

Studies on the Influence of Molecular Weight and Isotacticity of Polypropylene on the Formation of Mesomorphic Phase

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ABSTRACT: Polypropylene (PP) blends with various molecular weight and isotacticity were prepared through solution blending and subjected to rapid melt quenching. Structural changes in the PP matrix during mesomorphic phase formation were measured by FTIR spectroscopy and wide-angle X-ray diffraction measurements. The blends with different molecular weight and isotacticity provided the pathway to understand their influence on mesomor-

phic phase formation. It is observed that low molecular weight PP with low isotacticity forms mesomorphic phase, whereas high molecular weight and low isotactic PP does not lead to the formation of mesomorphic phase. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 3181–3186, 2009

Key words: polypropylene; mesomorphic state; isotacticity; molecular weight

INTRODUCTION

Polypropylene (PP) is one the most versatile thermoplastic polymer used for different end-use applications because of good mechanical properties, chemical resistance, excellent insulation characteristics, etc.¹ The key for the versatility of PP is the microstructure and molecular weight characteristic control through high-performance-supported Ziegler-Natta catalysts during stereospecific polymerization process.^{2–6} PP belonging to the class of crystalline polymers exhibits polymorphism.^{7,8} The physical properties of the PP are dependent on the crystalline structure, providing opportunity for multidimensional structural controls during production and processing for fine tuning product properties. The crystal phases found in isotactic polypropylene (iPP) are α (monoclinic), β (hexagonal), γ (orthorhombic) crystalline phases, and a mesomorphic phase.^{9–12} The crystalline structure of these phases are specified by four types of regular 3/1 helices, based on the combination of left and right handed helices and up and down stems, with reference to the CH₃ group.^{8,13}

Thin sections of molten iPP when quenched (cooling below 0°C with rate faster than 100°C/s), with

the cooling media in direct contact with the iPP, forms mesomorphic phase.^{13,14} Mesomorphic phase has important implications, predominantly in film and fiber products, where high clarity and gloss is critical for end applications. Cast Film is one such commercial product where mesomorphic phase, formed by extruding PP through die and further melt quenching on chilled rollers, imparts high transparency to the PP film for specialty applications.¹⁵ Mesomorphic phase is defined as the intermediate state between crystalline and amorphous phases.^{16–18} It has 3/1 helices but the packing of helices is not well defined as there is absence of orderly arrangement of left and right handed helices.^{19–27}

Natta and Corradini first defined mesomorphic phase as “smectic phase” characterized by parallel helices having disorder in lateral packing.⁷ Cohen and Saraf¹⁹ proposed that the state has systematic distortion in the adjacent helix registration with respect to the CH₃ group position. Study on the effect of isotacticity on the formation of mesomorphic state was reported by Konishi et al.¹⁴ which suggest that minimum mmmm pentad intensity (isotacticity) of 68% is required for the mesomorphic state formation. The formation mechanism and the parameters effecting its formation are still not well understood and is a scientific challenge.

The aim of the present study is to understand the influence of isotacticity and molecular weight on the formation of mesomorphic phase of PP. Samples with varying isotacticity and molecular weight,

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TABLE I
Details of the Polypropylene Samples

PP resin	mmmm%	$M_w \times 10^4$	$M_n \times 10^3$
PP1	92	33.2	67
PP2	83	24.8	29
PP3	30	7.5	12
PP4	33	1.4	4

prepared by solution blending, have been analyzed for the mesomorphic phase formation. WAXD analysis was done to study the local order in mesomorphic state, characterized by two broad peaks in WAXD.²⁰⁻²² Changes in 3/1 regular conformational helices with processing have been investigated by FTIR spectroscopy.

EXPERIMENTAL

Synthesis and materials

PP samples, PP1 (mmmm content 92%, $M_w = 33.2 \times 10^4$, $M_n = 67 \times 10^3$) and PP2 (mmmm content 83%, $M_w = 24.8 \times 10^4$, $M_n = 29 \times 10^3$), respectively, were synthesized using $MgCl_2$ supported titanium catalyst, as described in earlier publications.^{28,29} Heptane soluble part, PP3 (mmmm content of 30%, $M_w = 7.5 \times 10^4$, $M_n = 12 \times 10^3$) was extracted from the PP2 polymer by refluxing the polymer in heptane for 2 h. PP sample, PP4 with low isotacticity (mmmm content of 33%, $M_w = 1.4 \times 10^4$, $M_n = 4 \times 10^3$) was procured from Aldrich (Mumbai, India) and was used as obtained. The details of the PP samples used are given in Table I.

Polypropylene blending

Specified weights of the PP1 and PP4 were dissolved in boiling xylene in the presence of antioxidants (IRGANOX1010 and IRGAFOS168, Ciba Specialty Chemicals) and then precipitated into methanol

TABLE II
Blend Compositions of Polypropylene Resins

PP blend	%PP1	%PP4	mmmm%	$M_w \times 10^4$	$M_n \times 10^3$
B1	75	25	77	25.8	13
B2	50	50	63	17.9	7
B3	25	75	48	9.4	5

cooled with dry ice ($CO_2(s)$) with vigorous stirring. The resulting blends were dried at 60°C in vacuum; details of the blends are given in Table II. Solution blending was done to ensure uniform dispersion of the components for the blends having different molecular weight and isotacticity profiles.

Thermal processing

The polymer samples were subjected to thermal processing on hot stage under nitrogen atmosphere. The prequenched samples were prepared by melting the samples at 220°C and keeping at 40°C for 10 min. For annealing, the PP sample was melted at 220°C and annealed between steel plates at 115°C for 4 h for crystallization. The samples were melted at 220°C and quenched with ice/water system to ensure the rapid cooling below 0°C with rate faster than 80°C/s. All the samples after thermal processing were kept at room temperature prior to analysis. The details of thermal processing are given in Table III.

Characterization

X-ray diffraction measurements were carried on Bruker AXS, D8 Advance X-ray diffractometer at room temperature. The step size in WAXD measurements was 0.02° and the time per step of 4 s. Component analysis was performed using TOPAS software by Bruker AXS to understand the phase characteristics.

TABLE III
PP Samples and Thermal Processing

Sample	Starting material	mmmm%	$M_w \times 10^4$	$M_n \times 10^3$	Thermal processing
T1	PP1	92	33.2	67	220°C → 40°C (10 min)
T2	PP1	92	33.2	67	220°C → 115°C (4 h)
T3	T1	92	33.2	67	220°C → 0°C
T4	B1	77	25.8	13	220°C → 40°C (10 min)
T5	B2	63	17.9	7	220°C → 40°C (10 min)
T6	B3	48	9.4	5	220°C → 40°C (10 min)
T7	PP4	33	1.4	4	220°C → 40°C (10 min)
T8	B1	77	25.8	13	220°C → 0°C
T9	B2	63	17.9	7	220°C → 0°C
T10	B3	48	9.4	5	220°C → 0°C
T11	PP4	33	1.4	4	220°C → 0°C
T12	PP3	21	7.5	12	220°C → 0°C

Configurational differences can occur among the various propylene units, because each monomer unit in a PP polymer chain has an asymmetric carbon atom, resulting into polymer with vastly varying microstructure. It can be recognized from the steric pentad distributions obtained from the α -methyl resonances from the $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum. $^{13}\text{C}\{^1\text{H}\}$ -NMR experiments were performed in 50% (v/v) 1,2,4-trichlorobenzene and d_2 -tetrachloroethane solution with 10% (w/v) PP at 100.6 MHz on Bruker Avance-II 400 MHz instrument. The experiments were performed at 130°C with 30° pulse, 10,000 transients, 2-s delay time, and broadband proton decoupling. Isotacticity (mmmm content) determined from $^{13}\text{C}\{^1\text{H}\}$ -NMR spectroscopy is given in Tables I and II. It was measured by determining area under the peak corresponding to mmmm resonances to the total area under α -methyl resonances.^{30–32} The PP samples have isotacticity (mmmm pentad content) ranging from 92% to 30%.

FTIR analysis was performed on Perkin-Elmer spectrum GX instrument with 2 cm^{-1} resolution and 32 scans. FTIR spectral data was analyzed for studying relative changes in the conformation bands of long and short 3/1 regular helical sequences. Molecular weight distributions (M_w and M_n) were measured using high-temperature GPC with 1,2,4-trichlorobenzene as an eluent and calibration based on polystyrene standards on Polymer Laboratory PL-220 instrument at 145°C.

RESULTS AND DISCUSSION

Isotacticity, molecular weight profile, and thermal history are the structural parameters that define physical properties of PP matrix. Effect of processing on PP1 sample with mmmm pentad content of 92%, $M_w = 33.2 \times 10^4$, $M_n = 67 \times 10^3$ was studied to evaluate the effect of variable processing, annealing, and melt quenching on the structural parameters. Low iPP sample (mmmm content 30%, $M_w = 7.5 \times 10^4$, $M_n = 12 \times 10^3$) was subjected to melt quenching to study the effect of isotacticity on mesomorphic phase formation. PP blends with varying isotacticity and molecular weight profile were subjected to melt quenching. This provided the pathway to study the influence of molecular weight on the ability of PP samples with varying molecular weight and isotacticity to form the mesomorphic state.

Influence of processing

T1 and T2 samples processed through annealing at 40°C for 10 min and 115°C for 4 h, respectively, from same PP1 (mmmm content 92%, $M_w = 33.2 \times 10^4$, $M_n = 67 \times 10^3$) were subjected to WAXD profiling and FTIR spectroscopy to understand the

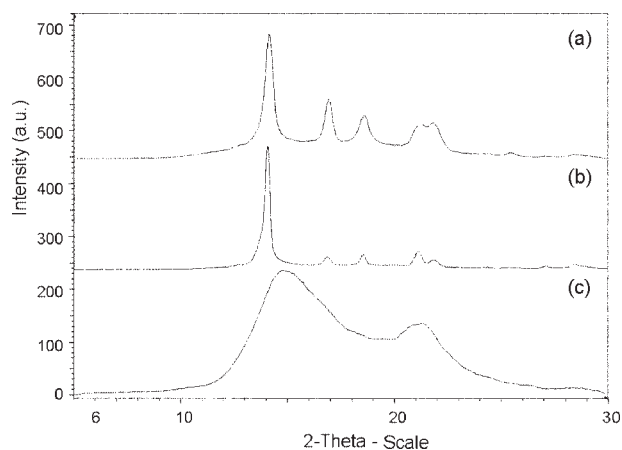


Figure 1 WAXD profile of (a) T1, (b) T2, and (c) T3 polypropylene samples.

effect of processing on the structure. WAXD profiles of T1 and T2 samples, Figure 1(a and b), respectively, show that intensity and sharpness of peaks increased substantially for T1 sample, indicating increase in crystallinity. Percent crystallinity calculated from the component analysis of WAXD indicates that crystallinity increased from 43% in T1 to 64% in T2 sample, with annealing at higher temperature for longer duration. T3 sample, prepared by melt quenching of T1 sample, shows two broad peaks in WAXD profile [Fig. 1(c)], characteristic of the mesomorphic phase. Mesomorphic phase determined from component analysis was 54%. The results indicate that PP with high isotacticity on annealing results in high crystallinity product and on quenching the molten state transforms into the mesomorphic state, ascertaining the critical effect of processing on PP properties.

FTIR spectral analysis in the region $750\text{--}1350\text{ cm}^{-1}$ provides information about the physical state and conformation of the iPP chains dictated by the 3/1 regular conformational helices. Absorption bands are related to the minimum number of monomer units in isotactic configuration (critical length, “ n ”) in a given regular conformational helical sequence. The absorption bands at 973 , 998 , 841 , and 1220 cm^{-1} have been assigned to $n = 3\text{--}4$, 10 , 12 , and ≥ 14 , respectively.^{11,33–36} Figure 2 (a–c) shows the FTIR spectra of T1, T2, and T3 samples, respectively, where one observes the characteristic bands in all the three cases but for T2 which is the annealed sample show sharp absorption bands in comparison with T1 and T3 samples.

To understand the relative differences in concentration of long ($n \geq 10$) and short ($n = 3\text{--}4$) regular helices, FTIR band at 973 cm^{-1} was used as the reference band to evaluate the relative intensity ratio variation corresponding to bands with high monomer units (998 , 841 , and 1220 cm^{-1}) arising due to

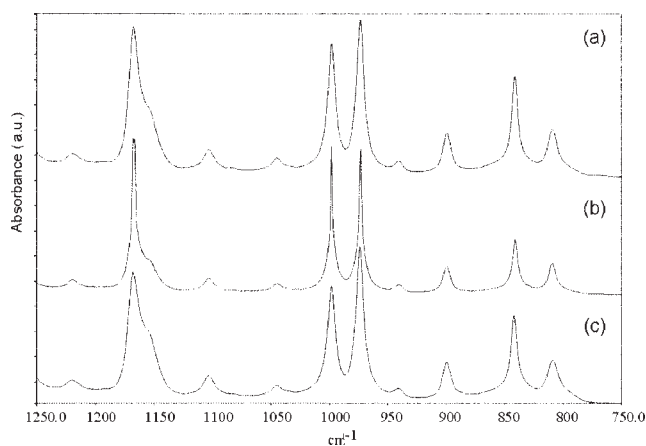


Figure 2 FTIR spectra of (a) T1, (b) T2, and (c) T3 polypropylene samples.

distinct processing. Figure 3 shows the variation in relative intensities with processing. Within a sample, the intensity varies for “ n ” as $10 > 12 > 14$, indicating that with increase in the critical length “ n ” there is decrease in concentration of helices. The order of relative intensity of long helical conformational sequences is T2 (annealed) $>$ T1 (prequenched) $>$ T3 (quenched). Thus, during crystallization short helices get converted into longer helices and during melt quenching longer helices get converted into short helical sequences, with the fact that long regular helices are still evident in quenched sample. The results indicate the strong correlation of structural features of PP with processing.

Influence of isotacticity

The sample T12, prepared from quenching low isotactic PP3 having mmmm content = 30%, $M_w = 7.5 \times 10^4$, and $M_n = 12 \times 10^3$ shows the absence of characteristic peaks corresponding to mesomorphic state in the WAXD profile (Fig. 4). WAXD has peaks that are characteristic of the monoclinic phase (α -

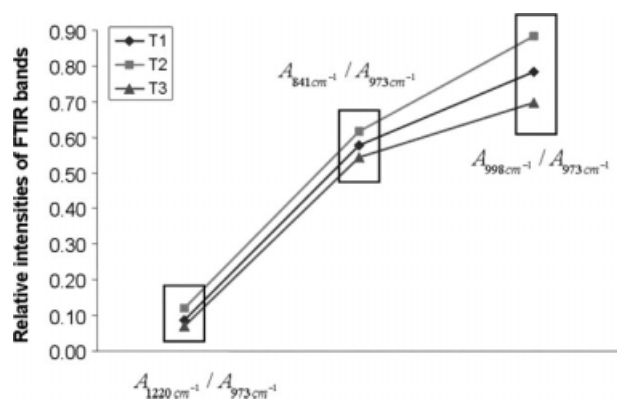


Figure 3 Relative intensities of different helical conformation bands for T1, T2, and T3 polypropylene samples.

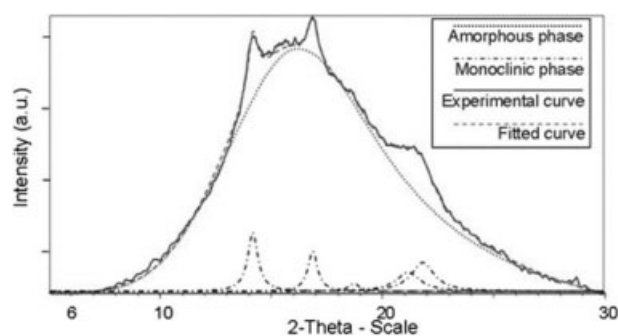


Figure 4 WAXD profile of T12 polypropylene sample.

crystalline peaks at 14.2, 16.9, 18.8, 21.2, and 21.9 2θ) and a broad hump for amorphous phase. This feature has been explained by Konishi et al. on the basis that critical length of rodlike segments, $L_c = 23.8 \text{ \AA}$, which corresponds to about 11 monomers in the isotactic block or isotactic sequence lengths ($\langle n \rangle_{iso}$) is required for formation of mesomorphic.¹⁴ They calculated that minimum mmmm content required for the formation of mesomorphic state is 68%. The sample T12 with mmmm content = 30% falls below this critical isotacticity requirement and thus does not form the mesomorphic state. High iPP (T1; mmmm = 92%) forms mesomorphic phase, whereas low isotactic sample (T12, mmmm = 30%) does not form the mesomorphic state; this indicates that isotacticity is critical for the formation of mesomorphic phase. The results prompted further investigations based on the hypothesis that as conversion of monoclinic phase to mesomorphic phase upon melt quenching is characterized by positional, orientational, and rotational movements of helices, addition of low molecular weight fraction owing to high diffusion may enhance the mesomorphic phase formation by providing more mobility to PP matrix.

Influence of molecular weight

PP samples, T1, T4, T5, T6, and T7 with decreasing molecular weight and isotacticity, were subjected to quenching upon melting, and the resultant quenched samples, T3, T8, T9, T10, and T11, were subjected to WAXD profile and FTIR analysis. Figure 5 shows the WAXD profile of the quenched samples. For T3 and T8 samples, since the mmmm content is greater than 68%, one is expected to observe the mesomorphic phase, which is seen as two broad peaks in WAXD [Fig. 5(a) and (b), respectively]. Interesting was the observation of two characteristic broad peaks of mesomorphic phase and absence of peaks corresponding to the α -form of PP for T9, T10, and T11 samples although the mmmm content of 63%, 48% and 33%, respectively. The variation in the mesomorphic and amorphous phase contents’ from

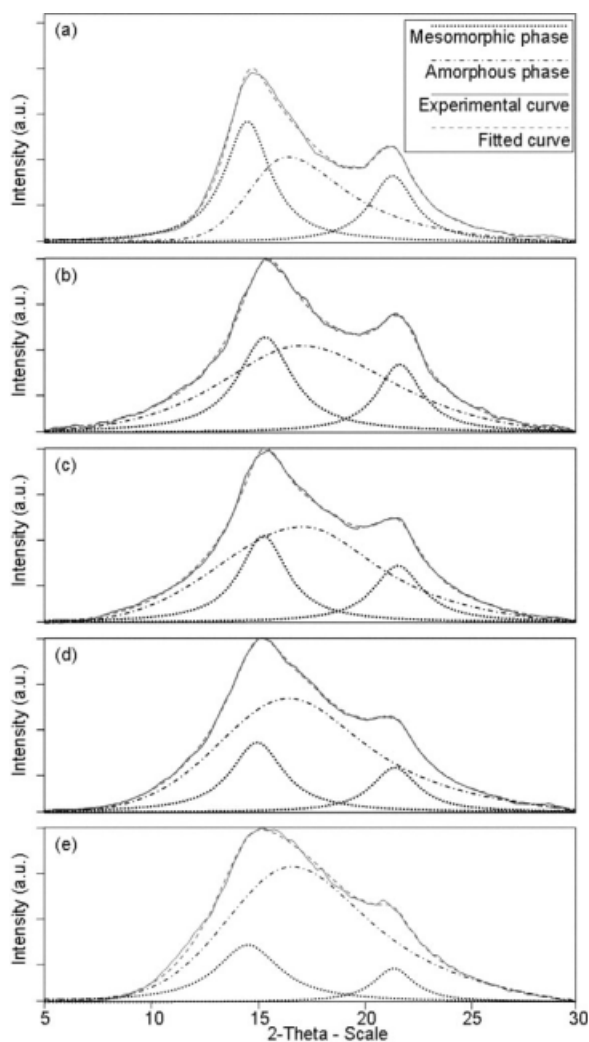


Figure 5 WAXD profiles of quenched polypropylene samples: (a) T3, (b) T8, (c) T9, (d) T10, and (e) T11.

component analysis is shown in Figure 6. The variation in mesomorphic phase content with isotacticity is almost linear for blends but increases sharply for T9 sample (mmmm content 92%). Low intensity for T8, T9, T10, and T11 samples may be attributed to low molecular weight fraction characterized by smaller helices and thus weaker diffraction. With the decrease in isotacticity and molecular weight, amorphous content increased. As even low isotactic samples in the presence of low molecular weight fraction are able to form mesomorphic state, the low molecular weight fraction thus plays a critical role for the formation of mesomorphic phase.

Figure 7 shows the relative FTIR intensity ratios for the prequenched and quenched samples. The difference in the variation of relative intensities of absorption bands corresponding to $n = 10, 12,$ and 14 with $n = 3-4$ with regard to isotacticity is quite evident. With increase in isotacticity, long regular helices ($n \geq 10$) increases that can be attributed to

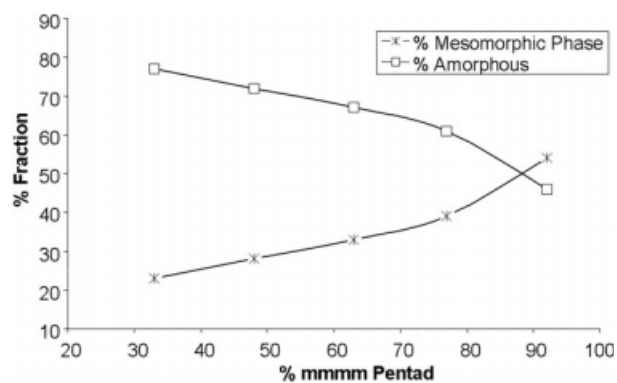


Figure 6 Variation in mesomorphic phase and amorphous phase in quenched polypropylene samples.

the higher structured packing of helices in the polymer matrix. Similar trend is observed for the quenched samples. For the samples T6/T10 and T7/T11 having low mmmm content of 48% and 33%, respectively, the absorptions bands for $n \geq 14$ helices are absent. This may be due to lower order in the PP matrix due to low isotacticity resulting in relatively more helices with shorter length in comparison to samples with high isotacticity. The relative variation of helical conformational sequences with melt quenching is shown in Figure 8 for T1 to T3

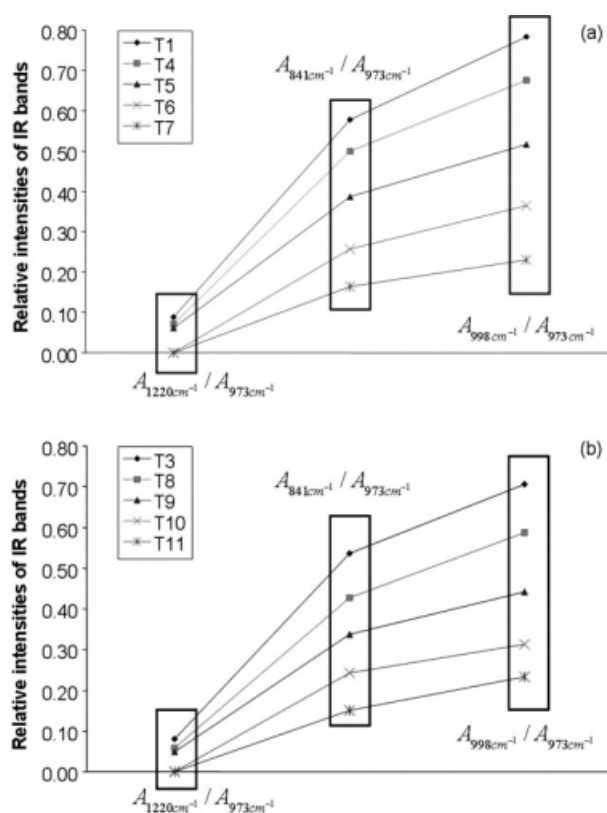


Figure 7 Relative intensities of different helical conformation bands of (a) prequenched and (b) quenched polypropylene samples.

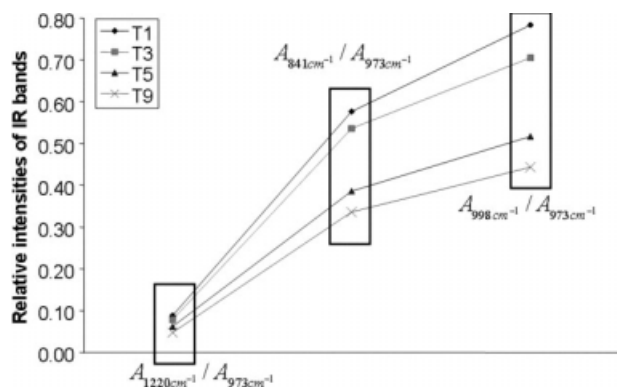


Figure 8 Variation in relative intensities of different helical conformation bands with quenching for T1 to T3 and T5 to T9 polypropylene samples.

and T5 to T9 samples. Similar trend was observed for rest of the samples. With the formation of mesomorphic phase (melt quenching), part of the longer helices get converted into short helical sequences, but long regular helices still remain in the quenched samples. The results specify that formation of mesomorphic phase is dependent on molecular weight, with low molecular weight fraction assisting in the formation of mesomorphic phase and isotacticity of PP.

CONCLUSIONS

Our studies indicate that low molecular weight is augmenting the formation of mesomorphic phase in PP. During mesomorphic phase formation, there are positional, orientational, and rotational changes of helices, which destroy the monoclinic unit cell of iPP, with the system going from ordered to disordered system. The high molecular mobility of low molecular weight chains results into fast diffusion and greater mobility of the PP matrix and of the helices thus assisting in the formation of mesomorphic phase. The same is demonstrated by WAXD profile analysis with mesomorphic phase formation even for low iPP samples containing low molecular weight fraction. Analysis of relative variation of long and short helical sequences through FTIR spectroscopy indicate the inter conversion of these sequences depending upon processing. Consequently, the formation of mesomorphic phase is dependent both on isotacticity and molecular weight of the PP in addition to the processing parameters.

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