Estimation of surface tension of poly(vinylidene fluoride-*co*-hexafluoro acetone) by corresponding states theory

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The theoretical surface tensions γ_S^T of poly(vinylidene fluoride-*co*-hexafluoro acetone) (hexafluoro acetone content: 6.5, 8.3, 10.4 mol%) were calculated according to Prigogine's corresponding states theory, as has already been extended to surfaces by Patterson and co-workers. The resulting γ_S^T was nearly consistent with the experimental surface tension γ_S^C evaluated by a $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plot based on the contact angle method.

(Keywords: poly(vinylidene fluoride-*co*-hexafluoro acetone); surface tension; corresponding states theory; contact angle)

Introduction

Surface tensions of various polymers have been obtained by the contact angle method[1–3]. In our previous study[4], we measured the contact angles of dispersion, polar and hydrogen bonding liquids on the surface of poly(vinylidene fluoride-*co*-hexafluoro acetone) [P(VDF-HFA)]. Then, the critical surface tensions γ_C of P(VDF-HFA) were estimated by $\cos\theta$ *versus* γ_L, $(1+\cos\theta)$ *versus* $1/\gamma_L^{0.5}$ and $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plots. The γ_C values estimated with the polar liquids were larger than those with the dispersion and hydrogen bonding liquids. It was suggested that the orientation and rearrangement of P(VDF-HFA) occurred and the $\cos\theta$ *versus* γ_L plot resulted in essentially a concave curve.

Siow and Patterson[5] pointed out that the theoretical surface tension of a polymer γ_S^T could be predicted with Prigogine's corresponding states theory by the following equation:

$$\tilde{\gamma}_S = \gamma_S^T/(k^{1/3}P^{*2/3}T^{*1/3}) \qquad (1)$$

$$\tilde{\gamma}_S\tilde{V}^{5/3} = 0.29 - (1 - \tilde{V}^{-1/3}) \times \ln[(\tilde{V}^{1/3} - 0.5)/(\tilde{V}^{1/3} - 1)] \qquad (2)$$

where P^* and T^* are the reference parameters for pressure and temperature, $\tilde{\gamma}_S$ and $\tilde{V}$ are the reduced surface tension and reduced volume and k is the Boltzmann constant. In this study, the relationship between γ_S^T calculated using equations (1) and (2) and the experimental surface tensions γ_S^C obtained by the $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plot for P(VDF-HFA) was examined.

Experimental

The polymer samples used were P(VDF-HFA) with HFA contents of 6.5 ($M_n = 30\,000$, $M_w/M_n = 4.23$), 8.3 ($M_n = 11\,600$, $M_w/M_n = 4.94$) and 10.4 mol% ($M_n = 35\,000$, $M_w/M_n = 4.63$).

The corresponding states parameters were calculated with the thermal expansion coefficient α and the thermal pressure coefficient κ, which were estimated by dilatometric measurements[6] and the equation $\kappa = \delta^2/T$ [where δ is the solubility parameter of P(VDF-HFA)], respectively. The dilatometric measurements obeyed Bekkedahl's method[7]. For dilatometry, a Pyrex glass dilatometer (length ~ 50 cm, thickness ~ 3 mm, inside diameter ~ 2 mm) containing mercury was used. The specific volumes V_{SP} of P(VDF-HFA) at various temperatures were calculated by the following equations:

$$V_{SP} = \frac{[V_t(T) + \Delta V_t - V_{tHg}]}{m_p}$$

$$V_t(T) = V(25°C) + S[N(T) + \Delta N - N(25)]$$

$$\Delta V_t = V(25)(T - 25) \times 10^{-5}$$

$$V_{tHg} = m_{Hg}(0.073554 + 0.0000134t)$$

$$t = T + (T - T_r)(T - T_l) \times 0.00017$$

$$\Delta N = 0.00017(T - T_r)(N - N_b)$$

where $V(25)$ is the specific volume at 25°C, $N(25)$ is the position of mercury at 25°C, N_b is the liquid temperature in an oil bath, $N(T)$ is the position of mercury at a temperature T, T_r is the room temperature, T_l is the liquid surface temperature before heating, S is the cross-section of the capillary, and m_p and m_{Hg} are the weights of the samples and mercury, respectively. After P(VDF-HFA) and mercury were put into the dilatometer, it was annealed for 2 h at 100°C. The dilatometer was placed in an oil bath, and the specific volumes of P(VDF-HFA) at the various temperatures (25–180°C) were measured. The heating rate was set at 2°C min^{-1}.

Results and discussion

Flory[8,9] defined the equation of state for the polymer fluid by means of Prigogine's corresponding states

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theory[10]:

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \frac{\tilde{V}^{1/3}}{\tilde{V}^{1/3}-1} - \frac{1}{\tilde{V}\tilde{T}} \qquad (3)$$

where $\tilde{P}$, $\tilde{V}$ and $\tilde{T}$ are the reduced parameters of pressure, volume and temperature, respectively. The reduced parameters are evaluated using α and κ as follows:

$$\tilde{V} = V_{SP}/V^* = \left(\frac{1+T\alpha}{1+4T\alpha/3}\right)^{-3} \qquad (4)$$

$$\tilde{P} = P/P^* = P/(\tilde{V}^2 T\kappa) \qquad (5)$$

$$\tilde{T} = T/T^* = (\tilde{V}^{1/3}-1)/\tilde{V}^{4/3} \qquad (6)$$

where P^*, V^* and T^* are the constant reference parameters. Therefore, γ_S^T can be calculated from equations (1) and (2) using the parameters P^*, T^* and $\tilde{V}$ which are obtained with α and κ. The slope of the V_{SP} *versus* temperature plot is α and κ can be estimated with δ as follows[11]:

$$\kappa = \delta^2/T \qquad (7)$$

The relationship between V_{SP} and T for P(VDF-HFA) with 6.5 mol% HFA content is shown in *Figure 1*. The phase transition of P(VDF-HFA) is revealed in the range ~90–150°C. Maeda *et al.*[12] found by d.s.c. that the melting point of P(VDF-HFA) with 6.5 mol% HFA content was around 130°C. It is considered that the phase transition of P(VDF-HFA) by dilatometry corresponds to the solid–liquid phase transition. Two straight lines are drawn using the least square approximation with a correlation coefficient of >0.99 with the following equations:

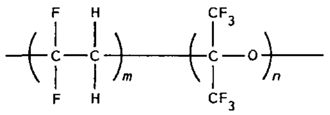
$$V_{SP} = 4.986 \times 10^{-4} T(°\mathrm{C}) + 0.583 \ (25\text{–}90°\mathrm{C}) \qquad (8)$$

$$V_{SP} = 5.975 \times 10^{-4} T(°\mathrm{C}) + 0.594 \ (150\text{–}180°\mathrm{C}) \qquad (9)$$

The slope of V_{SP} *versus* T is α. The thermal pressure coefficient κ of P(VDF-HFA) can be calculated with δ which is estimated by the molar attraction constant by means of Hoy's table[13]:

$$\delta = \sum F_i/V \qquad (10)$$

where F_i and V are molar attraction constant and molar volume, respectively. The structure of P(VDF-HFA) is represented by:



$$\left(\mathrm{CF_2{-}CH_2}\right)_m\left(\mathrm{C(CF_3)_2{-}O}\right)_n$$

$m + n = 1$

where m and n are the ratios of the VDF and HFA in P(VDF-HFA), respectively. Consequently, δ of P(VDF-HFA) is calculated with the monomer ratios m and n using the following equation:

$$\delta = \delta^m_{\mathrm{VDF}}\delta^n_{\mathrm{HFA}} = [\textstyle\sum F_{i(\mathrm{VDF})}/V_{\mathrm{VDF}}]^m[\sum F_{i(\mathrm{HFA})}/V_{\mathrm{HFA}}]^n \qquad (11)$$

The F_i and V values for VDF and HFA are shown in *Table 1*.

In P(VDF-HFA) with 6.5 mol% HFA content, the value of δ was 5.78. The state parameters at 20°C for P(VDF-HFA) are shown in *Table 2*. The state parameters were obtained with equation (9) in the range of 150–180°C, because the liquid state was reached.

Siow and Patterson[5] pointed out that γ_S^T was evaluated using equations (1) and (2) based on a state parameter. Stewart and Von Frankenberg[14] found that a reasonable γ_S^T for several polymers could be evaluated by equations (1) and (2). On the other hand, in our previous paper[4], we estimated γ_S^C of P(VDF-HFA) with the parameters ϕ and $\psi = 0.5 - a$ obtained by the contact angle method, where ϕ is the intercept of $(1 + \cos\theta)$ at $1/\gamma_L^{0.5} = 0$ in the $(1 + \cos\theta)$ *versus* $1/\gamma_L^{0.5}$ plot, ψ is the slope in the $\log(1 + \cos\theta)$ *versus* $\log(\gamma_L)$ plot and a is a constant showing the deviation from the geometric mean rule. The γ_S^T calculated with the state parameters and γ_S^C evaluated by the contact angle method for P(VDF-HFA) are shown in *Table 3*. The γ_S^T values nearly correspond to the γ_S^C values evaluated for dispersion liquids, whereas

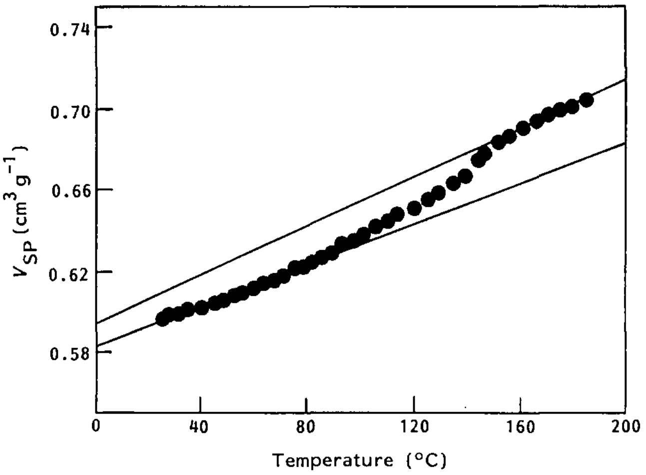


Figure 1 Relationship between specific volume V_{SP} and temperature for P(VDF-HFA) with 6.5 mol% HFA content

Table 1 Values of F_i and V for VDF and HFA

VDF				HFA			
Group	Number	F_i	V^a	Group	Number	F_i	V^a
$-\mathrm{CH_2}-$	1	131.5	15.85	$>\mathrm{C}<$	3	32.03	4.6
$>\mathrm{C}<$	1	32.03	4.6	$-\mathrm{F}$	6	41.33	10.9
$-\mathrm{F}$	2	41.33	10.9	$-\mathrm{O}-$	1	114.98	10.0
Sum		246.19	42.25	Sum		459.05	89.2

[a] Ref. 18

Table 2 State parameters for P(VDF-HFA) at 20°C

HFA content (mol%)	α ($\times 10^4$) (deg^{-1})	V_{sp} (cm^3 g^{-1})	V^* (cm^3 g^{-1})	$\tilde{V}$	T^* (K)	P^* (J cm^{-3})
6.5	5.975	0.595	0.514	1.159	7202	187.5
8.3	7.049	0.562	0.475	1.184	6451	195.0
10.4	6.312	0.753	0.646	1.167	6936	188.8

Table 3 Surface tension of P(VDF-HFA) at 20°C

HFA content (mol%)	6.5	8.3	10.4
γ_S^T (dyn cm^{-1})	21.1	19.1	20.4
γ_S^C (dyn cm^{-1})			
Dispersion	22.7	21.9	22.7
Polar	32.5	29.9	33.6
Hydrogen bonding	29.7	26.7	26.9

the γ_S^T values are smaller than the γ_S^C values obtained from polar and hydrogen bonding liquids. We consider that the orientation[15] of the polar group and the rearrangement[16,17] of the side chain in P(VDF-HFA) occurs near the polymer surface in contact with the polar and hydrogen bonding liquids. Therefore, it is predicted that the γ_S^T values are close to the γ_S^C values when orientation and rearrangement in the polymer bulk does not take place.

Conclusions

The γ_S^T of P(VDF-HFA) calculated with state parameters was close to the γ_S^C value evaluated by the contact angle method using dispersion liquids, whereas γ_S^T was smaller than γ_S^C in polar and hydrogen bonding liquids. Consequently, in polar and hydrogen bonding liquids, we assume the orientation and rearrangement have taken place in the P(VDF-HFA) bulk near the polymer surface. Further studies are required to confirm this.

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