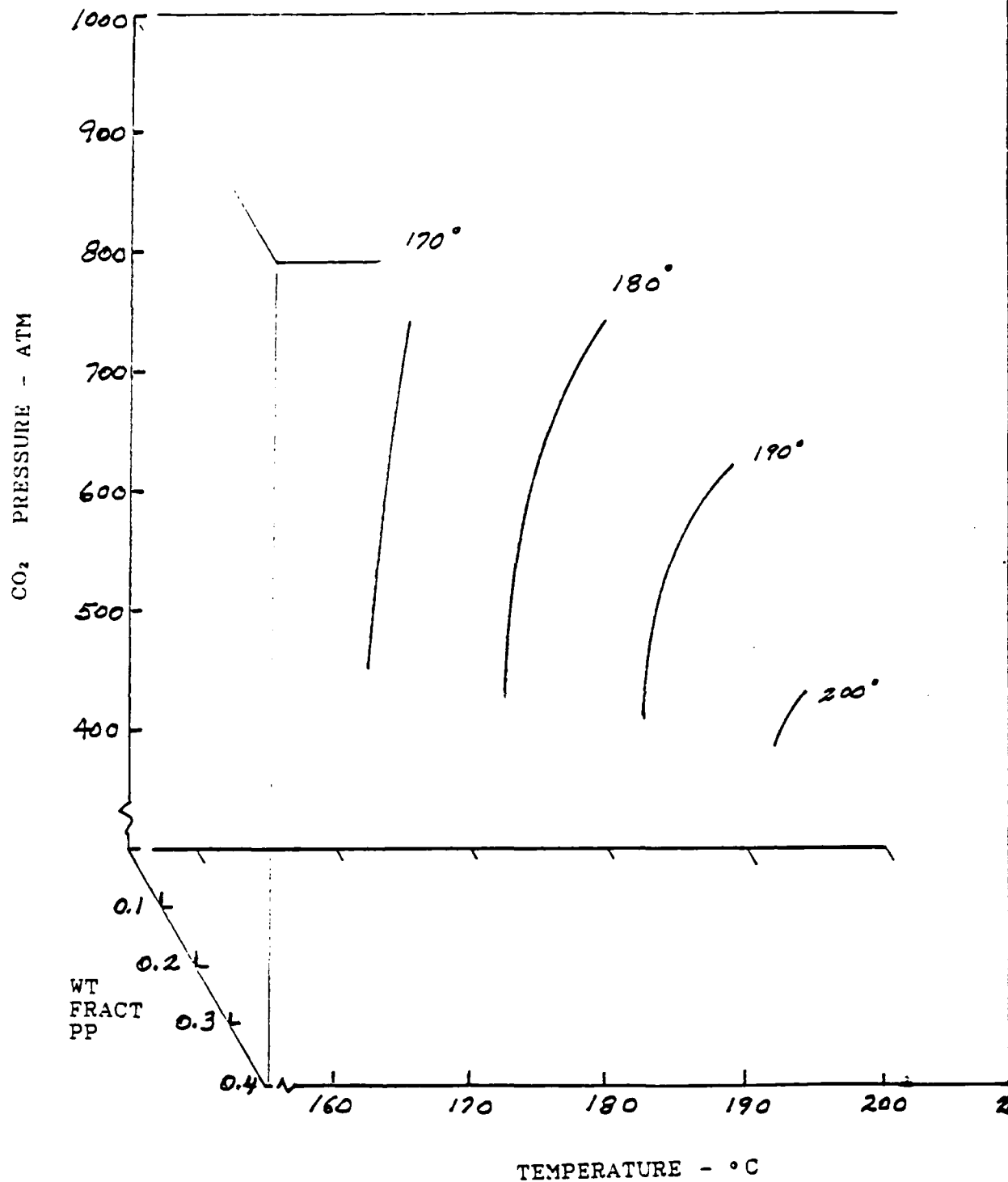
Figure 7 –   Plot of Pressure – Temperature – Concentration (X)
               Behavior of Solubility of Polypropylene in Carbon
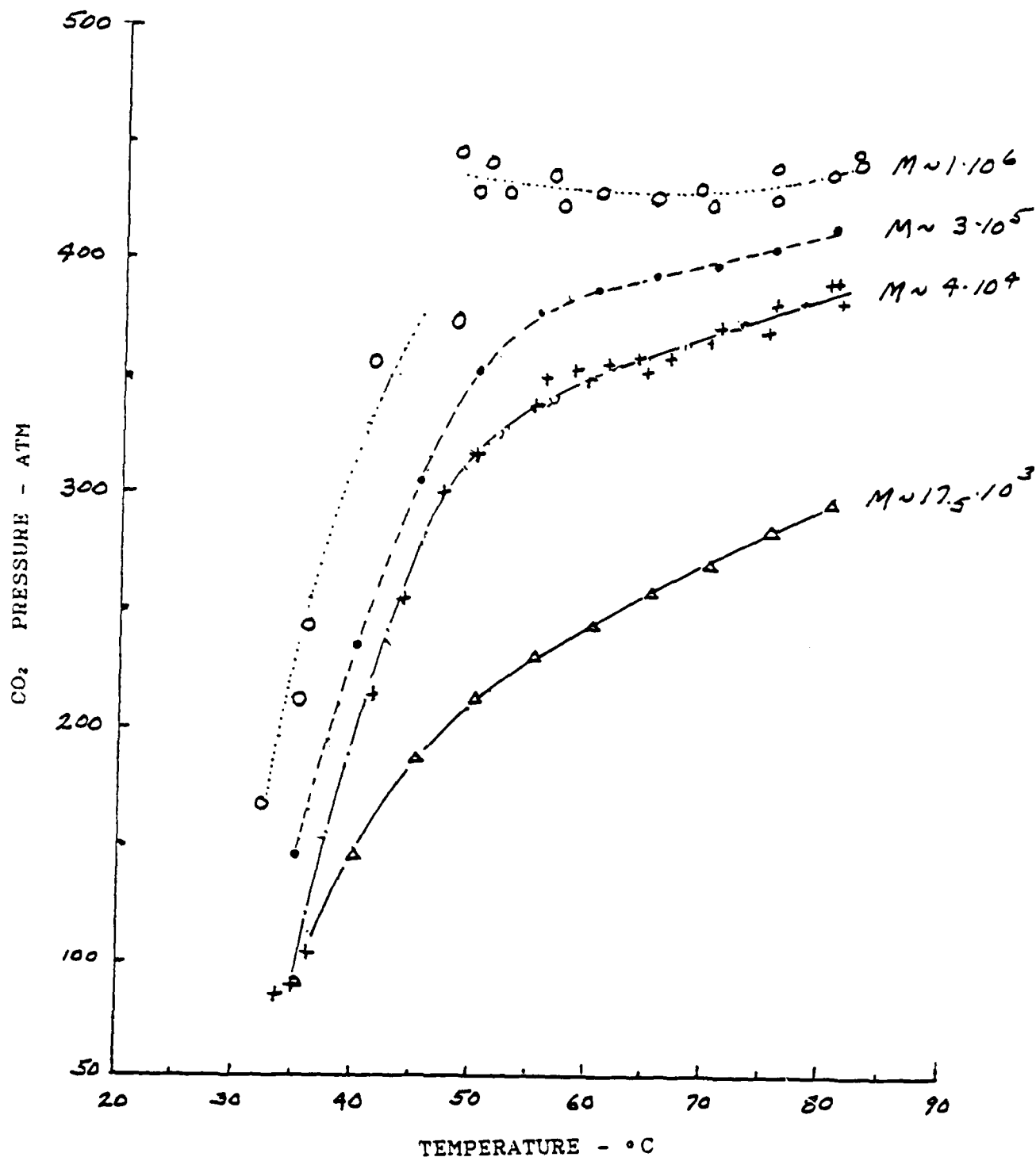   Dioxide.

Figure 8 - Effects of Molecular Weight on Solubility of
Polydimethylsiloxane in Carbon Dioxide, Plot of
CO_2 Pressures versus Temperatures for Solutions of
Polydimethylsiloxane of Various Molecular Weights
at 0.18 Weight Fraction PDMS.

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