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Rapid recrystallization of freshly melted spherulites

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Abstract

The effect of residual nuclei on recrystallization has been investigated for a copolyester of glycolide and lactide. Initial spherulitic textures were melted, as observed by hot stage polarizing microscopy, and recrystallized by quenching to a given crystallization temperature. It was noted that the previous melting temperature would strongly influence the morphology of the second crystallization clearly due to residual nuclei remaining from the initial melt. Investigation of the new crystalline texture as well as its influence on subsequent crystallization kinetics was investigated through an Avrami analysis. It was also demonstrated that no memory effects of the initial crystallization temperature were transmitted to the system that had been recrystallized. This was supported by the utilization of small angle x-ray scattering measurements of the long spacing.

Introduction

The growth of crystalline textures from supercooled melts and the crystallization kinetics of polymers have been widely studied (1-3) but very little attention has been reported on recrystallization after partial melting. This latter process refers to a semicrystalline polymeric solid sample being melted above its "ordinary" melting point (Tm) but below its equilibrium melting point (Tm^o) and recrystallized in the presence of "unmelted" material, sometimes referred to as residual nuclei. It appears, however, important to investigate the influence of such a thermal treatment which could in principle, occur on a processing line, and to note the final morphology of the recrystallized polymer.

Banks, Gordon and Sharples (4) studied what they termed "seeded" crystallization by the presence of unmelted material in polyethylene. They showed that the kinetics of this form of crystallization were greatly influenced when an already crystalline sample was partially melted and brought back to a specific crystallization temperature Tc. The most remarkable features of the seeded recrystallization were the retention of the shape of the previous crystalline superstructure and the quasi-instantaneity of the second crystallization when Tc was reached again after the initial melting (5,6).

In this brief paper, we report on the morphology of similarly transformed or recrystallized spherulites using both polarizing microscopy and SEM. In addition, the effect of the second crystallization temperature (Tc) will be considered with respect to the crystallization kinetics and the long spacing of the final crystalline form, using DSC and SAXS respectively.

Experimental

The polymer used for this study was a copolyester of glycolide and lactide of respective weight ratio of 90/10. This material is commercially denoted as Vicryl$^{(R)}$ when utilized in the form of an absorbable suture material (7). The glass transition temperature is Tg=43°C and the melting point Tm=200°C. (Peak by DSC at 20°C/min.). This material was kindly supplied through the courtesy of Ethicon Inc. The polymer, which was received in pellet form, was dried and then pressed above Tm at 240°C for 2 minutes to form films which were isothermally crystallized from the melt at 140°C to induce a distinct two dimensional isolated "disk" spherulitic morphology. The partially crystalline films were then heated to 205°C for one minute to melt the previous spherulitic texture, followed by rapid quenching to a given Tc.

The final morphology of these samples was then investigated using a Zeiss polarizer microscope and an ISI Super-IIIA Scanning Electron Microscope. Some of the samples were etched with a 50/50 solution of DMSO and water to reveal the fine crystalline structure according to the technique developed by Carter and Wilkes (8). The crystallization kinetics were studied with a Perkin-Elmer DSC-4. The samples were isothermally crystallized and a computerized method was used to perform an Avrami analysis of the DSC results. The long spacing of the lamellar textures was determined using SAXS with a M. Braun position sensitive detector (Innovative Technology).

Results and Discussion

The microscopic observation of the transformed spherulites showed the existence of a pronounced memory effect from the previous crystallization. However, the shape and perfection of the new crystalline structures were strongly related to the temperature used to melt the previous crystalline texture. Figure 1-a shows that when the temperature was raised to 205°C for one minute and then quenched again to 140°C, the new "speckled superstructure that instantaneously appeared retained the exact shape of the previous spherulite. However, instead of the well defined maltese cross pattern observed by polarizing optical microscopy for the initial spherulite, the recrystallized superstructure showed a fine granular morphology. On the other hand, when the initial melting temperature was raised to 210°C (also for one minute) the new crystalline form (developed at 140°C) showed a much lower "granular" nucleation density, leading with time, to an agglomerate of small spherulites as shown in Fig. 1-b. These observations confirm the results published by Banks et al (4) which directly related the amount of residual seeds acting as nuclei to the temperature of partial melting. Undoubtedly, melting time would also be influencial in a somewhat similar way.

Another interesting result was obtained from samples partially melted at 205°C and recrystallized at 140°C for several minutes. Figure 2-a shows that after the structure recovered their previous shape (which possessed the granular morphology) the transformed spherulite continued to grow as an ordinary one i.e, the optical microscope displayed a maltese cross with fibrillar like structure beginning at the boundary region of the granular spherulitic "core". This is confirmed in Fig. 2-b where the interfacial region between this core and the newly formed spherulitic "ring" on an etched sample is shown in an SEM micrograph. The picture shows a quite disordered core surrounded by an ordered fibrillar structure characteristic of the new spherulitic morphology.

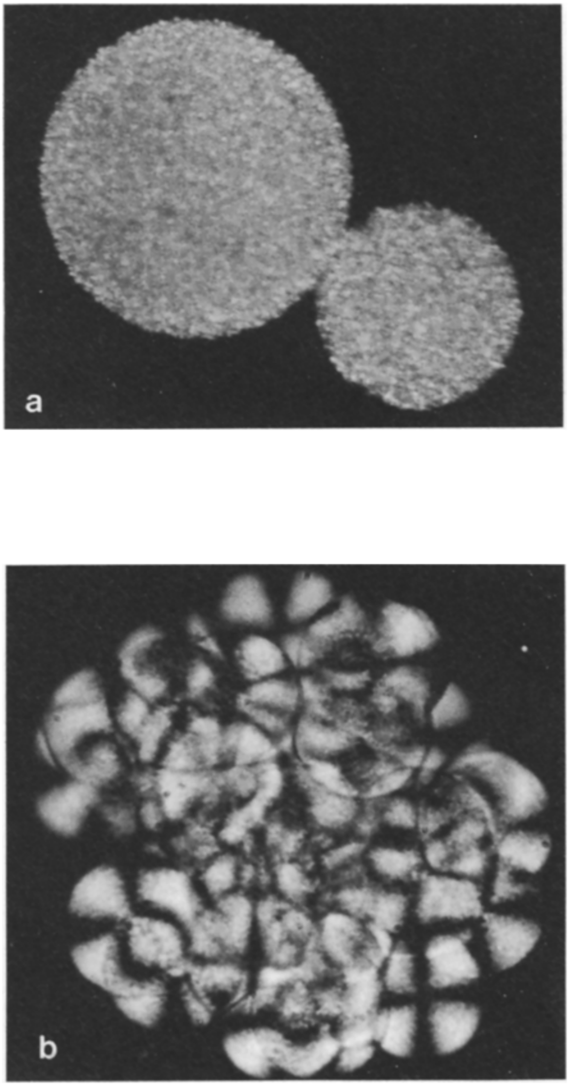
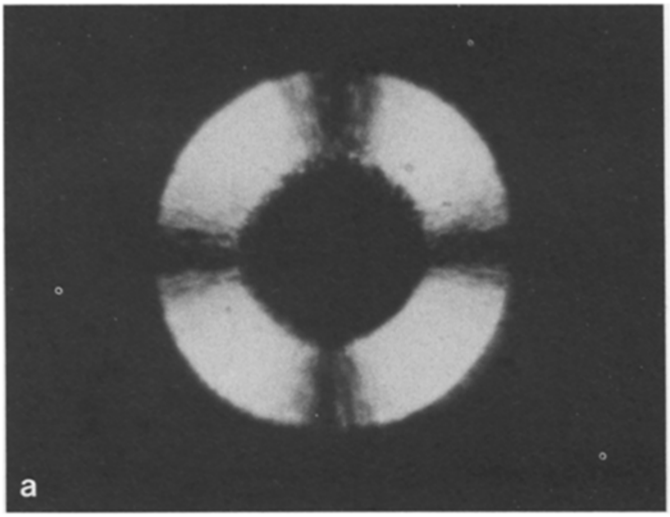


Figure 1: Optical micrographs of recrystallized or transformed spherulites; a) high primary nucleation density caused by residued nuclei, b) lower primary nucleation density caused by a greater time in the "melt" state.



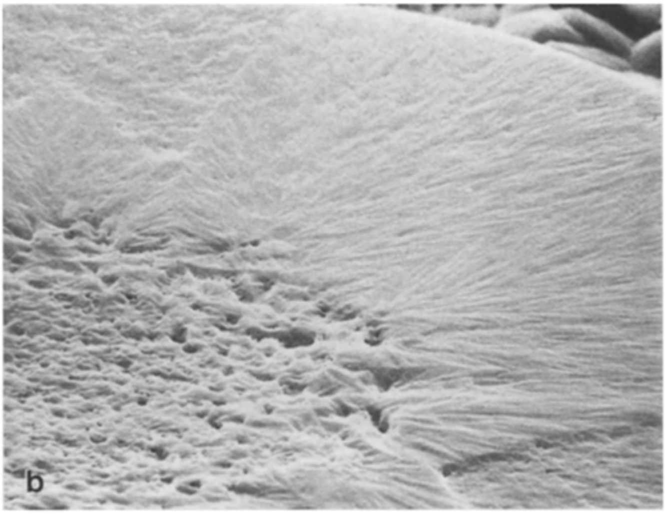


Figure 2: Recrystallization of transformed spherulite with further growth extending from the rapidly recrystallized core; a) optical microscopy - note the inner core was of granular texture but of low intensity relative to the outer fibrillar structure - hence the core also appears dark; b) SEM micrograph.

The last observation tended to support that the first and second crystallization followed the same mechanism. The kinetics seemed only to be accelerated by the remnant seeds. In order to verify this speculation, two samples were prepared as described before with a final Tc of either 140°C or 160°C respectively. The crystallization kinetics followed via heat flow using DSC are shown in Fig. 3. They indicate that the crystallization follows the well known Avrami relationship (see Eq. 1) for both, the initial first crystallization as well as for that from the growth of the fibrillar ringed regions of spherulitic-like textures.

$$Xam(t) = \exp(-Kt^{n}) \qquad (1)$$

Here Xam(t) is the amorphous fraction at time t, K is a kinetic constant, and n is the well known Avrami coefficient.

As expected from the microscopic observations, the overall kinetics of the second crystallization are much faster as expected. Moreover, they also are a function of the final Tc as shown by the values of $t_{1/2}$ (crystallization half-time) expressed in Table 1. However, the values of the Avrami coefficient (see Table 1) do not change greatly for the different samples, or crystallization type (initial vs. recrystallized) suggesting that there is no significant change in dimensionality of the growing crystalline structures (not those developed instantaneously) from first to second crystallization or as a function of the two different values of Tc.

The DSC results indirectly suggest that the "memory effect" observed for the rapid recrystallization of the initial melted structure (which retains the general shape of the initial spherulite) does not apply at the sub microscopic level. This conclusion is reached since the kinetics are a function of the final Tc. In order to support this point, the long spacing of the transformed spherulites was also investigated by SAXS as a function

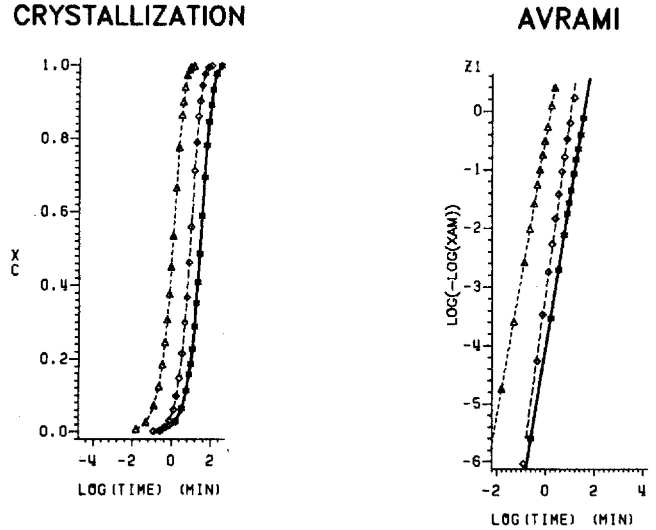


Figure 3: Results of the Avrami analysis; a) $X_{am}(t)$ versus log (time), b) $\log(-\log(X_{am}(t)))$ versus log(time).

of the final Tc. Specifically, three samples of the second or "recrystallized" textures (volume filling) were prepared as described before with final Tc's of 120°C, 140°C, 160°C respectively. The SAXS results from these materials were then compared to a pure volume filled spherulitic sample, crystallized only once at 140°C. The results for the SAXS experiments are reported in Fig. 4 and clearly show a shifting of the long spacing "peak" to small scattering angles for higher Tc for these three recrystallization experiments. The exact values of the long spacing are not provided since the peaks are from slit smeared experiments. However, the trend with Tc is clearly evident in that as expected from theory, the long spacing shifts to higher values as Tc increases. Therefore, it can be concluded that the parameter governing the lamellar thickness of the very rapidly seeded crystallization growth is the final Tc and that no memory effects from the previous crystallization are transmitted to the new crystalline lamellae through the remnant seeds.

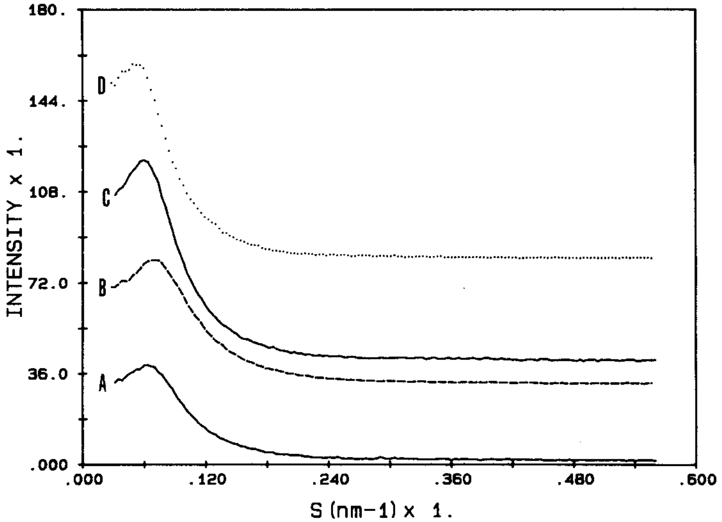


Figure 4: Slit smeared SAXS scans; a) spherulite, Tc=140°C; b) recrystallized spherulite, Tc=120°C; c) recrystallized spherulite, Tc=140°C; d) recrystallized spherulite, Tc=160°C. Note that both the 140°C scans, a) & c), show an equivalent long spacing.

Table 1: Crystallization half-time and Avrami coefficient as a function of the crystallization temperature.

	TEMP.(C)	HALF-TIME (min)	AVRAMI
FIRST CRYST.	140°C	4.28	2.4
SECOND CRYST.	140°C	1.05	2.3
SECOND CRYST.	160°C	2.53	2.7

Conclusion

The morphology and kinetics of the transformed spherulites are controlled by the final crystallization temperature and the amount of "seeds" left in the material after partial melting. The influence of the first crystallization is, however, important because of a memory effect which develop the new superstructures almost instantenously within the boundaries of the old ones. These results help to explain why semicrystalline polymers may possess a morphology different than might be expected at the end of a processing step if complete melting has not taken place.

Bibliography

1. J. D. Hoffman, J. I. Lauritzen Jr, J. Research of N.B.S, Phys. Chem., 65A (4), 297-335, (1961)
2. R. D. Icenogle, J.Pol.Sci., Pol. Phys. Ed., 23, 1369-1391,(1985)
3. A. J. Lovinger, D. D. Davis, F. J. Padden Jr., Polymer, 26, 1595-1604, (1985)
4. W. Banks, M. Gordon, A. Sharples, Polymer, 4(2) 289-302, (1963)
5. F. J. Padden, H. D. Keith., J.Appl.Phys., 30(10), 1479-84 , (1959)
6. H. G. Von Zachmann, H. A. Stuart, Makromol. Chem., 41, 148-172, (1961)
7. R. L. Kronenthal, in "Polymers in Medicine and Surgery," R. L. Kronenthal, Z. Oser, and E. Martin editors, Polymer Science and Technology, Vol. 8, Plenum Press, New York, 1979.
8. B.K.Carter and G.L.Wilkes in Polymers as Biomaterials, ed. S. W. Shalaby, A. S. Hoffman, B. D. Ratner and T. A. Horbert, Plenum Press, New York, 1984, pg. 67.

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