Influence of the liberation of heat of fusion on the temperature near the crystallization front in polymers

Ewa Piorkowska* **and Andrzej Galeski**
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, 90363 Lodz, Poland

(*Received 1 November 1991; revised 6 April 1992*)

The solution of the heat conduction equation with appropriate boundary and initial conditions makes it possible to determine the influence of the latent heat of fusion evolving during polymer crystallization on the temperature distribution near the crystallization front. It is shown that the increase in temperature at the crystallization front does not exceed a fraction of a degree.

(Keywords: crystallization; heat of fusion; poly(ethylene adipate); isotactic polypropylene)

INTRODUCTION

A special case of heat transport is that in which a substance undergoes a phase transformation with emission or absorption of heat. The essential feature of such a problem is the existence of a moving interphase at which the latent heat of fusion is liberated or absorbed. In metals and other low molecular substances the interphase at which the transformation occurs follows the isotherm of the melting point of the substance. The liquid phase could be substantially supercooled and the solidified phase overheated. It was determined that the time dependence of the position of the interphase is non-linear and is proportional to the square root of time.

There are several different treatments of this important mathematical problem of heat conduction during change of state. The most important exact solution is that of Neumann (see ref. 1) for a semi-infinite region ($x>0$) initially at a constant temperature which is greater than the melting point and with the surface ($x=0$) maintained at zero temperature. This solution was subsequently generalized for supercooled liquids assuming that the liquid in the region $x>0$ is initially at the temperature below the melting point and, since no heat is removed from the solid, the solidified material will thus have a constant temperature equal to the melting point.

A better approximation for solidification of metal cast in a mould was introduced by Schwarz[2]. He introduced a distinction between thermal properties of the melt and the solid, the solid is initially at zero temperature while the liquid is at a somewhat higher constant temperature. The method of solution follows the route of Neumann's solution.

A series of solutions has been presented for the case of solidification in the region $x>0$ when the liquid is initially at its melting point[3]. The generation of heat of fusion at the interphase was introduced to this formulation of the problem by assuming constant heat flux from the solid at $x=0$. By assuming a power series in time for the position of the interphase and a double power series for the temperature, exact solutions are found.

A simple exact solution for the surface of solidification moving with constant speed is due to Stefan (see ref. 4). It represents a solution of the problem of freezing in the region $x>0$ in which the liquid is initially at its melting point and the surface of solidification moves with constant speed. However, since the temperature at $x=0$ has to be given negative values which increase exponentially with time, the solution is of no great physical interest from the point of view of the problem of freezing.

Lightfoot[5] has contributed to solving the problem of solidification by elaborating a new method of solution if the thermal properties of the liquid and the solid are the same. The liberation of heat of fusion is represented by a moving source of heat. It is further assumed that the temperature at the interphase must always be equal to the melting point (see also ref. 3 for further discussion). The temperature at any point can be found by adding terms representing the effects of this moving source and the initial and boundary conditions.

Since polymer crystallization is controlled by the primary nucleation process the growth of crystalline aggregates–spherulites occurs in narrow zones on expanding circles or spheres around nuclei, often called a crystallization front. In those zones the latent heat of fusion is liberated due to the crystallization and is dissipated away from the crystallization front by heat conduction. For thin films there may be other heat sinks active, like surrounding air or cover glasses, where convection or heat conduction takes place. The heat flow away from the crystallization front results from the temperature gradient. Therefore, it is expected that the temperature at the crystallization front becomes higher than the temperature of the rest of the sample.

There is a substantial difference in the crystallization of polymers and metals. In contrast to low molecular weight substances the crystallization growth rate in polymers is usually constant with time. Based on that observation it was concluded in the past that the crystallization of polymers is not governed by the dissipation of heat of fusion. However, it is not necessarily true because polymers crystallize usually much below the melting point and the formed crystals are far from the equilibrium. The temperature at the crystallization front may be well below the equilibrium melting point but above the temperature of the supercooled liquid phase. Hence, the crystallization of polymers is a special case of heat

---

* To whom correspondence should be addressed

0032-3861/92/183985-05

transport and has not yet been considered in detail in the solution of the heat conduction problem on solidification.

Below, the possible temperature increase in the vicinity of the crystallization front in polymers is determined.

SOLIDIFICATION IN POLYMERS

We assume that the sample is infinite and at time $t=0$ consists of two phases: solid for $x<0$ and liquid for $x>0$, both at temperature $T(x,t)=T_0$ which is below the equilibrium melting point. At $t=0$ crystallization starts, hence the plane separating the two phases initially at $x=0$ begins to move along the x axis with a velocity, G, equal to the spherulite growth rate, and the latent heat of fusion, L, liberated at the crystallization front delivers an amount of heat Q per unit time per unit area of the crystallizing front. Such an approach makes it possible to consider the problem of heat transport as one-dimensional. Since a melt flows towards the crystallization front to compensate for the change in volume due to crystallization, convection in the melt as the mechanism for heat transport can be neglected. It is useful to introduce a system of coordinates moving with a velocity equal to the growth rate G. In the moving system of coordinates with the origin at the plane of phase separation where heat is liberated, the heat conduction equations take the following forms (see also ref. 6 for the formulation of these equations):

$$a_1\frac{\delta^2 T_1}{\delta x^2}+G\frac{\delta T_1}{\delta x}-\frac{\delta T_1}{\delta t}=0 \qquad \text{for} \quad x>0 \tag{1a}$$

$$a_2\frac{\delta^2 T_2}{\delta x^2}+G\frac{\delta T_2}{\delta x}-\frac{\delta T_2}{\delta t}=0 \qquad \text{for} \quad x<0 \tag{1b}$$

where x denotes a distance from the crystallization front, a_1 and a_2 denote thermal diffusivities of the liquid and the crystalline phases, respectively, and:

$$T_1(x,t)=T(x,t)-T_0 \qquad \text{for} \quad x>0 \tag{2a}$$

$$T_2(x,t)=T(x,t)-T_0 \qquad \text{for} \quad x<0 \tag{2b}$$

The functions T_1 and T_2 have to satisfy the following initial and boundary conditions:

$$T_1(x,0)=0 \tag{3a}$$

$$T_2(x,0)=0 \tag{3b}$$

$$T_1(\infty,t)=0 \tag{3c}$$

$$T_2(-\infty,t)=0 \tag{3d}$$

The assumptions of the continuity of the temperature function and the conservation of heat flux at the phase separation boundary result in the subsequent conditions:

$$T_2(0,t)=T_1(0,t) \tag{4a}$$

$$-K_1\frac{\delta T_1}{\delta x_{x=0}}+K_2\frac{\delta T_2}{\delta x_{x=0}}=Q \tag{4b}$$

where K_1 and K_2 denote the coefficients of thermal conductivity of the liquid and crystalline phases, respectively.

The differential equations (1a) and (1b) are solved with the conditions determined by equations (2a), (2b), (3a), (3b), (4a) and (4b) by Laplace transformation. After Laplace transformation, equations (1a) and (1b) assume the following forms:

$$a_1\frac{\mathrm{d}^2F_1}{\mathrm{d}x^2}+G\frac{\mathrm{d}F_1}{\mathrm{d}x}-pF_1=0 \qquad \text{for} \quad x>0 \tag{5a}$$

$$a_2\frac{\mathrm{d}^2F_2}{\mathrm{d}x^2}+G\frac{\mathrm{d}F_2}{\mathrm{d}x}-pF_2=0 \qquad \text{for} \quad x<0 \tag{5b}$$

where $F_1(x,p)$ and $F_2(x,p)$ are the Laplace transforms of the functions T_1 and T_2, respectively, and p is the transformation parameter. The conditions (3a), (3b), (4a) and (4b) are now in a form:

$$F_1(\infty)=0 \tag{6a}$$

$$F_2(-\infty)=0 \tag{6b}$$

$$F_1(0)=F_2(0) \tag{7a}$$

$$-K_1\frac{\mathrm{d}F_1}{\mathrm{d}x_{x=0}}+K_2\frac{\mathrm{d}F_2}{\mathrm{d}x_{x=0}}=\frac{Q}{p} \tag{7b}$$

The solutions of equations (5a) and (5b) fulfilling conditions (6) and (7) are described by the following expressions:

$$F_1(x,p)=\frac{2a_1a_2Q}{pV(p)}\exp\left[\frac{-G-(G^2+4a_1p)^{0.5}}{2a_1}x\right] \tag{8a}$$

$$F_2(x,p)=\frac{2a_1a_2Q}{pV(p)}\exp\left[\frac{-G+(G^2+4a_2p)^{0.5}}{2a_2}x\right] \tag{8b}$$

where

$$V(p)=K_2a_1[(G^2+4a_2p)^{0.5}-G] \\ +K_1a_2[(G^2+4a_1p)^{0.5}+G] \tag{9}$$

Since the amorphous phase is usually a worse heat conductor than the crystalline phase by substituting $a_2=a_1$ and $K_2=K_1$ the upper limit for the temperature increase is set due to the release of heat of fusion during crystallization. Denoting the degree of crystallinity of spherulites as s, the amount of heat released per unit time per unit area of the crystallization front can be expressed as follows:

$$Q=GLd_\mathrm{c}s \tag{10}$$

where d_c denotes the density of the crystalline phase.

Therefore, expressions (8a) and (8b) assume the following form:

$$F_1(x,p)=\frac{sa_1GLd_\mathrm{c}}{K_1p(G^2+4a_1p)^{0.5}} \\ \times\exp\left[\frac{-G-(G^2+4a_1p)^{0.5}}{2a_1}x\right] \tag{11a}$$

$$F_2(x,p)=\frac{sa_1GLd_\mathrm{c}}{K_1p(G^2+4a_1p)^{0.5}} \\ \times\exp\left[\frac{-G+(G^2+4a_1p)^{0.5}}{2a_1}x\right] \tag{11b}$$

Hence, the temperature function in the considered system can be described as follows:

$$T(x,t)=T_0+\frac{0.5Gsd_\mathrm{c}L}{(K_1d_\mathrm{a}c_\mathrm{p}\pi)^{0.5}} \\ \times\exp\left(-\frac{xG}{2a_1}\right)\int_0^t\exp\left(-\frac{x^2+G^2v^2}{4a_1v}\right)\frac{\mathrm{d}v}{v^{0.5}} \tag{12}$$

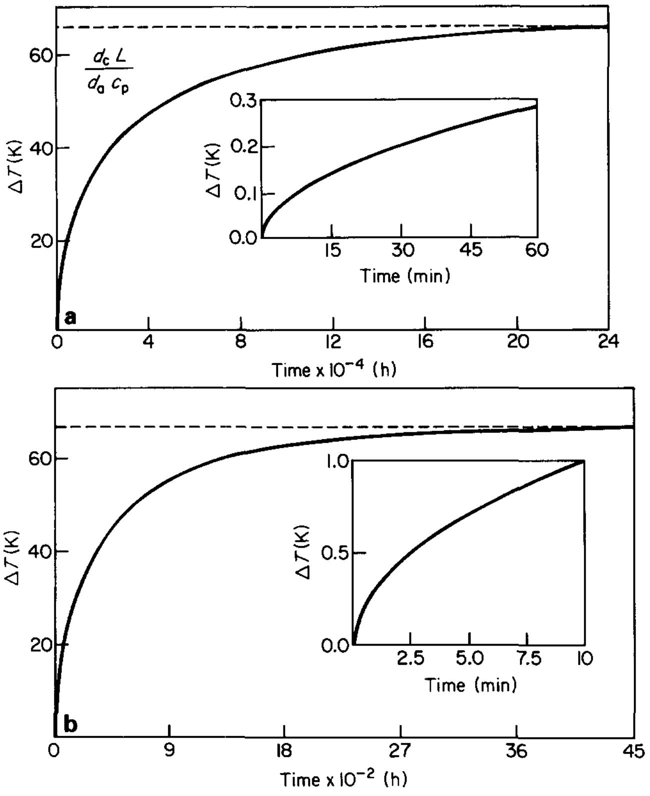

Figure 1 Time dependence of the temperature increase $\Delta T = T(0,t) - T_0$ at the crystallization front for: (a) PEA; (b) iPP. The broken line represents the level of the temperature increase at steady-state conditions

Equation (12) can be expressed in the following form:

$$T(x,t) = T_0 + \frac{sLd_c}{2d_a c_p}\left[\exp\left(-\frac{xG}{a_1}\right) \times \operatorname{erfc}\left(\frac{x - Gt}{2(a_1 t)^{0.5}}\right) - \operatorname{erfc}\left(\frac{x + Gt}{2(a_1 t)^{0.5}}\right)\right] \quad \text{for} \quad x \geqslant 0 \qquad (13a)$$

$$T(x,t) = T_0 + \frac{sLd_c}{2d_a c_p}\left[\operatorname{erfc}\left(\frac{-x - Gt}{2(a_1 t)^{0.5}}\right) - \exp\left(-\frac{xG}{a_1}\right)\operatorname{erfc}\left(\frac{-x + Gt}{2(a_1 t)^{0.5}}\right)\right] \quad \text{for} \quad x \leqslant 0 \qquad (13b)$$

where $\operatorname{erfc}(z) = 2\pi^{-0.5}\int_z^\infty \exp(-y^2)\,\mathrm{d}y$, and d_a and c_p denote the density of the amorphous phase and the specific heat capacity of the medium, respectively. The temperature at the phase boundary ($x = 0$) is expressed in the following form:

$$T(0,t) = T_0 + \frac{sLd_c}{d_a c_p}\operatorname{erf}\left(\frac{Gt^{0.5}}{2a_1^{0.5}}\right) \qquad (14)$$

where $\operatorname{erf}(z) = 2\pi^{-0.5}\int_0^z \exp(-y^2)\,\mathrm{d}y$.

Estimation of the temperature increase at the crystallization front of polymers was based on poly(ethylene adipate) (PEA) and isotactic polypropylene (iPP) which are often used for studying the spherulite growth rate. The spherulite growth rate[7] G of PEA at 28°C is $\sim 2\,\mu\mathrm{m\,min^{-1}}$, and d_c, d_a and L for PEA are $1.363\,\mathrm{g\,cm^{-3}}$, $1.221\,\mathrm{g\,cm^{-3}}$ and $29\,\mathrm{cal\,g^{-1}}$, respectively[8-10]. Assuming values of K_1 and c_p typical for polymer melts, $4 \times 10^{-4}\,\mathrm{cal\,cm^{-1}\,s^{-1}\,°C^{-1}}$ (refs 11 and 12) and $0.5\,\mathrm{cal\,g^{-1}\,°C^{-1}}$, respectively, and $s = 1$, the dependence of the increase in temperature at the crystallization front on time (*Figure 1a*) can be plotted. One can see that after 1 s, 1 min and 1 h of crystallization the temperature increase does not exceed ~ 0.005, 0.04 and 0.3 K, respectively. The temperature increase saturates and assumes quite a high value as time tends to infinity. However, in the considered case of PEA (broken line in *Figure 1a*) achieving the steady-state conditions would take >20 years of crystallization. Therefore, the steady-state solution of the problem, which has a form similar to that presented by Stefan[4], is of no practical importance.

During faster crystallization the same thermal effect is achieved in a shorter time since the temperature increase at the crystallization front is a function of $Gt^{0.5}$. This is illustrated in *Figure 1b*, where similar plots for iPP are shown. (The following values for the heat of fusion, and densities of the crystalline and amorphous phases were used[8]: $50\,\mathrm{cal\,g^{-1}}$, $0.946\,\mathrm{g\,cm^{-3}}$ and $0.854\,\mathrm{g\,cm^{-3}}$, respectively. The degree of crystallinity was assumed to be 0.6. The value of the growth rate of iPP spherulites used was $20\,\mu\mathrm{m\,min^{-1}}$ which corresponds to a temperature of crystallization of 121.5°C.) It should be mentioned, however, that the temperature at the crystallization front cannot increase greatly because the crystallization is also completed in a shorter time.

The temperature distributions in front of the crystallization front in PEA after 1 s, 1 min and 1 h of crystallization are plotted in *Figure 2a*. One can see that there is a gradual decrease in the temperature with increasing distance from the crystallization front. The range of the temperature rise increases with time. It is seen that after a longer time (1 min) of crystallization the zone of the temperature rise reaches a long distance from the crystallization front (6 mm) which is comparable with the size of the sample. The temperature distribution behind the crystallization front is very similar to that in front of it because the term $\exp(-xG/a_1)$ in equation (12) is close to 1 for the assumed values of G and a_1. *Figure 2b* shows similar plots for the case of iPP. In iPP the zone of increased temperature reaches similar distances from the crystallization front in similar time intervals as in the case of PEA, which is related to similar thermal diffusivities of melts of both polymers. However, the temperature increase at the crystallization front in iPP is approximately one order of magnitude larger (although still quite small, around 1K after 10 min of crystallization) than in the case of PEA which follows from faster growth rate, i.e. faster liberation of the latent heat of fusion.

Since the increase of the temperature at the crystallization front is quite slow it may be assumed that within a short time interval the growth rate is constant but different in different intervals as it follows from the temperature dependence of the growth rate. Equation (14) for the temperature at the crystallization front may now be modified in the following way:

$$T(0,t_k) = T_0 + \frac{0.5sLd_c}{(K_1 c_p \pi d_a)^{0.5}}\sum_{n=1}^{k} G(T_{n-1}) \times \int_{t_{n-1}}^{t_n} \exp\left[-\frac{G(T_{n-1})^2(t_k - t)}{4a_1}\right]\frac{\mathrm{d}t}{(t_k - t)^{0.5}} \qquad (15)$$

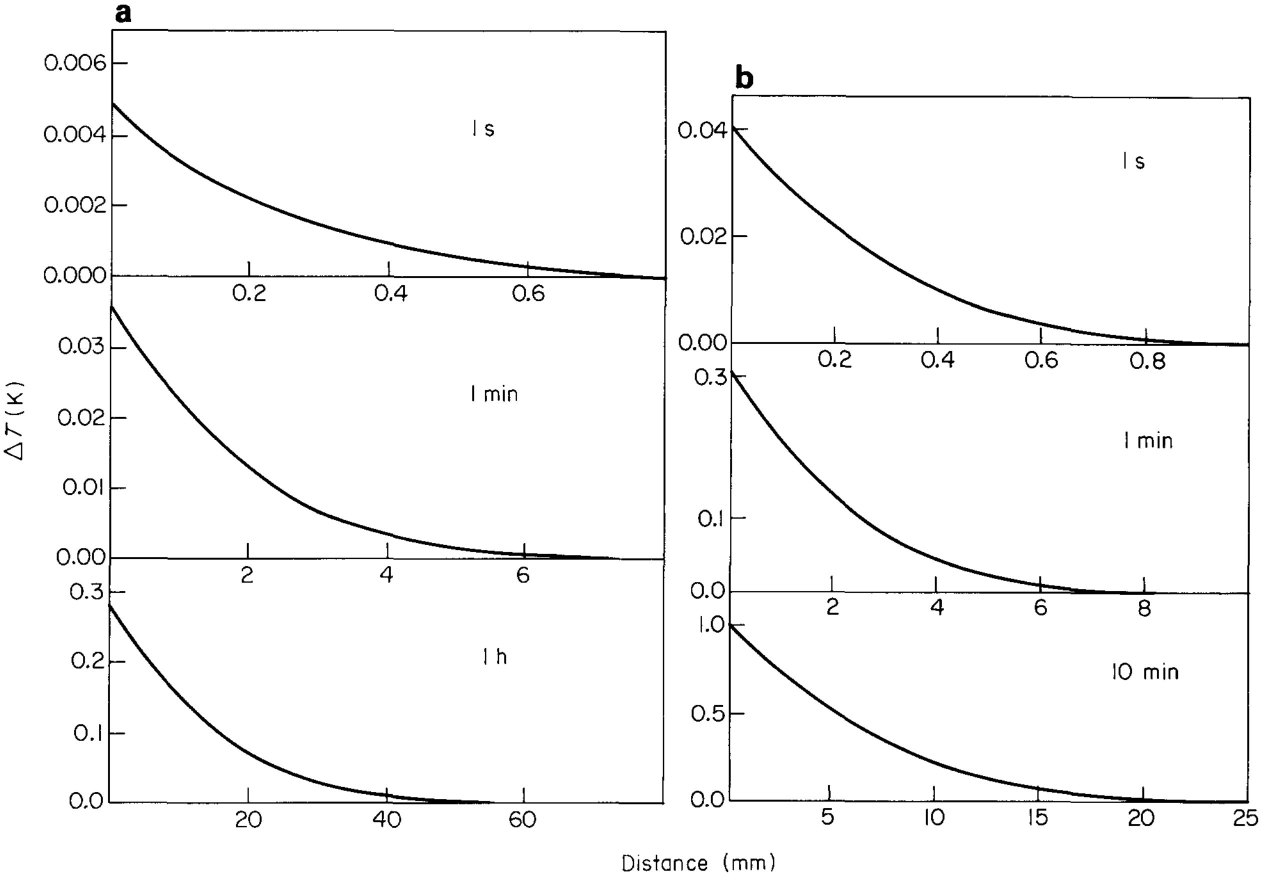

Figure 2 Temperature increase distribution in front of the crystallization front for: (a) PEA, after 1 s, 1 min and 1 h of crystallization; (b) iPP, after 1 s, 1 min and 10 min of crystallization

where $t_n - t_{n-1}$ denotes time intervals and $G(T_{n-1})$ is the growth rate for the temperature at the nth time interval. The equation represents a sum of positive contributions to the temperature rise from the subsequent time intervals and has continuously increasing character. In view of equation (15), any oscillations around a certain temperature are excluded.

In the above considerations a polymer melt flow towards the crystallization front resulting from the volume change during crystallization was neglected. From the mathematical point of view a melt flow means faster motion of the crystallization front with respect to a melt. Since the melt flow velocity does not exceed several per cent of the spherulite growth rate for most polymers, one should not expect any significant influence of a melt flow on a temperature distribution. However, the influx of a colder melt results in additional consumption of heat liberated during crystallization, therefore it can only cause a lowering of a temperature increase near the crystallization front.

DISCUSSION

In the above calculations, a constant crystalline phase growth rate was assumed, which in turn gave the continuously increasing temperature at the crystallization front and the surroundings. For an infinite time of crystallization the temperature rise may reach 50 to 60°C. The highest temperature increase above the initial temperature of the sample is found at the interphase. However, for most polymers the temperature increase is only a fraction of a degree in a reasonable time-scale (minutes or hours). Our estimation of the thermal effect due to crystallization was based on the assumption that there is no heat loss through cover glasses in the case of crystallization of thin films or through sample surfaces in the case of crystallization in bulk, that there is no convection in the melt and that the thermal properties of the crystalline phase are the same as those of the melt. Therefore, we have set the upper limit for the temperature increase due to crystallization.

An explanation for the crystallization of PEA in the form of banded spherulites is proposed in a paper by Foks[13]. The author concludes that the banding results from crystallization of polymer in alternating optically positive and negative zones due to the temperature in the vicinity of the crystallizing front and growth rate oscillations. Foks assumed that the oscillations of the temperature and the growth rate leading to the formation of banded spherulites occur during crystallization around the temperature of the maximum growth rate. The changes of the temperature are supposed to be caused by the liberation of the latent heat of fusion due to crystallization with the feedback on the change of the growth rate due to the temperature change. The hypothesis should be rejected on the basis of the conclusion of a continuous increase in the temperature at the crystallization front due to positive contributions to the temperature rise from subsequent time intervals. Also, since the temperatures at which optically negative and positive zones are observed during crystallization differ by at least 10K for PEA, the necessary temperature oscillations should be of the order of at least several degrees. The presented results do not indicate the possibility of a significant temperature change during the crystallization of PEA or other polymers. The order of magnitude of the calculated effect excludes the possibility of a temperature increase followed by a change in the growth rate and leading to oscillations in both values. In addition, the hypothesis of the origin of banding in spherulites by temperature oscillation at the interphase should be rejected in view of the growth rate data for fractionated PEA by Takayanagi and Yamashita[14]. In the temperature range where banded spherulites are observed in PEA, the growth rate remains constant with time throughout the entire growth process at a given crystallization temperature. The growth rate decreases with the temperature increase and no maximum is found within the temperature range where banded spherulites are observed.

REFERENCES

1 Carslaw, H. S. and Jaeger, J. C. 'Conduction of Heat in Solids', Clarendon Press, Oxford, 1959, pp. 282–291

2 Schwarz, C. *Arch. Eisenhuttenw.* 1931, **5**, 139; *Z. Angew. Math. Mech.* 1933, **13**, 202

3 Evans II, G. W., Isaacson, E. and McDonald, J. K. L. *Quart. Appl. Math.* 1950, **8**, 312

4 Carslaw, H. S. and Jaeger, J. C. 'Conduction of Heat in Solids', Clarendon Press, Oxford, 1959, p. 292

5 Lightfoot, N. M. H. *Proc. Lond. Math. Soc.* 1930, **31**, 97

6 Carslaw, H. S. and Jaeger, J. C. 'Conduction of Heat in Solids', Clarendon Press, Oxford, 1959, p. 12

7 Takayanagi, M. *J. Polym. Sci.* 1956, **19**, 200

8 Wunderlich, B. 'Macromolecular Physics, vol. 1, Crystal Structure, Morphology, Defects', Academic Press, New York, 1973, pp. 388–389

9 Hobbs, S. Y. and Billmeyer Jr, F. W. *J. Polym. Sci. A2* 1969, **7**, 1119

10 Hobbs, S. Y. and Billmeyer Jr, F. W. *J. Polym. Sci. A2* 1970, **8**, 1387

11 Fuller, T. R. and Fricke, A. L. *J. Appl. Polym. Sci.* 1971, **15**, 1729

12 Pattnaik, S. and Thompson, E. V. *Am. Chem. Soc. Polym. Prepr.* 1981, **22**, 199

13 Foks, J. *Polym. Commun.* 1990, **31**, 255

14 Takayanagi, M. and Yamashita, T. *J. Polym. Sci.* 1956, **22**, 552