Macromolecules **1996,** *29,* 5797−5804

Kinetics of Chain Organization in Ultrathin Poly(di-*n*-hexylsilane) Films[†]

M. M. Despotopoulou[‡] and C. W. Frank*

Department of Chemical Engineering, Stanford University, Stanford, California 94305-5025

R. D. Miller and J. F. Rabolt[§]

IBM Almaden Research Center, San Jose, California 95120-6099

Received August 15, 1995; Revised Manuscript Received June 10, 1996[⊗]

ABSTRACT: The effect of film thickness on the organization kinetics of ultrathin (50−1000 Å thick) spin-cast polymer films was studied using poly(di-*n*-hexylsilane) and UV absorption spectroscopy. We found an extensive reduction in the crystallinity as well as a reduction in the rate of crystallization for film thicknesses below 500 Å resulting from the constrained geometry. Modeling using polymer crystallization theories elucidated the surface-induced phenomena. We found that the dimensionality of the growth depended both on the film thickness and on the crystallization temperature. At low crystallization temperatures (below 0 °C) and for films thicker than 220 Å, the nucleation is bulk and the growth is three-dimensional. However, at higher crystallization temperatures (above 3 °C) and for low film thickness (below 150 Å), the growth is one-dimensional and heterogeneous nucleation becomes important. For 500 Å thick films, the transition between the two nucleation regimes occurs abruptly around 3 °C.

As ultrathin polymer films become more desirable in technological applications such as microelectronics, liquid crystal displays, and adhesive and passivation layers, the understanding of the role of the interface in altering the properties of an adjacent layer of organic material becomes necessary. The effect of geometric constraints on the crystallinity of a film is of considerable importance because both the properties and the topography of the film may be affected by the diminishing thickness. The potential significance of probing the chain organization in ultrathin films is that it may be related to the state of polymer organization in the region adjacent to a solid substrate in films of *any* thickness.

There is an extensive body of literature[1] examining the problem of chain organization and especially that of polymer crystallization. In several cases, the materials studied were thin films. For example, in order to observe crystallites under the optical microscope, the melt is usually confined between a slide and a cover glass to a layer that is often thinner than the dimensions of typical crystallites developed under unrestricted conditions. Also, in the case of some DSC measurements, a thin film of the material is deposited in the sample pan and thus it is important to know how the kinetics of crystallization are affected by the film configuration. There have been several attempts to model the kinetics of crystallization. One of the most widely used models is the Avrami−Evans theory,[2−5] which has been applied to a plethora of polymer systems. Efforts to adapt this theory to thin films were made, among others, by Stein and Powers[6] and later by Haudin and co-workers.[7−11]

The polysilanes offer a unique opportunity to study the chain organization in ultrathin polymer films with UV spectroscopy, a simple and well-understood technique. This is because polysilanes absorb strongly in the UV and the energy of the absorption maximum depends on the backbone conformation. In this work, we selected poly(di-*n*-hexylsilane) for our study. It is known that poly(di-*n*-hexylsilane) is a disordered solid above 42 °C, while at lower temperatures a crystalline, ordered phase develops.[12] In the disordered phase, the Si backbone assumes a disordered helical conformation, while in the crystalline phase it is in an extended all-trans conformation.[12] This is a first-order transition, as evidenced by the isosbestic point occurring in the UV absorption spectra.[13] At higher temperatures, this polymer does not undergo a transition to a melt phase but rather decomposes when heated above 250 °C. Chain extension in the all-trans conformation and the resulting crystallinity are developed by cooling a film that is initially in the disordered phase. In this polymer, the change of the backbone conformation from a disordered helix to an extended planar all-trans conformation produces a large change in the σ conjugation of the silicon chain, resulting in a 4180 cm^{-1} red shift in the absorption maximum for the crystalline material.[14] Thus, it is ideally suited for studying the chain organization in the thin region adjacent to a solid substrate which is often inaccessible for study in other polymers by such a simple technique.

For poly(di-*n*-hexylsilane), we have found[15] that extensive crystallization is prohibited in ultrathin films less than 150 Å thick. In order to gain a better understanding of the evolution of chain organization in this polymer and the effect of the interface on this process, we undertook a series of kinetic experiments, which are reported in this paper.[16]

Experimental Section

Substrate Preparation. The poly(di-*n*-hexylsilane) used in this study was synthesized as reported previously.[17] The weight-average molecular weight was 2.6 × 10^6 and the polydispersity 2.4. Solutions of the polymer were made in isooctane (2,2,4- trimethylpentane, 99+%, Aldrich Chemical Co.) in concentrations ranging from 0.1 to 2 wt %. The isooctane was used as received. The substrates used for the

---

[*] To whom correspondence should be addressed.

[†] Work first reported at the 1994 APS March Meeting, Pittsburgh, PA (*Bull. Am. Phys. Soc.* **1994**, *39*, 703).

[‡] Current address: Elf Atochem N.A. Inc., 900 First Ave., P.O. Box 61536, King of Prussia, PA 19406.

[§] Current address: Materials Science Program, Spencer Laboratory, University of Delaware, Newark, DE 19716.

[⊗] Abstract published in *Advance ACS Abstracts,* August 1, 1996.

S0024-9297(95)01196-X CCC: $12.00

UV absorption measurements were glass slides (VWR Scientific). They were cleaned in a mixture of H_2SO_4, H_2O_2, and H_2O (70/21/9 vol %) for 30 min at 120 °C.[18] After cooling to room temperature, the substrates were thoroughly rinsed with deionized water. All substrates were dried in an oven at 90 °C for 2 h and used immediately for film deposition.

Some quartz substrates were treated with octadecyltrichlorosilane (OTS) (United Chemical Technology). Long-chain *n*-alkyltrichlorosilanes, with more than 10 carbon atoms, form highly ordered, close-packed, self-assembled monolayers (SAMs) on quartz.[19] SAMs are very stable and mechanically robust and were used as an underlayer to study the potential interactions of the thin polymer film with the hydrophobic surface. All the solution preparations and reactions were done in a nitrogen atmosphere (Aldrich Chemical Co. Atmosbag) to avoid water-induced polymerization of OTS. Hexadecane (Aldrich Chemical Co.) was first dried by passing it through neutral alumina (Brockman Activity I) and then used to prepare a 2 mM solution of OTS. Quartz disks that had been cleaned and rinsed with deionized water were dried in a stream of nitrogen and immersed in the OTS silylating solution for 20 min. The substrates were wiped with 100% cotton tissues dipped in 2-propanol to remove any solution-deposited material (not bound to the surface), then rinsed with chloroform and ethanol, and dried with a stream of nitrogen. This procedure ensured the formation of a full OTS monolayer on the substrate.[20] The advancing contact angle was measured to be 112°, indicating a uniformly hydrophobic surface.

Film Preparation and Cooling System. The films were deposited by spin-casting at 3000 rpm for 40 s and then annealed at 100 °C for 15 min. The annealed films were slowly cooled to room temperature and later cooled further to the desired crystallization temperature. Accurate control of the crystallization temperature was provided by a U220-2 materials spectroscopy cryogenic research cooling system (MMR Technologies, Inc.) operating with high-purity (99.998%) N_2. The temperature stability of this system is ±0.05 °C. The cooling system was connected to a K-20 programmable temperature controller and a hand-held smart keyboard (MMR Technologies, Inc.) used to control the temperature and the other instrument functions. The cell had three quartz windows for use with a variety of spectroscopic techniques.

Ellipsometry. The film thickness of newly prepared films, deposited on a silicon wafer, was measured with an Auto EL^R-II automatic ellipsometer (Rudolph Research) with a He−Ne laser source (6328 Å).

Atomic Force Microscopy. A multimode Nanoscope III (Digital Instruments) atomic force microscope (AFM) was used, in the tapping mode, to image the surface of the glass substrate and characterize its roughness.

UV Spectroscopy. UV absorption spectra were obtained using a Cary 3 UV−vis spectrometer (Varian Analytical Instruments) with a clean substrate disk as reference. The baseline was recorded with another clean substrate disk in front of the sample beam. All film preparation was done under yellow lights in a class 100 clean room, thus avoiding any exposure of the films to UV light and airborne particulates before the crystallization studies. For each sample, several spectra were recorded and averaged when the peak positions were the same. The absence of a significant peak shift (more than 1 nm) was taken as an indication of film integrity, since exposure to UV light causes photodecomposition with a concurrent blue shift of the absorption maxima in polysilane films.[21]

Results and Discussion

Determination of Chain Organization and Crystallinity. The UV absorption spectra of the various polymer films were recorded continuously as the film crystallized isothermally at a specific temperature. A typical set of such spectra, for crystallization of a 160 Å film at −5 °C, is shown in Figure 1. As the film crystallization progresses, the intensity of the peak around 31 650 cm^{-1} starts to decrease, and a new peak, which grows with time, appears around 27 470 cm^{-1}. The low-energy UV absorption peak (27 470 cm^{-1}) corresponds to the crystalline phase absorption, while the high-energy absorption (31 650 cm^{-1}) is due to the disordered phase.[14] The isosbestic point observed around 30 000 cm^{-1} shows that this is a first-order transition[13] with the two phases in equilibrium. If we assume that the integrated absorption coefficients of the two phases are the same, the crystallinity of the film at any given time can be estimated by dividing the area under the low-energy peak (crystalline phase) by the total area under both peaks.

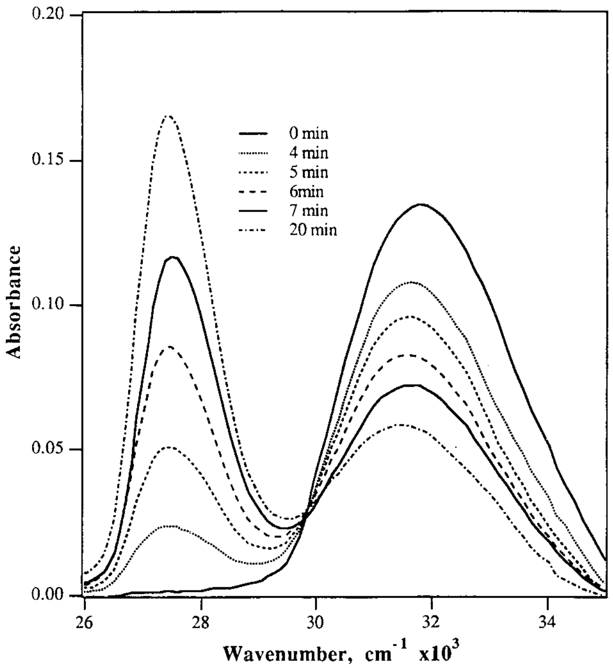

Figure 1. UV absorption spectra of a 160 Å thick film crystallized at −5 °C.

In poly(di-*n*-hexylsilane) films, the overall crystallinity of the sample is correlated with the presence of long trans or nearly trans segments. One of the fundamental characteristics of a crystalline phase is the existence of intermolecular interactions, and it has been shown that such interactions occur in poly(di-*n*-hexylsilane) and result in the extended all-trans backbone conformation.[12] Thus, although the UV absorption is directly related to the extent of the σ conjugation in all-trans segments, it is also an indirect measure of the intermolecular interactions in the crystalline phase. As a result, the sample crystallinity can be determined from the relative absorption of the all-trans and disordered segments in the sample.

To assess the validity of this approach, we may refer to literature results from X-ray and DSC measurements for similar materials. For example, the extent of crystallinity in equilibrated, solvent-cast films (tetrahydrofuran−methylene chloride) of poly(di-*n*-hexylsilane) of $M_w = 680\,000$ was estimated from X-ray diffractograms in the reflection mode to range between 56 and 69% depending on the crystallization temperature.[22] Moreover, the crystallinity of high molecular weight samples ($M_w = 2.6 \times 10^6$) has been estimated to be 61% using the heat capacities of the two phases calculated from differential scanning calorimetry.[23] Both of these estimates are in good agreement with our crystallinity results on thick films by UV spectroscopy, validating this technique. In this paper, we use the term crystallinity for the calculated crystallinity determined by UV

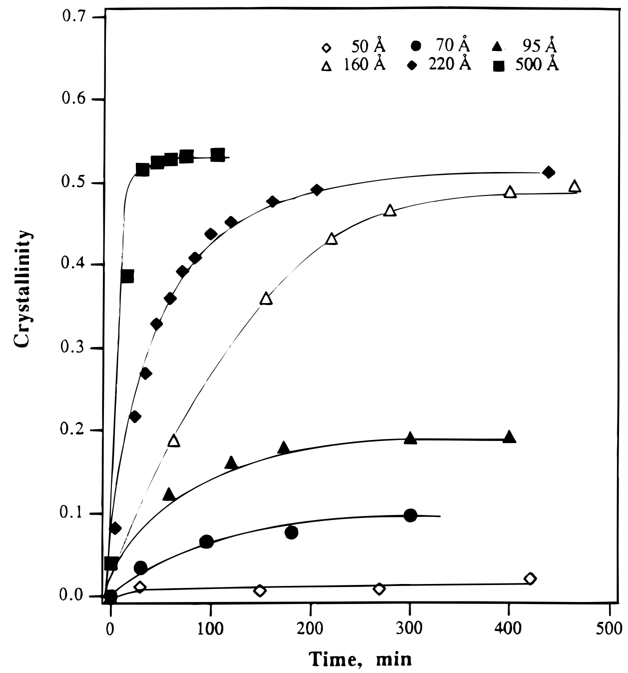

Figure 2. Kinetics of crystallization of poly(di-*n*-hexylsilane) films at 5 °C. The lines passing through the points are provided solely as a guide to the eye.

spectroscopy since our numbers are in good agreement with estimates obtained by other accepted macroscopic techniques.

Experimental Observation of Crystallization Kinetics. The UV spectrum of each film was initially recorded at room temperature before further cooling to the desired crystallization temperature. The observed absorption maximum was around 31 650 cm^{-1}, which corresponds to the amorphous polymer. Given the sensitivity of the UV absorption to the backbone conformation, this is good evidence that no crystallization has occurred prior to the beginning of the low temperature studies.

Figure 2 shows the dependence of the crystallinity with time for samples of various thicknesses cooled to 5 °C. We see that the crystallinity increases with time over a few hours and thicker films crystallize faster than thinner ones. Each film reaches a steady state after 8−9 h, but not all reach the same final crystallinity. For films thinner than 160 Å, the final film crystallinity is significantly lower, dropping from 52% to less than 20%, which suggests an inhibition in the growth of the microcrystallites in the restricted geometry of the thinner films.

Haudin and co-workers[7−9] found that a reduction in the rate of crystallization occurs for thin films when the size of the crystallite is of the same order of magnitude as the film thickness. Our observations show that there is a reduction in the crystallization rate in the 50−500 Å thickness range. Our results indicate that at 500 Å the thickness of the film is of the same order of magnitude as the crystallite size, which agrees with a previously estimated microcrystallite size of 290 Å[22] (see also Modeling of the Phase Change below).

After determining the rate of crystallization for poly(di-*n*-hexylsilane) films at 5 °C, we studied the effect of temperature. The results for crystallization at 0 °C are shown in Figure 3; the thicker films again crystallize faster than the thinner ones. Moreover, as seen in Figure 3, the 50 and 95 Å films do not attain the same final degree of crystallinity as the thicker films. This is exactly as observed for the crystallization at 5 °C. The final degree of crystallinity of the thicker films at 0 °C is 60%, which is slightly higher than the 52% observed at 5 °C. A similar set of experiments is shown in Figure 4 for crystallization at −5 °C. Again the thicker films crystallize faster than the thinner ones, but here even a 70 Å film is capable of reaching a very high final crystallinity (>50%). This is distinctly different from what was observed at higher temperatures, where films 95 Å thick or less did not reach a high crystallinity even after prolonged times (20% or less final crystallinity). The effect of temperature on a 500 Å film is more clearly shown in Figure 5. Obviously, the final film crystallinity increases with increasing supercooling down to a temperature of −5 °C. Also, it is clear that the rate of

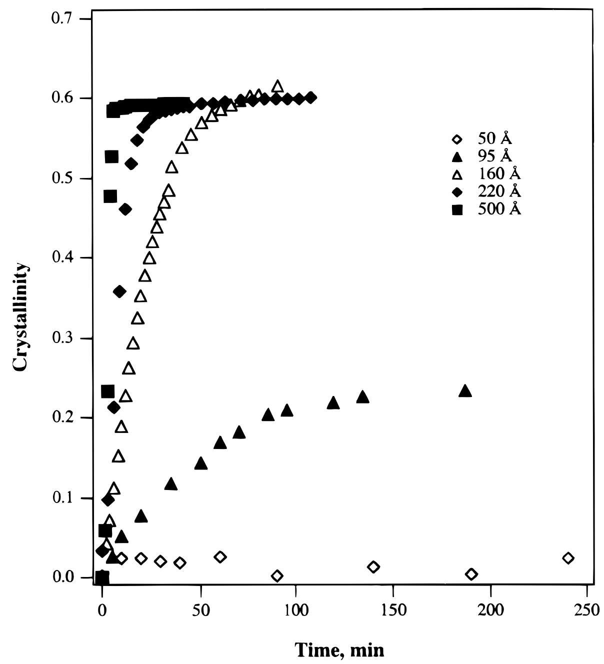

Figure 3. Kinetics of crystallization of poly(di-*n*-hexylsilane) films at 0 °C.

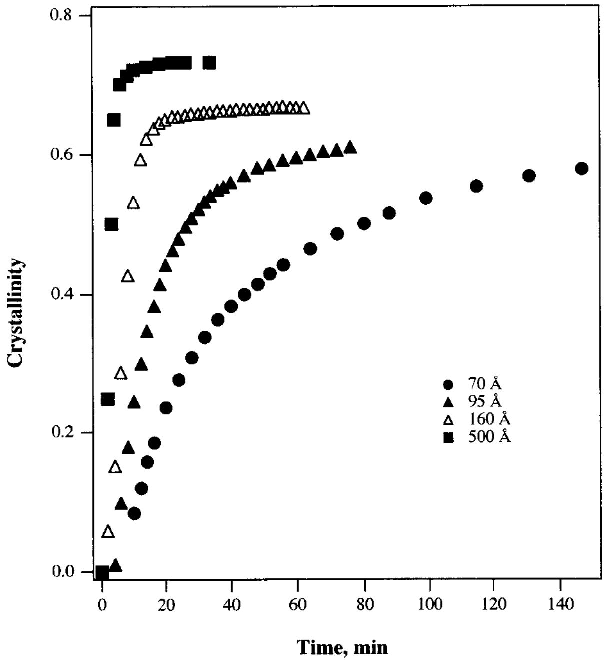

Figure 4. Kinetics of crystallization of poly(di-*n*-hexylsilane) films at −5 °C.

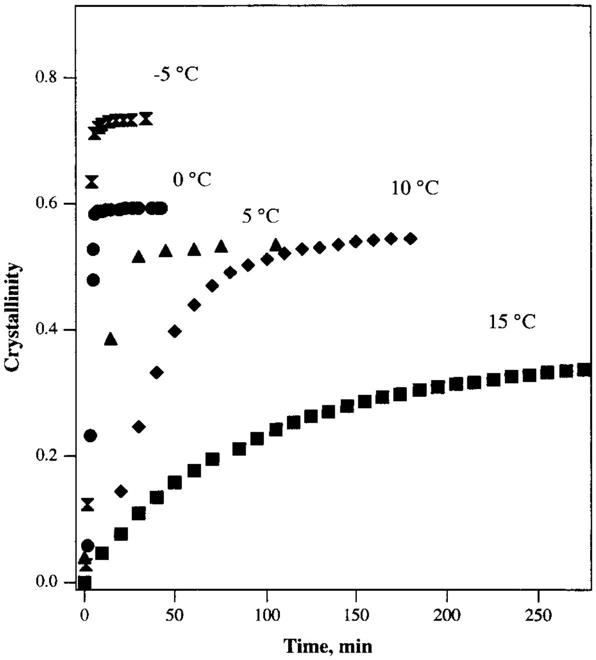

Figure 5. Kinetics of crystallization of a 500 Å film at several temperatures.

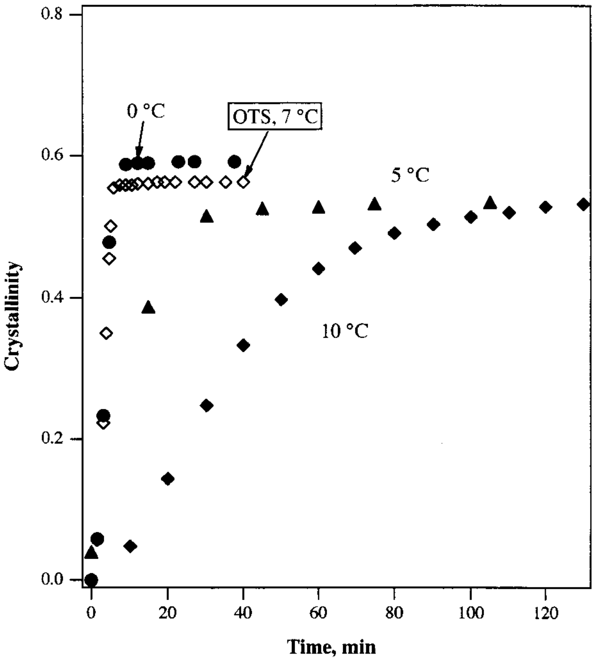

Figure 6. Kinetic data for crystallization of poly(di-*n*-hexylsilane) on OTS at 7 °C (open plotting symbols) shown relative to results on glass substrates (dark symbols) for 500 Å thick films.

crystallization is more than 10 times faster as the crystallization temperature decreases by 20 °C.

The effect of the substrate on the crystallization kinetics was also studied. Although it has been observed[24] that the nature of the substrate surface does not have any measurable effect on the final crystallinity of the films, it is possible that the kinetics could be affected. Figure 6 shows the kinetics of crystallization of a 500 Å thick poly(di-*n*-hexylsilane) film on an OTS-treated quartz surface (open plotting symbols) overlaid on the results for untreated glass substrate (solid symbols). The crystallization on the OTS SAM was carried out at 7 °C. If the kinetics of crystallization on the two substrates were the same, the data points for the OTS surface should fall between the 5 and 10 °C data of Figure 6. However, the crystallization process on OTS at 7 °C was found to be much faster, and this rate was comparable to that observed at 0 °C on glass. Thus, the surface has a pronounced effect on the kinetics of crystallization even though the final degree of crystallinity is the same, within experimental error, in each case.[24]

Crystallization Theories and Thin Films. In the Avrami−Evans theory, the volume percent crystallinity is calculated using geometrical or statistical arguments. The resulting equation is based on the view of crystallization as a macroscopic phenomenon, where nuclei appear at random points within the polymer volume and give rise to crystals that grow at a certain rate around the nuclei. The most widely used form of the Avrami equation is

$$v^{c} = 1 - \exp(-Kt^{n}) \tag{1}$$

where t is the crystallization time and K and n are two adjustable parameters. K depends on the experimental conditions, the type of nucleation, and the shape of the crystallite, while n is a parameter that depends on the dimensionality of growth. This form of the Avrami equation corresponds to isothermal crystallization and thermal or athermal nucleation. For athermal nucleation (all nucleation occurring at $t = 0$), n is 1, 2, or 3 for one-, two-, or three-dimensional growth, respectively. For thermal nucleation (nucleation occurring sporadically throughout time), n is 2, 3, or 4 for one-, two-, or three-dimensional growth, respectively. In the past, the Avrami exponent n has been used as the sole indicator of the dimensionality of growth, and considerable discussion has appeared in the literature regarding its meaning.[1] Although this dimensionality parameter cannot capture the details of each particular growth mechanism, it seems that the exponents obtained for a large number of polymers fall in the range predicted by the theory.[1]

Several attempts to adapt the basic Avrami−Evans theory to thin polymer films have appeared. Stein and Powers[6] derived the equations for a thin film by introducing a correction factor to account for the truncation in the spherical surface area due to the presence of a restraining upper boundary and concluded that the observed value of the Avrami exponent would be decreased by one relative to the value for unrestricted growth. A more detailed study of the effect of the restricted geometry on the kinetic law was done by Haudin and co-workers[7−11] in an effort to develop a model for both isothermal and anisothermal crystallization. This model allows the calculation of the crystallized volume anywhere in the film. Slower crystallization kinetics were observed not only because of the decrease in the number of activated (growing) nuclei due to truncations but also due to the decrease in the volume over which nucleation takes place. In addition to developing appropriate expressions[7] for the thin films, several simulations were carried out as well. The Avrami exponent was estimated by fitting the simulation results to eq 1. This overall exponent was smaller because the kinetics were slower in the restricted geometry. According to this theory, the ratio of the mean spherulite radius to the film thickness is of great importance. When this ratio approaches unity, the reduction in crystallization rate as well as the Avrami exponent is very pronounced. When, in addition to volume nucleation, surface nucleation occurs, trans-crystalline regions appear near the surface of the film if the density of the surface nuclei is high. In these regions the growth of crystallites is almost exclusively perpendicular to the surface because the close proximity of the surface nuclei hinders the transverse growth.

The Avrami–Evans theory and its modifications were widely used to model the crystallite growth in polymers prior to the appearance of the Lauritzen–Hoffman approach,[25–28] which explicitly considered the newly proposed concept of chain folding. In the present study, we have no information about the details of chain arrangement and are mainly concerned with the general aspects of the kinetics. The macroscopic treatment of Avrami and Evans does not assume a particular morphology for the nucleus or the growing crystal and is valid for any process where crystals grow with time, initiating at random positions throughout the medium. Moreover, there are no assumptions as to how these random points attain the critical nucleus size or the nature of the nucleus morphology. As mentioned above, the previously estimated microcrystallite size is 290 Å;[22] these microcrystallites are comprised of fully extended all-trans polymer chains. For such fully crystalline entities, the volume fraction overlapped by geometrical entities of the Avrami–Evans theory, v^c, and the transformed volume fraction measured here by UV spectroscopy are equivalent, and application of the Avrami–Evans approach is possible without further assumptions. Thus, this procedure is most appropriate for our purposes.

Obviously, trying to understand the crystallization of a particular polymer by examining the Avrami exponent alone does not provide adequate information for the complete characterization of the growth. Our aim is not to solely apply the Avrami–Evans theory blindly to yet another polymer beyond those already studied in the literature and to try to identify the type of growth by extracting the exponent. Rather, we have elected to carefully vary both the temperature and the thickness and determine their relative influence on the exponent. As only one parameter is varied at a time, and since we want to study the *relative* change of the Avrami exponent, this analysis can be extremely useful in elucidating the potential changes in the dimensionality of growth with decreasing thickness. From the work of Haudin and co-workers[7–11] we know the expected change in the Avrami exponent due to the restricted geometry. Any change beyond that predicted by this theory is not merely an effect of the restricted geometry, and other causal factors, such as a change in the nucleation type, should be considered as well.

Modeling of the Phase Change. The Avrami-Evans theory (as well as others) assumes that the polymer goes from a completely noncrystalline (0%) to a completely crystalline (100%) state. Thus, it is necessary to rescale the experimental data so that the maximum volume crystallinity corresponds to 1.0 (100% crystallinity), a procedure typically applied for the analysis of all semicrystalline materials. There are two different ways to fit the data to the functional form of eq 1 in order to estimate the parameters K and n. We can either directly apply a method for a nonlinear fit to eq 1 or linearize that equation (by taking a double logarithm) and use ordinary least-squares linear regression. As the fitting routine, we used the Levenberg–Marquardt method for a nonlinear fit.[29] This was favored over linearization of the Avrami equation primarily because the distribution of our data over time (more experimental points at longer times) skewed the v^c estimate of the linearized form, resulting in a poorer fit.

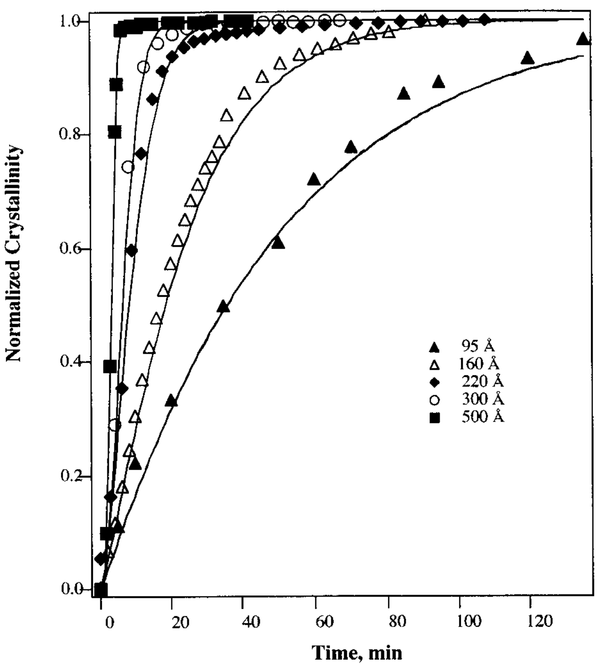

Figure 7. Nonlinear fit (continuous lines) of the Avrami equation to experimental data for crystallization at 0 °C.

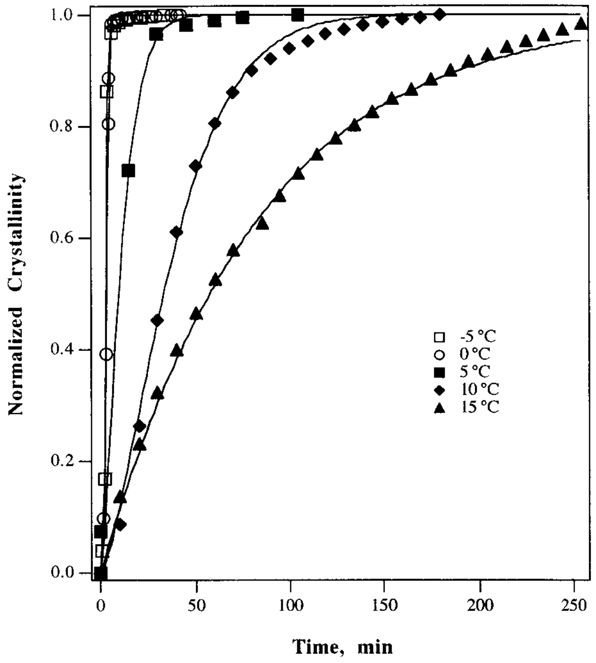

Figure 8. Nonlinear fit (continuous line) of the Avrami equation to experimental data for crystallization of a 500 Å film at various temperatures.

Typical results of the fits to eq 1 are shown in Figure 7 for films of various film thicknesses crystallized at 0 °C. Figure 8 shows the fits for a 500 Å film crystallized at a number of temperatures. The fits are relatively good. We did not try to fit eq 1 to data from films that reached less than 10% final crystallinity, e.g., the 50 and 70 Å films at 5 °C in Figure 2.

The values of the K and n parameters resulting from the nonlinear fits are shown in Figure 9 for each thickness and crystallization temperature. As expected, the effect of temperature and thickness on K is very

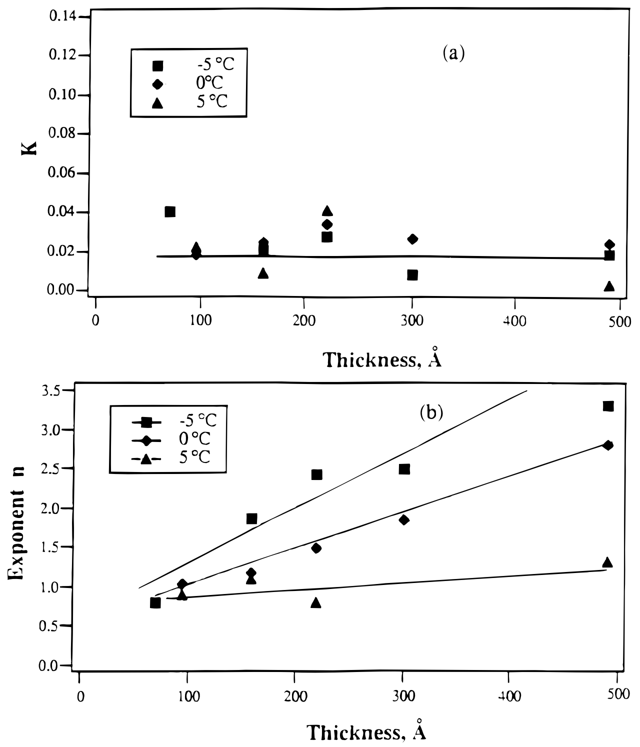

Figure 9. Dependence of (a) K and (b) the exponent n on the crystallization temperature and film thickness.

complicated since this parameter depends on a number of variables such as the shape of the crystallite, the growth rate, the number of potential nuclei, and their probability of nucleation. Unfortunately, we have no way to independently measure the number of nuclei or the growth rate to reduce the complexity. It can be seen that K varies around an average value of 0.019. This average has been calculated using the data for all thicknesses and temperatures. The effect of temperature and thickness on n is clear and more pronounced. We observe that the dimensionality parameter increases as the thickness increases and that the values of n are smaller for crystallization at higher temperatures. For example, the dimensionality parameter has a value close to unity at 5 °C for thin samples (50−200 Å).

It has been suggested[30] that the changes in K and n might be correlated and thus changes in K could mask the real changes in the dimensionality parameter. Since we cannot predict how the parameter K might change with thickness and temperature at this level of analysis, we performed another series of fits to eq 1 keeping K constant at its mean value of 0.019. The results of this one-parameter fit (using the same routine) are presented in Figure 10. The same trends are observed in the two- and one-parameter fitting results, making us confident that the changes we see in n are real and not an artifact created by correlated variation of K.

Figure 11 shows the results obtained for the exponent n by fitting eq 1 to the kinetic data for a 500 Å film crystallized at various temperatures. The dimensionality parameter changes abruptly around 3 °C from about 1 to about 3.5 as the temperature is lowered.

The fact that for thin samples and high crystallization temperatures the exponent is around 1 points to an athermal crystallization process. According to the Avrami−Evans theory, the only case where the exponent can be unity is when the growth is one-dimensional and athermal; i.e., the probability of nucleation is so high that almost all nucleation occurs at the beginning of the growth at $t = 0$.

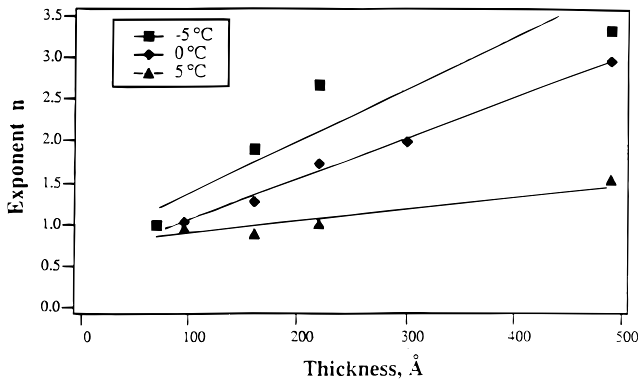

Figure 10. Dependence of the exponent n on the crystallization temperature and thickness. One-parameter fit, $K = 0.019$.

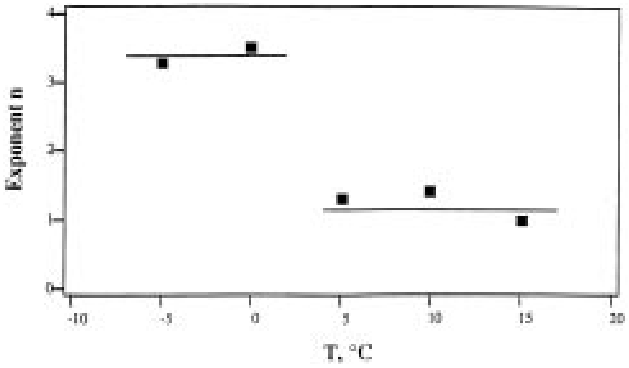

Figure 11. Dependence of the exponent n on temperature for a 500 Å film.

For crystallization at 5 °C, the exponent remains approximately constant and is equal to 1 for film thicknesses up to 500 Å (Figure 9). This means that the crystals do not encounter different constraints at different film thicknesses. However, when the crystallization occurs at somewhat lower temperatures, i.e., at 0 and −5 °C, we see that there is a continuous increase in the dimensionality of the growth as the thickness increases. The overall change in the value of the exponent Δn is larger than 1. This large change in the exponent cannot be explained by merely invoking the constraint on the growth imposed by the presence of the surface as indicated by the Haudin theory.[7−9] Therefore, we are led to believe that below 0 °C the crystallization process is different between thick and thin films. In addition to this observation of regime change with thickness at constant crystallization temperature, there is significant change of the dimensionality of the growth with temperature at constant film thickness, which is clearly shown in Figure 11.

All these observations can be explained in terms of nucleation theory.[1] It is known that when the supercooling is inadequate to lead to spontaneous nucleation and steady growth, the presence of a surface can provide an alternate way to decrease the Gibbs free energy of crystallization and thus initiate the crystallization. Since the presence of the surface creates a lower free energy, the critical nucleus size is reduced and steady growth can occur at a higher crystallization temperature (less supercooling). In several polymers, the temperature at which the transition occurs from heterogeneous nucleation to homogeneous (bulk) nucleation is well defined and can be easily identified from the sharp increase in the nucleation rate (see, for example, Cormia *et al.*[31] for polyethylene). In the case of ultrathin films, the surface is expected to play a role in the film crystallization. Examination of our results on the dependence of the dimensionality of growth on crystallization temperature shows that the growth is approximately one-dimensional at higher temperatures but becomes approximately three-dimensional at lower temperatures (increased supercooling). The transition is abrupt and occurs at a relatively well-defined temperature of 3 ± 2 °C (Figure 11). We interpret this as a change from heterogeneous to bulk nucleation as the temperature is lowered.

This interpretation can also explain the large change (of more than one) in the Avrami exponent (Δn) with thickness at constant crystallization temperature (Figure 9). As suggested in an earlier discussion, the restriction imposed by a boundary on the crystal growth can only lead to a maximum reduction of the Avrami exponent by one. Thus, there is a fundamental difference in the crystallization process of thin and thick films that must originate from the nucleation step. In the ultrathin films, it is difficult to achieve the size of the bulk critical nucleus, possibly due to the limited amount of material available. However, with the assistance of the surface, the size of the critical nucleus is reduced and stable crystallites can form and grow in one dimension. In this case, the crystal growth starts from the surface and develops one-dimensionally, i.e., toward the middle of the film. In the case of crystallization at high temperatures (5 °C), where the driving force (supercooling) is not large enough to effect bulk nucleation even in the thicker films, the nucleation remains heterogeneous throughout the thickness range studied. The constraint on the growth imposed by the opposite surface becomes independent of film thickness, as shown in the lower curve of Figure 9b, resulting in an exponent value of 1 for all thicknesses studied.

The fortuitous observation of much faster crystallization in two samples (220 Å at 5 °C and 160 Å at 0 °C) in which dust particles were visible on the films also points out the importance of heterogeneous nucleation for these films. These particles presumably acted as nucleation sites, considerably accelerating crystallization.

If heterogeneous nucleation is important for crystallization at high temperature and low thickness as proposed above, there are some additional implications about the overall development of crystallinity in these films. If the chains lie extended with the Si backbone axis parallel to the substrate, as concluded from transmission and grazing angle reflection FTIR data[24] and as reported for crystalline poly(hexylpentylsilane),[32] the only way substantial interaction among the chains can occur is by stacking of the poly(di-*n*-hexylsilane) in registry in a way that crystallinity develops from the surface to the middle of the film. At this point, we cannot differentiate between the effect of the substrate and the air surface; it is thus possible that either surface might affect the nucleation. In the proposed model of crystallization of ultrathin films, the development of crystallinity is one-dimensional and grows in a direction perpendicular to the film substrate.

Our kinetic measurements for a film deposited on an OTS surface offer some support for the hypothesis that heterogeneous nucleation is significant and that the surface plays an important role in the kinetics of crystallization under the conditions studied. One possible explanation for the acceleration in the rate of crystallization on the OTS surface may be the interdigitation and intermolecular interaction of the polymer hexyl side chains with the long alkyl chains of OTS on the substrate. In this case, the orientation of the side chains might be different than that found on quartz because of the additional favorable interaction between the side chains and the OTS. It is conceivable that the side chains are no longer extended parallel to the substrate as in the case of a pure glass substrate[24] but are instead oriented roughly perpendicular to the substrate in a way that maximizes their interaction with the OTS monolayer.

Any nuclei formed on a surface should be very sensitive to its roughness. Thus, we believe that the roughness of the glass substrate may also be an important factor in the development of the crystallinity of these ultrathin films. Using an AFM, we determined the mean substrate roughness (rms deviation of peak to valley height values) to be about 40 Å. The thinnest sample in which we saw any appreciable crystallization was 70 Å. This first 70 Å thick region of the polymer film might be aligned in the sense of having parallel disposition of chain segments, as predicted by several modeling studies,[33] but it cannot crystallize; i.e., it cannot attain the necessary all-trans extension and degree of intermolecular interactions to form organized crystalline material. The prevention of substantial intermolecular interactions might be due to the lack of sufficient material. Lovinger et al.[22] found an average crystallite size of about 290 Å in solvent-cast films by X-ray scattering. Although we have not attempted to measure the crystallite size in this work, we find it interesting that a preferred crystallite size of about 290 Å, coupled with a 70 Å noncrystalline region near the rough substrate, implies that a total thickness of at least 360 Å is needed for the development of a well-formed crystallite.

Thus, for the ultrathin films, there is an enhancement of nucleation due to the rough glass surface. In the case of an OTS substrate with a similar roughness, the possibility of intermolecular interactions between the hexyl side chains and the substrate led to a pronounced acceleration of nucleation and growth but did not affect the extent of final crystallinity.

The decrease in the rate of crystallization imposed by the constrained geometry was obvious below 500 Å in our experiments. This is in good agreement with the model assuming that a few noncrystalline polymer layers underlie the thicker films, presumably due to the substrate roughness. On the other hand, the relative importance of heterogeneous nucleation is dictated not only by the temperature but also by the substrate surface. Surface effects such as the heterogeneous nucleation may determine both the direction of crystal growth and the resulting crystal orientation.

Summary

We found that the development of long all-trans segments and overall chain organization in a crystalline phase, as measured by UV absorption spectroscopy, follows the general shape of the crystallinity vs time curve for a typical polymer. Thicker films crystallized faster than thinner ones, and in the temperature range examined (+15 to −5 °C) the rate of crystallization increased as the temperature decreased. The crystallization process was significantly slower when the thickness of the film was of the same order of magnitude as or smaller than the size of the crystallites. We used the Avrami−Evans theory to further analyze the di-

mensionality of growth and its dependence on thickness. At higher crystallization temperatures and for thin samples (below 150 Å), the growth was one-dimensional. There was an abrupt decrease, by more than one, in the Avrami dimensionality parameter as the temperature increased. These observations are consistent with a model of heterogeneous nucleation and growth starting at a surface and initially propagating one-dimensionally toward the middle of the film for ultrathin films and high temperatures. Finally, we have been able to identify both the surface effects and the effects of restricted geometry during the crystallization of ultrathin films and their interplay in determining the final film morphology.

Acknowledgment. We would like to thank Prof. A. P. Gast for helpful discussions. This work was supported in part by the Chemistry Program of the Office of Naval Research and in part by the NSF MRSEC Program through the Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA).

References and Notes

(1) Wunderlich, B. *Macromolecular Physics*; Academic Press: New York, 1976; Vol. 2.
(2) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103.
(3) Avrami, M. *J. Chem. Phys.* **1940**, *8*, 212.
(4) Avrami, M. *J. Chem. Phys.* **1941**, *9*, 177.
(5) Evans, U. R. *Trans. Faraday Soc.* **1945**, *41*, 365.
(6) Stein, R. S.; Powers, J. *J. Polym. Sci.* **1962**, *56*, S9.
(7) Escleine, J. M.; Monasse, B.; Wey, E.; Haudin, J. M. *Colloid and Polym. Sci.* **1984**, *262*, 366.
(8) Billon, N.; Escleine, J. M.; Haudin, J. M. *Colloid Polym. Sci.* **1989**, *267*, 668.
(9) Billon, N.; Haudin, J. M. *Colloid Polym. Sci.* **1989**, *267*, 1064.
(10) Billon, N.; Haudin, J. M. *Ann. Chim. Fr.* **1990**, *15*, 249.
(11) Billon, N.; Magnet, C.; Haudin, J. M.; Lefebvre, D. *Colloid Polym. Sci.* **1994**, *272*, 633.
(12) Patnaik, S. S.; Farmer, B. L. *Polymer* **1992**, *33*, 4443.
(13) Kuzmany, H.; Rabolt, J. F.; Farmer, B. L.; Miller, R. D. *J. Chem. Phys.* **1986**, *85*, 7413.
(14) Miller, R. D.; Hofer, D.; Rabolt, J. F.; Fickes, G. N. *J. Am. Chem. Soc.* **1985**, *107*, 2172.
(15) Despotopoulou, M. M.; Frank, C. W.; Miller, R. D.; Rabolt, J. F. *Macromolecules* **1995**, *28*, 6687.
(16) It has been brought to our attention that Sanji *et al.* (Sanji, T.; Sakamoto, K.; Sakurai, H.; Nakazato, A.; Ono, K. *Sendai International Symposium on the Frontiers of Organosilicon Chemistry*, Sendai, Japan, 1994, p 198) recently analyzed the kinetics of this process for a presumably thick, solvent-cast film. Although the morphology of solvent-cast films is different from spin-cast ones, the general conclusions on the dimensionality of growth of thick films are in agreement with our thick-film results. The actual film thickness or its effect on the kinetics were not mentioned.
(17) Rabolt, J. F.; Hofer, D.; Miller, R. D.; Fickes, G. N. *Macromolecules* **1986**, *19*, 611.
(18) The H_2SO_4/H_2O_2 mixtures are extremely corrosive and due care should be employed when used. The mixtures should be prepared in large-mouth containers.
(19) Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92.
(20) Mathauer, K.; Frank, C. W. *Langmuir* **1993**, *9*, 3446.
(21) Wallraff, G. M.; Miller, R. D.; Clecak, N.; Baier, M. *SPIE Proc.* **1991**, *1466*, 211.
(22) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2657.
(23) Varma-Nair, M.; Cheng, J.; Jin, Y.; Wunderlich, B. *Macromolecules* **1991**, *24*, 5442.
(24) Despotopoulou, M. M.; Miller, R. D.; Frank, C. W.; Rabolt, J. F., submitted to *J. Polym. Sci. Polym. Phys.*
(25) Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I., Jr. In *Crystalline and Noncrystalline Solids*; Hannay, N. B., Ed.; Plenum Press: New York, 1976; Vol. 3, Chapter 7.
(26) Hoffman, J. D.; Guttman, C. M.; Di Marzio, E. A. *Faraday Discuss. Chem. Soc.* **1979**, *68*, 177.
(27) Hoffman, J. D. *Polymer* **1982**, *23*, 656.
(28) Hoffman, J. D. *Polymer* **1983**, *24*, 3.
(29) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. R. *Numerical Recipes in FORTRAN, The Art of Scientific Computing*, 2nd ed.; Cambridge University Press: New York, 1992.
(30) Price, F. P. *J. Appl. Phys.* **1965**, *36*, 3014.
(31) Cormia, R. L.; Price, F. P.; Turnbull, D. *J. Chem. Phys.* **1962**, *37*, 1333.
(32) Factor, B. J.; Russell, T. P.; Toney, M. F.; Miller, R. D. *Acta Polym.* **1995**, *46*, 60.
(33) Theodorou, D. N. In *Physics of Polymer Surfaces and Interfaces*; Sanchez, I. C., Ed.; Butterworth-Heinemann: Boston, 1992; Chapter 7.

MA9511964