

## Inverse gas chromatographic observation of thermodynamic interaction between poly (vinylidene fluoride) and organic solvents

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### Summary

Inverse gas chromatography (IGC) has been applied to observe the interaction between poly(vinylidene fluoride) (PVDF) and organic solvent systems under conditions approaching infinite dilution of the volatile component.

The specific retention volumes ( $V_g^0$ ) were calculated from the retention volumes of the PVDF/solvent systems. The retention diagrams (RDs) which were plotted as  $\ln V_g^0$  vs. reciprocal temperature, corresponded with the thermodynamic behavior of PVDF. PVDF dissolves well in carbonyl-containing solvents at high temperatures. In these systems, the solution is converted easily to a thermoreversible gel by standing at room temperature. The Flory-Huggins interaction parameter ( $\chi_{12}$ ) and molar heat of sorption of probe absorbed by the amorphous part of PVDF ( $\Delta H_1^s$ ) calculated from the retention values indicated that the characteristics of the interaction between PVDF and the solvent (probe) varied with temperature and probe properties. The results of IGC of PVDF/solvent systems were discussed in relation to the dissolution and gelation behavior of PVDF.

### Introduction

Poly(vinylidene fluoride) (PVDF) is a semicrystalline piezoelectric polymer. Its crystallinity varies from 35 - 70%, depending on the method of preparation and the thermomechanical history. Crystallinity is an important factor that affects toughness and mechanical strength. Moreover, PVDF is highly insoluble and thermally stable. Experimentally, PVDF is resistant to most inorganic acids and organic solvents even at elevated temperatures. However, PVDF dissolves well in aliphatic or cyclic ketones at elevated temperatures, and the solution is converted easily into a thermoreversible gel at room temperature (1). In a series of PVDF/carbonyl-containing solvent systems, we used acetone (ACE), methyl ethyl ketone (MEK), and ethyl acetate (EA) as the solvents to study the thermoreversible gelation behavior of PVDF solution.

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Recently, we reported (2) the gelation of PVDF/aliphatic ketone systems in which the aliphatic ketone used has a large number of carbon atoms such as 3-octanone (3-OCTO), 3-heptanone (3-HEPO), 3-pentanone (3-PENO), cyclohexanone (c-HEXO), and cycloheptanone (c-HEPO). The gelation behavior of PVDF in carbonyl-containing solvents was investigated by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction measurement, and differential scanning calorimetry (DSC). The dissolution and gelation behavior of PVDF was considered in interpreting the results of the interaction between PVDF and the solvents. Leonard et al. (3) pointed out that through FTIR observation of the PVDF/PMMA systems, the major driving force leading to the compatibility between PVDF and PMMA is the formation of hydrogen bonds involving the carbonyl groups of PMMA and the CH<sub>2</sub> groups of PVDF. In this system, PMMA behaves as the solvent of PVDF. For the same reason, we considered that PVDF could be dissolved in this solvent, by forming hydrogen bonds with the carbonyl groups in the carbonyl-containing solvents. In our previous report (2), to observe the gelation dynamics of PVDF/carbonyl-containing solvent systems, the attenuated total reflection (ATR)-FTIR method was applied. It was assumed from the FTIR spectra that PVDF existing in the ketone solution exhibited a wide variety of conformations at the beginning of the gelation process, and that they aggregated to form chains in the later stage of gelation, leading to the TGTG conformation. However, the thermodynamics of PVDF dissolution and gelation remains to be clarified.

IGC is a useful method (4) to observe the interaction between polymer and solvent. The IGC technique utilizes conventional gas chromatography with minor modifications to measure the interaction between pure solvents (mobile phase, probes) and the polymer (the stationary phase) in terms of the retention time of the probes. The term "solute" is used to represent a low molecular weight volatile solvent that is usually injected into a gas chromatographic column.

In this study, the IGC method was applied to investigate the thermodynamic interaction between PVDF and solvents (probes), and to clarify the dissolution and gelation behavior of PVDF.

In IGC measurements, unretained gas such as methane or air which is inert to the stationary phase, was used as the marker. The time spent by the probe during passage through the stationary phase is expressed as:

$$t_N = t_R - t_M \quad [1]$$

where  $t_N$  is net retention time,  $t_R$  is probe retention time, and  $t_M$  is marker retention time. The measured net retention volume of the probe is

$$V = t_N \cdot F \quad [2]$$

where  $F$  is the volume flow rate of the carrier gas measured at room temperature ( $T_r$ ) at outlet pressure ( $P_o$ ). However, the volume flow rate is not constant along the column, i.e., it is higher at the outlet than at the inlet, because the inlet pressure  $P_i$  is greater than  $P_o$ . Therefore, the volume flow rate measured at  $P_o$  should be corrected to the volume flow rate in the column due to the compressibility of the gas. The correction factor derived by Purnell (5) is as follows.

$$J = \frac{3((P_i/P_o)^2 - 1)}{2((P_i/P_o)^3 - 1)} \quad [3]$$

Then, the net retention volume in the column is

$$V_N = t_N \cdot F \cdot J \quad [4]$$

Usually, the retention volume is obtained using the experimental peak maximum to define the retention time. The specific retention volume ( $V_g^0$ ) is calculated using

$$V_g^0 = \frac{V_N \cdot 273.15 \cdot (P_0 - P_w)}{w \cdot P_0 \cdot T_r} \quad [5]$$

where  $w$  is the mass of the polymeric stationary phase,  $P_0$  is pressure at the outlet,  $T_r$  is room temperature, and  $P_w$  is the vapor pressure of water at  $T_r$ .

The polymer/solvent interaction parameter ( $\chi_{12}$ ) is

$$\chi_{12} = \ln \frac{273.15 \cdot R \cdot v_2}{V_g^0 \cdot V_1 \cdot P_1^0} - 1 - \frac{P_1^0}{R \cdot T} (B_{11} - V_1) \quad [6]$$

where  $R$  is the gas constant,  $V_1$  is the molar volume of the probe,  $P_1^0$  is the vapor pressure,  $B_{11}$  is the second virial coefficient of the probe in the gaseous state, and  $v_2$  is the specific volume of the polymer at column temperature.  $V_1$ ,  $P_1^0$ , and  $B_{11}$  of the probe are calculated from the equations and values reported by Daubert and Danner (6). In IGC, the solute/solvent relationship is reversed as compared with that of an ordinary polymer solution. The solvent vapor becomes the solute dissolved in the polymer at infinite dilution so that subscripts 1 and 2 denote solvent and polymer, respectively.

## Experiments

The probes (solvents) used in this work are shown in Table 1. They were selected to represent several groups of chemically different families. They were

**Table 1** Physical properties of probes (solvents)

Probe	Abbreviation	Bp <sup>o</sup> C
n-hexane	n-HEX	69
n-octane	n-OCT	126
3-octanone	3-OCTO	167
3-heptanone	3-HEPO	149
3-hexanone	3-HEXO	123
3-pentanone	3-PENO	101
methyl ethyl ketone	MEK	79.6
acetone	ACE	56.3
cycloheptanone	c-HEPO	179
cyclohexanone	c-HEXO	155
$\gamma$ -butyrolactone	$\gamma$ -BL	204
dimethylacetamide	DMA	163
dimethylformamide	DMF	153
ethyl acetate	EA	77

purchased as reagent grade, and used without further purification. PVDF was Kureha w#1100 (supplied by Kureha Chemical Co.,  $M_w = 47 \times 10^4$ ,  $T_m = 177$  °C, Crystallinity = 59.5%).

Preparation of the gas chromatographic column proceeded as follows: An accurately weighed amount of PVDF was completely dissolved in DMF under

stirring. A solid support (Chromosorb WAW DMCS 60 - 80 mesh) coated with PVDF was dried in vacuum for 24 hr and packed into stainless steel columns having an inner diameter x length = 2.2 x 2000 mm. The column descriptions are shown in Table 2.

**Table 2** Column description and IGC conditions

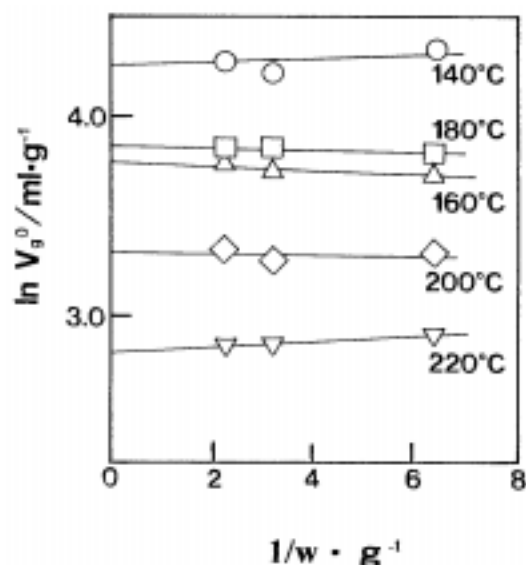
Column no.	PVDF weight/g	Support weight/g	Loading /%
1	0.159	1.79	8
2	0.319	1.79	15
3	0.450	1.79	20

Support: Chromosorb WAW DMCS 60 - 80 mesh;  
 Column: Stainless steel, inner diameter x length = 2.2 x 2000 mm; Carrier gas: He; Flow rate: 25 ml/min;  
 Marker: CH<sub>4</sub>; Detector: FID; Injection volume: < 0.1  $\mu$  l

IGC experiments were performed on a gas chromatograph (GC 380, G.L.Science Co.) equipped with a flame ionization detector (FID). Helium carrier gas was introduced at a flow rate of 25 ml/min, and measurements were made using a soap bubble flow meter at room temperature. Injection of probe vapor at infinite dilution mixed with methane gas as a marker was performed manually using a Hamilton microsyringe (full scale 1  $\mu$  l). The temperature of the injection port and the detector was 30 °C higher than the oven temperature. The retention time was determined from the maximum peak.

## Results and Discussion

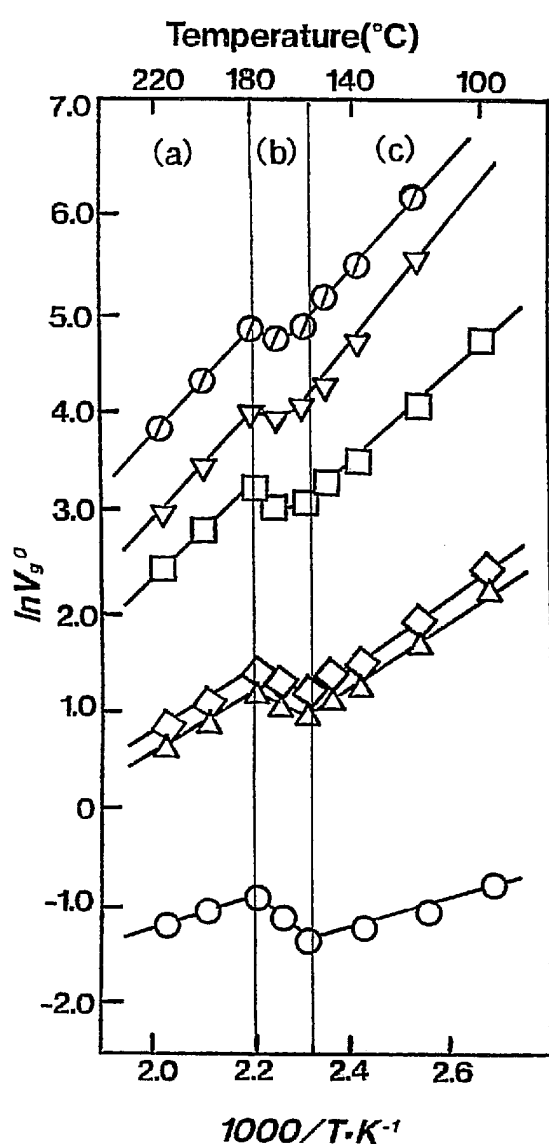
Figure 1 shows the dependence of the retention volume of DMA on PVDF loading measured below and above the melting temperature of PVDF (140 - 220 °C).



**Figure 1** Dependence of the retention volume of DMA on PVDF loading.

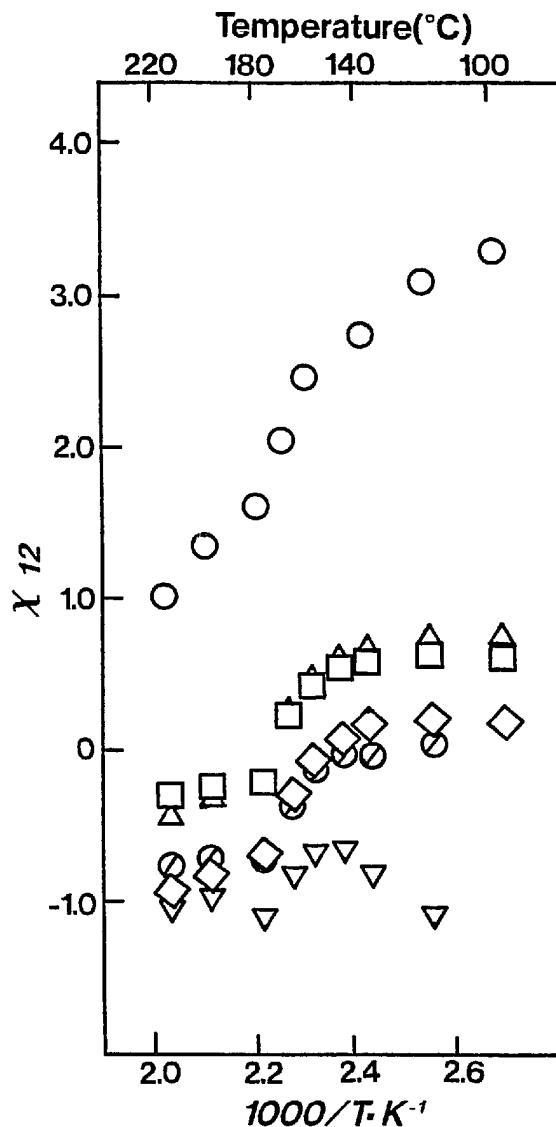
The retention volume data were extrapolated to infinite loading of the PVDF to eliminate probe absorption on the surface of the support. The plots of  $\ln V_g^0$  vs.  $1/w$

are almost linear and independent of the column loadings. This means that the values of the retention volumes obtained using 8, 15, and 20% loading columns will almost be the same if measurements are performed at the same column temperature. Consequently, we used the 15% loading column (column no.2 in Table 2) in subsequent experiments.



**Figure 2** Specific retention volumes of PVDF/probe systems at various temperatures as a function of reciprocal absolute temperature.

○:n-HEX, △:EA, ◇:ACE,  
□:c-HEXO, ▽:DMF, ⊙:γ-BL



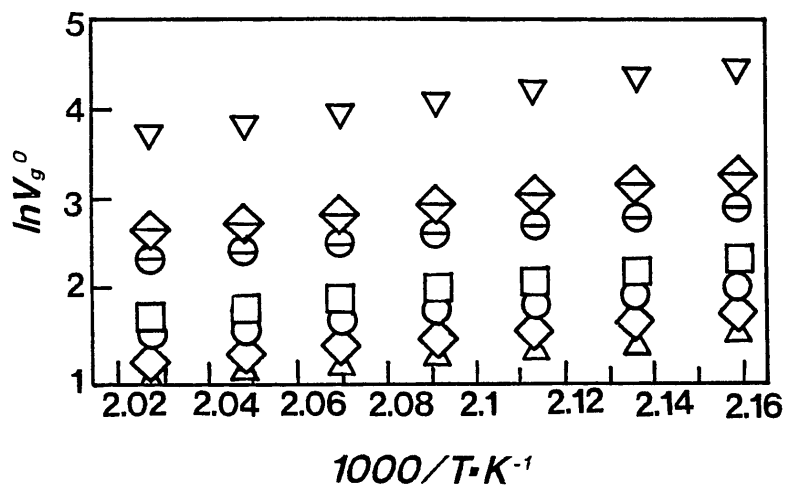
**Figure 3** Interaction parameter,  $\chi_{12}$  of PVDF/probe systems at various temperatures as a function of reciprocal absolute temperature.

○:HEX, △:EA, ◇:ACE,  
□:c-HEXO, ▽:DMF, ⊙:γ-BL

Figure 2 shows the specific retention volumes ( $V_g^0$ ) of different solvents (probes) by PVDF obtained over a wide temperature range of 110 – 220 °C. The  $\ln V_g^0$  of hydrocarbons such as n-HEX did not show remarkable adsorption. Only diffusion

took place when hydrocarbons were injected into the column as probes to measure the interaction between PVDF and solvent. However, when carbonyl-containing solvents such as ketones or ester (ACE, c-HEXO, or EA) were injected, the more the probe dissolved into the stationary phase, the greater the net retention volume per stationary phase became. For the semicrystalline polymer, crystalline and amorphous regions coexist in the bulk in the lower temperature region (c) in Figure 2. In this region, it can be assumed that the crystal is inert to the probe and vapor sorption occurs in the amorphous region. In region (b) in Figure 2, the crystal begins to melt, enlarging the amorphous region and leading to more vapor sorption, so that the curve turns upward until the end of the melting process. Above the melting temperature, region (a) in Figure 2, the curve turns downward.

The interaction parameters ( $\chi_{12}$ ) between PVDF and the probes were determined using equation [6] from  $V_g^0$  at different temperatures for some PVDF/solvent systems (Figure 3). Plots of  $\chi_{12}$  vs.  $1/T$  show different slopes depending on the PVDF phase behavior. The values (Flory-Huggins interaction parameters (7)) were smaller than 0.5 above the melting temperature of PVDF, which suggests that PVDF could dissolve such solvents at infinite dilution. The retention diagrams of other PVDF/carbonyl-containing solvent systems are shown in Figure 4. The PVDF solutions of 3-OCTO, 3-HEPO, 3-PENO, and c-HEXO formed gels at room temperature, similar to other carbonyl-containing solvents such as ACE or MEK.



**Figure 4** Specific retention volumes of PVDF/probe (ketone families) systems at various temperatures (above the melting temperature of PVDF) as a function of reciprocal absolute temperature.

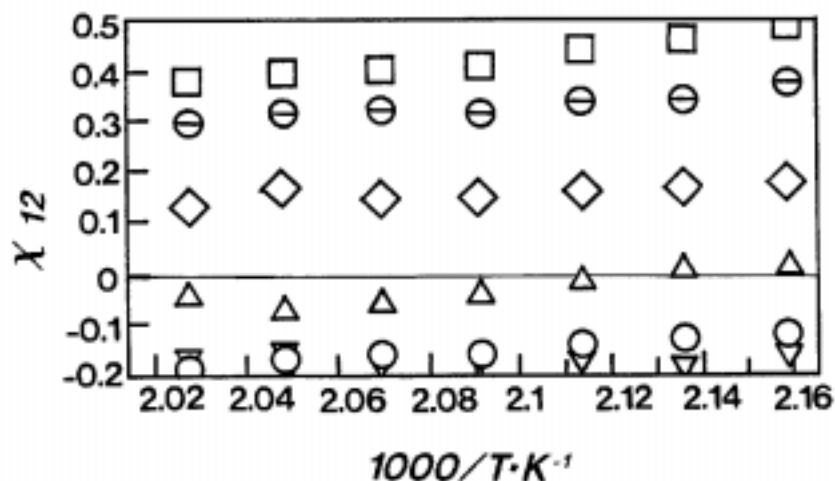
▽:  $\gamma$ -BL, ○: c-HEXO, ◇: c-HEPO, □: 3-OCTO, ○: 3-HEPO, ◇: 3-HEXO, △: 3-PENO

The  $\chi_{12}$  are shown in Figure 5. The molar heat of (enthalpy) sorption ( $\Delta H_1^s$ ) (8) of the probe was calculated, as follows:

$$\Delta H_1^s = -R \cdot \delta \ln V_g^0 / \delta (1/T) \quad [7]$$

The calculated  $\Delta H_1^s$  values are shown in Table 3.  $\Delta H_1^s$  (H) was -14.5 kJ/mol for n-hexane over the temperature range of 190 to 220 °C (above the melting temperature

of PVDF). However,  $\Delta H_1^s$  (H) was -29.5 kJ/mol for cyclohexanone. As summarized in Table 3, considerable differences in  $\Delta H_1^s$  (H) are found between hydrocarbons and



**Figure 5.** Interaction parameter,  $\chi_{12}$  of PVDF/probe systems at various temperatures as a function of reciprocal absolute temperature.

$\nabla$ :  $\gamma$ -BL,  $\circ$ : c-HEXO,  $\square$ : 3-OCTO,  $\ominus$ : 3-HEPO,  $\diamond$ : 3-HEXO,  $\triangle$ : 3-PENO

**Table 3**  $\Delta H_1^s$  (kJ/mol) obtained using equation [7] (molar heat of sorption of probe absorbed by the amorphous part of PVDF)

Probe	Column Temperature/ $^{\circ}$ C		$\Delta H_1^s$ (H) - $\Delta H_1^s$ (L)
	220 ~ 190	150 ~ 100	
	$\Delta H_1^s$ (H)	$\Delta H_1^s$ (L)	
n-HEX	-14.5	-15.9	1.4
n-OCT	-15.3	-17.7	2.4
3-OCTO	-33.8	-	-
3-HEPO	-25.5	-	-
3-HEXO	-25.5	-	-
3-PENO	-29.6	-	-
ACE	-26.1	-31.9	5.8
c-HEPO	-29.5	-	-
c-HEXO	-29.7	-38.4	8.7
$\gamma$ -BL	-29.1	-43.6	14.5
DMF	-51.7	-62.3	10.6
EA	-34.5	-35.6	1.1

carbonyl-containing solvents. DMF, a good solvent for PVDF, gave a  $\Delta H_1^s$  value of -51.7 kJ/mol. In the temperature range of 150 to 100  $^{\circ}$ C (below the melting temperature of PVDF),  $\Delta H_1^s$ (L) of n-hexane was -15.9 kJ/mol, which was approximately the same as that obtained above the melting temperature of PVDF. However, for carbonyl-containing solvents, there is a difference of 5 - 10 kJ/mol between the values obtained above and below the melting temperature of PVDF. It is reasonable to assume that the differences in  $\Delta H_1^s$  between PVDF/solvent systems could be one of the factors influencing the gelation of the solution.

## Conclusions

The inverse gas chromatography (IGC) method was applied for the thermodynamic characterization of semicrystalline PVDF. Using this method, information regarding the interaction between PVDF and organic solvents could be obtained over a wide temperature range of 100 to 220 °C, using many kinds of solvents (probes) containing carbonyl group or hydrocarbons. Although the hydrocarbons could only diffuse into PVDF, the specific retention volume in PVDF/n-HEX systems implied the phase transition of PVDF. The interaction parameter (Flory-Huggins interaction parameter) between PVDF and carbonyl-containing solvents showed that it was smaller than 0.5 above the melting temperature of PVDF, which means that PVDF could dissolve in such solvents. However, such solution easily gelled at room temperature. The dissolution and gelation of PVDF were discussed in relation to the molar heat of sorption of the probes absorbed by the amorphous regions of PVDF ( $\Delta H_1^s$ ).

Using the IGC method, the interactions between polymer and solvents could be observed over a relatively wide temperature range including the polymer phase transition.

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