



# A method for determination of thermodynamic and solubility parameters of polymers from temperature and molecular weight dependence of intrinsic viscosity

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## Abstract

An equation using the temperature dependence of intrinsic viscosity of a polymer was proposed for the determination of the partial molar entropy and enthalpy changes of the polymer for mixing in dilute solution. It was found that the partial molar entropy change of a polymer for mixing at a given temperature is proportional to the hydrodynamic volume or segment number of the polymer. The partial molar enthalpy change of the polymer for mixing was determined from the thermodynamic equilibrium property of polymer phases. The solubility or cohesion parameter of a polymer fraction was calculated by using the partial molar enthalpy change and repeat unit volume of the polymer. The solubility parameter of high molar mass polymer at a given temperature was determined by extrapolating solubility parameter values of polymer fractions to high molar mass by using the solubility parameter–segment number relation of polymer fraction. This relation gives a straight line. The solubility parameter of the polymer at a given temperature and the effective interchange energy parameter for polymer–solvent pair were obtained directly from the intercept and the slope of this line, respectively. These equations were applied to the intrinsic viscosity–temperature data of polystyrene fractions in decalin solutions, and polystyrene fractions in decalin, cyclohexane and dioctyl phthalate solutions at the theta temperatures and in toluene solutions at the given temperatures. The results obtained in this study coincide with the literature values. In addition, it was given a relation, which is derived from the blob theory for the temperatures above the theta point, for the estimation of the thermodynamic parameters of polymers for mixing.

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## 1. Introduction

The entropy and enthalpy changes of a polymer for mixing determined by the thermodynamic theories [1–5] of polymer solutions are not satisfactory. Therefore, the solubility parameter of a polymer cannot be determined directly from the experiment [6] and several indirect methods have been employed.

In our previous study [7], a method was proposed for the determination of thermodynamic and solubility parameters of polymers from critical volume fractions. In this study, an equation using the temperature dependence of intrinsic viscosity of a polymer will be proposed for the determination of the partial molar entropy and enthalpy changes of

a polymer for mixing in dilute solution. Also, the equations using the hydrodynamic volume or segment number of a polymer fraction for determination of the partial molar entropy change for mixing at a given temperature will be proposed. The partial molar enthalpy change for mixing is determined from the thermodynamic equilibrium property of polymer phases. The solubility parameter of a polymer fraction is calculated from the partial molar enthalpy change and the repeat unit volume of the polymer. Subsequently, the solubility parameter of the polymer is determined by extrapolating solubility parameter values of the polymer fractions to high molar mass by using the solubility parameter–segment number relation. A linear relationship is obtained. The solubility parameter of the polymer and the effective interchange energy parameter for the polymer–solvent pair introduced in the equation of state theory [2] are

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obtained directly from the intercept and the slope of this line, respectively.

In addition, the Han Eq. [8] which is derived from the blob theory for the asymptotic behavior of intrinsic viscosity at the good solvent limit is modified and used for the estimation of the thermodynamic parameters of polymers for mixing.

## 2. Theory

Mixing solvent (S) and polymer (P) can be represented schematically as a chemical equilibrium reaction with intermolecular interactions shown as dotted line [5]:



The equilibrium constant for this reaction can be written as,

$$K' = \frac{[S \dots P]}{[S][P]} \quad (2)$$

where [S] is the solvent, [S...P] and [P] are the mixed and unmixed polymer concentrations in molar units. In dilute polymer solutions, however, the concentration of solvent is large compared with the concentration of polymer and can be considered to be constant. Therefore, Eq. (2) can be written as,

$$K = K'[S] = \frac{[S \dots P]}{[P]} \quad (3)$$

In the mixing process, the measured intrinsic viscosity  $[\eta]$  is proportional to the mixed polymer concentration.

$$[\eta] = f[S \dots P] \quad (4)$$

Then, for the unmixed polymer concentration the following equation can be written.

$$[\eta]_L - [\eta] = f[P] \quad (5)$$

where  $[\eta]_L$  is the limiting intrinsic viscosity, which corresponds to the maximum swelling of the polymer and  $f$  is the proportionality constant.

Substituting Eqs. (4) and (5) into Eq. (3) gives

$$K = \frac{[\eta]}{[\eta]_L - [\eta]} \quad (6)$$

According to the second law of thermodynamics, the following equations

$$\overline{\Delta G}_2 = -RT \ln K \quad (7)$$

and

$$\overline{\Delta G}_2 = \overline{\Delta H}_2 - T\overline{\Delta S}_2 \quad (8)$$

are written. From Eqs. (6)–(8), the following equation is

obtained:

$$\ln\left(\frac{[\eta]_L - [\eta]}{[\eta]}\right) = \frac{\overline{\Delta H}_2}{RT} - \frac{\overline{\Delta S}_2}{R} \quad (9)$$

where  $\overline{\Delta G}_2$ ,  $\overline{\Delta H}_2$  and  $\overline{\Delta S}_2$  are the partial molar Gibbs free energy, enthalpy and entropy changes for mixing of a polymer fraction, respectively. A plot of  $\ln\{([\eta]_L - [\eta])/[\eta]\}$  versus  $1/T$  will give a straight line with a slope of  $\overline{\Delta H}_2/R$  and an intercept of  $-\overline{\Delta S}_2/R$ .

Then, the cohesion or solubility parameter  $\delta$  of a polymer fraction can be calculated from the following equation.

$$\delta = (\overline{\Delta H}_2/V^u)^{1/2} \quad (10)$$

where  $V^u$  is the volume per molar structural or repeat unit.

The relationship between  $[\eta]$  and  $M$  is given by the Mark–Houwink equation.

$$[\eta] = KM^a \quad (11)$$

where  $K$  and  $a$  are constants for a given polymer–solvent–temperature system. It was shown that  $a = 0.5$  under theta conditions, and that  $a$  increases to a limiting value of 0.8 with coil expansion [9]. If Eq. (11) is multiplied by  $M$ , the following equation is obtained.

$$[\eta]M = KM^{a+1} \quad (12)$$

where  $[\eta]M$  is the hydrodynamic volume of the polymer [9]. If  $x$  is taken as the number of segments of a polymer, Eq. (12) can be written as

$$[\eta]M = KM_s^{1+a}x^{1+a} \quad (13)$$

where  $M_s$  is the molecular weight of a segment. At the theta condition, from Eq. (13) the following equations

$$\frac{[\eta]_\theta M}{K_\theta M_s^{3/2}} = x_\theta^{3/2} \quad (14)$$

and

$$\left(\frac{M}{M_s}\right)^{3/2} = x_\theta^{3/2} \quad (15)$$

can be written, where  $M_{s\theta}$  is the molecular weight of a segment and  $x_\theta$  is the number of segments at the theta temperature, respectively.

It was shown in our previous study [7] that the partial molar entropy change of a polymer for mixing at the theta condition is given by the following equation.

$$\overline{\Delta S}_{2\theta} = -R \ln(\phi_{2\theta}/x_\theta) \quad (16)$$

Applying the thermodynamic criteria for the theta composition to the Flory–Huggins model yields [5].

$$\phi_{2\theta} = 1/(1 + x_\theta^{1/2}) \quad (17)$$

For high molecular-weight polymer  $x_\theta \gg 1$ , the Eq. (17) can be written as

$$\phi_{2\theta} = 1/x_\theta^{1/2} \quad (18)$$

Substituting Eq. (18) into Eq. (16), the following equations

$$\overline{\Delta S}_{2\theta} = -R \ln \phi_{2\theta}^3 \quad (19)$$

and

$$\overline{\Delta S}_{2\theta} = R \ln(x_{\theta}^{3/2}) \quad (20)$$

are obtained. Substituting Eqs. (14) and (15) into Eq. (20) gives

$$\overline{\Delta S}_{2\theta} = R \ln \left( \frac{[\eta]_{\theta} M}{K_{\theta} M_s^{3/2}} \right) \quad (21)$$

and

$$\overline{\Delta S}_{2\theta} = R \ln \left( \frac{M}{M_s} \right)^{3/2} \quad (22)$$

equations.

The temperature composition phase diagrams for polymer solutions show that two phases are at equilibrium at the theta  $\theta$  temperature. Then, the following equation can be written

$$\overline{\Delta H}_{2\theta} = \theta \overline{\Delta S}_{2\theta} \quad (23)$$

where  $\overline{\Delta H}_{2\theta}$  is the partial molar enthalpy change of a polymer for mixing at the theta temperature. Thus, the solubility parameter of a polymer fraction at the theta temperature can be calculated from Eq. (10).

According to the equation of state theory [2],  $\chi/\bar{X}_{12}$  is a linear function of  $1/T$ , where  $\chi$  is the Flory–Huggins polymer–solvent interaction parameter and  $\bar{X}_{12}$  is the effective interchange energy parameter [10]. At the critical

temperature  $T = T_c$ ,  $\chi$  can be substituted  $\chi_c$ . According to the Flory–Huggins model [5],  $\chi_c = 1/x_c^{1/2} + 1/2x_c + 1/2$ . Then,  $1/T_c$  should be linear with  $(1/\bar{X}_{12})(1/x_c^{1/2} + 1/2x_c)$ . It was shown in the previous study [7] that  $\delta^2$  is proportional to  $T_c$ , therefore,  $1/\delta_c^2$  should be a linear function of  $(1/\bar{X}_{12}) \times (1/x_c^{1/2} + 1/2x_c)$ . At the theta temperature,  $1/\delta_c^2$  and  $x_c$  can be substituted by  $1/\delta_{\theta}^2$  and  $x_{\theta}$ . Thus, the  $\delta_{\theta}$  values of polymer fractions at the theta temperature can be extrapolated to high molar mass of polymer  $\delta_{\theta\infty}$ , in which  $1/x_{\theta}^{1/2} \gg 1/2x_{\theta}$ , by means of the following equation.

$$1/\delta_{\theta}^2 = 1/\delta_{\theta\infty}^2 + (1/\hat{X}_{12})(1/x_{\theta}^{1/2}) \quad (24)$$

where the parameter  $\hat{X}_{12}$  is proportional to the effective interchange energy parameter  $\bar{X}_{12}$  and can be taken as the estimate of that parameter. A plot of  $1/\delta_{\theta}^2$  versus  $1/x_{\theta}^{1/2}$  will give a straight line with a slope of  $1/\hat{X}_{12}$  and an intercept of  $1/\delta_{\theta\infty}^2$ .

In a good solvent, the partial molar entropy change  $\overline{\Delta S}_{2g}$  for mixing of a polymer fraction can be obtained from

$$\overline{\Delta S}_{2g} = R \ln \left( \frac{[\eta]M}{KM_s^{1+a}} \right) \quad (25)$$

and

$$\overline{\Delta S}_{2g} = R \ln \left( \frac{M}{M_s} \right)^{1+a} \quad (26)$$

equations.

The partial molar enthalpy change  $\overline{\Delta H}_{2g}$  for mixing in a good solvent can be obtained approximately from the following equation.

$$\overline{\Delta H}_{2g} \approx T \overline{\Delta S}_{2g} \quad (27)$$

Table 1  
Intrinsic viscosities (dl/g) for polystyrene in decalin at various temperatures

$M_w$ (g/mol)									
$4.40 \times 10^6$		$1.56 \times 10^6$		$1.05 \times 10^6$		$6.22 \times 10^5$		$1.25 \times 10^5$	
$T$ (°C)	$[\eta]$	$T$ (°C)	$[\eta]$	$T$ (°C)	$[\eta]$	$T$ (°C)	$[\eta]$	$T$ (°C)	$[\eta]$
10.9	1.52	15.2	1.00	14.7	0.785	10.0	0.554	10.0	0.268
12.2	1.71	17.1	1.11	19.5	0.923	12.2	0.620	12.2	0.283
13.3	1.82	20.4	1.20	26.1	1.04	16.6	0.669	15.7	0.293
14.3	1.96	27.1	1.38	29.0	1.13	20.9	0.738	21.4	0.305
15.2	2.10	32.3	1.52	49.8	1.42	29.9	0.854	33.2	0.329
15.9	2.19	39.8	1.66	69.2	1.58	40.8	0.946	48.8	0.366
18.0	2.48	52.6	1.96	89.1	1.73	55.0	1.04	70.2	0.390
19.9	2.63	65.9	2.06	118.5	1.87	69.2	1.08	90.0	0.427
22.8	2.86	78.2	2.12			118.5	1.27	116.6	0.439
25.6	3.05	86.3	2.22						
29.9	3.39	100.5	2.33						
34.6	3.67								
39.4	3.85								
46.5	4.14								
55.9	4.45								
69.2	4.94								
84.4	5.17								

Obtained from Fig. 4 in Ref. [11].

The solubility parameter of a polymer fraction at the good solvent condition can then be calculated from Eq. (10).

Similarly, the solubility parameter values  $\delta_g$  of the polymer fractions at the good solvent condition can be extrapolated to high molar mass of polymer  $\delta_{g\infty}$  by means of the following equation.

$$1/\delta_g^2 = 1/\delta_{g\infty}^2 + (1/\hat{X}_{12})(1/\chi_g^a) \quad (28)$$

A plot of  $1/\delta_g^2$  versus  $1/\chi_g^a$  will give a straight line with a slope of  $1/\hat{X}_{12}$  and an intercept of  $1/\delta_{g\infty}^2$ .

### 3. Results and discussion

#### 3.1. Intrinsic viscosity and temperature data for polystyrene in decalin solutions

The intrinsic viscosity and temperature data for polystyrene in decalin solutions obtained from Fig. 4 in Ref. [11] are given in Table 1, where  $M_w$  is the weight-average molecular weight of polymer fraction in grams per mole. According to Eq. (9), the limiting intrinsic viscosity  $[\eta]_L$  must be previously determined. Therefore, the value of  $[\eta]_L$  is selected and substituted into Eq. (9). Then, the least squares fitting is applied to these data and the  $s_e^2$  and  $r^2$  statistical parameters used for the measures of the goodness of fit are calculated for each value of  $[\eta]_L$ .  $s_e^2$  is the residual variance and  $r^2$  is the coefficient of determination. These parameters are defined in Table 2. The values of  $[\eta]_L$ ,  $\overline{\Delta H}_2/R$  and  $-\overline{\Delta S}_2/R$ , and corresponding  $s_e^2$  and  $r^2$  values calculated for each polymer fractions were given in Tables 2–6. The minimum value of  $s_e^2$  gives the optimum values. The optimum values found for these polymer fractions were given in Table 7. Fig. 1 shows the plots of  $\ln\{([\eta]_L -$

Table 2

The limiting intrinsic viscosities  $[\eta]_L$  (dl/g), thermodynamics and goodness of fit parameters ( $s_e^2, r^2$ ) for polystyrene ( $M_w = 4.40 \times 10^6$  g/mol) in decalin solution

$[\eta]_L$	$-\overline{\Delta S}_2/R$	$\overline{\Delta H}_2/R$	$s_e^2 \times 10^{-2}$	$r^2$	$\overline{\Delta S}_{2\theta}/R^c$	$\overline{\Delta S}_{2g}/R^d$
5.27	-21.713	6408.3	5.981	0.9784		
5.30	-20.085	5930.8	2.697	0.9885		
5.40	-17.331	5130.0	1.644	0.9887		
5.50 <sup>c</sup>	-15.778	4683.4	1.285	0.9926		15.753
5.60	-14.679	4370.4	2.112	0.9835		
5.70	-13.828	4130.3	2.520	0.9781		
5.80	-13.135	3936.4	2.852	0.9728		
5.90	-12.553	3774.6	3.117	0.9678		
6.00	-12.052	3636.5	3.329	0.9632	12.026	

$$^a s_e^2 = (\sum_{i=1}^n (\hat{y}_i - y_i)^2)/(n - 2).$$

<sup>b</sup>  $r^2 = 1 - (\sum_{i=1}^n (y_i - \hat{y}_i)^2)/(\sum_{i=1}^n (y_i - \bar{y})^2)$ ; where  $n$  is the number of data points used in the fitting procedure,  $y_i$  denotes data point  $i$ , and  $\hat{y}_i$  is the calculated value.

<sup>c</sup> Calculated from Eq. (22) for the theta condition.

<sup>d</sup> Calculated from Eq. (26) for the good solvent condition.

<sup>e</sup> Corresponds to the optimum and good solvent condition.

Table 3

The limiting intrinsic viscosities, thermodynamics and goodness of fit parameters for polystyrene ( $M_w = 1.56 \times 10^6$  g/mol) in decalin solution

$[\eta]_L$	$-\overline{\Delta S}_2/R$	$\overline{\Delta H}_2/R$	$s_e^2 \times 10^{-2}$	$r^2$	$\overline{\Delta S}_{2\theta}/R$	$\overline{\Delta S}_{2g}/R$
2.35	-17.607	5193.6	19.6838	0.9162		
2.40	-14.538	4282.2	3.7999	0.9747		
2.41	-14.176	4176.1	3.0651	0.9784		13.990
2.45	-13.025	3841.7	1.6082	0.9865		
2.50	-11.980	3541.6	1.0622	0.9875		
2.55	-11.177	3314.2	0.9315	0.9885		
2.60 <sup>a</sup>	-10.528	3132.2	0.9299	0.9895	10.470	
2.65	-9.985	2981.5	0.9690	0.9865		
2.70	-9.519	2853.8	1.0178	0.9846		
2.75	-9.114	2743.6	1.0649	0.9826		
2.80	-8.756	2647.2	1.1063	0.9806		
2.85	-8.437	2562.1	1.1412	0.9787		
2.90	-8.149	2486.0	1.1697	0.9768		
2.95	-7.888	2417.7	1.1936	0.9751		
3.00	-7.650	2355.8	1.2105	0.9734		

<sup>a</sup> Optimum and theta condition.

$[\eta])/[\eta]$  versus  $1/T$  for the optimum values for polystyrene fractions.

#### 3.2. Intrinsic viscosities of polystyrenes in cyclohexane, decalin and dioctyl phthalate at the theta temperatures and in toluene at 12 and 15 °C

Perzynski, Delsanti and Adam [12] found experimentally that for polystyrene in cyclohexane for  $2.4 \times 10^4 \leq M_w \leq 6.77 \times 10^6$  g/mol.

$$C_\theta = \frac{40}{M_w^{1/2}} \quad (29)$$

Table 4

The limiting intrinsic viscosities, thermodynamics and goodness of fit parameters for polystyrene ( $M_w = 1.05 \times 10^6$  g/mol) in decalin solution

$[\eta]_L$	$-\overline{\Delta S}_2/R$	$\overline{\Delta H}_2/R$	$s_e^2 \times 10^{-2}$	$r^2$	$\overline{\Delta S}_{2\theta}/R$	$\overline{\Delta S}_{2g}/R$
1.88	-16.867	4992.8	26.9142	0.9128		
1.89	-15.363	4544.1	14.1718	0.9427		
1.90	-14.428	4266.8	8.8181	0.9589		
1.91	-13.740	4063.7	5.9534	0.9691		
1.92	-13.190	3902.4	4.2314	0.9760		13.317
1.93	-12.731	3768.2	3.1230	0.9809		
1.94	-12.336	3653.2	2.3771	0.9845		
1.96	-11.677	3462.6	1.4937	0.9891		
1.97	-11.396	3381.8	1.2312	0.9906		
1.98	-11.139	3308.2	1.0415	0.9916		
1.99	-10.903	3240.7	0.9043	0.9924		
2.00	-10.684	3178.5	0.8055	0.9930		
2.01	-10.480	3120.6	0.7351	0.9934		
2.02	-10.289	3066.7	0.6861	0.9936		
2.05 <sup>a</sup>	-9.7811	2924.1	0.6215	0.9936	9.8776	
2.10	-9.0915	2732.8	0.6448	0.9924		
2.11	-8.9714	2699.7	0.6578	0.9921		
2.20	-8.0736	2456.2	0.7993	0.9884		

<sup>a</sup> Optimum and theta condition.

Table 5  
The limiting intrinsic viscosities, thermodynamics and goodness of fit parameters for polystyrene ( $M_w = 6.22 \times 10^5$  g/mol) in decalin solution

$[\eta]_L$	$-\overline{\Delta S}_2/R$	$\overline{\Delta H}_2/R$	$s_c^2 \times 10^{-2}$	$r^2$	$\overline{\Delta S}_{2\theta}/R$	$\overline{\Delta S}_{2g}/R$
1.28	-15.862	4604.3	24.9842	0.9391		
1.29	-14.119	4091.0	6.6814	0.9632		
1.30	-13.058	3780.9	3.7409	0.9755		
1.31	-12.290	3558.1	2.3196	0.9828	12.427	
1.32	-11.686	3384.1	1.5605	0.9871		
1.33	-11.189	3241.6	1.1371	0.9897		
1.34	-10.765	3121.1	0.8996	0.9912		
1.35	-10.396	3016.8	0.7711	0.9919		
1.36	-10.070	2925.1	0.7088	0.9921		
1.37 <sup>a</sup>	-9.7776	2843.2	0.6877	0.9919		
1.38	-9.5124	2769.5	0.6922	0.9914		
1.39	-9.2702	2702.5	0.7129	0.9907		
1.40	-9.0473	2641.2	0.7433	0.9899	9.0910	

<sup>a</sup> Optimum condition.

where  $C_\theta$  is the solution concentration at the theta temperature in grams per centimetre cubed.

Chu and Wang [13] have given the following equation for the critical condition.

$$C_c = \phi_c \rho_p \quad (30)$$

where  $C_c$  is the critical solution concentration in grams per centimetre cubed,  $\phi_c$  is the critical volume fraction and  $\rho_p$  is the density of the polymer. At the theta condition, the following equation

$$C_\theta = \phi_\theta \rho_p \quad (31)$$

can be written. From Eqs. (18), (29) and (31), the following equations

$$\frac{1}{x_\theta^{3/2}} = \frac{40}{\rho_p M_w^{1/2} x_\theta} \quad (32)$$

Table 6  
The limiting intrinsic viscosities, thermodynamics and goodness of fit parameters for polystyrene ( $M_w = 1.25 \times 10^5$  g/mol) in decalin solution

$[\eta]_L$	$-\overline{\Delta S}_2/R$	$\overline{\Delta H}_2/R$	$s_c^2 \times 10^{-2}$	$r^2$	$\overline{\Delta S}_{2\theta}/R$	$\overline{\Delta S}_{2g}/R$
0.445	-13.230	3673.3	9.6858	0.9454		
0.450	-11.674	3222.8	4.6166	0.9655		
0.455	-10.658	2932.5	2.7009	0.9754		
0.460	-9.899	2718.1	1.7587	0.9812	9.6992	
0.465	-9.294	2548.8	1.2308	0.9850		
0.470	-8.791	2409.7	0.9108	0.9875		
0.475	-8.362	2292.2	0.7063	0.9893		
0.480	-7.986	2189.9	0.5611	0.9905		
0.490	-7.364	2023.1	0.4511	0.9919		
0.500 <sup>a</sup>	-6.859	1890.2	0.3815	0.9926	6.6841	
0.548	-5.292	1494.2	0.3898	0.9916		

<sup>a</sup> Optimum and theta condition.

Table 7  
The optimum values of thermodynamic parameters and limiting intrinsic viscosities, and the  $1/\delta_\theta^2$  ( $J/cm^3$ )<sup>-1</sup> and  $1/x_\theta^{1/2}$  parameters for polystyrene fractions

$M_w$ (g/mol)	$-\overline{\Delta S}_2/R$	$\overline{\Delta H}_2/R$	$[\eta]_L$	$(1/\delta_\theta^2) \times 10^{-2}$	$(1/x_\theta^{1/2}) \times 10^{-1}$
$4.40 \times 10^6$	-15.778	4683.4	5.50		
$1.56 \times 10^6$	-10.528	3132.2	2.60	0.3763	0.2966
$1.05 \times 10^6$	-9.781	2924.1	2.05	0.4031	0.3615
$6.22 \times 10^5$	-9.270	2702.6	1.39	0.4361	0.4697
$1.25 \times 10^5$	-6.859	1890.2	0.50	0.6236	1.0477

and

$$M_{s\theta} = \left( \frac{40}{\rho_p} \right)^2 \quad (33)$$

can be obtained; thus, the molecular weight of a segment of polystyrene in cyclohexane at the theta temperature can be

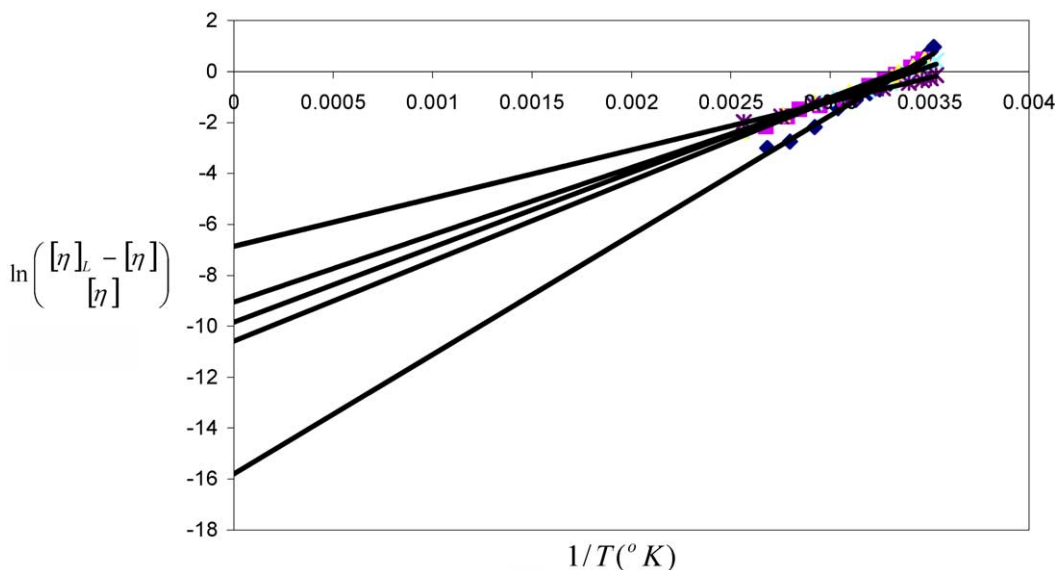


Fig. 1. Plots of  $\ln\{([\eta]_L - [\eta])/[\eta]\}$  versus  $1/T$  for  $M_w = 4.40 \times 10^6$  (◆),  $1.56 \times 10^6$  (■),  $1.05 \times 10^6$  (▲),  $6.22 \times 10^5$  (×),  $1.25 \times 10^5$  (★) g/mol of polystyrene in decalin solutions.



obtained from Eq. (33). The molecular weight of a segment of polystyrene at  $\theta = 34.5^\circ\text{C}$  was found to be 1451 g/mol from Eq. (33) by taking the density of polystyrene to be 1.05 g/ml. From this value, the number of monomers in a segment was found as  $n \approx 14$ . This value coincides with the value  $n = 15 - 20$  given by Flory [3]. Then, the segment number  $x_\theta$  of a polystyrene fraction at the theta condition can be calculated from the following equation.

$$x_\theta = \frac{M_w}{M_{s\theta}} \quad (34)$$

If the optimum values given in Table 7 for the polystyrene in decalin solutions are examined, it was found from Tables 2–6 that the values belonging to  $4.40 \times 10^6$  g/mol of polystyrene are related for the good solvent condition and the other values are for the theta conditions. The values of  $1/\delta_\theta^2$  calculated from these optimum values of  $\overline{\Delta H}/R$  and the values of  $1/x_\theta^{1/2}$  calculated from Eq. (34) are also given in Table 7. In these calculations, the repeat unit volume was taken as  $98 \text{ cm}^3/\text{mol}$ . Fig. 2 shows a plot of  $1/\delta_\theta^2$  versus  $1/x_\theta^{1/2}$  for data between  $1.25 \times 10^5$  g/mol and  $1.56 \times 10^6$  g/mol. The least-squares fitting gives  $\delta_{\theta\infty} = 18.8 \pm 1.2 (\text{J}/\text{cm}^3)^{1/2}$  and  $\hat{X}_{12} = 31.3 \pm 3.1 \text{ J}/\text{cm}^3$  ( $r^2 = 0.9996$ ).

The experimental values of  $M_w$  and  $[\eta]_\theta$  for polystyrene in cyclohexane at  $34.5^\circ\text{C}$  and  $[\eta]$  in toluene at  $15^\circ\text{C}$  solutions taken from Ref. [14] were given in Table 8. The value of  $a$  for polystyrene in toluene solution was found as 0.7 for the data between  $2.05 \times 10^4$  g/mol and  $1.32 \times 10^6$  g/mol of polystyrene. The molecular weight  $M_s$  of a segment of polystyrene at the good solvent condition and the number of monomers in a segment were found to be 416 g/mol and  $n = 4$ , respectively. The entropy changes for mixing of polystyrene fractions were determined from Eqs. (21) or (22) for cyclohexane, and from Eqs. (25) or (26) for toluene. The values calculated by using these data are also given in Table 8. Fig. 2 shows the plot of  $1/\delta_\theta^2$  versus  $1/x_\theta^{1/2}$  for polystyrene in cyclohexane solution. The least-squares

fitting of these data gives  $\delta_{\theta\infty} = 18.5 \pm 0.3 (\text{J}/\text{cm}^3)^{1/2}$  and  $\hat{X}_{12} = 39.4 \pm 1.3 \text{ J}/\text{cm}^3$  ( $r^2 = 0.9981$ ) for the data between  $2.05 \times 10^4$  g/mol and  $3.84 \times 10^6$  g/mol of polystyrene. Fig. 3 shows the plots of  $1/\delta_g^2$  versus  $1/x_g^{0.7}$  for polystyrene in toluene solution and the least-squares fitting gives  $\delta_{g\infty} = 18.0 \pm 0.5 (\text{J}/\text{cm}^3)^{1/2}$  and  $\hat{X}_{12} = 19.8 \pm 2.7 (\text{J}/\text{cm}^3)$  ( $r^2 = 0.9707$ ) for the data between  $2.05 \times 10^4$  g/mol and  $1.32 \times 10^6$  g/mol of polystyrene.

The intrinsic viscosities of polystyrene in cyclohexane, decalin and dioctyl phthalate at the theta temperatures and in toluene at  $12^\circ\text{C}$  taken from Ref. [11] are given in Table 9. As seen from this table, the values of  $[\eta]_\theta$  for polystyrene in cyclohexane, decalin and dioctyl phthalate solutions are close to each other for the same molecular weight of polystyrene and the  $K_\theta$  values calculated for these solutions are  $8.5 \times 10^{-4}$ ,  $8.2 \times 10^{-4}$  and  $8.6 \times 10^{-4} \text{ dl}/(\text{g}/\text{mol})^{1/2}$ , respectively. According to Eq. (14),  $x_\theta^{3/2}$  is proportional to  $[\eta]_\theta$ . Therefore, Eqs. (33) and (34) can also be used for the determination of  $M_{s\theta}$  and  $x_\theta$  for polystyrene in decalin and dioctyl phthalate solutions. The values calculated by using the data from Table 9 are given in Table 10. Fig. 2 also shows the plots of  $1/\delta_\theta^2$  versus  $1/x_\theta^{1/2}$  data for polystyrene in cyclohexane, decalin and dioctyl phthalate solutions. The least-squares fittings of these data give  $\delta_{\theta\infty} = 18.4 \pm 0.2 (\text{J}/\text{cm}^3)^{1/2}$ ,  $\hat{X}_{12} = 39.6 \pm 0.6 \text{ J}/\text{cm}^3$  ( $r^2 = 0.9996$ ) for the data between  $1.98 \times 10^4$  g/mol and  $1.56 \times 10^6$  g/mol of polystyrene in cyclohexane,  $\delta_{\theta\infty} = 18.0 \pm 0.3 (\text{J}/\text{cm}^3)^{1/2}$ ,  $\hat{X}_{12} = 35.9 \pm 1.1 \text{ J}/\text{cm}^3$  ( $r^2 = 0.9984$ ) for the data between  $1.98 \times 10^4$  g/mol and  $4.40 \times 10^6$  g/mol of polystyrene in decalin,  $\delta_{\theta\infty} = 18.0 \pm 0.2 (\text{J}/\text{cm}^3)^{1/2}$  and  $\hat{X}_{12} = 38.0 \pm 0.4 \text{ J}/\text{cm}^3$  ( $r^2 = 0.9994$ ) for the data between  $1.98 \times 10^4$  g/mol and  $1.56 \times 10^6$  g/mol of polystyrene in dioctyl phthalate solutions. Fig. 3 also shows a plot of  $1/\delta_g^2$  versus  $1/x_g^{0.7}$  data for polystyrene in toluene solution and the least-squares fitting of these data gives  $\delta_{g\infty} = 18.0 \pm 0.6 (\text{J}/\text{cm}^3)^{1/2}$  and  $\hat{X}_{12} = 19.5 \pm 3.0 \text{ J}/\text{cm}^3$  ( $r^2 = 0.9663$ ) for the data between  $1.98 \times 10^4$  g/mol and  $1.56 \times 10^6$  g/mol of polystyrene in toluene solution. The values of  $\delta_\infty$  and  $\hat{X}_{12}$

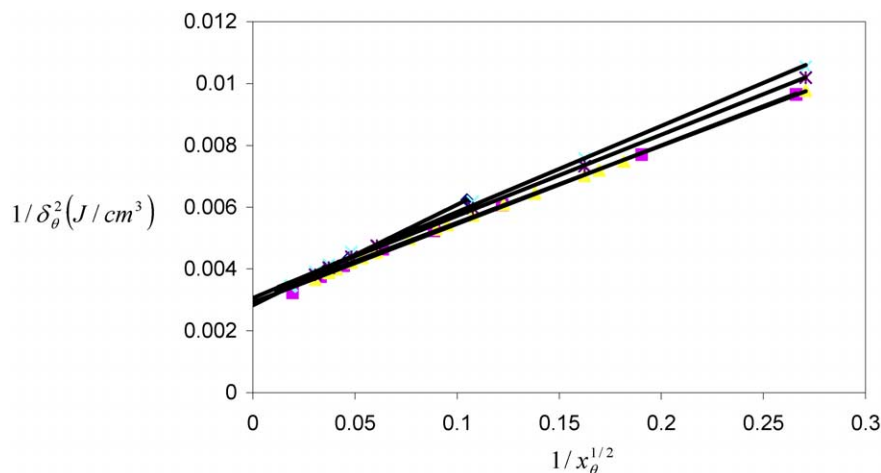


Fig. 2. Plots of  $1/\delta_\theta^2$  versus  $1/x_\theta^{1/2}$  for polystyrene: (◆) in decalin for the data from Table 7; (■) in cyclohexane at  $34.5^\circ\text{C}$  for the data from Ref. [14]; (▲) in cyclohexane at  $34.8^\circ\text{C}$ ; (×) in decalin at  $12.2\text{--}15.2^\circ\text{C}$ ; (★) in dioctyl phthalate at  $22.0^\circ\text{C}$  for the data from Ref. [11].

Table 8

Intrinsic viscosities (dl/g) of polystyrenes in cyclohexane at the theta temperature (34.5 °C) and in toluene at 15.0 °C, and the values of  $1/\delta_g^2$  ( $J/cm^3$ )<sup>-1</sup>,  $1/x_g^{1/2}$  and  $1/x_g^{0.7}$

Cyclohexane ( $\theta = 34.5$ °C)				Toluene (15.0 °C)		
$M_w$ (g/mol)	$[\eta]_\theta$	$(1/\delta_\theta^2) \times 10^{-2}$	$(1/x_\theta^{1/2}) \times 10^{-1}$	$[\eta]$	$(1/\delta_g^2) \times 10^{-2}$	$(1/x_g^{0.7}) \times 10^{-2}$
$2.05 \times 10^4$	0.123	0.9645	2.6604	0.156	0.6173	6.5333
$4.00 \times 10^4$	0.172	0.7701	1.9046	0.248	0.5269	4.0919
$9.73 \times 10^4$	0.273	0.6073	1.2212	0.467	0.4411	2.1963
$1.91 \times 10^5$	0.380	0.5234	0.8871	0.756	0.3925	1.3698
$3.59 \times 10^5$	0.512	0.4634	0.6357	1.18	0.3559	0.8806
$7.32 \times 10^5$	0.734	0.4103	0.4452	1.97	0.3219	0.5348
$1.32 \times 10^6$	0.981	0.3748	0.3315	2.91	0.2984	0.3540
$3.84 \times 10^6$	1.75	0.3224	0.1943	7.05	0.2635	0.1676

Results taken from Ref. [14].

Table 9

Intrinsic viscosities (dl/g) of polystyrene in cyclohexane, decalin and dioctyl phthalate at their respective theta temperatures and in toluene at 12.0 °C

$M_w$ (g/mol)	Cyclohexane $t = 34.8$ °C, $[\eta]_\theta$	Decalin $t = \theta^a$ , $[\eta]_\theta$	Dioctyl phthalate $t = 22.0$ °C, $[\eta]_\theta$	Toluene $t = 12.0$ °C, $[\eta]$
$1.98 \times 10^4$	0.119	0.123	0.150	0.156
$4.40 \times 10^4$	0.180			
$5.50 \times 10^4$	0.200	0.206	0.220	0.320
$7.60 \times 10^4$	0.245			
$9.62 \times 10^4$	0.266			
$1.25 \times 10^5$	0.290	0.283	0.310	0.548
$1.60 \times 10^5$	0.340			
$1.80 \times 10^5$	0.354			
$2.47 \times 10^5$	0.420			0.92
$3.94 \times 10^5$	0.545		0.500	
$4.06 \times 10^5$	0.550			
$5.07 \times 10^5$	0.600			
$6.22 \times 10^5$	0.660	0.62	0.600	1.64
$8.62 \times 10^5$	0.780			
$1.05 \times 10^6$	0.860	0.83	0.820	2.45
$1.56 \times 10^6$	1.06	1.00	1.02	3.55
$4.04 \times 10^6$		1.58		6.85
$4.40 \times 10^6$		1.71		8.00

Results taken from Ref. [11].

<sup>a</sup> Values of  $\theta$  are 15.2 °C for the data on  $1.56 \times 10^6$  g/mol and  $1.05 \times 10^6$  g/mol of polystyrene, and 12.2 °C otherwise.

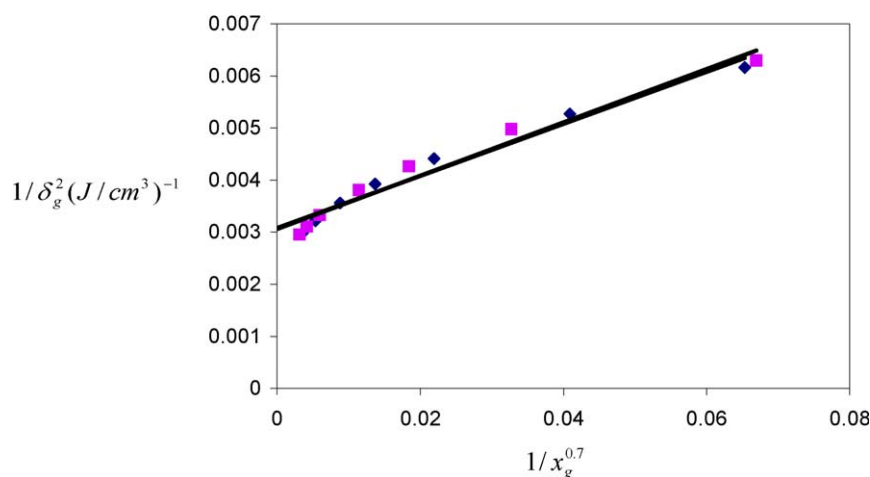


Fig. 3. Plots of  $1/\delta_g^2$  versus  $1/x_g^{0.7}$  for polystyrene: (◆) in toluene at 15 °C for the data from Ref. [14] and (■) in toluene at 12 °C for the data from Ref. [11].

Table 10

The values of  $1/\delta_\theta^2$  ( $\text{J}/\text{cm}^3$ )<sup>-1</sup> and  $1/x_\theta^{1/2}$  for polystyrene in theta solvents, and the values of  $1/\delta_g^2$  ( $\text{J}/\text{cm}^3$ )<sup>-1</sup> and  $1/x_g^{0.7}$  for polystyrene in toluene for the data given in Table 9

$M_w$	Cyclohexane		Decalin	Diocetyl phthalate	Toluene	
	$(1/\delta_\theta^2) \times 10^{-2}$	$(1/x_\theta^{1/2}) \times 10^{-1}$	$(1/\delta_\theta^2) \times 10^{-2}$	$(1/\delta_\theta^2) \times 10^{-2}$	$(1/\delta_g^2) \times 10^{-2}$	$(1/x_g^{0.7}) \times 10^{-2}$
$1.98 \times 10^4$	0.9764	2.7071	1.0537	1.0190	0.6295	6.6942
$4.40 \times 10^4$	0.7478	1.8159				
$5.50 \times 10^4$	0.7019	1.6242	0.7575	0.7324	0.4978	3.2742
$7.60 \times 10^4$	0.6446	1.3817				
$9.62 \times 10^4$	0.6084	1.2281				
$1.25 \times 10^5$	0.5726	1.0774	0.6180	0.5975	0.4262	1.8430
$1.60 \times 10^5$	0.5426	0.9523				
$1.80 \times 10^5$	0.5293	0.8978				
$2.47 \times 10^5$	0.4967	0.7664			0.3807	1.1441
$3.94 \times 10^5$	0.4553	0.6068		0.4751		
$4.06 \times 10^5$	0.4529	0.5978				
$5.07 \times 10^5$	0.4357	0.5350				
$6.22 \times 10^5$	0.4210	0.4830	0.4544	0.4393	0.3326	0.5994
$8.62 \times 10^5$	0.3995	0.4103				
$1.05 \times 10^6$	0.3875	0.3717	0.4139	0.4043	0.3104	0.4155
$1.56 \times 10^6$	0.3655	0.3050	0.3904	0.3814	0.2955	0.3149
$4.04 \times 10^6$		0.1895	0.3472		0.2648	0.1618
$4.40 \times 10^6$		0.1816	0.3434		0.2624	0.1524

are given in Table 11. These results show that the values of  $\delta_\infty$  depend on the temperature and slightly on the molecular weight values of the polymer. The following equation can be written for polystyrene at theta and good solvent temperatures.

$$\overline{\Delta S}_2 = (\overline{\Delta H}_2/T) \approx 109.6 \pm 1.4 \text{ J/mol } ^\circ\text{K} \quad (35)$$

The solubility parameter values found in this study for polystyrene coincide with the experimental values of  $17.7$ – $20.8$  ( $\text{J}/\text{cm}^3$ )<sup>1/2</sup>, calculated values of  $18.2$ – $20.2$  ( $\text{J}/\text{cm}^3$ )<sup>1/2</sup> and preferred value of  $18.5$  ( $\text{J}/\text{cm}^3$ )<sup>1/2</sup> for polystyrene at  $25$  °C [15].

The relationship between the effective interchange energy  $\bar{X}_{12}$ , interchange energy  $X_{12}$  and entropy  $Q_{12}$  parameters in the equation of state theory [2] has been given by the following Eq. [10].

$$\bar{X}_{12} = X_{12} - T\nu Q_{12} \quad (36)$$

where  $\nu$  is the reduced volume of the polymer, with  $\nu = 1.1528$  for polystyrene at  $25$  °C [2]. Flory and coworkers have found  $X_{12} = 42 \text{ J}/\text{cm}^3$  and  $Q_{12} = 0.023 \text{ J}/(\text{cm}^3 \text{ } ^\circ\text{K})$  for

polystyrene in cyclohexane [16], and  $X_{12} = 8.8 \text{ J}/\text{cm}^3$  and  $Q_{12} = -0.029 \text{ J}/(\text{cm}^3 \text{ } ^\circ\text{K})$  for polystyrene in ethylbenzene [17] solutions at  $25$  °C from osmotic pressure data. Ethylbenzene is a good solvent for polystyrene [17]. Using these values, Eq. (36) yields  $\bar{X}_{12} = 34.1 \text{ J}/\text{cm}^3$  for polystyrene in cyclohexane and  $\bar{X}_{12} = 18.8 \text{ J}/\text{cm}^3$  for polystyrene in ethylbenzene solutions at  $25$  °C. These results indicate that the values of  $\bar{X}_{12}$  are close to the values of  $\hat{X}_{12}$  found in this study for polystyrene in cyclohexane and toluene solutions.

### 3.3. Han's equation and thermodynamic parameters of polymers

Han [8] has obtained the following equations from the blob theory for the asymptotic behaviour of  $\alpha_\eta$  at the good solvent limit ( $N \gg N_r$ ) by using the static empirical approach to intrinsic viscosity of Mandelkern and Flory [8]

$$\alpha_\eta^3 = 0.416 \left( \frac{N}{N_r} \right)^{0.3} \quad (37)$$

Table 11

The values of  $\delta_\infty$  and  $\hat{X}_{12}$  parameters for polystyrene in theta and good solvents

Solvent	$\delta_\infty$ ( $\text{J}/\text{cm}^3$ ) <sup>1/2</sup>	$\hat{X}_{12}$ ( $\text{J}/\text{cm}^3$ )	$t$ (°C)	$M_w$ range
Cyclohexane	18.5	39.4	34.5 <sup>a</sup>	$2.05 \times 10^4$ – $3.84 \times 10^6$
	18.4	39.6	34.8 <sup>a</sup>	$1.98 \times 10^4$ – $1.56 \times 10^6$
Toluene	18.0	19.8	15.0	$2.05 \times 10^4$ – $1.32 \times 10^6$
	18.0	19.5	12.0	$1.98 \times 10^4$ – $1.56 \times 10^6$
Decalin	18.0	35.9	12.2–15.2 <sup>a</sup>	$1.98 \times 10^4$ – $4.40 \times 10^6$
Diocetyl phthalate	18.0	38.0	22.0 <sup>a</sup>	$1.98 \times 10^4$ – $1.56 \times 10^6$

<sup>a</sup>  $\theta$  points.



and alternatively by using the dynamic argument of Weill and des Cloizeaux [8]

$$\alpha_{\eta}^3 = 0.637 \left( \frac{N}{N_{\tau}} \right)^{0.3} \quad (38)$$

where  $\alpha_{\eta}^3 = [\eta]/[\eta]_{\theta}$ . Akcasu and Han [3] have calculated  $N/N_{\tau}$  using the following equation

$$\frac{N}{N_{\tau}} = \frac{M\tau^2}{M_0(n\alpha)} \quad (39)$$

where  $\tau = (T - \theta)/T$ ,  $M_0$  is the molecular weight per monomer and  $n$  is the number of monomer units in a statistical length. The product  $(n\alpha)$  is an adjustable parameter. When Eq. (39) and  $\tau$  are substituted into Eqs.(37) and (38), the following equations are obtained

$$\alpha_{\eta}^5 = 0.232 \left[ \frac{M}{M_0(n\alpha)} \right]^{1/2} - 0.232 \left[ \frac{M}{M_0(n\alpha)} \right]^{1/2} \frac{\theta}{T} \quad (40)$$

for the Mandelkern and Flory case, and

$$\alpha_{\eta}^5 = 0.471 \left[ \frac{M}{M_0(n\alpha)} \right]^{1/2} - 0.471 \left[ \frac{M}{M_0(n\alpha)} \right]^{1/2} \frac{\theta}{T} \quad (41)$$

for the Weill and des Cloizeaux case. A plot of  $\alpha_{\eta}^5$  versus  $1/T$  will give a straight line with a slope of  $\{c[M/M_0(n\alpha)]^{1/2}\theta\}$  and an intercept of  $\{c[M/M_0(n\alpha)]^{1/2}\}$ , where the parameter  $c$  is equal to the value of 0.232 or 0.471. The values of  $\alpha_{\eta}^5$  and  $1/T$  calculated from the data in Table 2 for the different molecular weights of polystyrene in decalin solutions are given in Table 12. Fig. 4 shows the plot of  $\alpha_{\eta}^5$  versus  $1/T$  for the data in Table 12. The values of slope and intercept calculated from the least-squares fitting

Table 12

The values of  $\alpha_{\eta}^5$  and  $1/T$  (°K) for the data given in Table 2 for polystyrene in decalin solutions

$M_w$ (g/mol)		$M_w$ (g/mol)		$M_w$ (g/mol)		$M_w$ (g/mol)		$M_w$ (g/mol)	
$4.40 \times 10^6$		$1.56 \times 10^6$		$1.05 \times 10^6$		$6.22 \times 10^5$		$1.25 \times 10^5$	
$\alpha_{\eta}^5$	$(1/T) \times 10^{-3}$	$\alpha_{\eta}^5$	$(1/T) \times 10^{-3}$	$\alpha_{\eta}^5$	$(1/T) \times 10^{-3}$	$\alpha_{\eta}^5$	$(1/T) \times 10^{-3}$	$\alpha_{\eta}^5$	$(1/T) \times 10^{-3}$
1.11	3.4907	1.18	3.4450	1.19	3.4174	1.13	3.4509	1.06	3.4622
1.25	3.4794	1.35	3.4063	1.53	3.3416	1.33	3.4009	1.13	3.3953
1.40	3.4679	1.71	3.3311	1.68	3.3102	1.70	3.2999	1.28	3.2641
1.51	3.4594	2.00	3.2743	2.44	3.0966	2.01	3.1853	1.54	3.1056
1.85	3.4341	2.39	3.1950	2.93	2.9209	2.28	3.0474	1.70	2.9128
2.04	3.4118	2.96	3.0696	3.41	2.7604	2.52	2.9209	1.98	2.7537
2.34	3.3791	3.32	2.9495	3.88	2.5535	3.26	2.5535	2.08	2.5658
2.66	3.3469	3.57	2.8461						
3.10	3.2999	3.71	2.7823						
3.53	3.2491	4.03	2.6765						
3.82	3.1998								
4.29	3.1287								
4.91	3.0386								
5.74	2.9209								
6.24	2.7970								
6.42	2.6833								

Table 13

The values of  $\{c[M/M_0(n\alpha)]^{1/2}\}$  and  $\{c[M/M_0(n\alpha)]^{1/2}\theta\}$  found from the data given in Table 12 for polystyrene in decalin solutions

$M_w$ (g/mol)				
$4.40 \times 10^6$	$1.56 \times 10^6$	$1.05 \times 10^6$	$6.22 \times 10^5$	$1.25 \times 10^5$
25.793 <sup>a</sup>	14.234 <sup>a</sup>	11.960 <sup>a</sup>	9.256 <sup>a</sup>	5.198 <sup>a</sup>
-6960.8 <sup>b</sup>	-3748.6 <sup>b</sup>	-3114.4 <sup>b</sup>	-2312.9 <sup>b</sup>	-1193.8 <sup>b</sup>
$r = -0.9857^c$	$r = -0.9913$	$r = -0.9954$	$r = -0.9911$	$r = -0.9941$

<sup>a</sup> gives  $\{c[M/M_0(n\alpha)]^{1/2}\}$

<sup>b</sup> gives  $\{c[M/M_0(n\alpha)]^{1/2}\theta\}$

<sup>c</sup> Correlation coefficient

of these data were given in Table 13. Han has proposed a value of  $n\alpha = 4$  for polystyrene. The values of  $\{0.232[M/416]^{1/2}\}$  parameters obtained from the Han equation for Mandelkern–Flory model,  $\{c[M/M_0(n\alpha)]^{1/2}\}$  parameters obtained in this study and thermodynamics parameters for the theta and good solvent conditions for polystyrene fractions are given in Table 14. These results show that the values of  $\{c[M/M_0(n\alpha)]^{1/2}\}$  coincide with the values obtained from Han's equation for the Mandelkern–Flory model. The values for  $1.56 \times 10^6$  and  $1.05 \times 10^6$  g/mol of polystyrene are close to the thermodynamics parameters for the good solvent conditions and the values for  $6.22 \times 10^5$  and  $1.25 \times 10^5$  g/mol of polystyrene are close to the thermodynamics parameters for the theta conditions. From the results given in Tables 13 and 14, the following equation is proposed for the estimation of the thermodynamics parameters of the polymers for the temperatures above the theta point.

$$\alpha_{\eta}^5 \approx \frac{\overline{\Delta S}_2}{R} - \frac{\overline{\Delta H}_2}{RT} \quad (42)$$

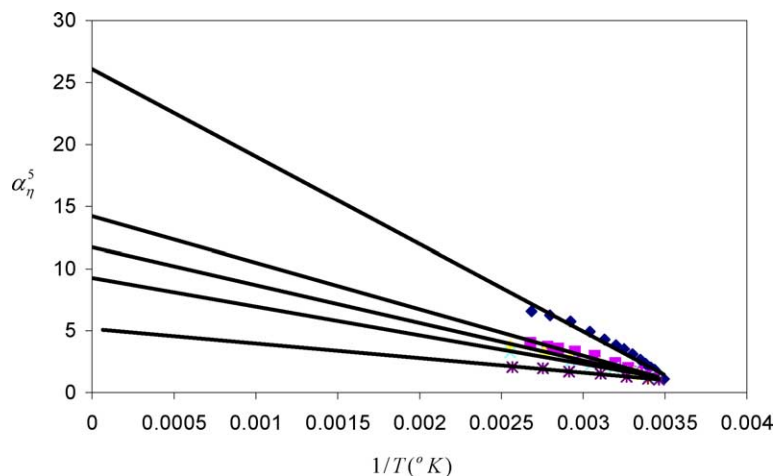


Fig. 4. Plots of  $\alpha_{\eta}^5$  versus  $1/T$  for  $M_w = 4.40 \times 10^6$  ( $\blacklozenge$ ),  $1.56 \times 10^6$  ( $\blacksquare$ ),  $1.05 \times 10^6$  ( $\blacktriangle$ ),  $6.22 \times 10^5$  ( $\times$ ),  $1.25 \times 10^5$  ( $\star$ ) g/mol of polystyrene in decalin solutions.

#### 4. Conclusions

No direct experimental method for determining the solubility parameter of a polymer exists. It is suggested on the basis of the results obtained in this study that the solubility parameter of a polymer can be determined experimentally by using the intrinsic viscosity–temperature relationships of the polymer. The effective interchange energy parameter of a polymer–solvent pair was estimated from the solubility parameter–segment number relation of polymer fractions. It was found that the partial molar entropy change of a polymer for mixing at the theta and good solvent temperatures has nearly a constant value. In addition, it was also found that the thermodynamics parameters of polymers for mixing can be estimated from the plot of  $\alpha_{\eta}^5$  versus  $1/T$  for the temperatures above the theta point. The equations proposed in this study were applied to the intrinsic viscosity–temperature data of polystyrene fractions in decalin solutions, and polystyrene

fractions in decalin, cyclohexane and dioctyl phthalate solutions at the theta temperatures and in toluene solutions at the given temperatures. The values of solubility parameters, the effective interchange energy parameters and the thermodynamic parameters of polystyrene in theta and good solvents obtained in this study were found to be coincided with the literature values.

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Table 14

Comparison of the values of  $\{c[M/M_0(n\alpha)]^{1/2}\}$  parameters and thermodynamics parameters of polystyrene

$M$ (g/mol)	$\{0.232[M/(104 \times 4)]^{1/2}\}^a$	$\{c[M/M_0(n\alpha)]^{1/2}\}$	$\overline{\Delta S}_{2\theta}/R$	$\overline{\Delta S}_{2g}/R$
$4.40 \times 10^6$	23.860	25.793	12.025	15.753
$1.56 \times 10^6$	14.207	14.234	10.470	13.990
$1.05 \times 10^6$	11.655	11.960	9.876	13.317
$6.22 \times 10^5$	8.971	9.256	9.091	12.427
$1.25 \times 10^5$	4.022	5.198	6.684	9.699

<sup>a</sup> Obtained from Han's equation for the Mandelkern–Flory model.