

## Functionalization of Isotactic Polypropylene with Citraconic Anhydride

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### Summary

Functionalization of isotactic polypropylene (*i*-PP) with citraconic anhydride (CA) was carried out in 1,2,4-trichlorobenzene solution with dicumyl peroxide as an initiator at 160°C under nitrogen atmosphere. Chemical and physical structures and thermal behavior of the synthesized graft copolymers with different anhydride units were determined by volumetric titration (acid number), FTIR and <sup>1</sup>H-NMR spectroscopy, X-ray powder diffraction, DSC and TGA thermal analyses. It was shown that the crystallinity and thermal behavior of grafted *i*-PP's depend on anhydride unit concentration in grafted *i*-PP; grafting reaction proceeds selectively which is not accompanied by oligomerization of CA and degradation main chain as in known maleic anhydride/PP system. This fact was explained by inhibition effect of  $\alpha$ -methyl group in CA grafted unit on the chain  $\beta$ -scission reactions and no homopolymerization of CA in chosen grafting conditions. Functionalized *i*-PPs showed high thermal stability in comparison with virgin *i*-PP.

### Introduction

Isotactic polypropylene (*i*-PP) has become one of the largest and fastest growing thermoplastics owing to its good impact strength, rigidity and chemical resistance and is low in cost [1,2]. However, the lack of reactive sites, poor hydrophilicity, adhesion and compatibility with other polymers and sensitivity to photo-oxidation significantly limit the area it application. These limitations may be overcome by the grafting or graft copolymerization of various functional monomers onto *i*-PP backbone via free radical mechanism [3-5]. Introducing polar functional groups into PP improves adhesion, paintability, affinity for dyes and printing agents, and compatibility [6] for preparation of multilayered barrier films, blends and composite materials.

In fact, anhydrides of unsaturated dicarboxylic acids such as maleic, citraconic and itaconic anhydride are strong hydrophilic monomers. If unsaturated dicarboxylic acids and their anhydrides are grafted onto polymers will carry a denser distribution of carbonyl or free carboxylic groups. These reactive groups can serve as sites for the further functionalization of grafted polymers. The grafting reaction of maleic anhydride (MA) with commercial polyolefins such as polyethylene (PE) [7,8],

polypropylene PP [9], ethylene-propylene (E-P) copolymer [10], in the presence of peroxide catalysts were investigated extensively.

The most investigations were related with MA grafting onto PP in the melt using various type of extruder and mixer [11-17]. The effect of MA and peroxide initiator concentrations on the amount of grafts and on the degradation was determined. A higher level of grafting occurred with an increased initial concentration of MA. Also, chain scission of PP is suppressed at high initial concentration of MA [13]. It was suggested that formation of oligomeric graft structures in maleated PP, is of minor importance for high-temperature PP grafting and in these conditions,  $\beta$ -scission of PP chain does not occur [16].

Alternatively, for the best understanding of mechanism grafting process, solution conditions can be used, where the polymer is dissolved in a suitable solvent at an appropriate temperature and MA is added with an initiator. Thus, the grafting of PP with MA in a xylene solution, using benzoyl peroxide as the initiator, has been reported by Ide et al. [18]. Little evidence of degradation of polymer product was found. The effect of solvent type and amount, catalyst type and amount, and the effect of initiator concentration on the MA grafting of PP were studied by Rengarajan et al. [19]. It was shown that all of these factors had a significant effect on the grafting degree of the PP. Borsig and Hrcakova [20] later compared the level of functionalization of *i*-PP using both solid phase and solution method. They found no significant effect differences in the grafting efficiency between the two methods. MA grafting of PP in a solution process and evaluation of the effects of monomer and initiator concentration, reaction time, and temperature on percentage grafting were investigated by Sathe et al. [21]. Recently, we have been reported the synthesis of the graft copolymers of PP (powder and granule) with maleic anhydride, using grafting in solution and reactive extrusion techniques and their main characteristics, as well as results of the structure-composition-property relationship studies [22-25].

The aim of this work was to functionalize *i*-PP with itaconic anhydride (CA) through solution radical grafting reactions and to investigate the effect of monomer concentration on the degree of grafting, rate of crystallization and crystallinity, as well as on the thermal behavior of grafted *i*-PPs.

## Experimental

### Materials

Isotactic PP was supplied by Petkim Petrochemical Company (Turkey). It has a melt flow rate (MFR) of 5 g/10 min (ASTM D 1238, 230°C, 2.16 kg), a melting point of 166°C and a degree of crystallinity of 32.4%; CA monomer (Aldrich) was purified by distillation under vacuum, before use; bp 213.5°C,  $n_D^{20}$  1.4712,  $d_4^{20}$  1.2468;  $^1\text{H-NMR}$  spectra: CH=, 1H quartet with 6.93-6.92 ppm and CH<sub>3</sub>, 3H doublet at 2.19 and 2.18 ppm; MA as a model monomer (Fluka) was purified by recrystallization from anhydrous benzene and sublimation in vacuum; mp: 52.8°C. Solvents, toluene, methanol and 1,2,4-trichlorobenzene (TCB), and the initiator, dicumyl peroxide (DCP) (Aldrich) were used without further purification.

### Grafting Procedure

The radical grafting of CA onto *i*-PP was performed in TCB solution at 160°C under nitrogen atmosphere in the presence of DCP as an initiator. For solution grafting,

given amounts of monomer (1.0-10 wt. %), the initiator (1.0 wt. %), and *i*-PP solution in TCB were charged into a Pyrex round-bottom-flask glass reactor equipped with a condenser, a heating unit, and a magnetic stirrer. Before the reaction, the solution was purged for 15 min with nitrogen, and a continuous nitrogen flow was maintained on the top of the condenser during the reaction process. The grafting process was controlled by titration of reaction mixture before and after grafting for chosen *t* time. The grafted polymers were isolated from reaction mixture by precipitation with methanol and then filtered and dried under vacuum at 100°C up to constant weight.

#### Polymer characterization

The amount of anhydride substituted onto PP chains during grafting reactions was determined by a standard titration method in which 0.4 g of the grafted polymer was dissolved in 100 ml toluene in a conical flask at 100°C (for anhydride grafted polymers, a few drops of water were added to hydrolyze all anhydride groups into carboxylic acid) then the hot solution was titrated with 0.05 N KOH (in methanol) in the presence of Thymol blue as an indicator. The reaction medium was continuously agitated in order to prevent precipitation of PP. The grafted monomer content was determined from the following equation [26]:

$$\text{Grafted Monomer Content (wt, \%)} = \frac{[(EW \times N \times V)]}{m \times 1000} \times 100 \quad (1)$$

Where *N* and *V* are the concentration (mol/L) and volume (L) of the titrant (potassium hydroxide-methanol solution), respectively, and *m* (g) is the weight of the grafted PP and EW is the equivalent weight of monomer (g).

FTIR spectra of the grafted polymers were recorded in a FTIR spectrometer (Shimadzu 800, Kyoto, Japan) in the range of 4000-400 cm<sup>-1</sup> range with 4 cm<sup>-1</sup> resolution. <sup>1</sup>H NMR spectra of 5.2 % solution of grafted polymers in TCB were recorded in a BRUKER DPX-400, 400 MHz high performance digital FT-NMR spectrometer with chloroform (CHCl<sub>3</sub>-*d*<sub>1</sub>) at 27°C.

Thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses of the grafted polymers were performed in a Thermal DSC-TGA-DTA Analyzer (Setaram Labsys, Caluire, France) and Shimadzu DSC-50 Analyzer (Kyoto, Japan), under nitrogen atmosphere at a heating rate of 10°C/min. The melting enthalpies were measured by using the areas under the melting peaks. The crystallinity values of the polymers were determined by using the following equation [27]:

$$\text{Degree of Crystallinity (\%)} = (\Delta H_f / \Delta H_f^\circ) \times 100 \quad (2)$$

Where, ΔH<sub>m</sub> is the melting enthalpy of the polymer and ΔH<sub>m</sub><sup>°</sup> is the enthalpy of 100 % crystalline PP (ΔH<sub>m</sub><sup>°</sup> = 209 J/g) [28].

X-ray powder diffraction (XRD) patterns of synthesized polymers were recorded using a Philips manual spectrogonometer employing CuK<sub>α</sub> (λ = 1.54184 Å) radiation between the range 5° ≤ 2θ ≤ 50°. Crystallinity degrees (χ<sub>c</sub>) of synthesized polymers were determined by area ratio method using the following equation [29]:

$$\chi_c = \int_0^\infty s^2 I_c(s) ds / \int_0^\infty s^2 I(s) ds \quad (3)$$

Where *s* is the magnitude of the reciprocal-lattice vector which is given by *s* = (2sinθ)/λ (θ is one-half the angle of derivation of the diffracted rays from the incident X-rays

and  $\lambda$  is the wavelength);  $I(s)$  and  $I_c(s)$  are the intensities of coherent X-ray scatter from both crystalline and amorphous regions and from only crystalline region of polymer sample, respectively, and  $d$  is interplanar spacing.

## Result and Discussion

### *Synthesis and characterization of graft copolymers*

It is known that the modification reactions of PP macroradicals depend on the temperature [5]. The grafting reaction of PP with monomers after radical generation is significant due to radical reactions in a narrow temperature range from 80 to 150°C. In the temperature range up to 180°C, branching and crosslinking are predominant and at temperatures above 180°C, the degradation reaction is dominant. Taking into consideration these known experimentally confirmed facts, radical-initiated grafting and graft copolymerization reactions of PP were carried out at 160°C. In this group of experiments, amount of anhydride monomers used were changed. The monomer/polymer ratio in the feed was also changed in the range of 1-10 (wt. %). The monomer unit content of the grafted *i*-PP and grafting yield, estimated from Eq. (1) and the changes of these parameters with the monomer content in feed are shown in Table 1. As seen from these data, the grafting degree of *i*-PP is a function of all the comonomer contents. In the experimental conditions applied in this study the grafted monomer unit content varies in the range of 0.012-0.56 mol %.

As a general behavior, the anhydride content firstly increases with the monomer content in the feed, reaches a maximum value and then decreases. When the MA content in the feed is low, there are enough initial radicals to combine with MA molecules and to initiate PP macroradicals. Therefore, the grafting degree (carboxylic acid content of the grafted PP) would increase with increasing the MA content in the feed. But with a further increase in the initial MA content, more and more radicals would be consumed in grafting reaction. The number of initial radicals to induce

**Table 1.** Effects of monomer unit content on the thermal behavior and crystallinity of the grafted *i*-PP's

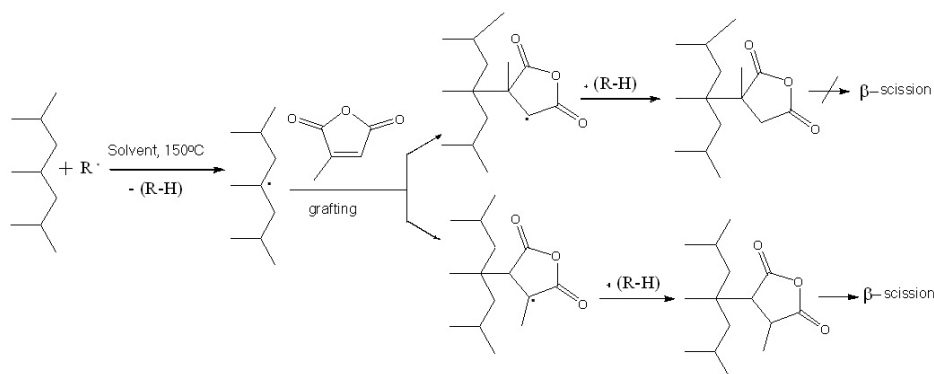
Monomer content in feed (wt %)	Acid number (mg KOH/g)	Grafted monomer contents (mol %)	$T_m$ (°C)	$\Delta H_m$ (J/g)	Crystallinity $\chi_c$ (%)		
					by DSC	by XRD	
Poly( <i>i</i> -PP-g-CA)							
1	0.14	0.01	163.2	78.2	37.4	–	
2.5	1.12	0.10	162.9	85.1	40.7	–	
5	2.46	0.22	161.9	92.4	44.2	45.9	
7.5	5.05	0.45	158.4	106.0	49.0	48.9	
10	1.68	0.15	162.5	90.5	43.3	–	
Poly( <i>i</i> -PP-g-MA)							
1	1.40	0.13	161.3	70.1	33.5	–	
2.5	5.61	0.50	158.5	90.1	43.1	–	
5	6.31	0.56	162.2	93.9	45.0	44.6	
7.5	4.21	0.38	163.3	89.2	42.7	43.6	
10	2.10	0.19	163.0	78.0	37.3	–	
Virgin <i>i</i> -PP	0.00	0.000	166.0	67.7	32.4	33.6	

considered other reactions would then decrease consistently. Therefore, the grafting degree of PP would decrease and a maximum of grafting degree of PP appears. In the case of CA, both the maximum grafting degree appears at higher CA content in the feed and the resultant carboxylic acid content is lower than those observed for MA grafting of PP. This may be a result of reactivity of CA molecules with radicals is lower than MA. That can be explained by relatively low electron-acceptor properties of citraconic double bond due to a  $\text{CH}_3$  group in the  $\alpha$ -position, as well as by steric effect of this group [25].

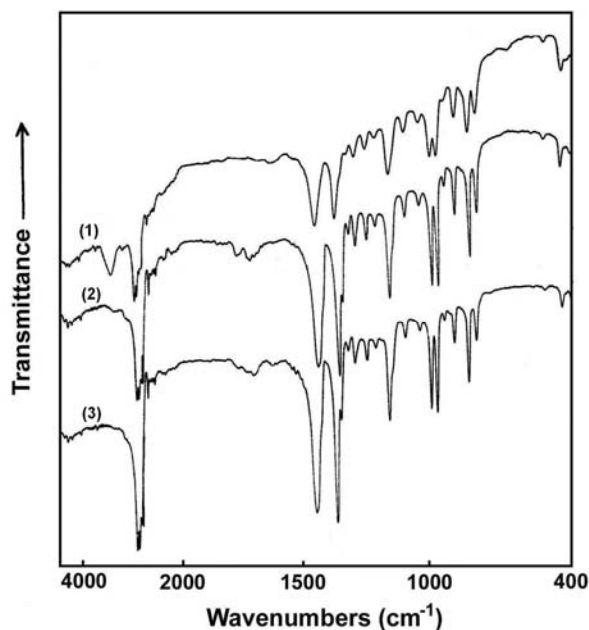
Thermal oxidation may also be a possible cause of degradation of *i*-PP chains; however in our case all the reactions were conducted under pure nitrogen atmosphere, therefore this side reaction could be neglected. Grafting reaction proceeds selectively which is not accompanied by oligomerization of CA and degradation main chain as in known maleic anhydride/PP system [5,30,31]. This fact was explained by inhibition effect of  $\alpha$ -methyl group in CA grafted unit on the chain  $\beta$ -scission reactions and no homopolymerization of CA in chosen grafting conditions. CA homopolymerization is additionally tried to perform under the same experimental conditions, however CA graft homopolymerization does not take place.

Although reactivity of CA radicals is lower than MA, grafting reaction of CA with *i*-PP is more selective than in the case of MA grafting reactions. That can be explained by relatively low electron-acceptor properties of citraconic double bond due to a  $\text{CH}_3$  group in the  $\alpha$ -position, as well as by steric effect of this group. This inhibition effect of chain scission of the  $\alpha$ -methyl groups may be due to the formation of quaternary carbon atom in CA grafted linkage (Scheme 1). As a result of this inhibition effect, one expects that the degree of grafting will be lower in the poly (*i*-PP-*g*-CA) than those for the (*i*-PP-*g*-MA) system similar grafting conditions [32].

The presence of the CA and MA units grafted onto *i*-PP was confirmed by using FTIR. Representative FTIR spectra of the CA or MA grafted *i*-PP are shown in Figure 1. As seen from the spectra of anhydride grafted polymers, the most significant difference in the spectral characteristics, as comparison with virgin *i*-PP spectra, correspond to carbonyl region ( $1900\text{--}1700\text{ cm}^{-1}$ ) which contains new bands at  $1835\text{ cm}^{-1}$  (antisym. C=O stretching) and  $1778\text{ cm}^{-1}$  (sym. C=O stretching) for the grafted anhydride unit,  $1735$  and  $1715\text{ cm}^{-1}$  for C=O stretching in ester and carboxylic groups,



**Scheme 1.** Schematic representation of CA grafting onto *i*-PP through hydrogen-transfer and  $\beta$ -scission mechanisms.

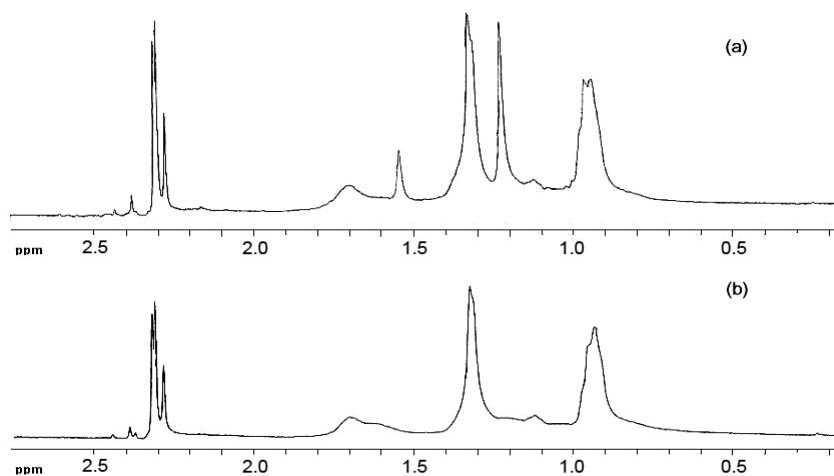


**Figure 1.** FTIR spectra: (1) ungrafted (virgin) *i*-PP; (2) CA grafted *i*-PP; (3) MA grafted *i*-PP.

respectively. The appearance of these two bands can be explained by partial esterification of anhydride unit in the conditions of high temperature precipitation of grafted polymers from TCB solutions by methanol at 100°C. Similar effect was observed for poly(*i*-PP-*g*-MA)s which were synthesized by homogeneous grafting of MA onto atactic PP in xylene over the 80-120°C temperature range with benzoyl peroxide initiator and precipitated by methanol, as well as by Sclavons et al. [33] in the case of high temperature chemical and alkali titrations of the MA grafted *i*-PP.

The visible change of intensity of stretching and deformation bands for CH, CH<sub>2</sub> and CH<sub>3</sub> groups, which are depended on the grafting degree, is also observed. The comparative analysis of spectra virgin *i*-PP and grafted polymers with different compositions indicated that the increase of intensity of the characteristic bands at 2961, 2923, 2874 and 2840 cm<sup>-1</sup> (C-H stretching in CH, CH<sub>2</sub> and CH<sub>3</sub> groups), 1470 and 1380 (CH<sub>2</sub> and CH<sub>3</sub> deformations) and 1162, 998, 974, 898 and 808 cm<sup>-1</sup>, which are associated with various vibrations of CH-CH<sub>3</sub> group conformation.

Grafted anhydride linkages are also characterized by <sup>1</sup>H NMR (400 MHz) spectroscopy. The <sup>1</sup>H NMR spectra are shown in Figure 2. <sup>1</sup>H NMR spectra of poly (PP-*g*-CA) contains relatively higher intensive and very weaker peaks between 0.9 and 2.45 ppm which are associated with protons of methyl, methylene and methine groups of ungrafted propylene units (more intensive peaks) and methylene group of grafted CA ring at 2.38 ppm (Fig. 2a). Poly(*i*-PP-*g*-MA) as a model copolymer synthesized in similar conditions shows the characteristic peaks of methyl, methylene and methine group of PP at 0.9 and 1.3 ppm respectively. Poly (*i*-PP-*g*-MA) also shows, in addition to the PP characteristic peaks, strong peaks at 2.38 and 2.42 ppm, which is related to the methylene and methine groups of grafted MA ring respectively (Fig. 2b).



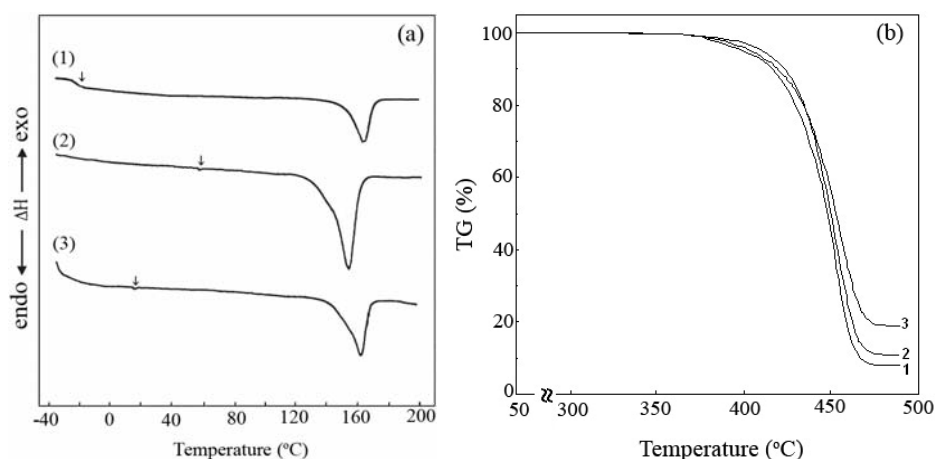
**Figure 2.**  $^1\text{H-NMR}$  spectra for (a) CA grafted *i*-PP and (b) MA grafted *i*-PP.

#### *Thermal behavior and crystallinity of graft copolymers*

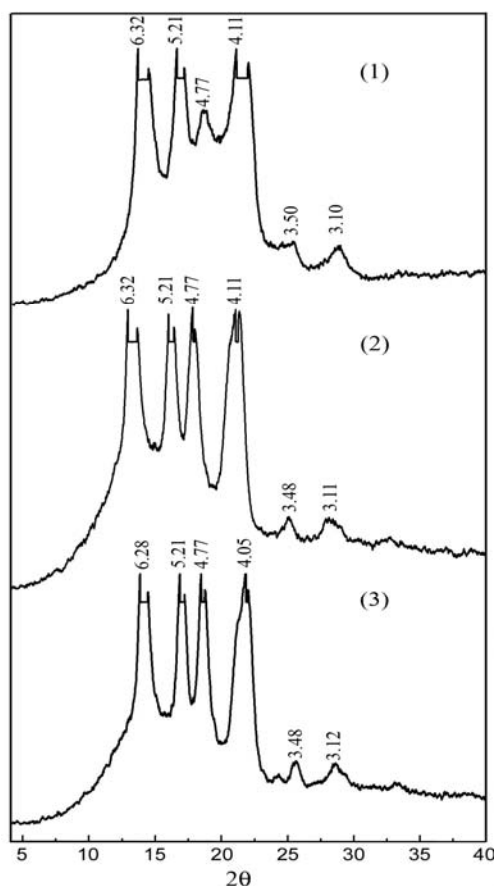
The effects of the composition on the thermal behavior, crystallization parameters, and crystallinity of synthesized functional *i*-PPs were determined with DSC, TGA and XRD analysis. The effect of variation of grafted monomer content on melting temperature ( $T_m$ ) is given in Table 1.

Figure 3 shows the DSC and TGA thermograms of copolymers prepared from the different monomer type. The thermograms showed sharp endotherms during heating. The grafted *i*-PP has a lower  $T_m$  than the ungrafted PP. This may be due to the grafting, which destroys the ordered structure of *i*-PP crystals. The chain degradation of *i*-PP during grafting may also result in a reduction of  $T_m$ .

The degree of crystallinity of the sample was determined by measuring the enthalpic change. The crystallinity values depend on carboxylic acid contents of the grafted



**Figure 3.** a) DSC and b) TGA curves of (1) virgin *i*-PP, (2) CA grafted *i*-PP, and (3) MA grafted *i*-PP.



**Figure 4.** XRD patterns (1) ungrafted (virgin) *i*-PP; (2) CA grafted *i*-PP; (3) MA grafted *i*-PP.

*i*-PPs. The observed differences between crystallinity values for all the grafted copolymers are related to carbonyl group contents of monomers onto *i*-PP backbone. It is known that the functionalization caused an increase in the polarity of the medium, intensifying the interaction forces between the grafted *i*-PP molecules, and then increased the polymer crystallinity [3,35]. The  $\Delta H_m$  results show that the crystallinity of grafted PP is higher than that of virgin PP.

The results obtained by TGA analysis indicate that the degradation reaction does not occur under the reaction conditions. The thermal stability was slightly increased by the presence of CA and MA. The initial decomposition temperature and overall degradation values of all the grafted copolymers are changed little compare with *i*-PP.

The X-ray diffraction patterns of *i*-PP and its grafts are shown in Fig. 4. The observed peaks around 14, 17, 18.6, 21.5 and 28.8° are common signals for all studied polymer systems. In all the grafted polymers, intensity of peak at 18.6° essentially increases. The overall degree of crystallinity is 33.6 % for virgin *i*-PP and around 49-43 % for the graft copolymers; it can be proposed that the strong polar grafted fragments have obvious effect on the nucleation mechanism and crystal growth model.



## Conclusion

Functionalized *i*-PP's were prepared in a solution grafting process at 160°C by using TCB as solvent and DCP as radical initiator. The effect of concentration on the anhydride content and grafting efficiency was investigated. In this study the grafted monomer content varies in the range of 0.01-0.56 mol %. As a general behavior, the grafted monomer content first increases with the comonomer content in the feed, reaches a maximum value and then decreases. The maximum grafting is achieved at 7.5 wt. % for CA monomer content in the feed. The result obtained by FTIR, DSC and XRD analyses indicated that the glass-transition temperature ( $T_g$ ) and crystalline properties of grafted *i*-PP were different from non-grafted *i*-PP. In addition, the melting point ( $T_m$ ) of the functionalized *i*-PP's changed little. It was shown that the structure, macro tacticity, crystallinity, crystallization and thermal behavior of synthesized *i*-PP grafts depend on the monomer unit concentration in polymers. It was shown that grafting reaction with CA proceeds more selectively than those for MA. That can be explained by relatively low electron-acceptor properties of citraconic double bond due to a CH<sub>3</sub> group in the  $\alpha$ -position, as well as by steric effect of this group. Obtained results will serve as basic data for our further studies of this CA/*i*-PP system in melt reactive extrusion for the preparation of the multilayered barrier PP films.

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