

## Temperature Dependence of Solubility Parameters of Polymers

K. K. Chee

Department of Chemistry\*, University of Malaya, Kuala Lumpur

\* Present Correspondence address: 37, Jalan Wangsa Budi 3,  
Wangsa Melawati, 53300 Kuala Lumpur, Malaysia.

**Abstract :** Two equations are proposed to describe the decrease of solubility parameter ( $\delta$ ) with increasing temperature ( $T$ ) for the polymers which exhibit the glass-rubber transition. They are derived by considering the temperature effects on the free volume and the enthalpy change of the glass-rubber transition. These derivations hinge on an enthalpy assumed to be inversely proportional to the fourth power in molar volume of liquid polymer. The predicted results over a significant range of temperatures are conveniently fitted to the linear equations of the form

$$\delta = \delta_g + m_i (T - T_g)$$

where  $\delta_g$  is the  $\delta$  at the glass transition temperature ( $T_g$ ), and the coefficient  $m_i = m_s$ ,  $m_l$  referring to the glassy and liquid polymers respectively. It has been found that  $m_l$  surpasses  $m_s$  consistently. The peculiarity of low-density polyethylene is explained. More important, the results of the present study compare favorably with the experimental  $\delta$  data obtained at 60 °C for two glassy polymers and two rubbery polymers. The implication of the present finding is discussed.

**Abstrak :** Dua persamaan telah dicadangkan untuk menggambarkan penurunan parameter kelarutan ( $\delta$ ) dengan kenaikan suhu ( $T$ ) bagi polimer-polimer yang mempertunjukkan peralihan fasa kaca-getah. Persamaan-persamaan itu adalah diterbitkan dengan mempertimbangkan kesan-kesan suhu atas isipadu bebas serta perubahan entalpi peralihan fasa kaca-getah. Terbitan tersebut di atas bergantung kepada suatu entalpi dianggap berkadar songsang dengan kuasa keempat dalam isipadu molar polimer cecair. Keputusan-keputusan diperolehi di atas dalam suatu lingkungan suhu yang bermakna, telah dikendalikan oleh persamaan-persamaan linear dalam suatu bentuk seperti berikut

$$\delta = \delta_g + m_i (T - T_g)$$

dengan  $\delta_g$  merupakan  $\delta$  pada suhu peralihan kaca ( $T_g$ ), dan pekali  $m_i = m_s$ ,  $m_l$  adalah masing-masing merujuk kepada polimer berkaca dan polimer cecair. Terdapat bahawa  $m_l$  sentiasa mengatasi  $m_s$ . Tambahan pula, keluarbiasaan polietilena bertumpatan rendah telah diterangkan. Yang penting sekali adalah bahawa keputusan-keputusan kajian ini berbanding baik dengan data  $\delta$  percubaan yang diperolehi pada 60 °C daripada dua polimer berkaca dan dua polimer bergetah. Implikasi hasil kajian ini telah dibincangkan.

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### Introduction

In classical thermodynamics, the solubility parameter ( $\delta$ ) of a substance is an important quantity in that it measures quantitatively the cohesive properties relevant to the intermolecular forces. This particular parameter has been commonly used to interpret the bulk and solution properties of polymers. In fact, the glass-transition temperature ( $T_g$ ) and surface tension of a polymer are closely related to its  $\delta$  [1,2]. Thermodynamically, the miscibility in polymer-solvent mixtures or polymer-polymer blends can be predicted if the solubility parameters of their components are precisely matched [3,4]. Indeed, the concept of  $\delta$  has formed the basis for the solvent selection procedure widely practised in the paint and related industries [5].

Despite its prominent role in the thermophysical studies of polymers, the information on  $\delta$  is mainly cited at ambient temperature [5,6]. Recently, we have obtained some  $\delta$  data at an intermediate temperature by studying the swelling behaviour of polymer networks [7]. However, these results seem to defy a plausible explanation. In this investigation, our primary objective is to establish a reliable relation between  $\delta$  and temperature ( $T$ ) to address the foregoing problem.

### Temperature Dependence of Solubility Parameters

When an amorphous polymer was heated it would undergo a phase transition from the glassy state to the rubbery state at the  $T_g$ , where the abrupt jumps in the thermal expansion and heat capacity

occurred. The present analysis deals with the polymers below and above the  $T_g$ .

By definition, the  $\delta$  is given by

$$\delta = \sqrt{E_c} \quad (1)$$

where  $E_c$  is the cohesive energy density. The  $E_c$  of a substance in a condensed state is equal to the decrease of internal energy per unit volume due to the presence of intermolecular forces

$$E_c = (U_g - U_i) / V_i \quad (2)$$

where  $U_g$  &  $U_i$  are respectively the molar internal energies in the gas state and the condensed state  $i$ , in which the molar volume of the substance is  $V_i$ . Hereafter, the condensed states of interest are designated by the subscript  $i = s, l$  standing for a solid, and a liquid state respectively. All physical quantities refer to a temperature  $T$ . Eq. (2) infers that  $E_c$  of ideal gas does not exist at all under any circumstance.

Since molar internal energy ( $U$ ) is related to molar enthalpy ( $H$ ) by  $H = U + pV$ , where  $p$  is the pressure and  $V$  is the molar volume, eq. (2) can be converted to

$$E_c = (\Delta H_{\text{vap}} - RT) / V_l \quad (3)$$

for a simple liquid, where  $\Delta H_{\text{vap}}$  is the molar heat of vaporization at  $T$ ,  $V_l$  is the molar volume, and  $R$  is the gas constant. Eq. (3) indicates that the cohesive energy is compensable by the heat of vaporization, which is experimentally accessible. Hence, it offers a practical means to assess the  $\delta$  of liquids via eq. (1). As polymers do not vaporize, a new approach for  $E_c$  is in order.

Applying eq. (2) to a polymer at  $T \geq T_g$  results in

$$E_c = (U_g - H_l) / V_l \quad (4)$$

where  $U_g$  and  $H_l$  refer to the  $U$  and  $H$  in their respective phases per mole structural unit at ambient pressure. Using statistical thermodynamic method [1], it has been found that

$$U_g = (3/2) RT \quad (5)$$

For liquid polymers, Tanaka [8] has developed an expression for  $H_l$  given as

$$H_l = (3/2) RT - H_c - RT^2 (\partial \ln v_f / \partial T)_T \quad (6)$$

where  $H_c$  is a composite enthalpy per mole structural unit at  $T$  consisting of a conformational and an intermolecular interaction component, and  $v_f$  is the fractional free volume. Combining eqs. (1), (4)-(6) leads to

$$V_l \delta^2 = H_c + RT^2 (\partial \ln v_f / \partial T)_T \quad (7)$$

We propose

$$H_c \propto V_l^{-4}$$

resulting in

$$H_c(T) = H_c(T_r) \exp(-4\alpha_l \Delta T) \quad (8)$$

where  $T_r$  is a reference temperature,  $\alpha_l$  is the coefficient of thermal expansion above  $T_g$ , and  $\Delta T = T - T_r$ . Since  $V_l = M/\rho$ , and  $\rho = \rho_r \exp(-\alpha_l \Delta T)$ , eqs. (7) and (8) give

$$\delta^2 = [\delta_r^2 - \rho_r RT_r^2 M^{-1} (\partial \ln v_f / \partial T)_{T_r}] \exp(-5\alpha_l \Delta T) + [\rho_r RT^2 M^{-1} (\partial \ln v_f / \partial T)_T] \exp(-\alpha_l \Delta T) \quad (9)$$

where  $M$  is the molecular weight of the structural unit,  $\rho$  is the density at  $T$ , and  $\rho_r$ ,  $\delta_r$  are the density and solubility parameter at  $T_r$  respectively. The fractional free volume of polymer is assumed to expand linearly with increasing  $T$  above  $T_g$

$$v_f = v_g + \Delta\alpha (T - T_g) \quad (10)$$

where  $v_g$  is the  $v_f$  at  $T_g$ , and  $\Delta\alpha$  is equal to the difference  $\alpha_l - \alpha_g$ , with  $\alpha_g$  being the coefficient of thermal expansion below  $T_g$ . By setting  $T_r = T_g$ , we obtain

$$\delta^2 = (\delta_g^2 - K) \exp(-5\alpha_l \Delta T) + K (T/T_g)^2 \exp(-\alpha_l \Delta T) / (1 + \Delta\alpha \Delta T / v_g) \quad (11)$$

for  $T \geq T_g$ , where  $\Delta T = T - T_g$ , and

$$K = \rho_g R \Delta\alpha T_g^2 M^{-1} v_g^{-1} \quad (11a)$$

with  $\rho_g$  and  $\delta_g$  being the  $\rho$  and  $\delta$  at  $T_g$ , respectively. Hence, the  $\delta$  as a function of  $T$  above  $T_g$  may be readily estimated from eq. (11).

We now proceed to consider the glassy polymers. By analogy, eq. (2) can be written for a glassy polymer in the form of

$$E_c = (U_g - H_s) / V_s \quad (12)$$

where  $H_s$  is the enthalpy per mole structural unit, and  $V_s$  is the molar volume at  $T \leq T_g$  and ambient pressure. The enthalpy change per mole structural

unit of a glass-rubber transition process occurring at T ( $\Delta H_{tr}(T)$ ) is defined by

$$\Delta H_{tr}(T) = H_l(T) - H_s(T) \quad (13)$$

By assuming  $\Delta H_{tr}(T_g)=0$ , we obtain

$$\Delta H_{tr}(T) = -M \int_T^{T_g} \Delta C_p(T) dT \quad (14)$$

where  $\Delta C_p(T)=C_{pl}(T) - C_{ps}(T)$ , with  $C_{pl}(T)$  and  $C_{ps}(T)$  being the specific heat capacities at constant p of the polymer in the liquid and glassy states at T respectively. Combining eqs. (2), (12)-(14) results in

$$V_s \delta^2 = U_g - H_l - M \int_T^{T_g} \Delta C_p(T) dT \quad (15)$$

Since the derivative in eq. (6) vanishes at  $T \leq T_g$ , eqs. (5), (6), and (15) lead to

$$V_s \delta^2 = H_c(T) - M \int_T^{T_g} \Delta C_p(T) dT \quad (16)$$

Substituting eq. (8) into eq.(16) gives

$$V_s \delta^2 = H_c(T_r) \exp(-4\alpha_l \Delta T) - M \int_T^{T_g} \Delta C_p(T) dT \quad (17)$$

With the aid of eq. (7) and setting  $T_r=T_g$  at which  $\rho_r = \rho_g$  and  $\delta_r=\delta_g$ , eq. (17) becomes

$$M \delta^2 / \rho_s = M \delta_g^2 / \rho_g \exp(-4\alpha_l \Delta T) - M \int_T^{T_g} \Delta C_p(T) dT \quad (18)$$

where  $\rho_s$  is the density of the polymer at  $T < T_g$ , and  $\Delta T=T-T_g$ . Since  $\delta_s = \delta_g \exp(-\alpha_g \Delta T)$ , eq. (18) can be written as

$$\delta^2 = \delta_g^2 \exp[-(\alpha_g + 4\alpha_l) \Delta T] - \rho_g \exp(-\alpha_g \Delta T) \int_T^{T_g} \Delta C_p(T) dT \quad (19)$$

The temperature functions of the specific heat capacities at constant p [10] are given by

$$C_{pl}(T) = C_{pl}' [1 + 1.2 \times 10^{-3} (T-298)] \quad (20)$$

$$C_{ps}(T) = C_{ps}' [1 + 3.0 \times 10^{-3} (T-298)] \quad (21)$$

where  $C_{pl}'$  and  $C_{ps}'$  are respectively the  $C_{pl}$  and  $C_{ps}$  at 298 K. Substituting eqs. (20) and (21) into eq. (19) yields

$$\delta^2 = \delta_g^2 \exp[-(\alpha_g + 4\alpha_l) \Delta T] + \rho_g A [1 + B (T+T_g)] / \Delta T \exp(-\alpha_g \Delta T) \quad (22)$$

for  $T \leq T_g$ , where  $\Delta T=T-T_g$ , and

$$A = (C_{pl}' - C_{ps}') - 0.3576 (C_{pl}' - 2.5C_{ps}') \quad (22a)$$

$$B = 6.0 \times 10^{-4} (C_{pl}' - 2.5C_{ps}') / A \quad (22b)$$

Eq. (22) would result in the  $\delta$  as a function of T for glassy polymers.

## Results and Discussion

In order to explore the utility of eq. (11), we take  $v_g=0.109$ , a theoretical value after Simha and Boyer [11]. Data for the other physical parameters appearing in eqs (11) and (22) are cited from the literature [2,7,10,12], and listed in Table 1 for four polymers particularly selected for the present investigation. The solubility parameter at 25 °C designated by  $\delta'$  is used to calculate  $\delta_g$ , which is not known *a priori*. The values of  $\delta_g$  so obtained using either eq. (11) or eq. (22), are shown in Table 2. After this exercise, the ensuing calculations are straightforward.

The values of  $\delta$  at various temperatures are obtained by eqs.(11) and (22). This study covers the temperatures varying from  $T_g-120$  K to  $T_g+120$  K, with the calculations extended to 60 °C for the rubbery polymers, namely natural rubber (NR) and low-density polyethylene (LDPE). Its results are represented by the following expression

$$\delta = \delta_g + m_i (T - T_g) \quad (23)$$

where  $m_i$  is an empirical constant with the subscript 'i' = s, l designating the polymers below and above the  $T_g$  respectively. The overall results are shown in Table 2. In the present analysis, eq. (23) registers a standard error in estimate on  $\delta$  equal to *ca* 0.04 (J/ml)<sup>1/2</sup>. Apparently, two straight lines joining at  $T_g$  and exhibiting distinct negative slopes can be used to depict the  $\delta$ -T profile of a polymer satisfactorily. In addition, the temperature gradients of  $\delta$  for liquid polymers (i.e.  $m_l$ ) are consistently steeper compared with their glassy counterparts. The strikingly low values of both  $m_s$  and  $m_l$  reported for LDPE in Table 2 may be attributed to its much-depressed  $T_g$  and M.

Knowledge of the change of  $\delta$  with T is essential in polymer systems, particularly in polymer blends. The miscibility of two polymers may be realized if their solubility parameters are adequately close [3,4]. In this connection, it is found that the poly(methyl methacrylate) (PMMA), polystyrene (PS), and NR included in Table 2 do not seem to produce any comparable solubility parameters over the practical

range of temperatures. This means that the foregoing polymers are grossly incompatible. On the contrary, NR and LDPE result in two straight lines intercepting at  $T=70$  °C with a common  $\delta=15.5$  (J/ml)<sup>1/2</sup>, indicating athermal mixing and miscibility. However, this particular thermodynamic outcome has never been realized experimentally [13,14], probably because of the characteristic morphological properties of LDPE, which melts at *ca* 110 °C and crystallizes rapidly to achieve the relatively high crystallinity on cooling.

Perhaps, the validity of eqs. (11) and (22) is best tested by some experimental data. The solubility parameters of PMMA, PS, NR, and LDPE have been determined using the equilibrium swelling method at 60 °C to be 19.2, 18.1, 16.0 and 15.8 (J/ml)<sup>1/2</sup> respectively [7]. Whereas the corresponding theoretical estimates are found to be 19.23, 18.02, 15.86 and 15.78 (J/ml)<sup>1/2</sup>, using eqs. (11) and (22). Clearly, these two sets of results on  $\delta$  at 60 °C are indeed consistent in that the difference between

measured and calculated solubility parameters of a polymer studied is always within 0.15 (J/ml)<sup>1/2</sup>. Certainly, more experimental data on  $\delta$  at different temperatures are required to support the generality of eqs. (11) and (22). However, this information seems to be hard to come by hitherto.

In conclusion, the temperature coefficients of molar volume, free volume and enthalpy change of glass-rubber transition are closely related to the cohesive energy density of polymers. Eqs. (11) and (22) are based on two basic proposals justified by the good agreement between the theoretical and empirical results on  $\delta$ . These semi-empirical models are believed to be useful for studying the solution and phase behaviour of polymer systems.

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**Table 1 :** Thermodynamic data of various polymers

| No. | Polymer                   | $T_g^{(a)}$<br>(K) | $\delta^{(b)}$<br>(J/ml) <sup>1/2</sup> | $\rho^{(c)}$<br>(g/ml) | $\alpha_g^{(d)}$<br>$\times 10^4$<br>(K <sup>-1</sup> ) | $\alpha_l^{(d)}$<br>$\times 10^4$<br>(K <sup>-1</sup> ) | $C_{ps}^{(d)}$<br>(J/g.K) | $C_{pl}^{(d)}$<br>(J/g.K) |
|-----|---------------------------|--------------------|---|------------------------|---|---|---------------------------|---------------------------|
| 1   | Poly(methyl methacrylate) | 378                | 19.8 <sup>(e)</sup>                     | 1.17                   | 2.2   | 6.2   | 1.37                      | 1.80                      |
| 2   | Polystyrene               | 373                | 18.6                                    | 1.05                   | 2.9   | 6.8   | 1.23                      | 1.71                      |
| 3   | Natural rubber            | 206                | 16.6                                    | 0.908                  | 2.0   | 6.7   | 1.59                      | 1.93                      |
| 4   | Low-density polyethylene  | 188                | 16.2                                    | 0.925 <sup>(f)</sup>   | 2.4   | 6.4   | 1.76                      | 2.26                      |

(a) Ref. (2), (b) Ref. (12) unless specified otherwise,  $\delta^* = \delta$  at 25 °C, (c) Ref. (10) unless specified otherwise,  $\rho^* = \rho$  at 25 °C, (d) Ref. (10), (e) Ref. (7), (f) Based on a crystallinity of 50%.

**Table 2 :** Parameters of eq. (23)

| No. | Polymer                   | $\delta_g^{(a)}$<br>(J/ml) <sup>1/2</sup> | $m_s^{(a)}$<br>(J/ml) <sup>1/2</sup> /K | $m_l^{(a)}$<br>(J/ml) <sup>1/2</sup> /K |
|-----|---------------------------|---|---|---|
| 1   | Poly(methyl methacrylate) | 18.50                                     | -0.0162                                 | -0.0209                                 |
| 2   | Polystyrene               | 17.38                                     | -0.0166                                 | -0.0217                                 |
| 3   | Natural rubber            | 18.85                                     | -0.0131                                 | -0.0241                                 |
| 4   | Low-density polyethylene  | 17.91                                     | -0.0037                                 | -0.0153                                 |

(a) The coefficients  $m_s$ ,  $m_l$  are defined by the following equation  $\delta = \delta_g + m_i (T - T_g)$ , where  $m_i = m_s$ ,  $m_l$ .

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