BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 7, pp. 1421–1424, 1995

0032-3861/95/$10.00+0.00

Combinatory entropy in crystalline polymer solutions

Susumu Saeki
Department of Materials Science and Engineering, Fukui University, Fukui 910, Japan
(Received 29 August 1994)

The combinatory entropy in the ternary solution of crystalline polymers (2), with n_c rod-like parts and c segments per part, with solvent (1) and holes (0) has been derived based on the Flory–Huggins theory, which is given by:

$$S_{\mathrm{P\ S\ H}}/R=(\phi_2/r)\ln\{[(z-1)/e]^{m-1}m\}-\phi_0\ln\phi_0-\phi_1\ln\phi_1-(\phi_2/r)\ln\phi_2-\theta\phi_2\ln\phi_2$$
$$+(1-\phi_2)\ln[A/(A+\theta\phi_2)]+(\phi_2/r)\ln[A(1+n_cc)/(A+\theta\phi_2)]+\theta\phi_2\ln[(\phi_2/r)(1+n_cc)/(A+\theta\phi_2)]$$

where R is the gas constant, z is the coordination number, e is communal entropy, $m=r-n_c(c-1)$, $A=[\phi_0+\phi_1+(\phi_2/r)]$, $\theta=n_cc/r$, r is the total number of segments per polymer chain, and ϕ_i is the volume fraction of component i. Two types of cluster formation by the rod-like parts in the crystalline polymer solution are considered: cluster formations by different polymer chains, and by a single polymer chain. Dependence of the cluster size on the length of the rod-like part or c has been determined based on the theory. An equation for the entropy of fusion for arbitrary crystallinity is also derived.

(Keywords: combinatory entropy; crystalline polymer solution; Flory–Huggins theory)

INTRODUCTION

The main purpose of this work is to obtain basic information on the formation of clusters or ordered regions in crystalline polymer solutions through calculations of combinatory entropy, which may help in the understanding of crystallization phenomena such as folded-chain and extended-chain crystals[1,2]. The entropy of fusion is an important quantity for characterizing the melting phenomena. A theory of fusion in crystalline polymers was proposed by Flory, where the combinatory entropy of a mixture of solvent and polymer molecules, which contains limited regions of perfect order or crystallites, is derived[3]. In this work, the entropy of fusion has been derived from the combinatory entropy in the ternary solution of a polymer with rod-like parts and flexible parts in solvent and holes, and the origin of the entropy of fusion is discussed. Comparisons are made between the Flory theory and the statistical thermodynamic theory of Oyama[4] and the theory in this work.

CALCULATION OF THE COMBINATORY ENTROPY IN THE TERNARY SOLUTION CRYSTALLINE POLYMER–SOLVENT–HOLE

It was shown in previous work[5] that the number of configurations in a flexible polymer solution given by the Flory–Huggins theory[6] is reduced to:

$$\Omega_{\mathrm{F-H}}=q_2^{N_2}\{(N_1+rN_2)!/[N_1!(rN_2)!]\}\phi_2^{N_2(r-1)} \tag{1}$$

where

$$q_2=z(z-1)^{r-2}r/e^{r-1} \tag{2}$$

and

$$\phi_2=rN_2/(N_1+rN_2) \tag{3}$$

Here r is the number of segments per polymer chain and z is the coordination number. In this work we assumed that a single polymer chain in a crystallizable solution consists of n_c rod-like parts with a length of c segments per rod-like part, and n_a flexible parts with a segments per flexible part, and the total number of segments per chain is $r=n_cc+n_aa$. The number of configurations for the ternary solution of N_2 polymers, N_1 solvent molecules and N_0 holes, based on the Flory–Huggins theory or equation (1) and an approximation that $z(z-1)^{r-2}\approx(z-1)^{r-1}$, is given by:

$$\begin{aligned}\Omega_{\mathrm{P-S-H}}=&\{[(z-1)/e]^{m-1}m\}^{N_2}\{(N_0+N_1+rN_2)!/\\&[N_0!N_1!(rN_2)!]\}\phi_2^{(r-1)N_2-x}\\&\times\{[(N_2+x)(N_2+x-1)\cdots(N_2+1)]/\\&[(N_0+N_1+N_2+x)(N_0+N_1+N_2+x-1)\cdots\\&(N_0+N_1+N_2+1)]\}\end{aligned} \tag{4}$$

where m is the effective number of flexible segments and is given by:

$$m=n_c+n_aa \tag{5}$$

Equation (5) suggests that a rod-like part in the chain behaves as a flexible segment. The first term in equation (4) is the number of configurations of N_2 polymer chains with m effective segments. The second term corresponds to the configuration for the ideal mixture of a solution of N_0 holes, N_1 solvent molecules and rN_2

segments, where the polymer chains are dismembered to rN_2 segments. The third term corresponds to the probability that $(r-1)N_2-x$ segments are fixed at their positions on the lattice. In the Flory–Huggins theory the factor is $\phi_2^{(r-1)N_2}$ or $x=0$, and therefore x segments are free in equation (4). The total number of rod-like parts in solution, x, is given by:

$$x=cn_cN_2 \tag{6}$$

Therefore x is a parameter characterizing the stiffness of a polymer chain and $x=0$ corresponds to the flexible polymer $n_c=0$. The fourth term in equation (4) gives the probability that the extra free x segments are fixed at the nearest-neighbour sites of free N_2 segments or combined with the N_2 segments to make rod-like parts in polymer chains.

The following two calculations are helpful in understanding the physical meaning of the fourth term and the probability mentioned above. The first calculation is that the number of configurations of a simple liquid mixture (SM) of N_1 molecules of component 1 and N_2 molecules of component 2 is given by:

$$\Omega_{\mathrm{SM}}=(N_1+N_2)!/(N_1!N_2!) \tag{7}$$

and the number of configurations when n_1 molecules of 1 are removed or disappear from the mixture, which is designated by $\Omega^R_{n_1}$ is given by:

$$\Omega^R_{n_1}=(N_1+N_2-n_1)!/[(N_1-n_1)!N_2!] \tag{8}$$

$$=\Omega_{\mathrm{SM}}\{[N_1(N_1-1)\cdots(N_1-n_1+1)]/[(N_1+N_2)(N_1+N_2-1)\cdots(N_1+N_2-n_1+1)]\} \tag{9}$$

The last ratio in equation (9) gives the probability that n_1 molecules of 1 are removed from the mixture when the total number of free molecules before the removal is $N_t=N_1+N_2$. The second calculation is that according to Tonks[7], the number of configurations for a one-dimensional system comprising N molecules each of length l^* and a space of length L is given by:

$$\Omega=(L-Nl^*)^N/N! \tag{10}$$

$$\simeq[(l-l^*)e]^N \tag{11}$$

where $l=L/N$ is the space available per molecule. This indicates that the number of configurations for a molecule is $(l-l^*)e$, where e is the communal entropy which comes from the fact that a molecule can move around the entire space and is not fixed at a position or cell. It is obvious that Ω decreases by $(l-l^*)e$ when a molecule is removed from the system. Let us return to the polymer solution or equation (4), where there are N_2+x free segments and $(r-1)N_2-x$ fixed segments. If one free segment is combined with the N_2 free segments, the number of configurations changes by $(z-1)/e$ because the segment loses the communal entropy e but gains an entropy from rotation about the bond, which is expressed by $(z-1)$ in the lattice model. In the case of a rigid bond or $z=2$, Ω decreases by e^{-1}, which is equal to the decrease of entropy due to the removal of a segment from solution when $[(l-l^*)e]^{-1}=e^{-1}$ or $l-l^*=1$ in equation (11). The fourth term in equation (4) means, from the first calculation, that x segments are removed from the solution with $(N_0+N_1+N_2+x)$ free molecules and segments. The second calculation shows that the removal of x segments is equivalent to the formation of x rod-like parts in the flexible polymer chains.

CLUSTER FORMATION IN CRYSTALLINE POLYMER SOLUTION

Two types of cluster formation by the rod-like parts in the crystalline polymer are considered: cluster formation by different polymer chains, and by a single polymer chain in solution. The probability that there are τ clusters in solution, which consist of v rod-like parts per cluster and c segments per rod-like part, and the rod-like parts in the cluster belong to many different polymers, is given by:

$$P_{\mathrm{cluster}}(v)=(n_cN_2)!/(v!)^\tau/\sum_{\tau=1}^{n_cN_2}(n_cN_2)!/(v!)^\tau \tag{12}$$

$$\simeq(1/v)^{N_2n_c} \tag{13}$$

where $n_cN_2=\tau v$ is the total number of rod-like parts in solution and is constant. Although the case of a polymer chain making a cluster is included in equation (12), the contribution is very small. The number of configurations for the ternary solution under the condition that there are τ clusters in solution with v rod-like parts per cluster is given by:

$$\Omega_{\mathrm{P\text{-}S\text{-}H,cluster}}=\Omega_{\mathrm{P\text{-}S\text{-}H}}(1/v)^{N_2n_c} \tag{14}$$

from which the entropy of the ternary solution with clusters is derived by $S=k\ln\Omega_{\mathrm{P\text{-}S\text{-}H,cluster}}$ where k is the Boltzmann constant. It is shown in equation (14) that the entropy $S_{\mathrm{P\text{-}S\text{-}H,cluster}}$ decreases with increasing v if n_c is constant. The maximum condition of the entropy with respect to n_c under n_cc is constant and constant concentration is given by:

$$[\partial(S_{\mathrm{P\text{-}S\text{-}H,cluster}}/R)/\partial n_c]_{n_cc,\phi i}=\ln[(z-1)/e]+[r-n_c(c-1)]^{-1}-(\partial n_c\ln v/\partial n_c)=0 \tag{15}$$

where R is the gas constant and ϕ_i is the volume fraction of component i. The following equation is derived from equation (15) by using an extreme boundary condition of a perfect crystal where $v=N_2$, $c=r$ and $n_c=1$, which is given by:

$$\ln v=\ln[(z-1)/e]+(c/r\theta)\ln\{[e/(z-1)]N_2r(1-\theta+\theta/c)\} \tag{16}$$

The entropy for the ternary solution is calculated by equation (4):

$$\begin{aligned}S_{\mathrm{P\text{-}S\text{-}H}}/R={}&(\phi_2/r)\ln\{[(z-1)/e]^{m-1}m\}-\phi_0\ln\phi_0\\&-\phi_1\ln\phi_1-(\phi_2/r)\ln\phi_2-\theta\phi_2\ln\phi_2\\&+(1-\phi_2)\ln[A/(A+\theta\phi_2)]\\&+(\phi_2/r)\ln[A(1+n_cc)/(A+\theta\phi_2)]\\&+\theta\phi_2\ln[(\phi_2/r)(1+n_cc)/(A+\theta\phi_2)]\end{aligned} \tag{17}$$

where $A=[\phi_0+\phi_1+(\phi_2/r)]$ and $\theta=n_cc/r$ gives a measure of crystallinity. The entropy $S_{\mathrm{P\text{-}S\text{-}H,cluster}}$ is given using equations (14), (17) and (16) by:

$$S_{\mathrm{P\text{-}S\text{-}H,cluster}}/R=S_{\mathrm{P\text{-}S\text{-}H}}/R-(n_c\phi_2/r)\ln v \tag{18}$$

$$\begin{aligned}={}&S_{\mathrm{P\text{-}S\text{-}H}}/R-(n_c\phi_2/r)\ln[(z-1)/e]\\&+(c/r\theta)\ln\{[e/(z-1)]\\&\times N_2r(1-\theta+\theta/c)\}\end{aligned} \tag{19}$$

It is interesting to examine the cluster formation by the same polymer in solution. The probability that there are N_2 clusters in solution which consist of v rod-like parts and c segments per part, and the v rod-like parts belong to a single polymer chain is given by:

$$P_{\mathrm{cluster,s}} = \{[n_c!/v!(n_c - v)!]/2^{n_c}\}^{N_2} \qquad (20)$$

The entropy $S_{\mathrm{P\ S\text{-}H,cluster,s}}$ is given using equations (17) and (20) by:

$$S_{\mathrm{P\ S\text{-}H,cluster,s}} = S_{\mathrm{P\text{-}S\text{-}H}} + k \ln P_{\mathrm{cluster,s}} \qquad (21)$$

The maximum condition of the entropy with respect to v, with n_c and c constant, is given by:

$$v = n_c/2 = r\theta/(2c) \qquad (22)$$

It is also shown that $\ln P_{\mathrm{cluster,s}}(v = n_c/2) = 0$ and therefore $S_{\mathrm{P\text{-}S\text{-}H,cluster,s}} = S_{\mathrm{P\text{-}S\text{-}H}}$ at $v = n_c/2$.

RESULTS AND DISCUSSION

It is reasonable to consider the cluster of rod-like parts as the crystallite and the flexible parts as the amorphous region in a typical crystalline polymer. Therefore the parameter τ corresponds to the number of crystallites, v to the number of structural units in a crystallite, and c to the average length of the unit in number of segments. Dependences of v on c for two types of cluster formation, i.e. a multiple cluster formation (equation (16)) and a single cluster formation (equation (22)), are shown in *Figures 1* and *2*, where $\ln v$ increases linearly with increasing c in equation (16), but $\ln v$ in equation (22) decreases with increasing c. The former behaviour shows that a parallel arrangement of the rod-like parts or cluster formation occurs more frequently with increasing the length of the rod-like part c, because the arrangement is favoured entropically and there are many partners. It is shown in *Figure 1* that $\ln v$ decreases with increasing θ at constant c, and therefore many crystallites of smaller size are formed with increasing θ. On the other hand, the latter behaviour shows that v decreases with increasing c or decreasing n_c, because in this case the partners are restricted to the rod-like parts of the same polymer chain.

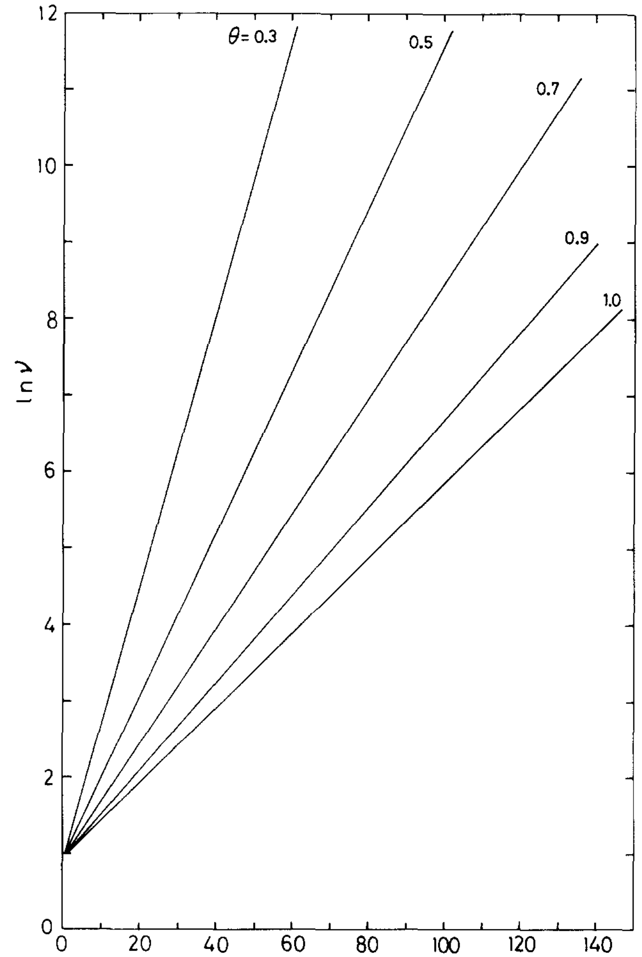

Figure 1 Plot of cluster size $\ln v$ *versus* length of structural unit in number of segments c in equation (16), with $z=8$, $r=1000$ and $N_2 r = 6 \times 10^{23}$, for various values of $\theta = cn_c/r$ in multiple cluster formation

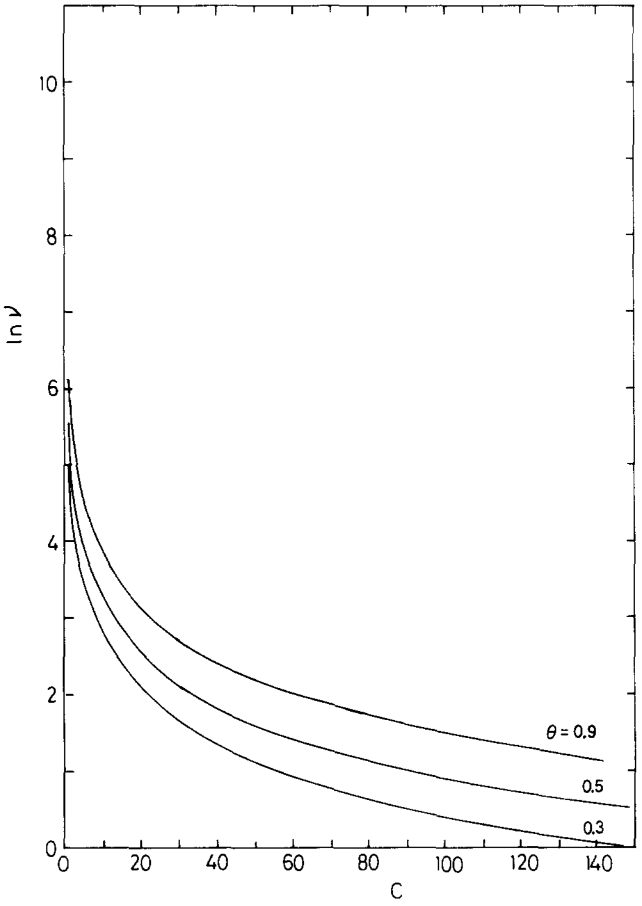

Figure 2 Plot of cluster size $\ln v$ *versus* length of structural unit in number of segments c in equation (22), with $z=8$, $r=1000$ and $N_2 r = 6 \times 10^{23}$, for various values of θ in single cluster formation

It is interesting to calculate the entropy of fusion in the crystalline polymer based on equation (4), which is given using equation (19) by:

$$\Delta S_F/R = S_{\mathrm{P\text{-}S\text{-}H}}(\phi_{0,1}, \phi_1 = 0, m = r)/R - S_{\mathrm{P\text{-}S\text{-}H,cluster}}(\phi_{0,s}, \phi_1 = 0, m = m)/R \qquad (23)$$

where $\phi_{0,1}$ and $\phi_{0,s}$ are the volume fraction of holes for liquid and solid states, respectively, by which the volume change at the melting point can be taken into account. The contribution of crystallinity on ΔS_F is also included in equation (23). The expression $\Delta S_F/R$ in equation (23) is given by:

$$\Delta S_F/R = (\phi_{2,1} - \phi_{2,s} + \theta\phi_{2,s})\ln[(z-1)/e] + (\phi_{2,1}/r)\ln r - \phi_{0,1}\ln\phi_{0,1} + (\phi_{2,s}/r)\ln\{N_2/[r\theta(\phi_{0,s} + \phi_{2,s}r^{-1})]\} - \theta\phi_{2,s}\ln\theta + (\phi_{0,s} + \theta\phi_{2,s})\ln(\phi_{0,s} + \theta\phi_{2,s}) \qquad (24)$$

In the special case of $\phi_{2,l}=\phi_{2,s}$, $\Delta S_F/R$ is reduced to:

$$\Delta S_F/R=\theta\phi_2 \ln[(z-1)/e]+(\phi_2/r)\ln\{N_2/[(\phi_0+\phi_2 r^{-1})]\} - \phi_0 \ln \phi_0-\theta\phi_2 \ln \theta+(\phi_0+\theta\phi_2)\ln(\phi_0+\theta\phi_2) \tag{25}$$

In the derivation a condition $r \gg 1$ is used. In the case of no holes in the solid state or $\phi_{0,s}=0$, equation (24) is given by:

$$\Delta S_F/R=(\theta-\phi_{0,l})\ln[(z-1)/e]+(\phi_{2,l}/r)\ln r-\phi_{0,l}\ln \phi_{0,l} +(r^{-1})\ln(N_2/\theta) \tag{26}$$

The term $\ln[(z-1)/e]$ in these equations is due to the entropy change from the chain conformation; $\phi_{0,l} \ln \phi_{0,l}$ is due to a distribution of holes in the liquid state, and the other terms containing θ are due to the intermolecular contribution from the change of chain stiffness from rod-like to flexible polymer. The term $\ln N_2$ comes from the extreme boundary condition of a perfect crystal.

The entropy of fusion ΔS_F of a linear crystalline polymer has been discussed through its separation into several contributions. Starkweather and Boyd[8] separated ΔS_F into three parts: first, the entropy due to the increase in volume on melting; second, the entropy due to the appearance of long-range disorder; and third, the entropy of rotational isomerism due to many configurations in the melt through rotation about skeletal bonds. Kirshenbaum[9] and Tonelli[10] separated ΔS_F into two contributions: first, the entropy change at constant volume, which may be identified as the change in the intramolecular configurational entropy of a polymer chain; and second, the entropy change made by the change in volume at melting. Karasz *et al.*[11] argued against the separation of the entropy of fusion. It is shown in equation (24) that contributions from the volume change $\phi_{2,l}-\phi_{2,s}$ and the chain stiffness to ΔS_F are included in the first term due to the entropy change from the chain conformation, and the chain stiffness also affects the intermolecular configurational entropy through $\theta=n_c c/r$. Therefore it is very difficult to separate ΔS_F into the inter- and intramolecular contributions.

It is very interesting to compare the theory in this work with that by Flory[3], in which a basic starting point is a single linear chain joined by all the polymer and solvent molecules, and the number of different arrangements of the N_1 and N_2 polymer molecules in the chain is given by:

$$\Omega_{\text{chain}}=(N_1+N_2)!/(N_1!N_2!) \tag{27}$$

The configurational entropy S_c of the semicrystalline polymer–solvent mixture in the Flory theory consists of four terms. The first term is calculated from equation (27) and the fourth is calculated from the probability of the pairing off of molecule ends. The second term is related to the entropy arising from the numerous configurations available to the single chain at the expense of communal entropy e, which is $k \ln[(z-1)/e]$. The third term is related to the probability that the crystallites are suitably occupied by polymer molecules, which means that the first cell of a given crystalline sequence of cells is occupied by polymer and by a proper segment of the structure unit, and that the ends of the molecules involved do not occur within the sequence; these considerations are not taken into account in this work. However, the probability of cluster formation and the chain stiffness of the polymer are taken into account in this work.

The statistical thermodynamic theory of crystalline polymer solution has been derived by Oyama[4], where the crystal structure, which is energetically stabilized, and the amorphous structure are assumed for the segments of crystallizable polymer; the theory also shows the possibility of phase separation into two phases which are different not only in concentration but also in the degree of crystallinity of the segment. In previous work[5] it was shown that phase separation occurs if the stiffness of the polymer chain or x increases, where x is expressed by $x=\alpha\phi_1 r N_2$ and α is a constant. A full discussion of phase separation in crystalline polymer solutions is possible if the enthalpy term in the solution is evaluated.

In a crystalline polymer solution, x is given by $x=n_c c N_2$, which is different from $x=\alpha\phi_1 r N_2$ in the semiflexible polymer solution[5]. In a crystalline polymer solution, cluster formation is essentially important because the formation leads to a stable state at the crystallization temperature, where the change of entropy due to cluster formation in solution (ΔS_{CF}) is negative and the change of enthalpy due to cluster formation (ΔH_{CF}) is negative, and ΔH_{CF} is a dominant factor in the crystallization. On the other hand, in a polymer solution with no clusters, the entropy of mixing ΔS_M and the enthalpy of mixing ΔH_M are both positive in most cases; ΔS_M is a dominant factor and no strong correlation between polymer chains exists, even in the pure polymer state. The chain configuration in a Θ solution is the same as that in the bulk state. The x in the semiflexible polymer solution, which is zero at the limit of $N_2=0$ (dilute polymer solution) and $N_1=0$ (pure state polymer), means that the intra- and intermolecular configurational contributions to the combinatory entropy are the same as those in the Flory–Huggins theory. The value of x in the crystalline polymer solution, which is not zero at the limit of $N_1=0$ but zero at $N_2=0$, suggests that the intra- and intermolecular contributions to S_{comb} are not the same as those in the Flory–Huggins theory. The intramolecular contribution to the combinatory entropy is the term containing $\ln[(z-1)/e]$, while the intermolecular contribution is the remainder of equation (17) in this work.

REFERENCES

1 Keller, A. *Phil. Mag.* 1957, **2**, 1171
2 Wunderlich, B. 'Macromolecular Physics' Vol. 1, Academic Press, New York, 1976
3 Flory, P. J. *J. Chem. Phys.* 1949, **17**, 223
4 Oyama, T. *Kobunsikagaku* 1961, **18**, 420, 426
5 Saeki, S. *Polymer* 1993, **34**, 1444
6 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, 1953
7 Tonks, L. *Phys. Rev.* 1936, **50**, 955
8 Starkweather, H. W. and Boyd, R. H. *J. Chem. Phys.* 1960, **64**, 410
9 Kirshenbaum, I. *J. Polym. Sci. Part A* 1965, **3**, 1869
10 Tonelli, A. E. *J. Chem. Phys.* 1970, **52**, 4749
11 Karasz, F. E., Couchman, P. R. and Klempner, D. *Macromolecules* 1977, **10**, 88