

Crystallization kinetics and morphology of polymer blends of poly(tetramethyl-*p*-silphenylene siloxane) fractions*

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The crystallization behaviour of polymer blends or mixtures of the same system has been studied over a wide range of molecular weight and crystallization temperatures. Blends were made by mixing fractionated polymer samples. The spherulitic growth in these mixtures is dependent upon the number-average molecular weight of the system at the shorter chain lengths, but then becomes insensitive to molecular weight values when about 10^5 to 10^6 are reached. The growth rate kinetics of mixtures can be described by a kinetic model used for fractionated poly(tetramethyl-*p*-silphenylene siloxane) (TMPS) polymers. The crystal surface energies deduced from these rate data are molecular weight dependent as are the pre-exponential and transport factors in the rate equation. These parameters are explained in terms of the crystallite morphology. Mixtures (as well as fractions themselves) of all polymer fractions ranging from the monomer to the highest molecular weight (10^6 approximately) have similar morphological features and form negatively birefringent spherulites. Although molecular weight segregation appears to play an important role in crystallization at comparatively small undercoolings, its influence seems to be minimal at large undercoolings (close to or below the growth rate maxima). Very low molecular weight additives significantly affect the overall crystallization kinetics. Compared to the undiluted sample, mixtures so formed have lower observed melting points and glass transition temperatures. Rates of crystallization are generally facilitated by the diluent with the peak in the growth rate being displaced to lower temperatures. The growth rates for diluted over the undiluted polymer at similar undercoolings are usually larger. At high molecular weights the log of the spherulitic growth rate varies as $M_n^{-1/2}$, over a considerable range, but at low molecular weight values the rate depends more strongly on M_n approaching a limit of $M_n^{-1.2}$ as the monomeric state is approached.

INTRODUCTION

Almost a decade ago, preliminary crystallization studies¹ of blends of poly(tetramethylsilphenylene siloxanes) (TMPS) revealed that the spherulitic growth rate of blends of fractions of these polymers could be related to the number-average molecular weight. In these crystallization experiments, it was noted that the rate of growth of spherulites in a given mixture of high and low molecular weight fractions was observed to increase in a manner determined 'by the enhanced free volume effect and by the balance of diffusion processes arising from the addition of shorter chains present'. Since this paper, which was primarily concerned with the crystallization rate of polymer fractions, more extensive and detailed investigations have been made on intimate mixtures of these same polymer fractions. Studies have covered a wide range of molecular weights and crystallization temperatures. The purpose of these experiments was to ascertain the following:

(a) If the kinetic growth rate model^{2,3} could be used to describe spherulitic growth successfully in polymer blends¹. Prior to this work on polymer mixtures, there were no detailed results on this topic reported in the literature;

(b) To establish how the spherulitic growth rate in blends depends on polymer chain length;

(c) To determine if the molecular weight dependence for blends is similar to that already noted for polymer fractions^{1,3};

(d) To find out if there was a significant relationship between the pre-exponential factor in the growth rate equation and the molecular weight;

(e) To determine if molecular segregation played a significant role, particularly at comparatively larger undercoolings.

This paper considers these various factors and attempts to give some rational answers. Currently accepted theories of polymer crystallization^{3,4} are re-examined in the light of these results on polymer blends. Data from earlier papers on fractionated TMPS polymers^{1,5,6} are included for purpose of comparison.

EXPERIMENTAL

Sample blend preparation

Fractionated TMPS polymers used in earlier studies^{1,5,6} were blended using several different methods to ensure homogeneous mixing. Blends[†] were prepared from mixtures of polymer fractions by (a) freeze drying and (b) film casting.

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† In this paper the words 'blend' and 'mixture' are used interchangeably.

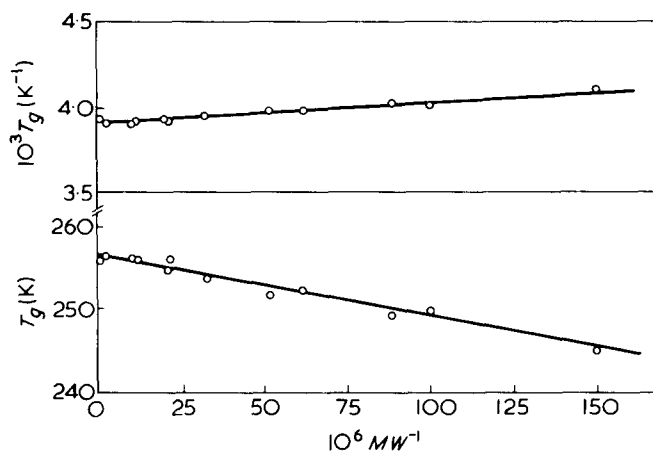


Figure 1 Glass temperature versus number-average molecular weight (M_n) plots of TMPS polymers

Low molecular weight plasticizer and polymer were also intimately blended with polymer fractions and measurements were made on these blends.

Spherulitic growth rates

Conventional time-lapse photography using a Bolex 16 mm movie camera with Kodak plus-x and tri-x film was used. Samples mounted between clean dry cover slips were melted on a thermostatted hot stage at 200°C for 5 min and then crystallized isothermally on a Mettler FP2 stage at the desired crystallization temperature. The experimental fusion conditions used here were established previously for TMPS polymers¹. A wide range of molecular weights mixtures spanning several decades were examined by this technique.

Examination of samples

Spherulites produced during crystallization of polymer blends were examined microscopically between crossed polars during isothermal crystallization and again after crystallization was completed. The melting temperature for each blend was determined as a function of crystallization conditions. The extrapolation method⁷ was used to estimate the thermodynamic melting temperature T_m of each fraction or mixture which was crystallized isothermally at different temperatures over a wide span. Figure 1 shows the dependence of T_m on molecular weight[†]. Glass transition temperatures, T_g , were determined on quenched glassy samples using a Perkin-Elmer differential scanning calorimeter (d.s.c.)^{1,8}. Each sample was measured at a variety of heating rates, and the results extrapolated to zero rate in order to obtain meaningful values for T_g .

Results

Spherulitic growth rates displayed in Figure 2 for different molecular weight compositions were found to be linear functions of time at all crystallization temperatures in the early stages of growth. The growth rates, G , are expressed in $\mu\text{m}/\text{min}$. Each curve refers to a particular mixture made by mixing well-defined TMPS fractions^{1,5}. A wide range of molecular weights are included and the spherulitic growth rates span a temperature interval from just below room temperature to about 20°C below the estimated thermodynamic melting temperature, T_m of each mixture.

† Unless otherwise specified, molecular weights referred to in this report represent number-average values, M_n

Optical micrographs of some blends are shown (Figure 3) for samples crystallized on either side of the growth rate maxima in Figure 2. All mixtures were examined with the optical microscope during the kinetic measurements and after spherulites growth was 'completed'.

DISCUSSION

Kinetic studies

Spherulitic growth rate theory. It is generally accepted³ that the spherulite growth for a homopolymer can be described by an equation of the form:

$$G = G_0 \exp\left(\frac{-\Delta E_D^*}{RT}\right) \exp\left(\frac{-\Delta G^*}{RT}\right) \quad (1)$$

where the first exponential (transport) term is best written as $\exp[-A/R(T - T_\infty)]$ and the second exponential involving the free energy for nucleation may be designated $\exp(-BT_m/T\Delta T)$ for two dimensional lamellar surface nucleation. When the rate equation is expressed as:

$$G = G_0 \exp\left(\frac{-A}{R(T - T_\infty)}\right) \exp\left(\frac{-BT_m}{T \cdot \Delta T}\right) \quad (2)$$

then G_0 , A , T_∞ , B and T_m are parameters appropriate for the polymer mixture, comprised of two or more polymer fractions, or a diluent and a polymer fraction(s). G_0 is a pre-exponential factor, T_m is the estimated thermodynamic melting temperature pertinent to each sample under investigation. ΔT is the undercooling ($T_m - T$), R is the gas constant, A is a transport parameter and T_∞ is a temperature below the glass transition temperature (T_g) where the segmental motion associated with molecular transport to the crystal growth face is insignificant. For many polymeric materials this temperature seems to lie about 40° to 50°C below T_g . B is a parameter usually expressed as $4b_0 \sigma \sigma_e / \Delta h_f k$ where σ is the lateral and σ_e is the transverse surface (interface) energy of the crystalline lamellae, comprising

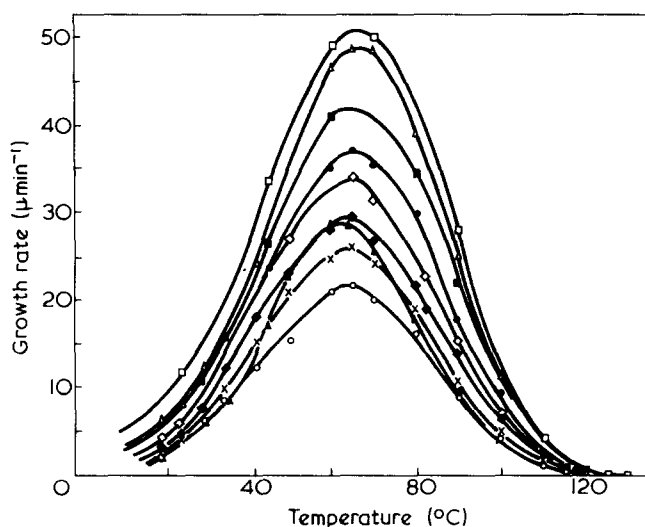


Figure 2 Plot of the growth rate G ($\mu\text{m}/\text{min}$) vs. crystallization temperature, T , for polymer blends including TMPS monomer as a diluent in one instance. \square , 1.83×10^4 ; \triangle , 2.70×10^4 ; \blacksquare , 4.25×10^4 ; \diamond , 5.50×10^4 ; \blacklozenge , 8.04×10^4 ; \times , 1.07×10^5 ; \circ , 3.50×10^5 ; \blacktriangle , 3.32×10^5 with 1.17% monomer diluent

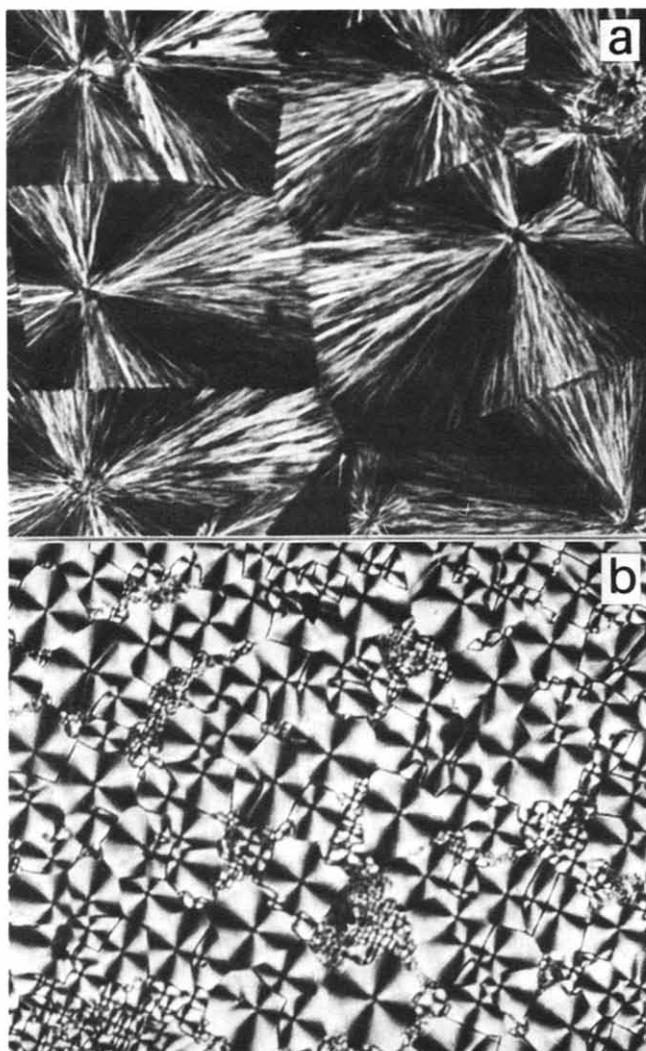


Figure 3 Spherulite growth habits at (a) 100°C and (b) 35°/25°C; i.e. above and below the maximum in the growth rate temperature plots of Figure 2 for $2.7 \times 10^3 \bar{M}_n$ from mixed fractions

the spherulites, R is the gas constant, b_0 the interplanar separation in the growth direction and Δh_f is the heat of fusion.

A recent modification of this theory (see for example ref 3) leads, in some circumstances, to $B = 2b_0 \sigma \sigma_e / \Delta h_f k$ if there is a change in morphology and mode of nucleation that deviates from a spherulitic-like crystal habit. An analytical solution by Frank⁹ showed that the ratio of the substrate length to distance apart of nucleation events, must exceed 10^3 — a condition most likely to be met at smaller undercoolings. Where such changes take place the magnitude of $\sigma \sigma_e$ (or σ_e) but not the trend in these values with molecular weight will be altered. Details of this model have been tested using polyethylene¹⁰ where precise measurements at relatively small undercooling have been made on sharp fractions.

Surface energy considerations. Spherulitic growth rates for each molecular weight (Figure 2) were fitted to expression (2) by computer. The data on the right hand limb (nucleation controlled region) of this diagram were also analysed by plotting either

$$\log G + A/R(T - T_\infty) \text{ vs. } 1/T\Delta T \quad (3)$$

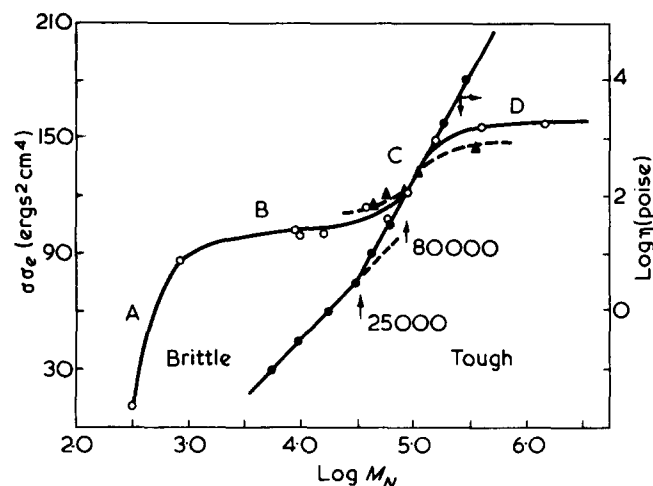


Figure 4 Surface or interfacial energy values as a function of \bar{M}_n for TMPS blends and fractions. The parameter σ_e is the chain-fold surface (interfacial) energy and σ is the lateral surface energy of the crystal lamellae. Note that σ is assumed to be independent of crystallization temperature and \bar{M}_n . The melt viscosity data at 217°C are from Fox and Allen (1964)

when a series of straight lines were obtained, increasing in slope with increasing molecular weight (not shown). From the slopes the value of the surface energy product $\sigma \sigma_e$ (erg^2/cm^4) (or J^2/m^4) was deduced using the well-known relation:

$$\sigma \sigma_e = \frac{2.3R\Delta H_f (\text{Slope})}{4b_0 \cdot T_m} \quad (4)$$

For a given blend, the surface energy values obtained by the graphical technique agreed very well with values derived by computer curve fitting the *entire* growth rate data for a given molecular weight. However, it must be emphasized⁵ that a meaningful pre-exponential factor G_0 , is not obtained by this linear plotting procedure. Indeed, $\ln G_0$ values that are negative have been reported in the literature¹¹ in order to model some experimental results. Such a situation is an unrealistic one.

Figure 4 contains the derived surface energy values from the growth rate-temperature plots. An upward trend with increasing chain length is observed for all samples in the manner previously noted for $\sigma \sigma_e$ or σ_e TMPS fractions alone assuming σ is a constant^{1,5,3}. From Figure 4 it is clear that the sharp rise in σ_e obtained on going from the monomer to the oligomers (region A) corresponds to the transition from an extended to folded-chain morphology[§]. Recall^{6,9} that here the lower chain-fold step height for TMPS corresponds to 75 Å approximately, i.e. about 10 monomer units. The further but gradual rise (region B)[§] can be attributed to a mixed contribution arising from chain-folding and chain ends, the latter diminishing in magnitude as the molecular weight increases through region C. Chain-folding is feasible in the molecular weight range 3000 and above. Region C corresponds to the chain length where intercrystallite links become relatively abundant and may affect molecular motion in the polymer melt. Under such conditions the change in σ_e

§ Hoffman and coworkers (see ref 3) have made a detailed analysis of the complicated behaviour associated with regime I and II growth morphologies, but the experimental data in this paper has not been made sufficiently close to the melting point to permit a worthwhile analysis of this situation.

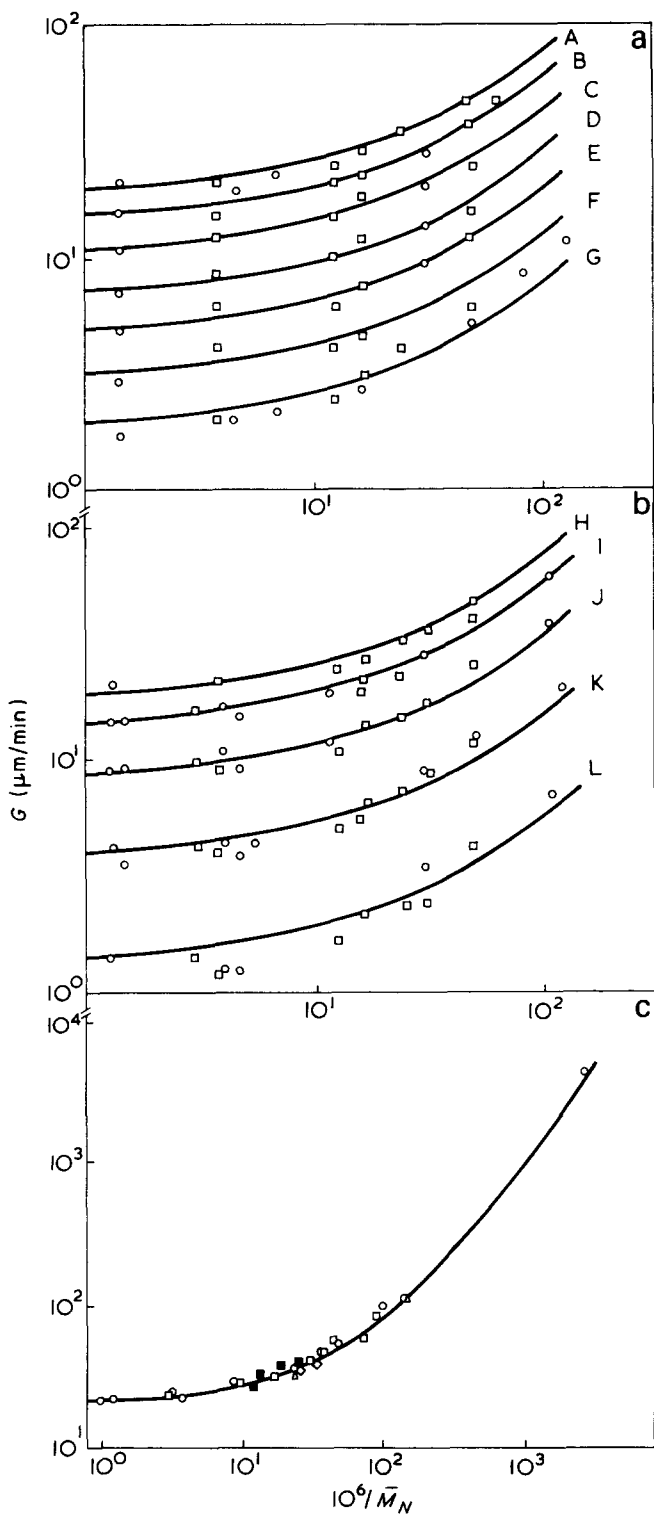


Figure 5 Crossplots of data from Figure 2 containing plots of $\log G$ ($\mu\text{m}/\text{min}$) versus $(\bar{M}_n)^{-1}$ for blends and fractionated samples. (a) Above G_{max} of $G-T$ plots: A, 60; B, 50; C, 42.5; D, 35; E, 30; F, 25; G, 20. (b) Below G_{max} of $G-T$ plots: H, 70; I, 80; J, 90; K, 100; L, 110. (c) At G_{max} only: polymer fractions (\circ), blends (\square); unfractionated specimens (\diamond); freeze-dried samples (\bullet); upquenching from the glassy state (\triangle)

obtains from a compromise amongst contributions from (a) chain-folding, σ_f ; (b) crystallite links, σ_x , and chain end, σ_t contributions. The influence of σ_t must be insignificant in region D of Figure 4, but σ_f contributions persist while σ_x might be expected to intensify at larger molecular weights. The relative magnitudes of σ_f and σ_x are unknown at present,

but it seems that the density of tie molecules between lamellae in the solid state are considerably less abundant than the entanglements density of chains associated with the zero shear viscosity, η . For TMPS below a critical molecular weight ($M_c = 25\,000$ approximately), η varies as the first power of the weight molecular weight, M_w . Above M_c where entanglements¹² play a very important role through interchain interaction, the viscosity varies as the 3.4 power of M_w . From an analysis of our rate measurements there is no *a priori* or indeed *a posteriori* evidence or reason to believe that entanglements in the polymer melt have an equivalent rôle to play in the formation of crystalline polymeric solid even though they manifest themselves to an important degree through enhancing the mechanical integrity of high over low molecular weight specimens. However, the insensitivity of spherulitic growth rates to chain length at high molecular weights and the concomitant rise in primary nucleation under these conditions probably obtains from chain immobility (see Figure 5). In fact, at sufficiently high molecular weights the molecular chain length between entanglements may become the rate controlling parameter in kinetics of crystallization. The point will be discussed in the next section of the paper. Certainly, there is evidence that a non-spherulitic structure is found in high molecular weight polyethylene specimens¹³.

Dependence of growth rate of molecular weight. It has been clearly demonstrated elsewhere⁵ that the spherulitic growth rate of TMPS fractions is very sensitive to chain length. Extensive data ranging from the monomer to fractions in excess of 10^6 molecular weight have been reported^{1,5}. Similar behaviour is now noted for polymer blends. These results show that above molecular weights of 5×10^4 the growth rate is essentially insensitive to length of the polymer chain in accord with the rationale that the growth rate is largely free-volume dominated. Figure 5 shows a plot of these earlier data¹ on fractions plus the new results obtained from polymer blends. All results are found to lie on well defined curves, when plotted as an inverse function of \bar{M}_n . Figures 5a–5c illustrate the spherulitic growth rate dependence on chain length at comparatively large undercoolings. All curves have a similar shape in these isothermal plots. Curves of a similar form can also be obtained for plots of $\log G$ versus inverse \bar{M}_n at constant ΔT when the corrected melting temperature is employed for each molecular weight. The slope of all these plots expressed as $\partial \log G / \partial (\bar{M}_n)^{-1}$ tends to zero at the high molecular weight end of the scale, to approximately 1.2 in the vicinity of the monomer itself. This overall change is only illustrated in Figure 5c where typical data at the growth rate maximum, G_x , is illustrated under conditions where factors affecting each limit of the $G-T$ curves of Figure 2 are comparable in equation (2). From 6×10^3 to about 1.4×10^6 molecular weight, the logarithm of the growth rate ($\mu\text{m}/\text{min}$) varies almost as the square root of \bar{M}_n^{-1} . The actual equation* describing this behaviour for TMPS polymers has the form:

$$G = A \exp B/[\bar{M}_n]^\alpha \quad (5)$$

where $\alpha = 0.54$ in the range $6 \times 10^3 < \bar{M}_n \leq 1.4 \times 10^6$ where B is a constant equal to 219 and A is a parameter dependent upon the crystallization conditions. It can be

* This form must be general for all polymers but the parameters are expected to vary from one material to another.

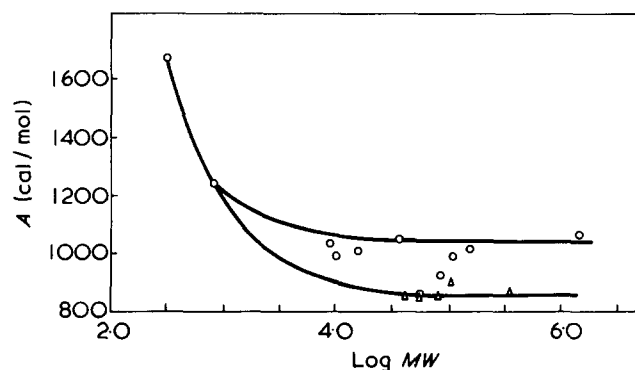


Figure 6 Relationship between A (cal/mol repeat units) and molecular weight from monomer through polymers of high molecular weight for TMPS. Δ , Blends; \circ , fractions

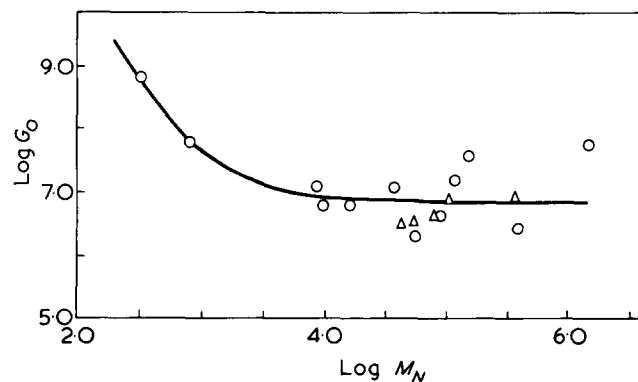


Figure 7 Plots of the pre-exponential G_0 as a function of molecular weight for TMPS materials. \circ , Fractions; Δ , blends

expressed as $A'f(T)$ when $A' = 17.46$ and $f(T) = \exp\{-[(T - T_x)^2/870] - [(T - T_x)^{3/2}/2000]\}$ for $T > T_x$ (the temperature where the growth rate is a maximum). For $T < T_x$ $f(T) = \exp\{-(T - T_x)^2/870\}$ also fits the data well. Hence it follows that A and B are fitting parameters and $f(T)$ is invariant for a given isothermal. The parameter α is dependent upon chain length. (Note that the plots in Figure 5 are logarithm to the base 10.) For short chains the exponent of M_n increases fairly rapidly reaching a limiting value ($\alpha = 1.2$) at the monomer. It is important to note that a general polymeric relationship cannot be deduced based upon limited molecular weight data. It is worth remarking, however, that polymer history does not affect spherulitic growth rates (whereas the overall transformation kinetics are enormously changed by past sample conditions⁶). Blends, fractions, whole polymers as well as freeze dried specimens of TMPS (Figure 5c) fall on a common spherulitic growth curve. Similarly, spherulitic transformation from the quenched glassy state or the melt will, at the same isothermal crystallization temperature, proceed at the same rate.

Effect of shorter chains on $\sigma\sigma_e$ (or σ_e)

When a low molecular weight fraction such as 1.58×10^2 is mixed homogeneously with a much higher fraction like 1.4×10^6 a noticeable decrease in $\sigma\sigma_e$ is found (see region D, Figure 4). In terms of current theory³ this lowering of $\sigma\sigma_e$ or σ_e can be explained by the increased concentration of cilia or chain ends on lamellae interfaces. It was previously shown that this change is in accord with the results from another surface study of TMPS single crystal surfaces¹³, which suggested that chain ends were predominately rejected from these crystals. In the 'transition' region C which is above the molecular weight where entanglements predominately enhance macroscopic fluid transport, the $\sigma\sigma_e$ values lie along the arbitrary line drawn through the experimental data points for both blends and fractions. However, in regime B the $\sigma\sigma_e$ values for blends (\blacktriangle) tend to fall higher than the values determined for homopolymer fractions, but the differences lie on the borderline of experimental error. The gradual rise in $\sigma\sigma_e$ with molecular weight suggests (other things being equal) that the surface energy associated with a cilia and a chain-fold cannot be too different in TMPS. Theory predicts that σ_f is much less than σ_t in polyethylene³⁴.

Dependence of transport parameters on molecular weight

Figure 2 illustrates how the activation term A in equation (2) changes with molecular weight. The decrease in A on

going from monomer to polymer[†] suggests that the activation energy associated with segmental diffusion needed to deposit polymer segments on a substrate is less than that required to move individual polymer segments from within the supercooled melt mix to the vicinal crystal surface. Consideration of this result leads one to the conclusion that polymer segments because of their chain connectivity may possess a higher affinity for the crystal substrate than isolated monomer units in their own environment[‡]. Certainly, from an entropic viewpoint there will be a distinct difference between the two conditions⁴.

Pre-exponential factor, G_0 . Figure 7 illustrates changes in this factor with increasing molecular weight. Only the trend need be considered, not the absolute values cited. A general levelling-off is noted at higher molecular weights even though there are significant fluctuations in G_0 , which form a theoretical viewpoint features orientational, entropic and other factors associated with accommodation of segments at the crystal interface³. Presumably some limiting condition is asymptotically attained for longer chains. It is worth noting that G_0 for the polymer is less than G_0 for the monomer itself.

Universal relation for crystallization

The results of Figure 2 and spherulitic growth rates determined for polymer fractions can be readily reduced to a single curve when plotted as $\ln(G/G_x)$ versus θ where $\theta = (T_m - T)/(T_m - T_\infty)$ and $0 \leq \theta \leq 1$. The growth rate at the maximum G_x in the $G - T$ plots and the other symbols have been defined previously. The corresponding states plot normalizes all growth rate data in dimensionless form G/G_x , whence it follows that polymeric materials peak on the abscissa where $\theta \sim 0.41$. This coincidence of all curves from just below 10^4 to above 10^6 in molecular weight (because of the overcrowding only typical examples of data are shown) must mean that the molecular weight and temperature dependences of both $\sigma\sigma_e$ and Δh_f in each equation must be similar. This normalization procedure is useful in testing data for consistency and in extrapolating sparse growth rate results to other regions where data is experimentally non-existent or not readily inaccessible. Elsewhere¹⁵, it has been demonstrated that this reducing equation is applicable to a wide range of different types of polymers.

[†] Only the trend is significant, not the absolute magnitude of the energy.

[‡] Note that these values are less than values encountered for comparable molecular weights for macroscopic melt transport.

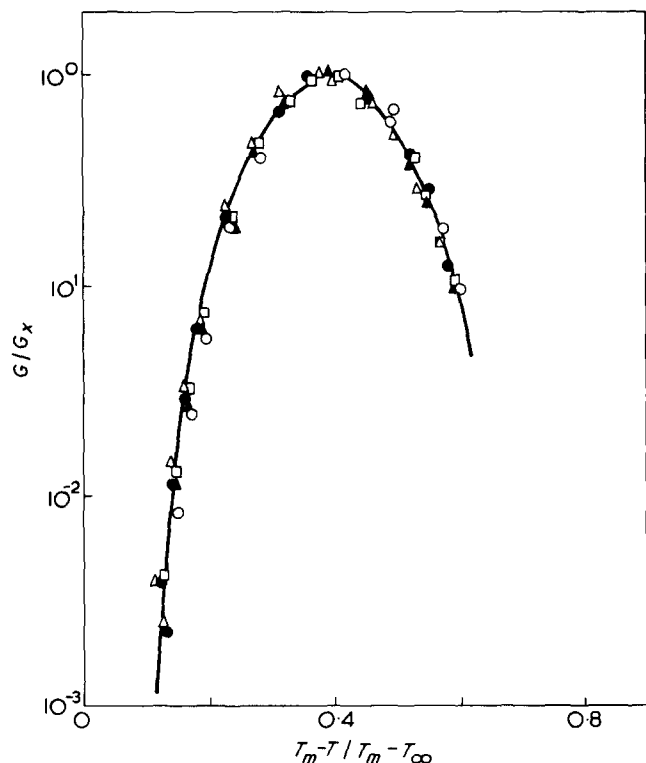


Figure 8 Dimensionless plots of spherulite growth rate expressed as $\log(G/G_x)$ vs. reduced temperature $(T_m - T)/(T_m - T_\infty)$ where $T_\infty = (T_g - 50)$ for various samples. G_x is the maximum observed growth rate, T_m is the thermodynamic melting point and T is the crystallization temperature and T_g is the measured glass transition temperature. \bar{M}_n values: \triangle , 4.25×10^4 ; \bullet , 5.50×10^4 ; \square , 8.04×10^4 ; \blacktriangle , 1.07×10^5 ; \circ , 3.50×10^4

Fractionation during crystallization

One of the clearest demonstrations of the inhibiting role of impurities on crystallization of spherulitic polymers is demonstrated¹⁶ by the non-linear dependence of spherulitic radius with time under isothermal growth conditions. Mostly this type of behaviour has been shown to occur in the presence of a non-crystallizable impurity (e.g. atactic polystyrene in the presence of the isotactic polymer). Experimentally such growth differences are only manifest at comparatively low undercoolings where sufficient mobility and free volume exists in the melt to allow diffusion of different species to occur. At comparatively large undercoolings, certainly in blends of molecular weight fractions of TMPS, no clear cut segregation is manifested where both low and high molecular weight species are crystallizable and the differences in properties arising via the ΔT term are small, far from the respective T_m values of the individual crystallizing species. At large undercoolings crystallite size is essentially independent of temperature over a wide crystallization range. It has been demonstrated that the fold thickness in a high polymer is independent of molecular weight at large undercoolings, contrary to earlier theoretical predictions¹⁹. This lower limiting crystal dimension in the chain direction has also been demonstrated for polystyrene¹⁶ and TMPS¹⁷ nylon-6,6¹⁸. Certainly, for obvious reasons, no change in observed melting with crystallization conditions is measured at large degrees of supercoolings. Sanchez⁴ predicts that broad molecular weight distributions tend to suppress molecular segregation effects rendering them more difficult to observe directly by experiment. In mixtures of widely different molecular weight

fractions, segregation is generally manifest in polymer properties at relatively small undercoolings, via melting point behaviour, small-angle X-ray scattering periodicities, and other property sensitive parameters. However, at large undercoolings these properties are generally independent of all isothermal crystallization conditions of the TMPS polymers where the small-angle X-ray spacing is invariant with the degree of undercooling^{17,18}.

CONCLUSIONS

(1) The general spherulitic growth rate equation(s) apply equally well to polymer fractions and mixtures of fractions if the extrapolated melting temperature is used in the analysis.

(2) The isothermal growth rate, $G(T)$, - molecular weight dependence for both fractions and blends can be described by the formalism:

$$G(T) = A \exp B/\bar{M}_n^\alpha$$

where A and B are constants and α is a molecular weight dependent parameter, $0.5 < \alpha < 1.2$.

(3) The surface (or interfacial) energy product $\sigma\sigma_e$ (or σ_e) for mixed fractions follow a pattern akin to that previously established for fractionated samples. The diluent effect of chain ends is noted particularly when short and long chain specimens are blended.

(4) The transport parameter A (kcal/mol units) in the crystal growth equation and the pre-exponential factor G_0 ($\mu\text{m}/\text{min}$) decrease asymptotically towards high molecular weight limiting values.

(5) A reduced equation may be used to put all growth data (fractions or mixtures) on a single master curve (except for very low molecular weight samples).

(6) Molecular weight segregation is not evident at large undercoolings where crystallite size becomes independent of chain length.

ACKNOWLEDGEMENTS

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REFERENCES

- 1 Magill, J. H. *J. Appl. Phys.* 1964, **35**, 3249
- 2 Hoffman, J. D. and Lauritzen Jr, J. I. *J. Res. Nat. Bur. Stand. (A)* 1961, **65**, 297
- 3 Hoffman, J. D., Davis, G. T. and Lauritzen Jr, J. I. in 'Treatise on Solid State Chemistry', (Ed. N. B. Hannay), Plenum Press, New York, 1976, Vol 3, ch. 7
- 4 Sanchez, I. C. *J. Macromol. Sci. (C)* 1974, **10**, 113
- 5 Magill, J. H. *J. Polym. Sci. (A-2)* 1967, **5**, 89; 1969, **7**, 1187
- 6 Magill, J. H. *J. Polym. Sci. (B)* 1968, **6**, 853
- 7 Hoffman, J. D. and Weeks, J. J. *J. Chem. Phys.* 1965, **42**, 4301
- 8 Magill, J. H. unpublished results
- 9 Frank, F. C. *J. Cryst. Growth* 1974, **22**, 233
- 10 Hoffman, J. D., Ross, G. S., Frolen, L. J. and Lauritzen Jr, J. I. *J. Res. Nat. Bur. Stand. (A)* 1975, **79**, 671
- 11 van Antwerpen, F. and van Krevelan, D. W. *J. Polym. Sci. (A-2)* 1972, **10**, 2049, 2423
- 12 Berry, G. C. and Fox, T. G. *Adv. Polym. Sci.* 1968, **5**, 261

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|----|---|----|--|
| 13 | Haller, M. N. and Magill, J. H. <i>ACCG Conf. Cryst. Growth</i> August 1969 | 18 | Pollack, S. S. and Magill, J. H. <i>J. Polym. Sci. (A-2)</i> 1969, 7, 551 |
| 14 | Fox, T. G. and Allen, V. R. <i>J. Chem. Phys.</i> 1964, 41, 344 | 19 | Girolamo, M., Magill, J. H. and Keller, A. to be published |
| 15 | Gandica, A. and Magill, J. H. <i>Polymer</i> 1972, 13, 595 | 20 | Price, F. P. in 'Nucleation', (Ed. A. C. Zettlemeyer), Marcel Dekker, New York, 1969, Ch.8 |
| 16 | Keith, H. D. and Padden, F. J. <i>J. Appl. Phys.</i> 1964, 35, 1286 | 21 | Haller, M. N. and Magill, J. H. <i>J. Appl. Phys.</i> 1969, 40, 4261 |
| 17 | Jones, D. H., Lathman, A. J., Keller, A. and Girolamo, M. <i>J. Polym. Sci. (Polym. Phys. Edn)</i> 1973, 11, 1759 | | |