

Effect of Negative Pressure on Melting Behavior of Spherulites in Thin Films of Several Crystalline Polymers

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ABSTRACT: The melting behavior of spherulites in thin films of isotactic polypropylene, poly(ethylene oxide), poly(methylene oxide), and poly(ethylene adipate) crystallized isothermally at various temperatures has been studied by polarized light microscopy. The local increase of melting temperature in regions surrounding cavities and multiple boundary points, dependent on the crystallization temperature, was observed in all studied polymers. In pockets of occluded melt an arising negative pressure lowers an equilibrium melting temperature; hence, decreases an undercooling, which results in the increase of lamellae thickness and their melting temperature. The elevation of melting temperature and the negative pressure buildup depend on the polymer and the crystallization temperature. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1380–1385, 1999

Key words: spherulites; crystallization; melting; negative pressure; polypropylene

INTRODUCTION

In the course of crystallization the pockets of melt are occluded by impinging spherulites.^{1,2} Crystallization in those pockets is accompanied by the buildup of negative pressure due to lower specific volume of a solid. The negative pressure can grow to the limit, beyond which the melt fractures, which results in cavities preferably present near multiple boundary points inside a spherulitic structure.^{3–6} Local stresses or holes weaken a material; hence, the areas occluded during crystallization constitute “weak spots” of spherulitic structure. It was recently shown that cavitation in films of isotactic polypropylene occurs preferably at solid–liquid interface.⁷ In thin films the negative pressure arises only during crystallization of a polymer layer between two plates, while

in films crystallized with free surface the thinning of a sample within a weak spot occurs instead.

The negative pressure in weak spots lowers the equilibrium melting temperature, T_m^0 ; hence, decreases the undercooling. It was demonstrated in previously⁸ that negative pressure in weak spots causes a significant decrease of growth rate of isotactic polypropylene spherulites. The local decrease of undercooling also results in the crystallization of thicker lamellae. After the negative pressure relaxation by removing a cover glass from thin film or microtoming of a bulk sample the lamellae in weak spots exhibit higher melting temperature, T_m . The increase of melting temperature, ΔT_m , of spherulites in weak spots was observed in high-density polyethylene and in isotactic polypropylene.^{8,9} The changes in morphology of spherulites inside weak spots in isotactic polypropylene were also observed, suggesting reduced crosshatching.¹⁰

In the presented work an effort was made to demonstrate that the increase of lamella thickness and/or perfection, reflected in local elevation of T_m , is a common effect during crystallization of

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polymers. Local ΔT_m was measured in wide range of crystallization temperature T_c . Based on ΔT_m and on the dependence of T_m on T_c , the decrease of the undercooling, equal to the drop of T_m° , was calculated for several polymers. Then, the values of negative pressure in occluded pockets of melt were estimated by extrapolating the empirical dependence of T_m° on pressure p^{11-15} to a negative pressure range.

EXPERIMENTAL

The following polymers were chosen, known as crystallizing in a form of large spherulites well visible in light microscope: two brands of isotactic polypropylene (iPP)—Polysciences product having an $M_n = 17,000$ and an $M_w = 220,000$ (iPP1) and Montedison product Moplen S 30 G, melt flow index 1.75 g/10 min at 230°C (iPP2); poly(ethylene adipate) (PAE), Poles 60/20, Polish product of $M_n = 2000$; poly(ethylene oxide) (POE), Polysciences, $M_w = 4,000,000$, and poly(methylene oxide) (POM), Du Pont product, Delrin 150, melt flow index 2.0 g/10 min. IPP and POE films of thickness 30–40 μm and PAE films of thickness 10–20 μm were obtained by compression molding. POM films having thickness of 30–40 μm were cast from 4 wt % solution of dimethylformamide. The films were placed between two cover glasses, and then melted, melt annealed, cooled, and isothermally crystallized in the Linkam Hot Stage mounted on the light microscope. The precision of the temperature control was within 0.1°. The time and temperature of melt annealing were: 5 min at 220°C for iPP, 10 min at 60°C for PAE, 5 min at 100°C for POE, and 1 min at 190°C for POM.

T_c ranges were: 116–139°C for iPP, 43–58°C for POE, 27–40°C for PAE, and 152–166°C for POM. At lower T_c , small spherulites crystallized in not completely isothermal conditions, while at higher T_c crystallization was too slow, possibly accompanied by segregation of low molecular fractions and by degradation in the case of iPP and POM. The formation of spherulitic structure was monitored to determine the localization of weak spots. The upper cover glass was removed after crystallization to release the stresses in sample, and then the melting behavior of a sample was studied during heating in the Linkam Hot Stage. For iPP, where the local increase of melting temperature, ΔT_m , was best seen, also the melting behavior of samples with the unre-

upper glass was occasionally observed. Usually, several samples crystallized at the same T_c were examined. The heating procedure for the best observations of ΔT_m of the spherulites was chosen on the basis of preliminary studies; samples were heated up fast to the temperature by 5 K lower than T_m , to minimize annealing effects, and then slowly to observe the melting behavior of samples. The fast and slow heating rates were: 80 K/min and 5 K/min for iPP and POE, 120 K/min and 5 K/min for POM, and 10 K/min and 3 K/min for PAE. The crystallization and melting of samples were monitored by light microscope with crossed polarizers. The microscope was connected with a closed-circuit TV (CCTV) camera, CCTV display, and VHS video recorder. To correlate the melting behavior with the regime of crystallization, the spherulite growth rate, G , for iPP was also determined from the position of crystallization front in successive time intervals for T_c until 141°C. For $T_c = 125^\circ\text{C}$, the drop of G inside a weak spot was also recorded.

RESULTS AND DISCUSSION

The observation of thin polymers films, crystallized between glass plates, showed that there is a local increase of T_m of spherulites in regions of weak spots where the melt was confined between spherulites during crystallization. The local increase in T_m indicates the difference in undercooling during crystallization. At isothermal conditions the change of undercooling in weak spots

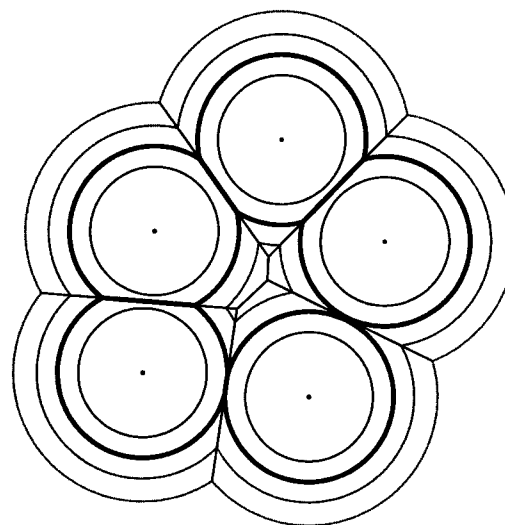


Figure 1 The scheme of a weak spot formation.

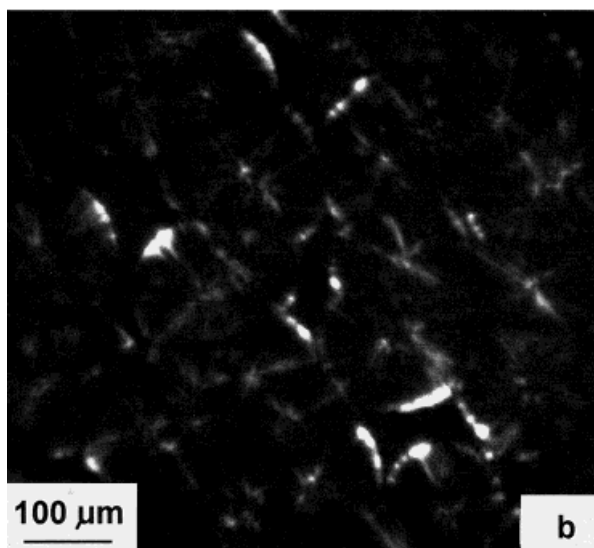
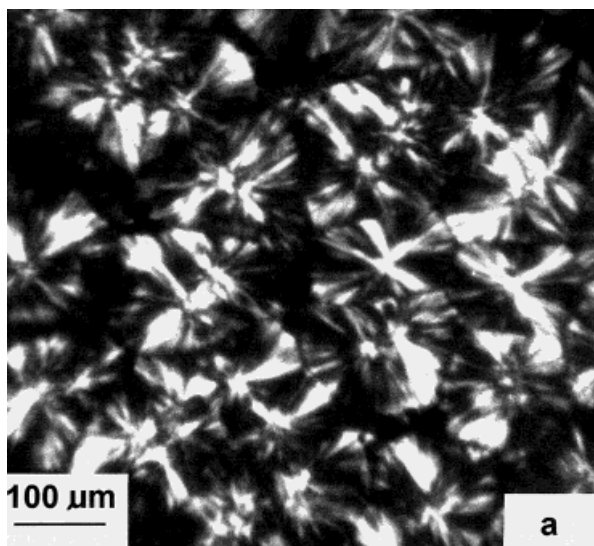


Figure 2 The micrographs of a weak spot and its surrounding in iPP1 thin film crystallized between glass plate at 128°C. Crossed polarizers: (a) room temperature, (b) 165.5°C.

results from the local decrease of T_m° caused by negative pressure. The dependence of T_m on T_c for spherulites outside weak spots permits calculation of the change of undercooling from the shift of T_m . Hence, the local increase of T_m in weak spots allows us to calculate the drop of T_m° caused by the negative pressure.

The ΔT_m in weak spots was observed in POM and POE in the entire range of T_c studied, for $T_c < 136^\circ\text{C}$ in the case of iPP, and in the range $30^\circ\text{C} < T_c < 39^\circ\text{C}$ for PAE. Although ΔT_m was observed

locally in weak spots, it was invisible in other parts of the same spherulites outside weak spots. In the case of iPP thin films, if the upper glass was not removed from a sample, the effect of the T_m increase was seen on the next day after crystallization, indicating slow stress relaxation in spherulitic structure in contrast to immediate release of negative pressure in melt caused by cavitation described in ref. 8. The removal of upper glass accelerated the relaxation and permitted to

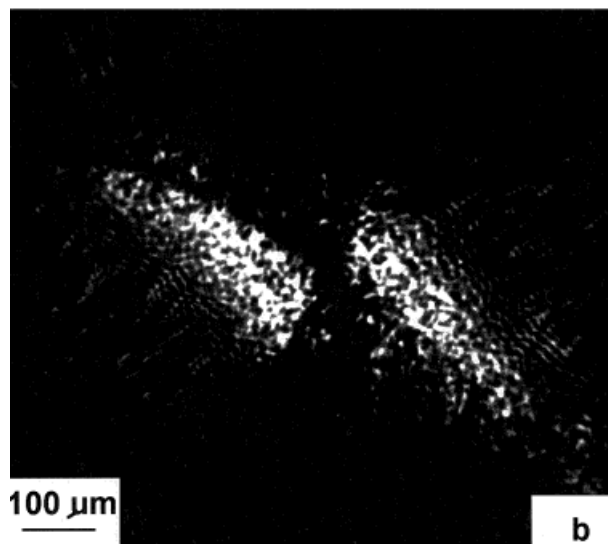
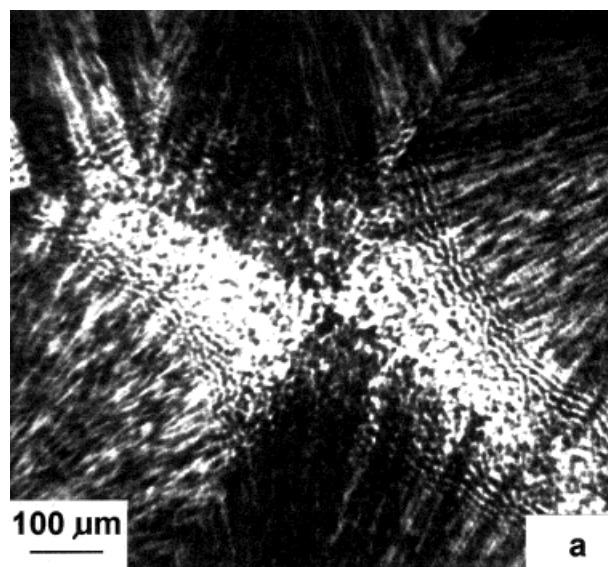


Figure 3 The micrograph of a weak spot and its surrounding in PAE thin film crystallized between glass plates at 34°C. Crossed polarizers: (a) room temperature, (b) 45.5°C.

observe ΔT_m even right after completion of crystallization.

Figure 1 shows the scheme of a weak spot formation as a result of spherulites impingement. The thickest line corresponds to the moment of melt pockets formation by occlusion by spherulites. In Figures 2–3, the exemplary microphotographs show the differences in melting behavior between weak spots area and their surroundings

in iPP1 and PAE thin films. The effect is best visible as brightenings of peripheral fans of spherulites upon melting, and it depends on polarizers positions. The residual birefringent regions were seen in parts of spherulites crystallized after confinement of melt. If the negative pressure in weak spots was released by cavitation of melt, only the portions of spherulites crystallized after confinement, but prior to cavitation

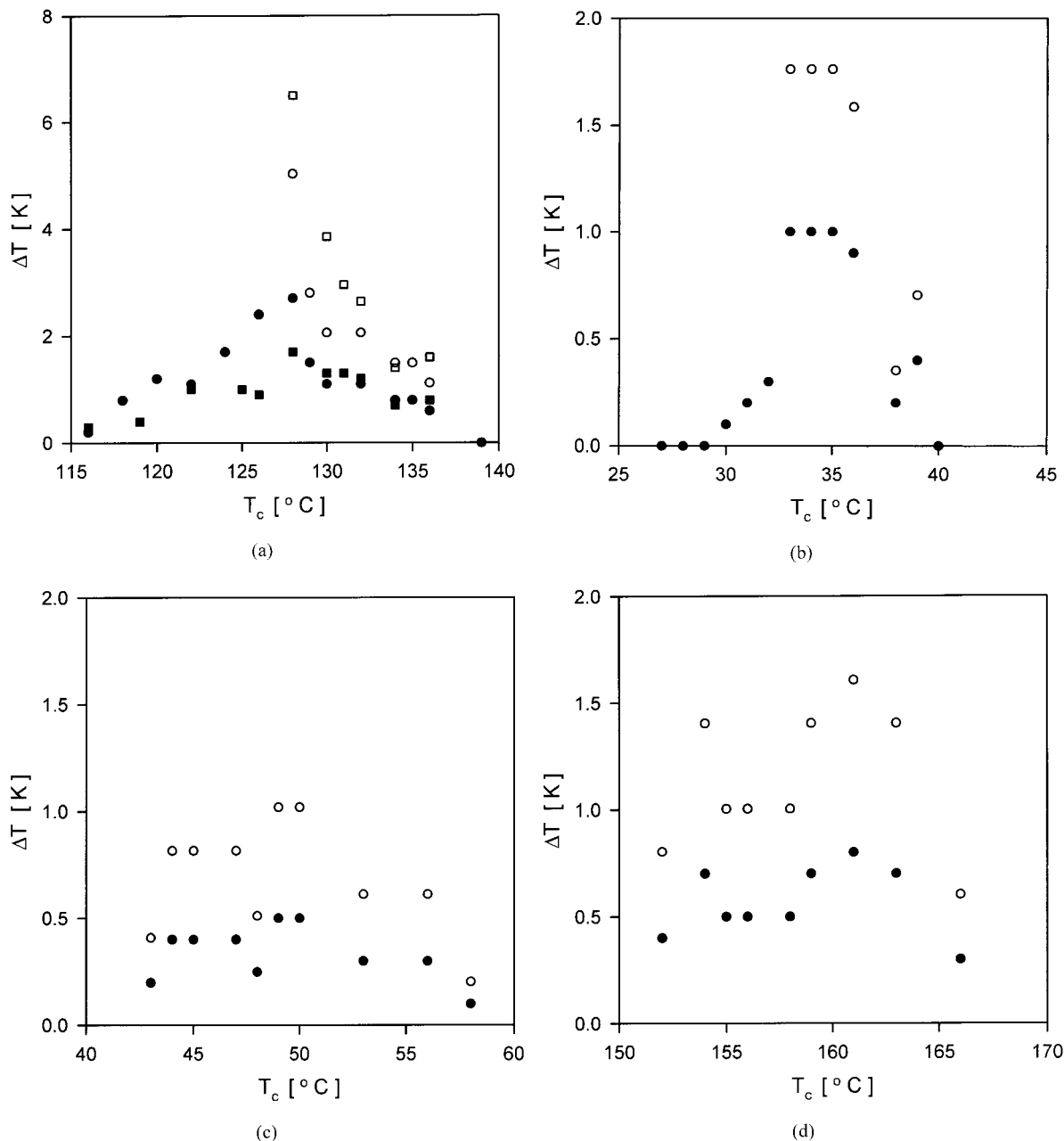


Figure 4 The increase of ΔT_m (filled symbols) and ΔT_m° (open symbols) in weak spots vs. T_c : (a) iPP1 (circles) and iPP2 (squares), (b) PAE, (c) POE, (d) POM.

exhibit the increased melting temperature. In addition, in iPP, after cavitation the nucleation of β spherulites was observed in weak spots,^{16,17} leading to lower melting temperature of that part of the weak spot interiors.

ΔT_m measured for different weak spots in samples of the same polymer crystallized at the same T_c varied significantly, indicating different levels of negative pressure buildup. In Figure 4(a)–(d) the highest values of ΔT_m , measured for thin films of all studied polymers, are plotted against T_c . Pronounced maxima of dependence of ΔT_m on T_c are visible for both iPPs and PAE, while for POM and POE the dependence of ΔT_m on T_c is flatter. Also in Figure 4 the equilibrium melting temperature difference, ΔT_m° , calculated from ΔT_m and the dependence of T_m on T_c are shown. For POE and POM ΔT_m° was calculated for the entire ranges of T_c studied using the values dT_m/dT_c , which were 0.49 and 0.57, respectively.^{11–15} For iPP and PAE, the values of ΔT_m° were computed only for T_c higher than 126 and 31°C, respectively. The recrystallization was observed for samples crystallized at lower T_c during the second step of heating, resulting in a significant increase of T_m . The values of dT_m/dT_c used for calculations of ΔT_m° were as follows: 0.57 for PAE above 33°C, 0.54 for iPP1 above 128°C, while for the iPP2 dT_m/dT_c value was 0 for 128–131°C, and then increased to 0.5. The dependence of ΔT_m° on T_c obtained for both iPPs is similar. ΔT_m° decreases strongly with the T_c increase in PAE and in both iPPs, while for POE and POM ΔT_m° dependence on T_c is weaker.

In ref. [9] ΔT_m in weak spots in high-density polyethylene was observed only in samples crystallized in Regime III. In the present study Regime III \rightarrow Regime II transition for both iPPs studied was determined on the basis of the plot $\ln G + U[R(T_c - T_\infty)]^{-1}$ on $[T_c(T_m^\circ - T_c)]^{-1}$, assuming $T_m^\circ = 458.2$ K, and $T_\infty = 231.2$ K, and was found at $136 \pm 1^\circ\text{C}$, close to values reported by others.^{6,18,19} The clear tendency of decline of ΔT_m and T_m° is visible in Figure 4(a) for both iPPs near the regime II/III transition temperature. For POE and POM ΔT_m and ΔT_m° of weak spots are seen in Figure 4(c) and (d) for T_c in both Regimes II and III.^{20–22} In PAE ΔT_m is visible in weak spots for T_c in the range in which banded spherulites crystallize; ΔT_m and ΔT_m° decrease upon the approach to the temperature of transitions to positively birefringent spherulites.²³

The highest observed values of ΔT_m were: 2.7 K for iPP1, 1.7 K in iPP2, 1.0 K for PAE, 0.8 K for

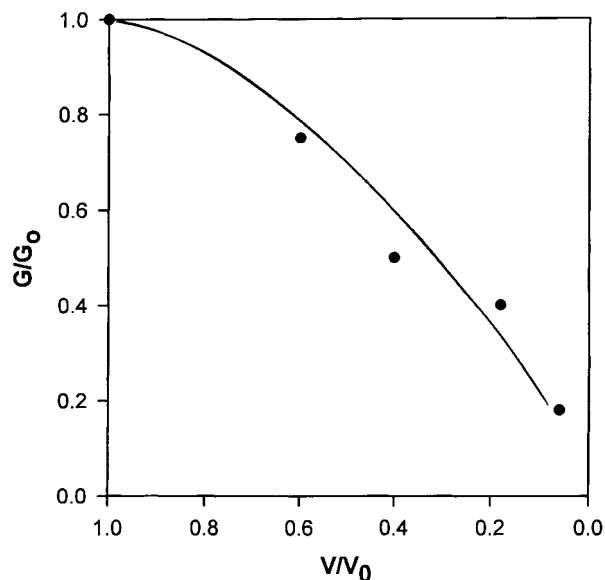


Figure 5 The ratio of momentary spherulite growth rate, G , in weak spot to spherulite growth rate outside weak spot, G_0 , against the ratio of momentary area of weak spot, V , to the initial area of that weak spot, V_0 , at the moment of occlusion of a melt by spherulites in iPP1 at $T_c = 125^\circ\text{C}$.

POM, and 0.5 K for POE, which correspond to T_m° : 5.0, 6.5, 1.8, 1.6, and 1.0 K, respectively. Taking into account the values dT_m°/dp for iPP (0.38 K/MPa,¹³ 0.338 K/MPa¹²) we obtain the maximum negative pressure: 13–15 MPa in iPP1 and 17–19 MPa in iPP2. dT_m°/dp and calculated values of p for PAE, POM, and POE are: 0.15 K/MPa¹⁵ and 12 MPa, 0.156 K/MPa¹² and 10 MPa, 0.157 K/MPa¹⁴ and 6 MPa, respectively. The highest value of negative pressure was obtained for iPP2, while the lowest for POE.

In iPP the reason of ΔT_m drop for $T_c < 128^\circ\text{C}$ is the lack of sensitivity of T_m to T_c in this region of temperature due to lamella thickness independent of T_c (e.g., ref. 6). Therefore, the ΔT_m difference was calculated from the depression of spherulite growth rate G in weak spots, using the Hoffman formula: $G = G^* \exp(-U[R(T_c - T_\infty)]^{-1}) \exp(-K_g T_c^{-1} [T_m^\circ - T_c]^{-1})$.²¹ For iPP1 at $T_c = 125^\circ\text{C}$, the difference in ΔT_m° was found at the level of 6.4 K (Fig. 5). The value of $K_g = 3.3 \times 10^5$ K² was determined from the dependence of $\ln G + U[R(T_\infty - T_c)]^{-1}$ on $[T_c(T_m^\circ - T_c)]^{-1}$ for Regime III. The calculated value of 6.4 K is higher than the maximum ΔT_m° determined from ΔT_m measurement for iPP1, indicating significant negative pressure buildup also when the drop of ΔT_m with the decrease of T_c was observed.

The decrease of ΔT_m and ΔT_m° with increasing T_c , observed in all polymers studied, indicates the lowering of negative pressure, which is probably due to coarser lamellar structure, lower melt viscosity, and slower growth of spherulites; hence, easier compensation of volume deficiency in weak spots by displacement of the amorphous phase in spherulites. Another reason is the cavitation occurring at lower negative pressure at higher temperature.

The results obtained indicate that the negative pressure buildup, resulting in local lowering of undercooling, occurs during the crystallization of various polymers and it is influenced by the crystallization temperature.

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REFERENCES

- Galeski, A.; Piorkowska, E. *J Polym Sci Polym Phys Ed* 1983, 21, 1313.
- Galeski, A.; Piorkowska, E. *J Polym Sci Polym Phys Ed* 1983, 21, 1323.
- Galeski, A.; Koenczoel, L.; Piorkowska, E.; Baer, E. *Nature* 1986, 325, 40.
- Galeski, A.; Piorkowska, E.; Koenczoel, L.; Baer, E. *J Polym Sci Part B Polym Phys* 1990, 28, 1171.
- Schultz, J. M. *Polym Eng Sci* 1984, 24, 770.
- Monasse, B.; Haudin, J. M. *Coll Polym Sci* 1985, 263, 822.
- Thoman, R.; Wang, Ch.; Kressler, J.; Mulhaupt, R. *Macromol Chem Phys* 1996, 197, 1085.
- Pawlak, A.; Galeski, A.; *J Polym Sci Part B Polym Phys* 1990, 28, 1813.
- Piorkowska, E.; Galeski, A. *J Polym Sci Part B Polym Phys* 1993, 31, 1285.
- Olley, R. H.; Basset, D. C. *Poster on Polymer Physics*, Bristol, UK, April 1991.
- Wunderlich, B. *Macromolecular Physics*, Vol. 3., *Crystal Melting*; Academic Press: New York, 1980, p. 95.
- Karl, V.; Asmussen, F.; Uberreiter, K. *Makromol Chem* 1977, 178, 2037.
- Leute, U.; Dolhopf, W.; Liska, E. *Coll Polym Sci* 1978, 256, 914.
- Tsujita, Y.; Nose, T.; Hata, T. *Polym J* 1974, 6, 51.
- Jenckel, E.; Rinkens, H.; *Z Elektrochem* 1956, 60, 970.
- Varga, J.; Ehrenstein, G. *Polymer* 1996, 37, 5959.
- Kolasinska, J.; Piorkowska, E. Nowacki, R., in preparation.
- Clark, E. J.; Hoffman, J. D. *Macromolecules* 1984, 17, 878.
- Cheng, S. Z. D.; Janimak, J. J.; Zhang, A.; Cheng, H. N. *Macromolecules* 1990, 23, 298.
- Cheng, S. Z. D.; Chen, J.; Janimak, J. J. *Polymer* 1990, 31, 1018.
- Hoffman, J. D. *Polymer* 1983, 24, 3.
- Pelzbauer, Z.; Galeski, A. *J Polym Sci Part C* 1972, 38, 23.
- Takayanagi, M.; Yamashita, T. *J Polym Sci* 1956, 22, 552.