Macromolecules **1988**, *21*, 3327–3328 3327

(15) Balke, S. T.; Hamielec, A. E.; Leclair, B. D.; Pearce, S. L. *Ind. Eng. Chem. Prod. Res. Dev.* **1969**, *8*, 54.
(16) Geacintov, C.; Smid, J.; Szwarc, M. *J. Am. Chem. Soc.* **1962**, *84*, 2508.

Modification of the Avrami Treatment of Crystallization To Account for Nucleus and Interface

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Introduction and Review of the Avrami Treatment

The kinetics of crystallization of polymers is often fitted to the Avrami treatment.[1] Identical treatments were proposed earlier than the one by Avrami,[2] by Kolmogoroff[3] and Johnson and Mehl[4], and later, by Evans.[5] All can be related to the problem of impinging waves, first solved by Poisson.[6] The solution can be briefly stated for the case of three dimensions by saying that the probability of a point not to be overrun by expanding spheres, $P_{\mathrm{o}}(t)$, is equal to $\exp(-E)$, where E is the expectation volume fraction for interpenetrating spheres expanding unhindered by impingement. The value of E increases from zero at time zero without limit to values beyond one as time increases.

For the application to crystallization of macromolecules, a number of specific modifications are usually made. First, nucleation is assumed to lead to negligible amounts of crystal formation and is either athermal (i.e., all N nuclei per unit volume are preformed and active at time zero) or thermal (i.e., the number of nuclei in the uncrystallized volume increases as a function of time $N(t) = at$). Second, the linear crystal growth rate, v, is assumed to be constant from nucleation to impingement, and the impingement leads to a negligible volume fraction of interface. These two assumptions lead to the following expectation volume fraction (also called the free growth approximation of the crystallization kinetics)

$$E = 4\pi N v^3 t^3/3 \qquad (1)$$

for athermal nucleation,[1] and

$$E = \pi a v^3 t^4/3 \qquad (2)$$

for thermal nucleation.[1] The corresponding Avrami equation is usually cast in the form

$$1 - v^{\mathrm{c}} = \exp[-Kt^n] \qquad (3)$$

where $1 - v^{\mathrm{c}}$ is the volume fraction of polymer outside the spherically expanding crystal, K is the collection of constants that can be evaluated by comparison with eq 1 and 2, and n is the "Avrami exponent", in the present cases 3 and 4, respectively. In this paper, both assumptions will be modified to account for a crystallization that approaches the case of "cold crystallization",[7,8] a case of crystallization from a highly viscous state that permits only minimum rearrangement of the crystallizable units. A similar model of crystallization has been proposed as an "Erstarrungsmodell"[9] and has also been fitted to the computation of the statistics of crystallization of macromolecular anisotropic melts.[10]

Further assumptions that are implied in the use of eq 3 for the description of crystallization of macromolecules are an isometric crystal morphology so that the probability $P_{\mathrm{o}}(t)$ does not depend on direction from the nearest nucleus. The spherulitic crystal superstructure often seen in macromolecules[11] ideally fulfills this condition but needs a special correction for partial crystallization within the spherulite boundaries, usually effected by normalizing the crystallinity at infinite crystallization–time to one. A frequent complication is continuing an approach to crystalline perfection within the spherulite. It has been corrected for the case of slow rates by additional term in eq 3.[1] Additional complications such as those due to volume change on crystallization, different crystal geometries, and different crystal branching have been described in detail and can be added to the modification proposed here when necessary.

All of these modifications have led to Avrami exponents of one or larger. Recent experiments have, however, shown an increasing number of cases of very small Avrami exponents,[12–14] in some cases even approaching zero. It will be shown in this paper that these low exponents could find an explanation in large nuclei numbers followed by rather limited growth slowed down by the production of rigid amorphous portions[15–19] between the microphase-separated crystals (soft impingement, see below).

Crystallization with Nonnegligible Volume Fraction of Nuclei

Usually, one does not take the volume fraction of nuclei into account since it is often very small and less than 1% of the total crystallinity in a polymeric system. However, when the volume fraction of nuclei increases up to 10% or more, the influence of such a large volume fraction of nuclei to overall crystallization becomes obvious.

Recent observations of the kinetics involving condis crystals show that a nonnegligible volume fraction of nuclei does exist and plays an important role in their overall crystallization behavior. For example, in the cases of thermotropic copolyesters produced by Celanese [with different 1,4-hydroxybenzoic acid (HBA) and 2,6-hydroxynaphthoic acid (HNA) compositions], a fast solidification process can be found within seconds during quenching the materials from their anisotropic melts. About 0.5–0.8 kJ/mol of heats of transition is formed. This corresponds to at least 5–10% or more of the total (condis) crystallinity.[12,20,21] It is also found that these earlier grown crystals grow slowly at later times and hamper further crystal growth under isothermal conditions.[12] It indicates that the earlier crystals as nuclei of further growth are being exhausted, and the number of active nuclei decrease with increasing time. Assuming that such a decrease can be cast in the form

$$N(t) = N_{\mathrm{o}} t^a \qquad (4)$$

where a is negative [$a = 0$ if a constant number of nuclei (athermal) are considered], the Avrami equation (eq 3) can now be written as

$$\log\,[-(\ln\,(1 - v^{\mathrm{c}}))] = \log g + \log N_{\mathrm{o}} + n \log v + (n + a) \log t$$

$$\log\,[-(\ln\,(1 - v^{\mathrm{c}}))] = \log K_1^* + (n + a) \log t \qquad (5)$$

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where $K_1^* = gN_0v^n$, and g is a geometrical factor (which is $4\pi/3$ for spheres as in eq 1 and 2). The slope in eq 5 for the relationship between log $[-(\ln (1 - v^c)]$ and log t, $(n + a)$, is smaller than n, its original Avrami exponent.

Crystallization with Changing Growth Rate

Linear crystal growth rates that change as crystallization proceeds have been observed earlier and mainly been linked to the influence of transport processes on crystallization.[1] For example, crystallization from dilute solution at large supercooling showed a nonlinear crystal-size increase with time,[22] and copolymers were shown to exhibit a sizable slow-down in spherulitic growth rate on close approach of two spherulites.[23,24] Such slow-down of crystal growth can often be treated as a Stefan problem[25] and leads usually to a boundary position that changes with the square root of time.[1] More substantial reduction in crystal growth rate is possible if the interface volume is large and crystallization leads to increasing restriction of the amorphous fraction, as can occur in the production of major fractions of rigid amorphous polymers.[15-19] In the cases of copolymers, such as in the HBA/HNA copolyesters,[12,21] a translational motion along the chain direction is largely hindered by the earlier grown crystals, and noncrystallizable counits cannot thus diffuse out from the growth-front of the crystal surface. We call such a phenomenon a "soft impingement." To treat this case, we assume that the crystal growth rate is a fraction of time:

$$v = v_o t^m \qquad (6)$$

where m is negative when v decreases with increasing time. Equation 3 can now be cast in the form of

$$\log [-(\ln (1 - v^c))] = \log g + \log N + n \log v_o + n(m + 1) \log t$$

$$\log [-(\ln (1 - v^c))] = \log K_2^* + n(m + 1) \log t \qquad (7)$$

where $K_2^* = gNv_o^n$, and $n(m + 1)$ is the slope of log t. Such a slope is smaller than n since m is negative. If the crystal growth is diffusion-controlled, for instance, in which case v would scale as $t^{-1/2}$,[26] according to eq 7, the slope of log t becomes $0.5n$, and it would be 0.5, 1, and 1.5 for one-, two-, and three-dimensional growth, respectively.

Combining these two effects of nonnegligible volume fraction of nuclei and changing crystal growth rate, we may have

$$\log [-(\ln (1 - v^c))] = \log g + \log N_o + n \log v_o + [n(m + 1) + a] \log t$$

$$\log [-(\ln (1 - v^c))] = \log K^* + [n(m + 1) + a] \log t \qquad (8)$$

where $K^* = gN_0v_o^n$, and $n(m + 1) + a$ is called as an apparent coefficient of log t. Both negative contributions (m and a) lead to the smaller value of the apparent coefficient one observed from experiments.

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References and Notes

(1) Wunderlich, B. *Macromolecular Physics. Crystal Nucleation, Growth, Annealing*; Academic: New York, 1976; Vol. 2.
(2) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103; **1940**, *8*, 212; **1941**, *9*, 177.
(3) Kolmogoroff, A. N. *Izv. Akad. Nauk SSSR, Ser. Math.* **1937**, *1*, 335.
(4) Johnson, W. A.; Mehl, R. T. *Trans. Am. Inst. Min., Metall. Pet. Eng.* **1939**, *135*, 416.
(5) Evans, U. R. *Trans. Faraday Soc.* **1945**, *41*, 365.
(6) Poisson, S. D. *Recherches sur la Probability des Jugements en matière criminelle et en matière civile*; Bachelier: Paris, 1837; p 206.
(7) Dole, M. *Kolloid Z.* **1959**, *165*, 40.
(8) Wunderlich, B. *J. Chem. Phys.* **1958**, *29*, 1395.
(9) Fischer, E. W. *Pure Appl. Chem.* **1978**, *50*, 1219.
(10) Hanna, S.; Windle, A. H. *Polymer* **1988**, *29*, 207.
(11) Wunderlich, B. *Macromolecular Physics. Crystal Structure, Morphology, Defects*; Academic: New York, 1973; Vol. 1.
(12) Cheng, S. Z. D. *Macromolecules* **1988**, *21*, 2475.
(13) Bhattacharya, S. K.; Misra, A.; Stein, R. S.; Lenz, R. W.; Hahn, P. E. *Polym. Bull. (Berlin)* **1986**, *16*, 465.
(14) Grebowicz, J.; Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 675.
(15) Suzuki, H.; Wunderlich, B. *Makromol. Chem.* **1985**, *189*, 1109.
(16) Cheng, S. Z. D.; Cao, M.-Y.; Wunderlich, B. *Macromolecules* **1986**, *19*, 1868.
(17) Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1987**, *20*, 1630.
(18) Cheng, S. Z. D.; Wu, Z. Q.; Wunderlich, B. *Macromolecules* **1987**, *20*, 2082.
(19) Cheng, S. Z. D.; Wunderlich, B. *Macromolecules* **1988**, *21*, 789.
(20) Butzbach, G. D.; Wendorff, J. H.; Zimmermann, H. J. *Polymer* **1986**, *27*, 1337.
(21) Cao, M.-Y. Ph.D. Thesis, Rensselaer Polytechnic Institute, Troy, NY 12180–3590, 1988.
(22) Holland, V. F.; Lindenmeyer, P. H. *J. Polym. Sci.* **1962**, *57*, 589.
(23) Price, F. P.; Kilb, R. W. *J. Polym. Sci.* **1962**, *57*, 395.
(24) Barnes, W. J.; Luetzel, W. G.; Price, F. P. *J. Phys. Chem.* **1961**, *65*, 1742.
(25) Stefan, J. *Ann. Phys. (Leipzig)* **1891**, *42*, 269.
(26) Schultz, J. *Polymer Materials Science*; Prentice-Hall: Englewood Cliffs, NJ, 1974.

Multiple Scattering Correction to the Second Virial Coefficient Measured by Small-Angle Scattering

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Introduction

When solutions are very dilute, the elastic scattering from the individual solute molecules adds linearly, so the intensity of radiation scattered coherently with wavevector transfer, Q, is just proportional to the mass of the molecule, M, the concentration, c, and the single-chain form factor, $P(Q)$. For larger concentrations, interparticle interferences become important, and the scattering then depends upon higher powers of the concentration. Zimm[1] derived an approximate expression for the coherent partial differential cross section by assuming that two molecules interact at only one point at any one time:

$$\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}(Q) \approx KcMP(Q)[1 - 2A_2(Q)cMP(Q)] \qquad (1)$$

$P(Q)$ is defined here to be unity at zero Q. In the small Q limit, A_2 is the second virial coefficient in the power series expansion of the osmotic pressure and indicates deviations from van't Hoff's law for ideal solutions. The second virial coefficient is an important quantity because it represents the strength of the intermolecular interactions.[2] It is usual to write eq 1 in the reciprocal,

$$Kc\left(\frac{\mathrm{d}\Sigma}{\mathrm{d}\Omega}\right)^{-1} \approx \frac{1}{MP(Q)} + 2A_2c \qquad (2)$$

because this form comes closer to accounting for neglected higher order terms than does eq 1.

Equation 2, known as the Zimm equation, has been the basis for analyzing low Q scattering data for many years.

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