

Special Issues –International Symposium on Polymer Crystallization 2007– Branching and Higher Order Structure in Banded Poly(vinylidene fluoride) Spherulites

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The formation mechanism of banded spherulites of poly(vinylidene fluoride) has been examined experimentally by optical and atomic force microscopies. We have confirmed the proportional relationship between the band spacing and the maximum lateral width of lamellar crystals at the growth front, and the square root dependence of the maximum width and the band spacing on the growth rate. The square root dependence suggests a splaying instability of the growth front regulated by a gradient of free energy in the liquid side, and the proportional dependence suggests the dominant effect of torsional re-orientation on the occasion of splaying in the period determination of band spacing.

KEY WORDS: Spherulites / Poly(vinylidene fluoride) / Branching /

Crystallization of polymers from the melt evolves as a higher-order structure of spherulite with radiating and space filling branches. A number of polymer spherulites accompany concentric ring pattern in them and are called banded (or ringed) spherulite. The formation mechanism of spherulites in general and that of banded spherulites specifically have been studied for many years, but the fundamental mechanism of the pattern formation has not been clarified yet.^{1,2}

The concentric ring pattern in polymer spherulites is caused by an optical birefringence of lamellar crystallites which have twisting correlation along the radial axis.^{3–10} Concerned with the origin of the torsional stress, folded chains in the upper and lower surface regions of lamellar crystals are supposed to give rise to a residual asymmetric stress which has non-zero component of the torsional stress. The stress is called unbalanced surface stresses¹¹ and can get stronger by the reorganization of folding surfaces with lamellar thickening.¹² The molecular origin of the torsional stress is therefore dependent on the specific nature of each polymer, such as molecular chirality¹³ or asymmetric higher-order structures of the crystals.^{14,15}

In our recent studies, we have been focusing not on the molecular origin of the inherent stress but on the mechanism of the structural formation of spherulites in a mesoscopic scale, *i.e.*, the mechanism of branching and re-orientation of lamellar crystals in the spherulites. We have examined the banded spherulites of polyethylene and non-banded spherulites of polybutene-1 in our recent studies.^{16,17} The present paper is therefore for the further confirmation of the following proposed mechanism on the banded spherulites of poly(vinylidene fluoride), PVDF.

In our proposed modeling of the branching and re-orientation of lamellar crystals, we have suggested the possibility of a splaying instability of the growth front as the source of branching; the lateral width of each lamellar crystal is limited at a critical width, *i.e.*, maximum lateral width, above

which the crystal splays into branches. After the branching, the branches will be spontaneously re-oriented due to torsional inherent stress in the case of banded spherulites. Then, the reorientation results in the independent growth of each branch, and the growth front will undergo the repeated cycles of the lateral growth up to the critical value, branching, and re-orientation, as shown in Figure 1. In this way, we have suggested the branching and re-orientation mechanism with the frequency high enough to fill in the 3-d space of a spherulite with thin lamellar crystallites by the re-orientation on the occasion of branching.

The mechanism of branching and re-orientation in the banded spherulites is related with the selection mechanism of ring periodicity. It is probable that the period selection is not simply determined by the pitch of continuous twist of a lamellar crystal. Instead, the discrete twisting on the occasion of branching can be the possible source of the twisting along the radial direction. If the discrete re-orientation is the dominant factor in twisting, the band spacing, P , is determined by the average distance between successive branching along the radial axis, Λ , and the torsional re-orientation angle on the occasion of the branching, $\Delta\theta$, as $P = (\pi/\Delta\theta)\Lambda$. By simple geometrical consideration, the ratio of Λ and the maximum lateral width for splaying, λ_m , is determined by the ratio of growth rates in the axial and tangential directions, g . The band spacing is then expressed by the maximum lateral width, λ_m , as,

$$P = (\pi g / \Delta\theta) \lambda_m \quad (1)$$

with the form factor, g , of the order of one for most polymers.

Concerned with the splaying instability at the growth front as the source of branching, the possibility has been discussed for many years mainly by Keith and Padden without decisive experimental confirmations.^{18–20} We have recently suggested a splaying instability due to a gradient field of free energy at the growth front and experimentally confirmed the predicted

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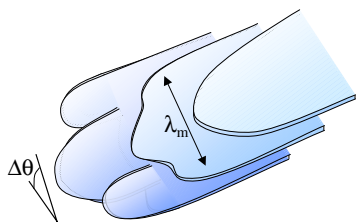


Figure 1. Schematic illustrations of the evolution of crystal splaying at the critical width, λ_m , coupled with the re-orientation due to intrinsic torsional strain.

dependence for the case of banded polyethylene spherulites and non-banded polybutene-1 spherulites.^{16,17} As the splaying instability of growth front, we have suggested two possibilities of the gradient in free energy at the growth front formed by (1) compositional gradient of non-crystallizing fractions (Mullins–Sekerka’s type^{21,22}) and by (2) pressure gradient due to the difference in densities of the crystal and the melt (Saffman–Taylor’s type^{23,24}). The gradient in free energy accelerates the fluctuation of the growth front and the surface tension suppresses the fluctuation; the balance of those two effects determines the critical lateral width, λ_m . The compositional gradient means the segregation of molecular species which are rejected at the growth front. Segregation is not unrealistic for synthetic polymers with inevitable molecular weight distribution. On the other hand, due to the density difference between the crystal and the melt, there must be mass flow near the growth front to supply the stationary growth of the spherulites. Therefore, the pressure gradient will also be one of realistic candidates of the gradient field.

We have supposed that the critical width of the splaying instability corresponds to the maximum lateral width of lamellar crystals at the growth front of spherulites. The dependence of the maximum lateral width, λ_m , on the growth condition is then expressed as follows for the compositional gradient and pressure gradient, respectively,

$$\lambda_m \propto (VD^{-1})^{-1/2}, \quad (V\eta)^{-1/2} \quad (2)$$

where V represents the growth rate, D the mass diffusion coefficient, and η the viscosity of the melt. Here, the possibility of thermal diffusion of latent heat can be excluded due to much faster thermal diffusion in comparison with mass diffusion of polymer molecules. It is also noted that the temperature dependence of D and μ^{-1} are both expressed by WLF type,

$$D_T = (D/D_0) = \eta_T^{-1} = (\eta/\eta_0) = \exp\{-[U^*/R(T - T_\infty)]\} \quad (3)$$

with the constants, $U^* = 4210$ cal/mol and $T_\infty = T_g - 51.6$ K, where T_g represents the glass transition temperature.²⁵ For this reason, the two cases are not distinguishable by the examination of the temperature dependence of λ_m .

In our previous papers, we have reported successful confirmation of the predicted square root dependence of λ_m on VD^{-1} (or $V\eta$) in terms of the temperature dependence for polyethylene¹⁶ and polybutene-1,¹⁷ irrespective of the higher order structures of banded and non-banded spherulites. For the banded spherulites of polyethylene, the proportional relation-

ship between P and λ_m in eq 1 has also been confirmed. In the following of this paper, we therefore suggest additional supporting evidences of the following dependences,

$$P \propto \lambda_m \propto (VD_T^{-1})^{-1/2}, \quad (V\eta_T)^{-1/2} \quad (4)$$

with PVDF banded spherulites by examining the growth rate and the band period by polarizing optical microscopy (POM) and the microscopic morphology of lamellar crystals at the growth front by atomic force microscopy (AFM) associated with quenching.

EXPERIMENTAL

We used PVDF of KF1000 ($M_w = 2.5 \times 10^5$ and $M_w/M_n = 2.1$, Kureha Chemical Industries, Co., Ltd.). For the crystallization from the melt, a film of 15 μm thick was prepared on a cover glass by press. The samples placed in a hot stage (THMS600 controlled by LK-600, Linkam) under nitrogen atmosphere were examined by POM (BX51, Olympus Corp.) for the measurements of growth rate, V , and the band spacing, P . As the sample preparation for the examination by AFM, the samples were crystallized isothermally for a certain time interval, and then quenched in a coolant (Fluorinert FC-77, 3M Co., Ltd.) kept at about -30°C by dropping the samples from the crystallization cell. In order to crystallize PVDF in the α form having concentric banding in the spherulites, the samples were firstly crystallized at 150°C and then the temperature was raised to the preset temperatures of isothermal crystallization.

For the microscopic examination of lamellar crystals at the growth front of spherulites by AFM, we need to remove surrounding micro-crystallites and amorphous portions formed on quenching. For this purpose, the sample surface of PVDF was washed with hot acetone kept at around 50°C for 10 min or so. By doing this softly, the lamellar crystals embedded in the quenched portions were visible by AFM. When quenched portions were dissolved away completely, the growth front of spherulites was like a cliff, so that the observation of lamellar crystals at the growth front by AFM became impossible. We have observed the crystals at the growth front, and supposed that the maximum size of the lateral width of lamellar crystals corresponds to the critical width, λ , for the onset of splaying; we have averaged the size of several large crystals. AFM (SPI3800N, Seiko Instruments Inc.) was in a dynamic force mode in air and silicon cantilevers (SI-DF20, Seiko Instruments Inc.) with a resonance frequency of 110–150 kHz were used for the observations.

RESULTS AND DISCUSSION

Figures 2 and 3 show the POM images of PVDF spherulites and the AFM images of the lamellar crystals at the growth front. It is clearly seen in those figures that both of the band spacing and the lateral width of lamellar crystals at the growth front increases with crystallization temperatures in a similar way, as indicated by double arrows in Figure 3 for the lateral width.

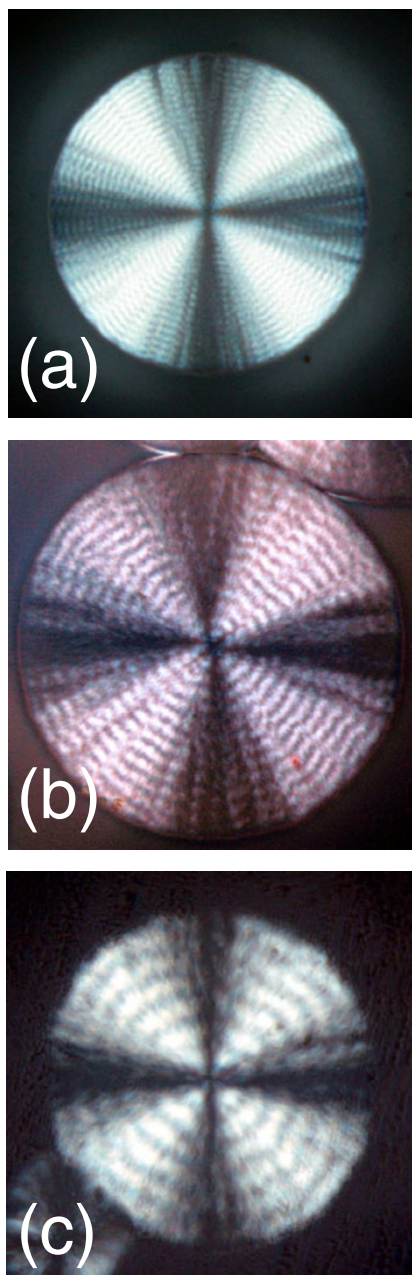


Figure 2. $180 \times 180 \mu\text{m}^2$ POM images of PVDF banded spherulites grown from the melt at (a) 166.0, (b) 169.5, and (c) 172.0°C, respectively.

Figure 4a shows the logarithmic plots of the growth rate and that divided by the factor in eq 3, VD_T^{-1} (or corresponding $V\eta_T$), against crystallization temperatures. We have also plotted the maximum lateral width of crystals at the growth front of spherulites, λ , and the band spacing, P , in Figure 4b. Due to the narrow temperature range examined, those data points can be fitted by straight lines, and the factor, D_T^{-1} has only a minor effect as seen in Figure 4a. As is shown by the fittings, the ratio of the slopes of the fitting lines of $\text{Log}[VD_T^{-1}]$, $\text{Log}[\lambda_m]$, and $\text{Log}[P]$ in Figure 4 is close to $-2:1:1$ and satisfies the predicted relationship of eq 4. The successful

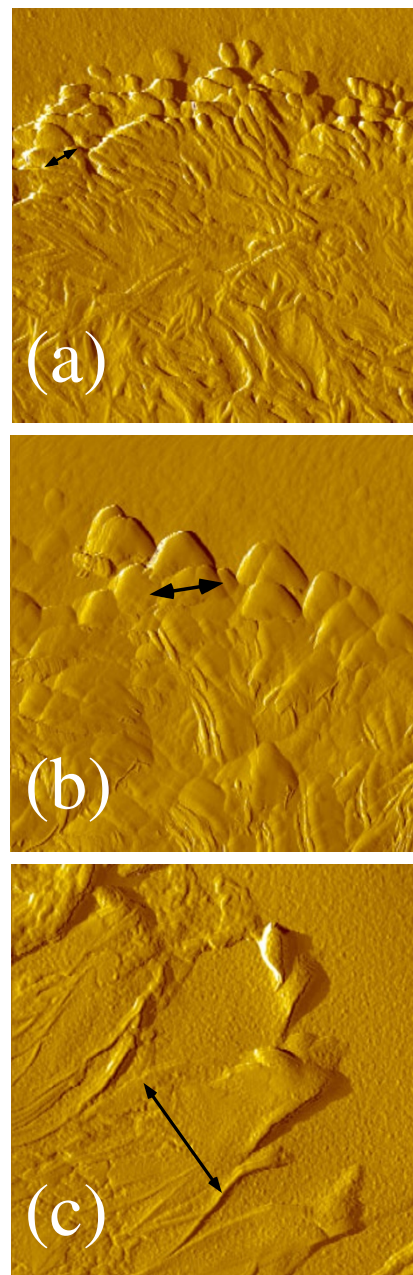


Figure 3. $6 \times 6 \mu\text{m}^2$ AFM amplitude images near the growth front of PVDF spherulites grown from the melt at (a) 166.0, (b) 169.5, and (c) 172.5°C, respectively.

confirmation can also be seen in the double logarithmic plots of $\text{Log}[\lambda_m]$ and $\text{Log}[P]$ against $\text{Log}[VD_T^{-1}]$ in Figure 5, where the slope -0.5 represents the predicted relationships and the data points are on the fitting lines.

The proportional relationship of eq 1 between λ_m and P suggests that the discrete re-orientation on the occasion of splaying is the dominant factor in the torsional angle determination of twist, irrespective of the cause of the splaying of branches. On the other hand, the square root dependence of λ_m and P on VD_T^{-1} (or $V\eta_T$) supports the prediction of eq 4 for the splaying instability due to a gradient in free energy at the

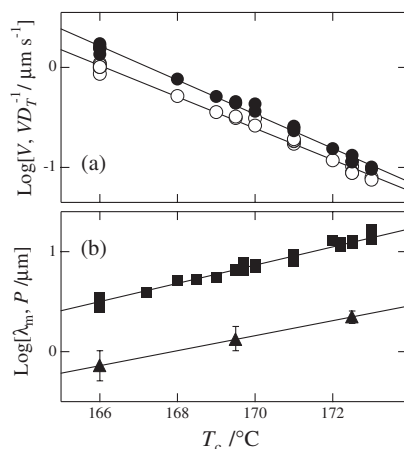


Figure 4. Logarithmic plots of (a) V (○) and VD_T^{-1} (●), (b) λ_m (▲) and P (■) against crystallization temperature. The slopes of the fitting lines are (a) V -0.16 , VD_T^{-1} -0.17 and (b) λ_m 0.075 , P 0.091 , respectively. VD_T^{-1} in (a) is divided by a constant, 2000, to overlap with V .

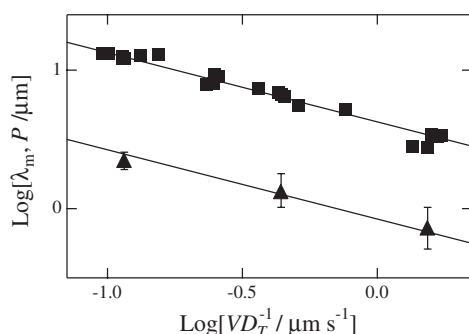


Figure 5. Double logarithmic plots of λ_m (▲) and P (■) against VD_T^{-1} . The slopes of the straight lines are -0.5 .

growth front. Because of the acute angle ($\sim 55^\circ$) of the growth tip made by the $\{110\}$ sectors of PVDF crystals as seen in Figure 3, for the splaying of the growth front, we suppose side branching as shown in Figure 1. The acute angle is in contrast with the obtuse angle ($\sim 112^\circ$) of the growth tip of polyethylene crystals. The examination of the width at the growth front must be essential for the successful confirmation of the relationship, because the width behind the growth front can get wider on crystallization even after the branching.

As the possible gradient, we have proposed two possibilities of splaying instability by the compositional gradient of non-crystallizing fractions and by the pressure gradient due to the density difference between the crystal and the melt. Because of the same temperature dependence of the WLF type of D_T^{-1} and η_T in eq 4, the distinction between them is not possible by the examination of the temperature dependence shown in Figures 4 and 5; we expect the same dependence of λ_m and P on VD_T^{-1} and on $V\eta_T$ by changing temperature.

At the final part of the discussion, it is noted that we do not exclude the possibility of continuous twist of lamellar crystals by the inherent stress. Actually, for the miscible blends of Poly(ϵ -caprolactone), PCL, and Poly(styrene-co-acrylonitrile),

SAN, it was reported that the addition of SAN brought drastic changes on the nucleation density as well as on the band spacing of PCL spherulites,²⁶ suggesting possible direct interaction between PCL and SAN by, *e.g.*, physical adsorption of SAN molecules on the nuclei and on the crystal surfaces of PCL probably to cause the drastic decrease in nucleation density and continuous twist of lamellar crystals, respectively. It is also noted that the proportional relationships of P and λ_m can be expected from continuous re-orientation, if the re-orientation is limited by the width of lamellar crystals, as has been speculated by Muthukumar.²⁷

CONCLUSION

We have experimentally examined the mesoscopic structure of the branching and re-orientation of lamellar crystals in the banded spherulites of PVDF by POM and AFM after the application of quenching. Due to the quenching, we could examine the lateral width of lamellar crystals at the growth front of spherulites, where the quenched portions were washed away by a solvent. We have measured the growth rate, the band spacing, and the maximum lateral width for different crystallization temperatures and confirmed the proportional relationship between the band spacing and the maximum lateral width and the square root dependence of the maximum width and the band spacing on the growth rate. The proportional relationship indicates that the discrete twisting on branching is dominant in the framework of the present modeling. On the other hand, the square root dependence suggests that the maximum width is limited by the splaying instability caused by a gradient field of free energy at the growth front. We have suggested two possibilities for the instability by the compositional gradient and by the pressure gradient; the distinction between them was not possible by the examination only of the changes with temperature. Further investigation of the behaviors by examining, *e.g.*, molecular weight dependence will be required.

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REFERENCES

1. P. H. Geil, "Polymer Single Crystals," John Wiley, New York, 1963.
2. J. H. Magill, *J. Mater. Sci.*, **36**, 3143 (2001).
3. A. Keller, *Nature*, **169**, 913 (1952).
4. J. J. Point, *Bull. Acad. R. Bel.*, **41**, 982 (1953).
5. H. D. Keith and F. J. Padden Jr., *J. Polym. Sci.*, **39**, 123 (1959).
6. F. P. Price, *J. Polym. Sci.*, **39**, 139 (1959).
7. A. Keller, *J. Polym. Sci.*, **39**, 151 (1959).
8. Y. Fujiwara, *J. Appl. Polym. Sci.*, **4**, 10 (1960).
9. Y. Nozue, R. Kurita, S. Hirano, N. Kawasaki, S. Ueno, A. Iida, T.

- Nishi, and Y. Amemiya, *Polymer*, **44**, 6397 (2003).
10. H. Tanaka, T. Ikeda, and T. Nishi, *Appl. Phys. Lett.*, **48**, 393 (1986).
 11. B. Lotz and S. Z. D. Cheng, *Polymer*, **46**, 577 (2005).
 12. D. C. Bassett, *J. Macromol. Sci.*, **B42**, 227 (2003).
 13. C.-Y. Li, S. Z. D. Cheng, J. J. Ge, F. Bai, J. Z. Zhang, I. K. Mann, F. W. Harris, L.-C. Chien, D. Yan, T. He, and B. Lotz, *Phys. Rev. Lett.*, **83**, 4558 (1999).
 14. H. D. Keith and F. J. Padden Jr., *Polymer*, **25**, 28 (1984).
 15. H. D. Keith and F. J. Padden Jr., *Macromolecules*, **29**, 7776 (1996).
 16. A. Toda, M. Okamura, K. Taguchi, M. Hikosaka, and H. Kajioka, *Macromolecules*, **41**, 2484 (2008).
 17. H. Kajioka, M. Hikosaka, K. Taguchi, and A. Toda, *Polymer*, **49**, 1685 (2008).
 18. H. D. Keith and F. J. Padden Jr., *J. Appl. Phys.*, **34**, 2409 (1963).
 19. H. D. Keith and F. J. Padden Jr., *Polymer*, **27**, 1463 (1986).
 20. D. C. Bassett and A. S. Vaughan, *Polymer*, **27**, 1472 (1986).
 21. (a) W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.*, **34**, 323 (1963),
(b) W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.*, **35**, 444 (1964).
 22. J. S. Langer, *Rev. Mod. Phys.*, **52**, 1 (1980).
 23. P. G. Saffman and G. I. Taylor, *Proc R. Soc. London, Ser. A*, **245**, 312 (1958).
 24. R. J. Fields and M. F. Ashby, *Philos. Mag.*, **33**, 33 (1976).
 25. J. D. Hoffman, G. T. Davis, and J. I. Lauritzen Jr., "Treatise on Solid State Chemistry," Plenum Press, New York, 1976, vol. 3, Chapter 7.
 26. H. D. Keith, F. J. Padden Jr., and T. P. Russell, *Macromolecules*, **22**, 666 (1989).
 27. M. Muthukumar, Presented at the 234th ACS National Meeting, Boston, August 19–23, 2007, Paper no. PMSE 455.