Influence of Molecular Weight Distribution on the Structure and Properties of Melt-Spun Polypropylene Filaments

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SYNOPSIS

The role of molecular weight distribution on the spinnability, structure, and properties of melt-spun isotactic polypropylene filaments was studied with the aim of clearly distinguishing the effect of the breadth of the distribution from the effect of the average molecular weight and resin melt flow rate (MFR). Nine resins were chosen for this purpose, ranging in MFR from 16 to 78 and in polydispersity from 2.6 to 5.4. It was observed that the spinnability, structure, and properties of the spun filaments were all strong functions of the breadth of the distribution. Spinnability decreased with increasing breadth. At given spinning conditions and polydispersity, an increase in the weight-average molecular weight (decrease in MFR) produces an increase in crystallinity, birefringence, tensile strength, and tensile modulus. But at given spinning conditions and resin MFR, broadening the molecular weight distribution (increasing the polydispersity) produces an increase in crystallinity, tensile modulus, and elongation-to-break while birefringence and tensile strength decrease. The major influence of the polydispersity on the structure and properties developed was attributed to its effect on both the elongational viscosity of the resin and the ability of high molecular weight tails in the distribution to influence the stress-induced crystallization that occurs in the spinline. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

This is the fourth research article in a series from our group dealing with the subject of the influence of resin characteristics on the development of the properties and structure of melt-spun isotactic polypropylene filaments. The first two articles,[1,2] referred to as Parts I and II, dealt with several aspects of the influence of molecular weight and its distribution; they showed that spinnability and the resulting structure and properties are affected by both the weight-average molecular weight (M_w) and the breadth of the distribution (polydispersity). The third article,[3] Part III, dealt with factors that modify substantially the quiescent crystallization kinetics, such as the influence of the addition of nucleating agents or of copolymerizing with a small amount of ethylene. The results and conclusions in the first two articles, Parts I and II, were incomplete because the number of resins studied (three) was too small to separate out completely the relative influence of molecular weight level from the effect of the breadth of the distribution. The primary objective of the present article is to supplement the first two articles in this respect; we study here nine different resins chosen so that we can separate out the relative significance of the molecular weight level from the breadth of the molecular weight distribution (MWD).

The early studies of melt spinning of isotactic polypropylene were reviewed extensively in our earlier articles.[1-3] The reader is referred to these, especially the first two, for a detailed discussion of the key references prior to about 1985. More recent articles of interest include Bodaghi et al.,[4] Fan et al.,[5] Kloos,[6] and Andreassen et al.[7] In particular, Fan et al. did the first study indicating the major signifi-

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cance of MWD on the structure and properties of polypropylene spun and drawn filaments. Both Kloos and Andreassen et al. added some additional insights.

EXPERIMENTAL

Materials

Nine isotactic polypropylene resins were supplied by Exxon Chemical Co. Based on both qualitative and quantitative information provided by them, the as-received resins can be divided into three groups in terms of their melt flow rates (MFR), viz., 16–18, 35–42, and 74–78 MFR. At each particular range of MFR, three samples of varying MWD, indicated qualitatively as narrow, medium, and broad, were provided as shown in Table I. The molecular weight averages computed from GPC data on four of these samples, measured in the "as-received" state by Exxon Chemical Co., are summarized in Table I. It is to be noted that the weight-average molecular weight (M_w) increases somewhat with both a decrease in MFR level and the broadening of the MWD. Further, the M_z and M_{z+1} averages increase rapidly with broadening of the distribution at similar MFR levels. Increases in these two averages indicate a greater fraction of longer molecules present in the resin.

It should be noted that extrusion of polypropylene inevitably leads to some thermal/oxidative degradation. This effect will be characterized and discussed in the Results section.

Melt Spinning

Filament spinning was carried out in the same equipment used for our earlier studies,[1-3] and the reader is referred to those articles for more detail. Generally, the filaments were prepared using a monofilament spinline equipped with a constant displacement melt pump which provided a constant extrusion rate. Molten polymer from the melt pump was forced through a filter mesh and then a capillary die of diameter 0.762 mm and an L/D ratio of 5.0. The filament exiting the die was drawn down by an airjet drawdown device. The air pressure applied to this device determines the air drag and, hence, the spinline stress and take-up velocity of the spinning filament. Depending on the viscous properties of the polymer, spinning speeds up to about 6000 m/min could be achieved (air pressures up to about 80 psig). The spinline length from extruder to the airjet drawdown device was held constant at 250 cm (2.5 m) throughout.

Density and Birefringence Measurements

Densities of as-spun filaments were measured using an isopropyl alcohol/water density gradient column maintained at 23°C. The reported crystallinities were estimated from the density using the expression

$$X = \rho_c(\rho - \rho_{am})/\rho(\rho_c - \rho_{am}) \quad (1)$$

where ρ is sample density and ρ_c and ρ_{am} are the densities of crystalline and amorphous polypropylene, respectively. The values of the latter two quantities were the same as those quoted by Samuels.[8]

Table I Characterization of As-received Resins

Resin No.	MFR	Qualitative MWD	M_n	M_w	M_z	M_w/M_n	M_z/M_w
1	16	Narrow	59,240	175,300	325,640	3.0	1.9
2	16	Medium					
3	18	Broad	42,300	228,260	858,060	5.4	3.8
4	35	Narrow					
5	37	Medium					
6	42	Broad					
7	78	Narrow	45,790	118,490	196,020	2.6	1.7
8	74	Medium					
9	75	Broad	36,510	138,410	448,060	3.8	3.2

The birefringences of the as-spun filaments were measured in the usual way using a polarizing microscope and a Berek compensator. The as-spun filament diameters were measured with a filar eyepiece.

Wide-angle X-ray Diffraction Patterns

X-ray patterns were obtained using a flat plate camera and a Philips Norelco X-ray generator. Nickel-filtered CuKα radiation was used.

Mechanical Properties

The tensile properties of the as-spun filaments were measured with an Instron tensile testing machine. Fibers of initial gauge length 25 mm were stretched at a crosshead speed of 50 mm/min. The diameter of each tensile sample tested was measured using an optical microscope and a filar eyepiece. All filaments tested were conditioned at room temperature for several days prior to testing. The reported results are the average of tests carried out on 10 tensile test specimens.

On-line Measurements

The techniques used to measure the profiles of diameter, birefringence, and temperature as a function of distance from the spinneret have been previously described. The reader is referred to Refs. 2, 9, and 10 for details of these techniques. The diameter is measured using a Zimmer diameter monitor. This instrument operates on a noncontact electrooptic principle, and it has a diameter resolution of ± 0.5 μm. Birefringence profiles were obtained using an Olympus polarizing microscope and an Olympus four-order Berek compensator. The microscope is mounted on a movable stand used to position the microscope at the appropriate points along the spinline for on-line measurements.

The on-line temperature profiles were measured using a Hughes PROBEYE 3300 infrared thermal imaging system. The technique involves calibration of the effective filament emissivity for variations in filament diameter. The technique has been discussed in detail in Ref. 10.

RESULTS AND DISCUSSION

Preliminary Studies of Spinnability and Degradation

Preliminary spinning experiments showed that spinnability decreased as the MWD broadened. The spinnability of a given resin, as measured by maximum air pressure (applied to the drawdown device) for a continuous spinline, increased with increase in extrusion temperature, up to a certain point, and then tended to slowly decrease again. The narrow MWD samples could be spun over a wide range of extrusion temperatures and air pressures applied to the airjet drawdown device (corresponding to a wide range of take-up velocities). This range of conditions decreased as the MWD was broadened. At higher air pressures, the broad MWD resins and some of the medium MWD resins showed unsteadiness (spinline vibrations) and frequent breaking of the spinline. Even stable spinlines exhibited more diameter variation with time at a given point in the spinline as the MWD became broader. As polypropylenes are known to thermally degrade more with increasing extrusion temperature, the optimum spinning temperature for our study was chosen to be the lowest temperature at which continuous steady spinning could be carried out at reasonable take-up speeds. In the present experiments, all samples could be spun at an extrusion temperature of 210°C; hence, most of the comparisons are made at this spinning temperature. The air pressure applied to the drawdown device was limited to 25 psig in order to avoid breaking of the spinline for the broader MWD samples. The broader MWD samples, especially the 18 MFR sample, exhibited less vibration and more stable spinning at somewhat higher temperatures, so some data were obtained with a spinning temperature of 240°C.

As noted above, thermal degradation of polypropylene during spinning is typically observed.[4,6,7,11] Such degradation can lead to changes in both the average molecular weight and the MWD. As the present study is intended to show the effects of these variables on the spinnability and the structure and properties of spun filaments, it is necessary to examine the extent of polymer degradation under the chosen spinning conditions. This was done by measuring the MFR and the MWD (by GPC) for extrudate samples which were extruded using the chosen extrusion conditions. These measurements were again carried out by Exxon Chemical Co. and are reported in Table II. These data show that the samples exhibited substantial degradation during extrusion, but the basic differences among the resin samples remained qualitatively similar to those of the as-received resins. Higher extrusion temperatures resulted in greater degradation, as expected. There was a tendency for the broad MWD resins to undergo greater change in their MFR than for the other

Table II Influence of Extrusion Conditions on MFR and MWD

Resin No.	Qualitative MWD	Extrusion Temp (°C)	Postextrusion MFR	M_n	M_w	M_z	M_w/M_n	M_z/M_w
1	Narrow	210	19	55,350	171,810	317,840	3.1	1.85
1	Narrow	240	24	54,360	168,970	305,070	3.1	1.8
2	Medium	210	17	51,940	183,980	390,000	3.5	2.1
2	Medium	240	22	47,960	169,420	350,880	3.5	2.1
3	Broad	210	22	44,090	210,850	704,070	4.8	3.3
3	Broad	240	32	38,290	182,080	536,310	4.8	3.0
4	Narrow	210	40	49,930	141,790	251,270	2.8	1.8
5	Medium	210	45	39,090	143,850	285,650	3.7	2.0
6	Broad	210	44	40,480	162,680	479,130	4.0	3.0
7	Narrow	210	85	42,170	118,920	199,980	2.8	1.7
8	Medium	210	86	38,480	132,260	320,680	3.4	2.4
9	Broad	210	95	34,490	136,060	408,280	3.9	3.0
9	Broad	210	84[a]	38,020	145,200	500,160	3.8	3.4

[a] Nitrogen purge used for extruder.

samples, and the MWD seemed to narrow slightly. To maintain similar MFRs after extrusion, it was necessary to use a nitrogen gas purge of the extruder and hopper for resin no. 9, the broad MWD resin with an as-received MFR of 75. In subsequent references and characterizations of the filaments, we use the postextrusion MFRs rather than the as-received ones.

Structure and Properties of As-spun Filaments

For the study of structure development during spinning, each sample was spun with two different air pressures applied to the airjet drawdown device at the selected spinning temperatures. The two air pressures resulted in two take-up velocities for each resin, but the take-up velocities varied from resin to resin. The processing conditions are summarized in Table III. The indicated spinning speeds are determined from application of the continuity equation to the on-line diameter measured at 220 cm from the spinneret where the take-up velocity had been achieved for all samples. The lower spinning speeds for each polymer were obtained by using a constant air pressure of 5 psig in the drawdown device, whereas the higher speeds were obtained, in most cases, with an air pressure of 25 psig. Generally, the spinning speed increased with extrusion temperature, with increase in MFR or with narrowing of the MWD for a given air pressure applied to the drawdown device.

The average diameters of the as-spun filaments are presented and compared with the corresponding on-line values measured at 220 cm from the spinneret in Table III. It is noteworthy that the off-line diameters tend to be slightly higher than the on-line values. This apparently is due to the elastic contraction occurring in the filaments when the drawdown stress is removed. The difference between the on-line and off-line (as-spun) diameters clearly decreases with increase in spinning temperature, as expected. Trends with molecular weight or MWD are not as apparent, though the overall behavior seems to indicate that the difference in on-line and off-line diameters increases with increase in molecular weight (decrease in MFR) at a fixed extrusion temperature.

The birefringence, density (and crystallinity as computed from the density), and the tensile mechanical properties of the as-spun filaments are presented in Table IV. Since the spinning speeds of the various samples varied, a graphical representation of the data as a function of the take-up velocity provides a method for comparing different samples while accounting for the variation in spinning speeds. The density of the samples spun at 210°C is plotted vs. take-up velocity in Figure 1. As seen from this figure, the crystallinity increases with spinning speed, but this increase with spinning speed is greater for the narrow and medium MWD resins than for the broad MWD resins, because the latter have rather high crystallinities even at low spinning speeds. The crystallinity tends to increase as the

Table III Processing Conditions for Polypropylene Filaments

Resin No.	Postextrusion MFR	Qualitative MWD	Extrusion Temp (°C)	Single-hole Extrusion Rate (g/min)	Drawdown Device Air Pressure (psig)	On-line Filament Diameter[a] (μm)	Off-line Filament Diameter (μm)	Spinning Speed (m/min)
1	19	Narrow	210	1.55	5	37.2	45.3	1580
1	24	Narrow	240	1.64	5	34.8	39.6	1920
2	17	Medium	210	1.55	5	39.3	46.4	1420
2	22	Medium	240	1.53	5	35.2	41.9	1740
3	22	Broad	210	1.55	5	52.0	65.5	810
3	32	Broad	240	1.55	5	38.4	42.3	1440
4	40	Narrow	210	1.62	5	34.1	38.2	1960
5	45	Medium	210	1.59	5	32.9	38.5	2080
6	44	Broad	210	1.61	5	39.8	42.3	1440
7	85	Narrow	210	1.69	5	32.6	37.7	2250
8	86	Medium	210	1.70	5	36.1	42.9	1840
9	84	Broad	210	1.69	5	37.0	41.5	1740
1	19	Narrow	210	1.55	25	27.4	35.1	2910
1	24	Narrow	240	1.64	25	26.3	29.2	3350
2	17	Medium	210	1.55	25	32.0	39.0	2600
2	22	Medium	240	1.53	25	25.9	31.4	3230
3	22	Broad	210	1.55	25	32.6	46.4	2060
3	32	Broad	240	1.55	15	33.0	36.9	2010
4	40	Narrow	210	1.62	25	26.4	29.0	3270
5	45	Medium	210	1.59	15	27.5	33.6	2970
6	44	Broad	210	1.61	10	37.1	40.4	1650
7	85	Narrow	210	1.69	25	24.7	30.9	3900
8	86	Medium	210	1.70	25	26.6	29.9	3380
9[b]	84	Broad	210	1.55	25	27.4	33.0	2910
9	95	Broad	210	1.69	15	32.7	34.8	2230

[a] Measured at 220 cm from the spinneret.
[b] Using nitrogen purge in extruder.

MFR decreases (molecular weight increases), and for the same range of MFR and at low to modest spinning speeds, the filaments spun from the broad MWD resins tend to develop higher crystallinity while the filaments obtained from the narrow MWD resins have the lowest crystallinity. Interestingly, the breadth of the distribution seems to be as significant in determining the crystallinity as is the MFR level. The results shown in Figure 1 are quite consistent with those obtained several years earlier and published in Part I. In that article, data are given for samples with 12 MFR, 35 MFR, and 300 MFR (as-received values). The latter two resins had a narrow MWD while the 12 MFR resin had a broad MWD. The density data for the 300 MFR filaments lie below those for the present 85 MFR narrow MWD results and the 12 MFR data lie above those for the present 22 MFR broad MWD results shown in Figure 1. The 35 MFR resin studied in Part I was nearly identical to resin no. 4 (35 MFR as-received and 40 MFR postextrusion) of the present investigation. The density data for the two cases superimpose on the same curve when plotted together. In that respect, there were more spinning speeds studied in Part I and the variation of the densities, birefringence, etc., with spinning speed is better judged from those results than from the two speeds studied here.

The birefringences of the filaments spun at 210°C are plotted in Figure 2. The birefringence increases with spinning speed, and it tends to be higher for the narrow MWD resins, whereas the broad MWD resins, in the same range of MFR, have the lowest birefringences in the range of spinning speeds investigated.

Figures 3–5 show the plots of the tensile elastic modulus, tensile strength, and elongation-to-break of the filaments spun at 210°C as a function of take-up velocity. The tensile modulus increases with increased spinning speed, and it tends to be higher as

Table IV Characteristics of As-spun Filaments

Resin No.-Extrusion Temp	Post-extrusion MFR-Air Pressure	Qualitative MWD	Birefringence (× 1000)	Density (g/cm³)	Crystallinity (%)	Young's Modulus (GPa)	Tensile Strength (MPa)	Elongation to Break (%)
1-210	19-5	Narrow	17.9	0.8996	60.6	1.56	173	400
1-240	24-5	Narrow	16.2	0.8967	57.0	1.00	180	315
2-210	17-5	Medium	16.8	0.9026	64.3	1.41	150	500
2-240	22-5	Medium	17.5	0.8993	60.2	0.97	123	405
3-210	22-5	Broad	13.4	0.9027	64.5	1.20	86	750
3-240	32-5	Broad	15.5	0.9029	64.7	1.00	97	615
4-210	40-5	Narrow	18.4	0.8975	57.9	1.15	158	310
5-210	45-5	Medium	16.9	0.9004	61.6	1.43	117	380
6-210	44-5	Broad	14.1	0.9013	62.7	1.48	95	540
7-210	85-5	Narrow	16.1	0.8922	51.2	0.90	146	270
8-210	86-5	Medium	14.5	0.8995	60.5	1.08	87	450
9-210	84-5	Broad	13.1	0.9010	62.3	1.26	84	675
1-210	19-25	Narrow	18.1	0.9022	63.8	2.83	175	380
1-240	24-25	Narrow	20.7	0.9026	64.3	1.78	183	300
2-210	17-25	Medium	17.1	0.9027	64.5	2.41	156	450
2-240	22-25	Medium	17.7	0.9029	64.7	1.10	125	370
3-210	22-25	Broad	15.2	0.9029	64.7	2.10	104	620
3-240	32-15	Broad	15.7	0.9032	65.1	1.02	99	610
4-210	40-25	Narrow	19.1	0.9023	64.0	1.48	162	250
5-210	45-15	Medium	18.7	0.9037	65.7	1.47	140	360
6-210	44-10	Broad	14.7	0.9014	62.8	1.47	91	550
7-210	85-25	Narrow	21.5	0.8967	57.0	1.49	170	200
8-210	86-25	Medium	17.1	0.9018	63.3	1.37	108	370
9-210[a]	84-25	Broad	14.5	0.9001	61.2	2.2	90	590
9-210	95-15	Broad	14.8	0.9013	62.7	1.29	86	560

[a] Using nitrogen purge in extruder.

the MFR decreases and the MWD is broadened (Fig. 3). Figure 4 shows that the tensile strength of the as-spun filaments decreases with broadening of MWD and with increase in the MFR. This trend is reversed for the elongation-to-break, i.e., the elongation to break tends to be lower as the MFR increases and as the MWD narrows (Fig. 5). Both the elongation-to-break and the tensile strength seem to be affected more by the breadth of the MWD than by the range of MFR for the resin, in the range of spinning speeds studied.

Wide-angle X-ray patterns for selected resins and spinning conditions are shown in Figures 6 and 7. Figure 6 shows the patterns for each resin spun at 210°C with 5 psig air pressure applied to the airjet drawdown device. Each row of Figure 6 corresponds to resins in the same MFR range and shows the variation of the X-ray patterns as the breadth of the MWD is changed. Each column compares the patterns from resins with different MFR but qualitatively similar MWD. Most of the patterns indicate that the spun filaments contain the monoclinic α-phase. However, the patterns of the narrow MWD resins appear to indicate a mixture of monoclinic and smectic structure, with the fraction of smectic phase increasing somewhat as the MFR increases. This finding is similar to that reported previously in Part I, where it was also shown that spinning speed is an important determinant of the relative amount of smectic and α-form. The smectic phase tends to occur at low spinning speeds and high MFRs (low M_w), corresponding to low spinline stresses and low solidification temperatures. The data shown in Figure 6 show that broadening the MWD tends to produce a more well-developed α-monoclinic structure in the same MFR range. The differences observed in the X-ray patterns are qualitatively consistent with the measured differences in density described above.

The patterns of Figure 6 also indicate qualitatively similar levels of crystalline orientation in these samples (though there are observable differences on careful examination). This latter finding is evidently traceable to the filaments being spun under the same air pressure in the drawdown device and, hence, similar (though not identical) stress levels developed in the spinline, but different take-up velocities. Previous investigators[1,11,12] suggested that molecular

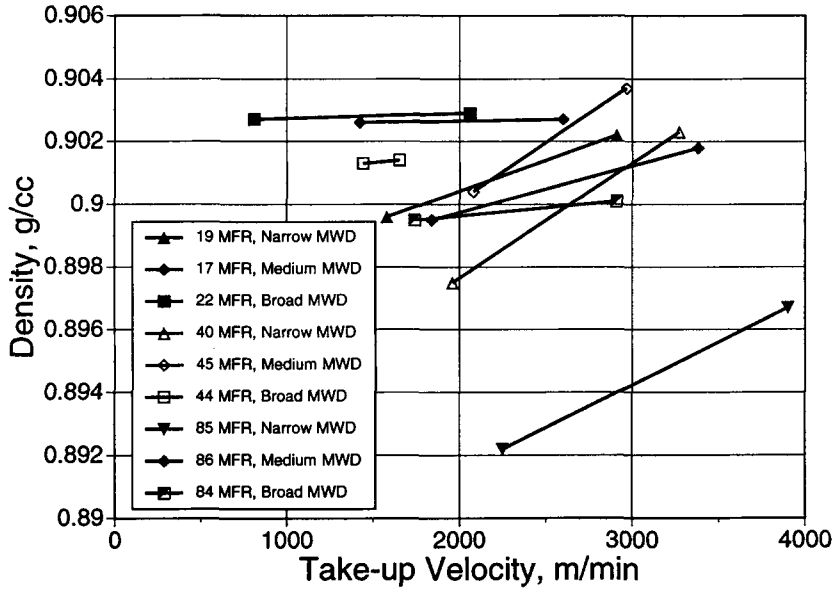

Figure 1 Effect of resin characteristics on the density of filaments spun at 210°C.

orientation developed by melt spinning tends to correlate with the level of spinline stress existing at the point at which crystallization begins in the spinline. For a given resin, increase in air pressure applied to the drawdown device or increase in take-up velocity increases the level of molecular orientation as illustrated by comparing Figure 7 to Figure 6.

On-line Profiles

The diameter profiles measured on the running spinlines for resins in the 40–45 MFR range for melt spinning at 210°C with 5 psig air pressure applied to the drawdown device are given in Figure 8. The relative behavior of the broad, medium, and narrow MWD resins observed in this figure was also observed in the other two MFR ranges. The broad MWD sample approaches its final diameter closer to the spinneret than does the narrow MWD sample. The medium MWD sample draws down in between the broad and narrow MWD samples. The data of Part II established that at a given MWD decreasing the MFR (increasing the M_w and the viscosity) causes the drawdown to occur closer to the spinneret. This trend is also observed in the present results. For example, the 19 MFR and 86 MFR narrow MWD samples approach their final diameters at distances 120 and 170 cm from the spinneret, respectively. The 40 MFR narrow MWD sample approaches its final diameter at a distance in between the above two values, viz., at 140 cm from the spinneret. Further, as the spinning speed increases, the filament draws down closer to the spinneret because of higher stress on the fiber which causes higher drawdown in the section of the spinline where the filament is hot and the local viscosity is lower. At 25 psig, the 40 MFR narrow MWD fiber approaches its final diameter at a distance of 70 cm from the spinneret, whereas at 5 psig, it reaches its final diameter at 140 cm from the spinneret. Although the effects of spinning speed and MFR were observed earlier,[2] the effects observed here due to the breadth of the MWD have not been reported before, in any detail, to the authors' knowledge. Note that the slight difference in MFR within a given MFR range (i.e., 45 vs. 40 in Fig. 8) is in the wrong direction to explain the major effect of MWD.

The nature of the on-line temperature profiles of different polypropylene samples in the same range of MFR are illustrated in Figure 9, where the temperature profiles of the three different samples in the MFR range of 84–86 for 5 psig air pressure are given. Although the differences between the curves are small and nearing the limitations of our measurement technique, the temperature profiles indicate that the more rapid drawdown of the broad MWD sample in the upper part of the spinline results in a slightly faster cooling of the broad MWD sample, compared to the narrow MWD sample. In the lower part of the spinline (below about 70 cm from the spinneret), there is a crossover of the cooling curves. This would appear to be related to the

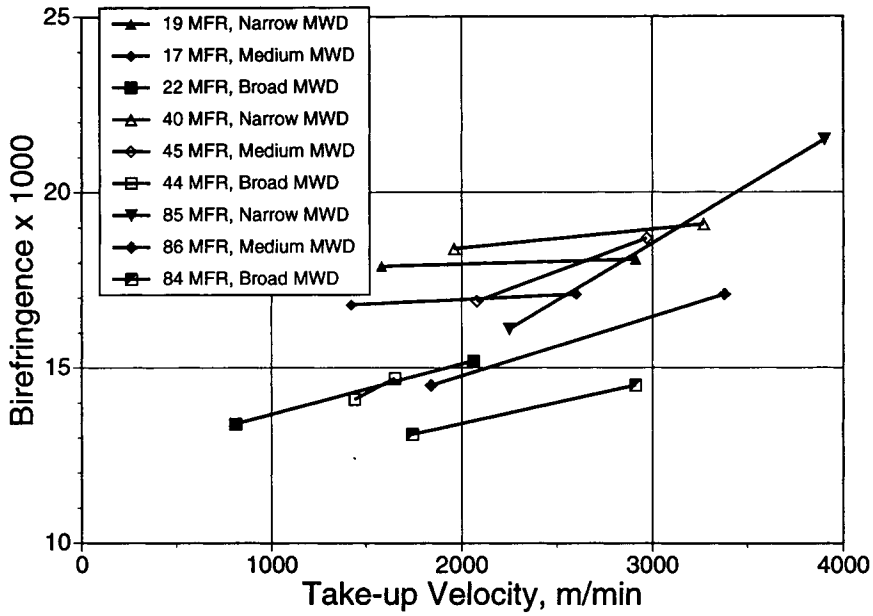

Figure 2 Effect of resin characteristics on the birefringence of filaments spun at 210°C.

influence of the heat of crystallization given up during crystallization, as will be discussed further below.

On-line birefringence profiles are shown in Figures 10 and 11. Figure 10 gives the profiles for the resins in the 19–22 MFR range spun at 240°C and 5 psig applied to the drawdown device. Figure 11 gives a direct comparison of the development of birefringence along the spinline for the six samples in the MFR ranges of 40–45 and 84–86 which were spun with the same extrusion temperature of 210°C and 5 psig air pressure. These birefringence profiles show that the broad MWD samples tend to have lower final birefringence than that of the narrow MWD samples of the same range of MFR, in agree-

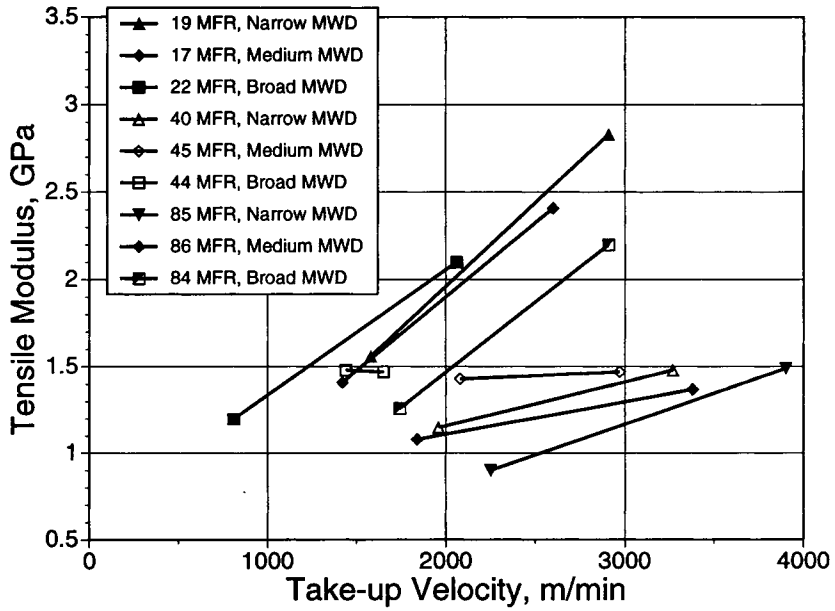

Figure 3 Effect of resin characteristics on the tensile elastic modulus of filaments spun at 210°C.

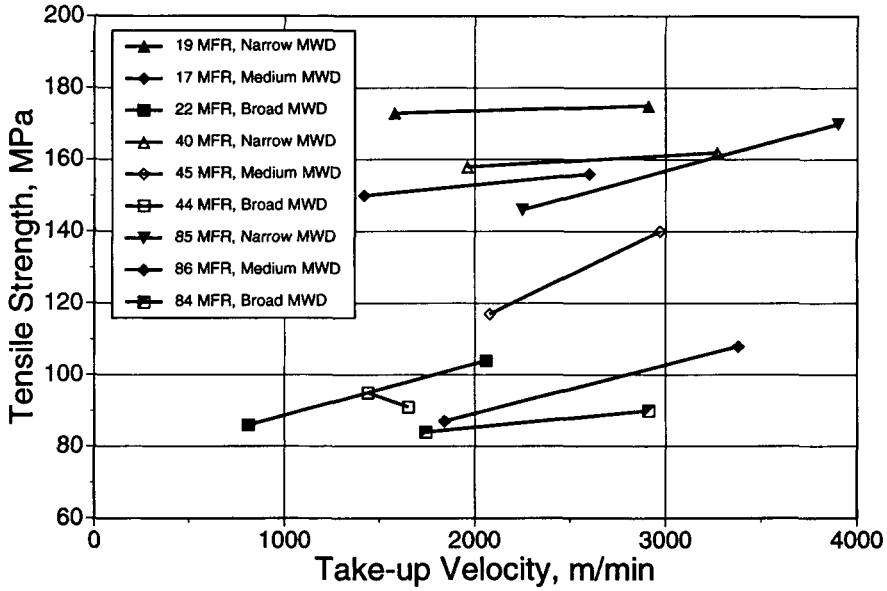

Figure 4 Effect of resin characteristics on the tensile strength of filaments spun at 210°C.

ment with the trends observed in the as-spun samples. As seen, e.g., in Figure 10, the rapid birefringence increase occurs closest to the spinneret for the broad MWD resin (even though it has the higher MFR) and farthest from the spinneret for the narrow MWD resin. However, once the birefringence starts to increase rapidly, it develops faster for the narrow MWD resin and reaches a higher value than for the broad MWD resin. This behavior with change in MWD is a common feature in all the three MFR ranges, as can be ascertained from examination of Figure 11. Figure 11 also provides an interesting direct comparison between samples of different MFR levels. In particular, comparison of 40 MFR narrow MWD to 85 MFR narrow MWD, 45 MFR medium MWD to 86 MFR medium MWD, and 44 MFR

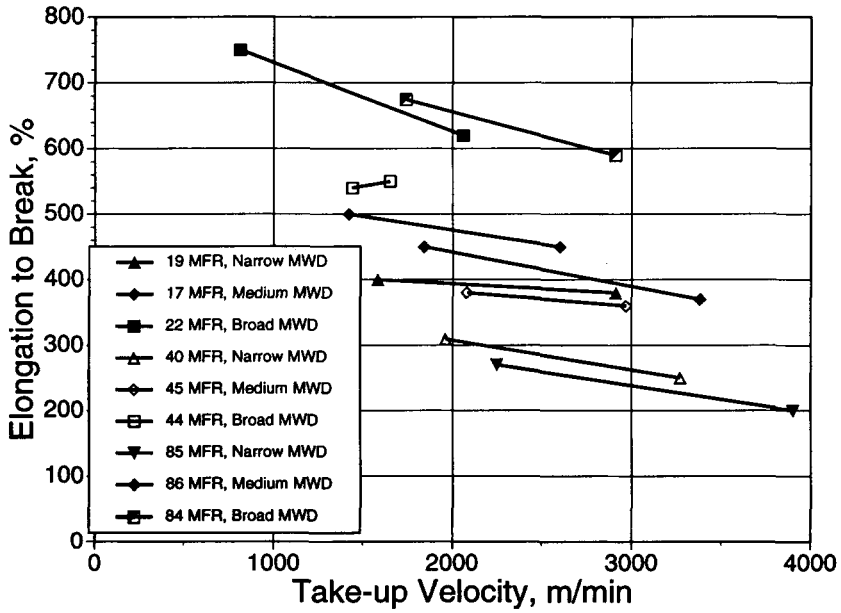

Figure 5 Effect of resin characteristics on the elongation-to-break of filaments spun at 210°C.

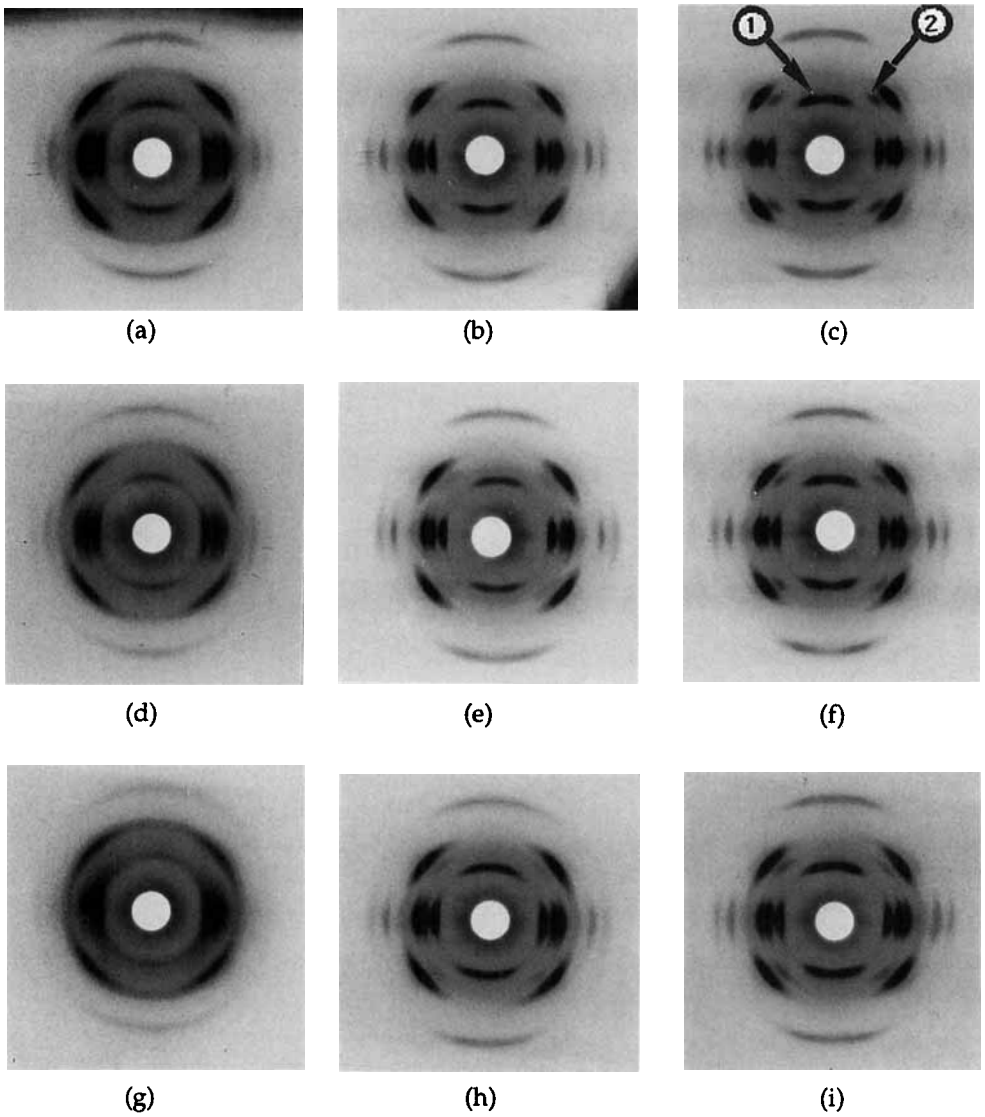

Figure 6 Wide-angle X-ray patterns of filaments spun at 210°C and 5 psig air pressure: (a) 19 MFR narrow MWD; (b) 17 MFR medium MWD; (c) 22 MFR broad MWD; (d) 40 MFR narrow MWD; (e) 45 MFR medium MWD; (f) 44 MFR broad MWD; (g) 85 MFR narrow MWD; (h) 86 MFR medium MWD; (i) 84 MFR broad MWD.

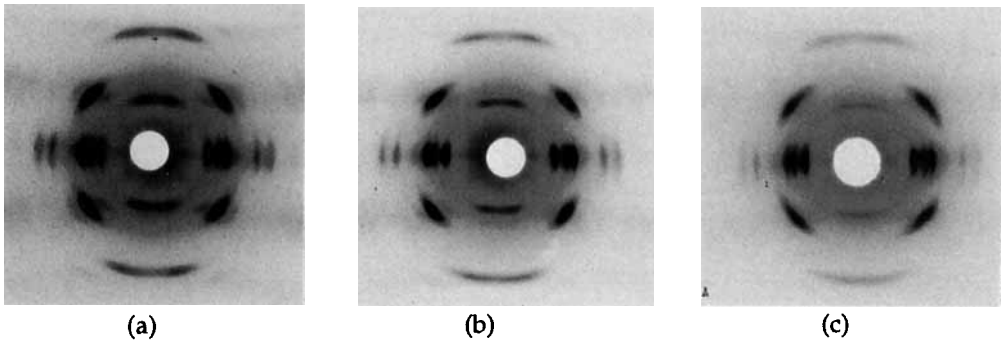

Figure 7 Wide-angle X-ray patterns of filaments spun at 210°C and 25 psig air pressure: (a) 19 MFR narrow MWD; (b) 40 MFR narrow MWD; (c) 85 MFR narrow MWD.

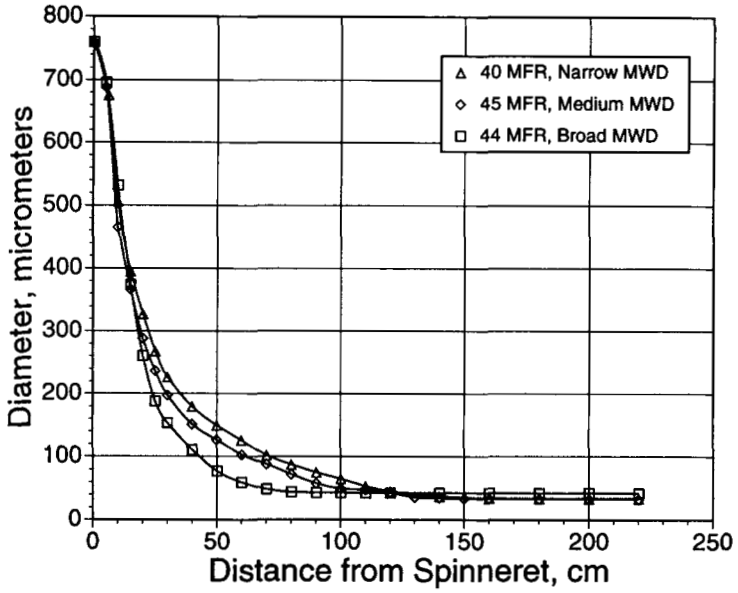

Figure 8 On-line diameter as a function of distance from the spinneret showing the effect of varying MWD with similar MFR. Example is for resins in the 40–45 MFR range spun with an air pressure applied to drawdown device of 5 psig and a spinning temperature of 210°C.

broad MWD to 84 MFR broad MWD shows that birefringence develops closer to the spinneret with decreased MFR (or increased viscosity) for samples of similar MWD. Also note that the birefringence curves of the medium and broad MWD samples in the 84–86 MFR range rise closer to the spinneret than does the 40 MFR narrow MWD sample in spite of the lower MFR of the latter resin.

The birefringence profiles of the filaments spun at the higher spinning speeds (higher air pressure applied to the drawdown device) have many of the same features as those described above for the sam-

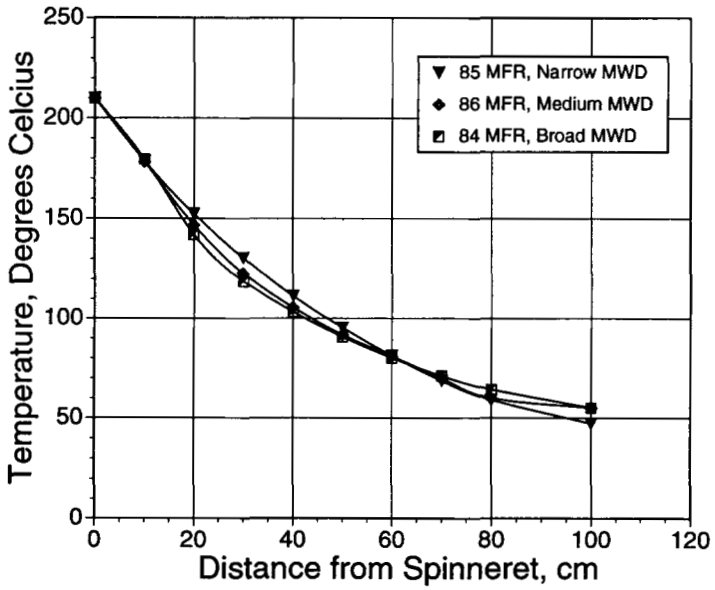

Figure 9 On-line temperature as a function of distance from the spinneret for resins in the 84–86 MFR range.

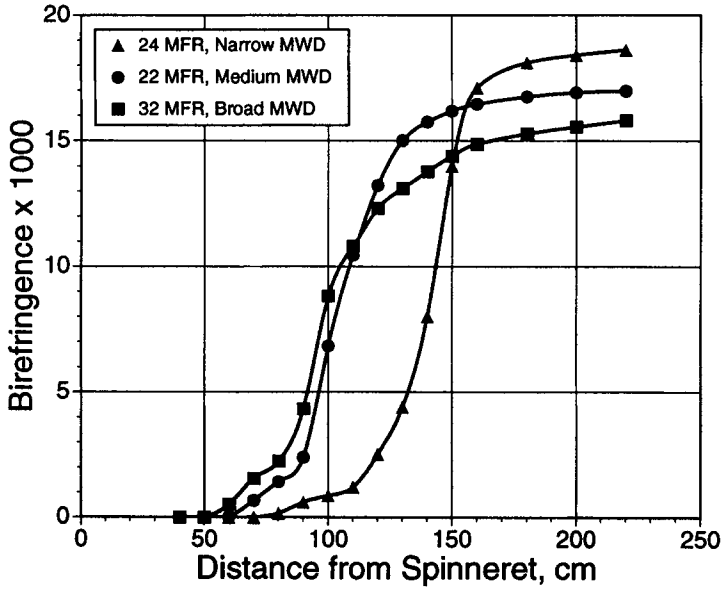

Figure 10 On-line birefringence as a function of distance from the spinneret for resins in the MFR range spun at 240°C and 5 psig air pressure showing the effect of varying MWD.

ples spun with 5 psig air pressure. The major differences are that the rapid birefringence rise occurs closer to the spinneret and there is not as much difference between the positions at which this rise occurs with change in MWD. These changes are illustrated in Figure 12. A detailed discussion and implications of the on-line profiles as well as the off-line data is given in the following section.

Discussion of Results

The tables and figures presented above are all consistent in indicating the major influence of MWD on the spinnability, structure, and properties of polypropylene filaments. Narrowing the MWD at the same MFR tends to improve spinnability, decrease crystallinity, initial elastic modulus, and elongation-to-break and to increase the birefringence and tensile strength of the as-spun filaments. As shown in Table II, the broadening of the MWD at the same MFR in the present resins was accomplished by allowing the number-average molecular weight, M_n, to decrease while the weight-average, M_w, and the z-average molecular weight, M_z, increased. This produced broader distributions as measured by the polydispersity, M_w/M_n, and the ratio M_z/M_w. This results in some variation of M_w within the same range of MFR, but there remains a clear distinction in M_w value from one MFR range to another, as might be expected from the well-known variation of polymer viscosity with M_w.[13] It must be kept in mind that the MFR is only a single measurement of viscosity under fixed conditions of temperature and load application. Dynamic viscosity measurements were also made on the present resins in the as-received condition at 180°C and as a function of angular frequency. These data show that, over a wide range of frequencies ($10^{-1} < \omega < 5 \times 10^2$ rad/s), the viscosities of the 16–18 MFR resins all lie above that of the 35–42 MFR resins and the latter all lie above that of the 74–78 MFR resins, as might be expected from their MFR values. However, the data also show that, at low frequencies, the broad MWD resins have higher dynamic viscosities than do their narrow MWD counterparts, but they are more "shear thinning" and their viscosity decreases faster with increase in frequency and eventually crosses and drops below the curve for the narrow MWD resin in the same MFR range. Thus, the dynamic viscosities are consistent with the resin MFRs, but they also give an indication of why the different MWDs behave so differently in the spinline as discussed below.

Two factors primarily affect the fiber drawdown during melt spinning of semicrystalline polymers. They are (i) rheological effects and (ii) crystallization effects. One aspect of the rheological effect on fiber drawdown during melt spinning of polymers is

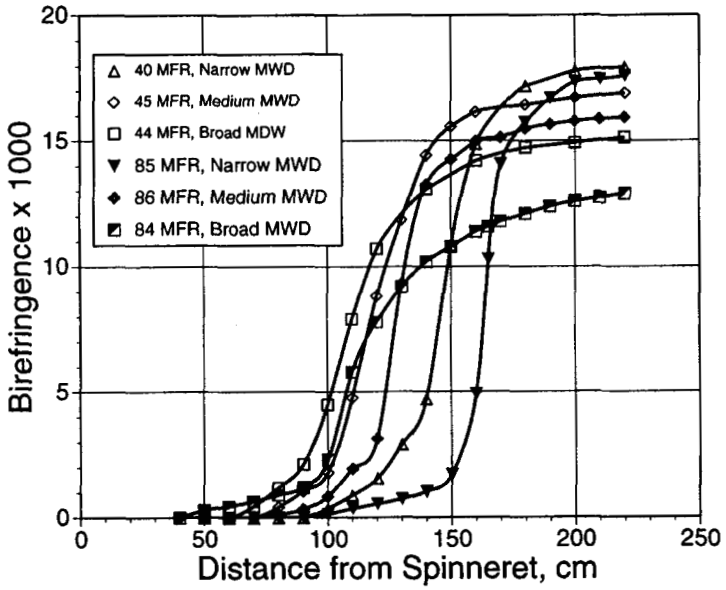

Figure 11 Comparison of on-line birefringence for resins in the 40–45 MFR and 84–86 MFR ranges spun at 210°C and 5 psig air pressure.

well understood. For a given overall drawdown ratio, a higher viscosity polymer draws down closer to the spinneret where the molten polymer is hotter and, hence, the local viscosity is lower. This largely explains the difference in drawdown rate for the samples of different MFR (different viscosity) with similar MWD and was discussed previously in Part II. Kloos[6] suggested that differences in elongational viscosity vs. elongation rate between broad and narrow MWD resins are responsible for the difference in drawdown and in structure and property development. Since our broad MWD samples have higher viscosity at low frequencies (or shear rates by the Cox–Merz rule,[14]) this difference might produce a tendency to drawdown more rapidly than for the narrow MWD resins in the same MFR range. It must

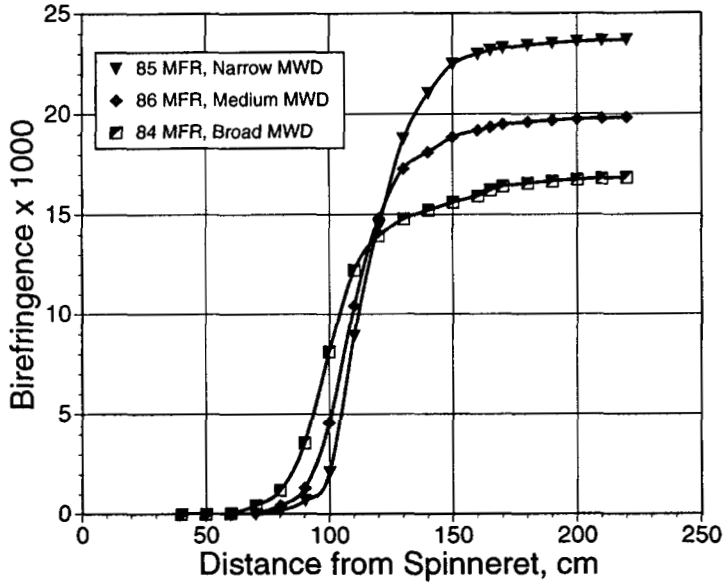

Figure 12 Comparison of on-line birefringence for resins in the 84–86 MFR range spun at 210°C and 25 psig air pressure.

be kept in mind that the rheological property of the polymer changes as the volume element moves away from the spinneret because of the change in temperature of the polymer. Also, the elongation rate first increases and then decreases. Polypropylenes are elongation-thinning polymers and the viscosity would be expected to decrease some with increase of elongation rate. In the upper part of the spinline, this effect would counter, to some extent, the increase in viscosity due to decreased temperature. Further, the elongation-thinning behavior can be expected to be different for the samples with different MWD even if they are in the same range of MFR as shown by their different shear-thinning behavior observed in their dynamic viscosities. This array of possible effects makes it difficult to ascertain with certainty the relative magnitude and role of these effects in controlling the drawdown process in the spinline in the absence of an adequate detailed rheological model. We will attempt to develop such a model in a future article.

Crystallization effects in the spinline superimpose on the melt rheological effects. Onset of crystallization increases the local viscosity of the polymer and causes the fiber to drawdown closer to the spinneret where it is not crystallizing. Thus, earlier crystallization (higher crystallization rates) will also tend to make the polymer drawdown closer to the spinneret. This was confirmed by recent work from our laboratory, Part III, in which the polymer crystallization kinetics were varied systematically without appreciable variation in the resin rheology.[3] Crystallization also contributes to the rapid rise in birefringence observed in the on-line profiles due to the fact that the crystals nucleate and grow in an oriented manner.[2,11,15,16] Thus, the position at which crystallization is occurring can be judged by the point at which the rapid rise in birefringence occurs. An interesting comparison is the relative behavior of the diameter and birefringence profiles of the 40 MFR narrow MWD sample and the broad and medium MWD samples in the MFR range of 84–86. When spun with 5 psig air pressure applied to the drawdown device, both the 84 MFR broad MWD sample and the 86 MFR medium MWD sample draw down faster and approach their final diameter at a distance of about 100 cm from the spinneret, whereas the 40 MFR narrow MWD sample approaches its final diameter at a distance of 140 cm from the spinneret, in spite of the fact that the dynamic viscosity of the 40 MFR narrow MWD sample is higher than either the 84 MFR broad MWD or the 86 MFR medium MWD samples at 180°C over the entire range of angular frequencies measured ($10^{-1} < \omega < 5 \times 10^2$ rad/s). Further, Table II shows that the value of M_w is greater for the 40 MFR narrow MWD resin than for either the 84 MFR broad or 86 MFR medium MWD resins, as would be expected on the basis that viscosity correlates with M_w. Therefore, the faster drawdown and more rapid rise of birefringence as a function of distance from the spinneret of the latter samples must be attributed to a higher crystallization rate during fiber spinning that overrides the effect of lower melt viscosity of the 84 and 86 MFR resins. The higher density and crystallinity (Table IV and Fig. 1) of the broad MWD resins relative to the narrow MWD resins also suggests that the broad MWD resins are crystallizing at higher temperatures than are the narrow MWD resins in the same MFR range. This behavior is also consistent with the crossover of the temperature profiles shown in Figure 9 being caused by the reduced cooling rate resulting from the heat of crystallization given up by the broad MWD resin at a higher position in the spinline.

It is now well established that the crystallization rates in the spinline are enhanced by molecular orientation, i.e., the process involves "stress-induced" crystallization and frequently results in row-nucleated structures.[12,15,17–20] The above data and discussion suggest that crystallization occurs at greater rates and at higher temperatures in broad MWD resins because they are more susceptible to stress-induced crystallization than are their narrow MWD counterparts. A possible explanation for this difference is related to the fact that the broad MWD resins have a larger number of relatively longer chain molecules than do the narrow MWD resins as measured by the M_z values listed in Table II. It is suggested that these longer molecules may be more readily oriented due to more entanglements and serve as the source of the row nuclei which seed the stress-induced crystallization. Fan et al.[5] and Andreassen et al.[7] made a similar suggestion to explain the effect of MWD on the structure and properties of polypropylene filaments prepared in their studies. This would explain why the 84 MFR broad and 86 MFR medium MWD resins crystallize closer to the spinneret than does the higher viscosity 40 MFR narrow MWD resin. Examination of Table II shows that the M_z values for the 84 MFR broad MWD and the 86 MFR medium MWD resins are both substantially above that of the 40 MFR narrow MWD resin, while their M_w values, and, hence, viscosities, are lower. More generally, there is a fairly strong correlation of the distance from the spinneret at which crys-

tallization starts and the value of M_z for the resin. This is illustrated in Figure 13, which shows the distance from the spinneret (estimated from the birefringence profiles) at which crystallization begins for the various resins, when spun at 210°C and 5 psig air pressure, as a function of the value of M_z measured on the as-spun filaments. Although the spinning process is very complicated with many variables, this figure shows a very definite correlation of the start of crystallization with M_z, the crystallization occurring nearer the spinneret the larger the value of M_z. This correlation suggests that M_z may be a reasonable molecular parameter to use in judging the sensitivity of a polymer to stress-induced crystallization. It should be emphasized that all the results plotted in Figure 13 are for nearly identical spinning conditions; it is noted that the actual crystallization distances in Figure 13 are valid only for the spinning conditions used in our experiments, though the relative behavior would be expected under differing conditions.

Two other features of the measured birefringence profiles require further discussion. It was noted above that once the rapid rise in birefringence begins (due to the onset of oriented crystallization), the curve rises more rapidly and reaches a higher ultimate birefringence for the narrow MWD resins than for the broader ones. A higher ultimate birefringence indicates higher overall molecular orientation in the filaments, once the process of crystallization is complete. On first examination, the X-ray patterns of Figure 6 indicate that the crystalline orientation is slightly higher in the broad MWD resins than in their narrow MWD counterparts (slightly shorter arcs on the Debye rings for the broader MWD patterns). This would suggest that, since this trend is opposite to the birefringence trend, the amorphous orientation in the narrow MWD resins must be higher than in their broad MWD counterparts. On careful reexamination of the X-ray patterns, another, more likely, possibility may be suggested. As is commonly observed for polypropylenes crystallized in extensional flows, the X-ray patterns indicate a bimodal crystalline orientation in which the "primary" component of the orientation distribution has its polymer chains (the crystal c-axis) tending to be parallel to the fiber axis (in the normal way) and a "secondary" component has its chains nearly perpendicular to the fiber axis.[21,22] This distinctive bimodal orientation is shown by the presence of what appear to be extra reflections on the first layer line of the pattern. These reflections are labeled "1" and "2" on one of the diffraction patterns in Figure 6. The presence of this "secondary component" of the orientation texture clearly will reduce the birefringence compared to a sample which has only the "primary" orientation. Careful examination of Figure 6 indicates that the relative amount of the secondary component of the texture increases with an increase in the breadth of the MWD. A similar trend was also noted by Kloos[6] and Andreassen et al.[7] It was suggested by Peterlin[19] that a possible reason

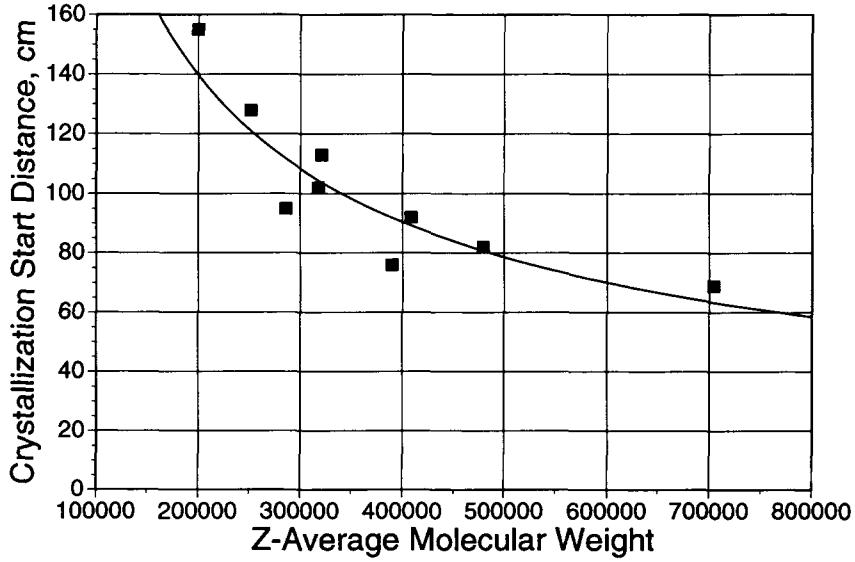

Figure 13 Distance from the spinneret at which crystallization begins as a function of M_z for resins spun at 210°C and 5 psig air pressure.

for the formation of the bimodal orientation distribution is that row nuclei formed during stress-induced crystallization eventually carry so much of the tensile load that the remaining melt can relax and crystallize epitaxially in the secondary population. Since the broader MWD resins are more subject to stress-induced crystallization, it stands to reason that they might exhibit a greater secondary component of the orientation distribution. In any case, we conclude that the greater amount of secondary component, not a large difference in amorphous orientation, is most probably the cause of the lower ultimate birefringence in the broad MWD resins. Of course, we cannot rule out the possibility that there is also a difference in amorphous orientation in these filaments as well. The presence and rate of development of this secondary component of the texture may also explain why the birefringence curve rises more slowly for the broad MWD resin. Another possible explanation is that the lamellae growth rate is higher in the narrow MWD case due to lower growth temperature as a result of greater supercooling prior to nucleation. It is well known that lamellae growth rates are highly temperature-dependent and that the dependence is in the right direction to explain the observed results.[23,24]

As noted above, the effect of MWD on structure development becomes less pronounced as the spinning speed increases. This appears to be associated with either (1) a saturation of the influence of stress on nucleation of crystallization or (2) the result of the elongation thinning nature of the broad MWD resin. In the latter case, the higher spinning speeds (and elongation rates) may cause the viscosities of the resins to approach each other. An effect somewhat related to the former case was earlier observed[3] in the case of samples with differing quiescent crystallization kinetics but identical rheology. In that case, increasing the spinning speed reduced the effect of differences in quiescent crystallization rates, presumably because stress-induced crystallization began to overtake the influence of the factors that produced the differences in quiescent crystallization. In agreement with the results at lower spinning speeds, the ultimate birefringence values decrease with broadening of MWD. This indicates that the differences in morphology that produce these differences in birefringence are not eliminated by changing the take-up velocity. In spite of the fact that the overall orientation level increases with take-up velocity, the differences in the amount of material in the secondary component of the bimodal orientation continues to be greater for the broad MWD resins.

Examination of the tensile test data shows that the mechanical properties of the filaments are greatly influenced by the MWD as well as by the MFR level. These effects on properties can largely be traced to the effects of MWD on the crystallinity and phase distribution (density) and orientation (birefringence) developed under the given spinning conditions. At lower spinning speeds, the narrow MWD resins tend to form the smectic mesophase rather than the α-monoclinic phase. Broadening the distribution produces the α-phase under similar spinning conditions because the freezing occurs at a higher position and temperature in the spinline as a result of greater stress-induced crystallization. The tensile strength and elongation-to-break are affected more by orientation and, consequently, their behavior is fairly highly correlated to the birefringence as shown in Figures 14 and 15. In these two figures, all data obtained in the present study are plotted. They correlate with birefringence, in an overall sense, independent of spinning conditions, MFR, or MWD. The correlations with birefringence observed here are similar to those published earlier for samples that have similar MWD, but which were prepared so as to have a broad range of birefringence.[4,25] It is noteworthy that the data shown on Figures 14 and 15 tend to cluster in groups corresponding to the broad, medium, and narrow MWD resins. We caution that it should not be assumed from this result that, e.g., broad MWD filaments with high birefringence, tensile strength, and low elongation to break cannot be made. We suggest that the clustering of the broad MWD results at lower birefringence, tensile strength, and higher elongation-to-break is a result of the limited conditions of filament preparation and the interaction of the resin rheology and stress-induced crystallization kinetics with the chosen spinning conditions, as discussed above.

Though the tensile strength and elongation-to-break are largely determined by orientation (birefringence) as discussed above, the tensile moduli of the filaments are more complex. Orientation clearly has an effect on the filament modulus, but the filament crystallinity (density) also has a major influence. This can be seen readily by examination of the data in Table IV or by comparison of the plots in Figures 1–3. Therefore, the factors which tend to increase crystallinity in the as-spun filaments, such as broader MWD and lower MFR, also tend to increase the tensile modulus of the as-spun filaments.

Finally, it must be noted that we have studied only the properties of as-spun filaments here. The effects

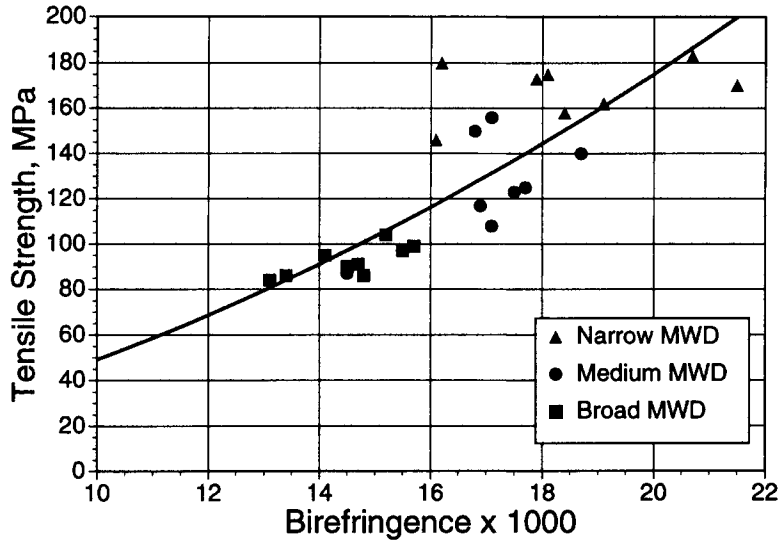

Figure 14 Tensile strength as a function of filament birefringence for the filaments spun in this study.

of second-stage drawing and annealing on the structure and properties of polypropylene filaments have been studied by many investigators,[4,5,25–28] but most recently by Andreassen et al.[7] who examined the influence of MWD. In agreement with previous investigators, they found that the draw ratio was the most important variable in determining the properties of drawn polypropylene filaments and that the tensile strength increases with M_w for the same spinline drawdown ratio and second-stage draw ratio due to greater spinning and drawing stresses which lead to greater molecular orientation. The effects of MWD were complex. They observed that at low draw ratios broad MWD fibers had the highest tensile modulus and elongation-to-break and the lowest tenacity at break. These results are similar to those reported here for as-spun fibers, and they reflect the influence of the MWD on the spinning-stage properties. Increasing the draw ratio increases the tensile strength and modulus and reduces the elongation-to-break for both broad and narrow MWD fibers. But Andreassen et al. found that the increase in

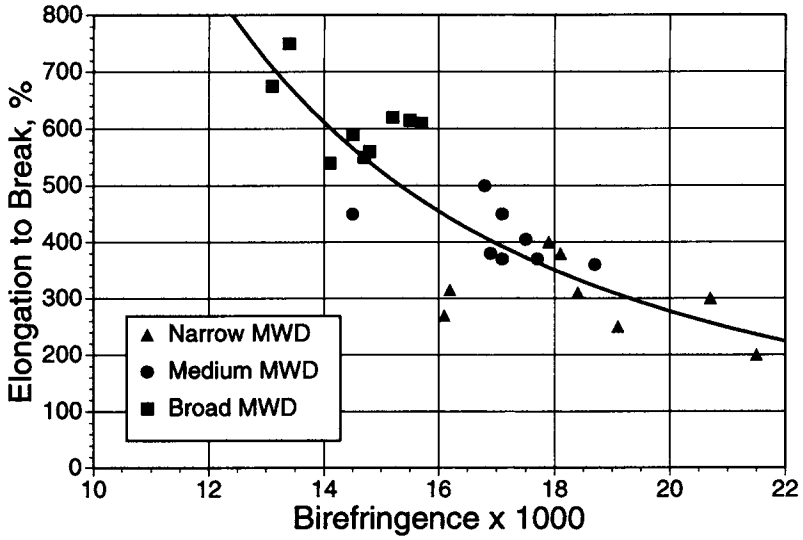

Figure 15 Elongation-to-break as a function of filament birefringence for filaments spun in this study.

tensile modulus was greater for narrow MWD fibers, so that at high draw ratios the narrow MWD fibers had a higher tensile modulus than that of the broad MWD fibers.

SUMMARY AND CONCLUSIONS

The spinnability, structure, and properties of melt-spun filaments prepared from nine different resins having a range of MFRs and MWDs were studied. At any MFR level, spinnability as judged from the maximum filament spinning speed without frequent breaks and from filament diameter fluctuations increased with narrowing of the MWD.

As expected, the well-established effects of MFR and M_w were observed. Increasing the M_w (decreasing the MFR) for a given polydispersity leads to higher spinline stresses, faster filament drawdown, higher crystallization rates, and higher levels of crystallinity and orientation, higher tensile strength, and lower elongation-to-break for the filaments when spun under similar processing conditions (extrusion temperature, cooling conditions, take-up velocity, mass throughput, etc.). These effects were also documented in an earlier article: Part I.[2] It was also found that the spinline behavior and structure and properties of the filaments were greatly influenced by the breadth of the MWD. Examination of the characteristics of the as-spun filaments reveals that the fibers spun from the broad MWD samples develop higher crystallinity and lower birefringence than do the samples spun from the narrow MWD samples of similar MFR. Also, the fibers spun from the narrow MWD samples have higher tensile strength and lower elongation-to-break than those of the filaments obtained from the broad MWD samples in the same range of MFR. On-line profiles during the melt spinning of these samples showed that the filament draws down faster and approaches its final diameter closer to the spinneret with the broadening of MWD. Further, the birefringence profile of the fiber starts to rise earlier along the spinline but develops more slowly and reaches a lower final value with the broadening of MWD.

The filament drawdown behavior could be attributed to the influence of MWD (in the same range of MFR) on the elongational viscosity and the propensity to undergo stress-induced crystallization. It was argued that the broad MWD resins are more elongation-thinning, but have a higher elongational viscosity at low elongation rates than do the narrow MWD resins. This assertion is consistent with dynamic (shear) viscosity data on the resins. The higher propensity to undergo stress-induced crystallization for the broader MWD resins is attributed to the influence of the high molecular weight tail in the MWD. It can be speculated that the longer chains in the high molecular weight tail give rise to "row nuclei" due to greater entanglement and orientation than do the shorter chains, thus causing onset of crystallization earlier along the spinline and, hence, at a higher temperature. This further results in higher crystallinity for the broad MWD filaments relative to their narrow MWD counterparts.

The lower final birefringence of the broad MWD resins was attributed to the presence of a bimodal crystalline orientation in polypropylene crystallized under stress and an observed increase in the "secondary component" with increasing polydispersity. Based on the speculation of earlier authors,[7,19] it is suggested that this may also be related to the greater propensity for stress-induced crystallization with increased polydispersity.

The tensile strength and elongation-to-break of the as-spun filaments correlated with birefringence (orientation) in the same way as previously discussed in the literature, independent of the MWD. However, MWD did influence the value of the birefringence, and, hence, the tensile properties developed, due to its influence on the rheology and stress-induced crystallization behavior of the resin. The tensile modulus exhibited a more complex behavior than that of tensile strength in which the crystallinity was a greater determinant than was the molecular orientation.

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