

Comparison of Maleic Anhydride Grafting onto Powder and Granular Polypropylene in the Melt by Reactive Extrusion

Yılser Güldoğan, Sinan Eğri, Zakir M. O. Rzaev, Erhan Pişkin

Chemical Engineering Department, Faculty of Engineering, Hacettepe University, Beytepe, 06532 Ankara, Turkey

Received 25 August 2003; accepted 13 November 2003

ABSTRACT: The grafting of powder and granular polypropylene (PP) with maleic anhydride (MA) was investigated in a reactive extrusion process with dicumyl peroxide (DCP) as an initiator. The effects of the MA and DCP contents in the feed on grafting were investigated. Under the experimental conditions applied in this study, the grafted monomer unit content was varied from 0.023 to 0.5%. The MA grafting efficiency of powder PP was higher than that obtained for the granular form of PP. In general, the grafting degree first increased with the MA or DCP content in the feed, then reached a maximum value, and finally decreased because of several possible alternative reactions during the grafting. The grafting of powder PP was more successful

because of better initial mixing and less diffusional resistance during the grafting. An increase in the MA content in the feed caused significant reductions in the melt-flow index of the graft copolymers. The results obtained with Fourier transform infrared, differential scanning calorimetry, and X-ray powder diffraction analyses indicated that the structure, macrotacticity, crystallinity, crystallization, and thermal behavior of PP changed with grafting and depended on the grafting degree. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3675–3684, 2004

Key words: poly(propylene) (PP); melt; reactive extrusion

INTRODUCTION

Polypropylene (PP) has gained an important position among polyolefins because of its versatile and broad range of applications. However, it also has limitations, such as a lack of reactive sites, poor hydrophilicity and dye uptake, low melting and sticking temperatures, poor compatibility with other polymers, and sensitivity to photooxidation. These limitations may be overcome by the graft copolymerization of various functional monomers onto the PP backbone via a free-radical mechanism.^{1–4}

The functionalization of polyolefins through the melt grafting of unsaturated polar groups onto the polymer backbone with organic peroxides as free-radical initiators has received considerable attention in recent years. The free-radical grafting of monomers is one of the most attractive methods of chemically mod-

ifying polymers. It involves the reaction between a polymer and a vinyl-containing monomer, which is able to form grafts onto the polymer backbone in the presence of free-radical-generating chemicals such as peroxides.^{5–7}

The grafting of PP with maleic anhydride (MA) represents one of the oldest attempts to bind polar groups to the PP chain to improve the compatibility of PP with polar polymers or its adhesion to polar surfaces such as glass and inorganic materials. The functionalization of PP through grafting with MA in the presence of an organic peroxide as an initiator has received much attention over the past decades. Such modifications are generally aimed at obtaining single-monomer grafts or short-length grafts that substantially change the polymer's chemical or reactive properties but not its mechanical properties.^{8–11}

Various monofunctional and bifunctional monomers have been used for the grafting of PP through different routes. Functionalized PP has been achieved successfully with solution-state,¹² melt-state,^{13,14} and solid-state routes.^{15,16} The melt-state process is called the reactive extrusion method; the molten polymer is mixed with a monomer and an initiator in an extruder at an elevated temperature. In the solution process, the polymer is dissolved in a suitable solvent at an elevated temperature, and a monomer is added with an initiator; the graft reaction mainly involves the ap-

Correspondence to: E. Pişkin (piskin@hacettepe.edu.tr).
Contract grant sponsor: Turkish Academy of Sciences.
Contract grant sponsor: State Department; contract grant number: 02 K 120 290-16.
Contract grant sponsor: POLINAS Plastic Industry & Commercial Co.
Contract grant sponsor: Turkish Scientific Technical Research Council; contract grant number: MİSAG-158.

pending of an MA molecule to ternary carbons along the PP backbone. Grafting in the melt is more economical and continuous (i.e., high production rates) and does not require any removal of solvents. The mechanism of the free-radical grafting or graft copolymerization of functional monomers onto PP and the selectivity of the grafting process have been studied in detail.^{17–20}

In this study, we investigated the grafting of MA onto PP in two different forms, a virgin form (powder) and a compounded form (granular), in the presence of dicumyl peroxide (DCP), with a twin-screw extruder system.

EXPERIMENTAL

Materials

Two different forms of isotactic polypropylene (iPP), powder and granular, were used, and both were supplied by Petkim Petrochemical Co. (Izmir, Turkey). The powder PP was virgin polymer (i.e., not compounded) taken directly from the PP polymerization reactor, whereas the granular PP was the final product marketed by Petkim Petrochemical. They had similar properties: melt-flow rate = 5 g/10 min (ASTM D 1238, 230°C and 2.16 kg), melting point = 166°C, and degree of crystallinity (χ_c) = 32.4%. The MA monomer (Fluka, Buchs, Switzerland) was purified by recrystallization from anhydrous benzene and by sublimation *in vacuo*; its melting point was 52.8°C, and the ¹H-NMR spectra showed a signal at 7.34 ppm (CH=, 2H singlet). The solvents toluene, methanol, and 1,2,4-trichlorobenzene (TCB) and the initiator DCP (Aldrich, Milwaukee, WI) were used without further purification. Calcium stearate, tetrakis methane, tris(2,4-di-*tert*-butylphenyl) phosphite, and tris(3,5-di-*tert*-butyl-4-hydroxybenzyl) isocyanurate were supplied by Petkim Petrochemical and were used as received.

Reactive extrusion

Granular PP

The grafting reaction was carried out in a twin-screw extruder. Before the extrusion, to homogeneously mix the initiator (DCP) with the PP granules, MA and DCP were dissolved in acetone and mixed with the granules, and the acetone was removed by evaporation.

A specially designed laboratory-size twin-screw extruder was used. The ratio of the length to the diameter of the extruder was 13.35. The temperature profile of the extruder zones was as follows: $T_1 = 165^\circ\text{C}$, $T_2 = T_3 = 130^\circ\text{C}$, and $T_4 = 175^\circ\text{C}$. The screw speed was set at 14 rpm, and all samples were extruded under a nitrogen atmosphere.

The MA-grafted PP was dissolved in TCB at 150°C under nitrogen, precipitated with methanol at 80–100°C, and then dried *in vacuo* at 100°C for 24 h.

Powder PP

Before the extrusion, powder PP was mixed with various stabilizers as recommended by the producer [Petkim Petrochemical; for 1 g of PP, 500 ppm calcium stearate, 470 ppm tetrakis methane, 312 ppm tris(2,4-di-*tert*-butylphenyl) phosphite, and 312 ppm tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)isocyanate] and then with the proper amounts of MA and DCP. The powder PP was extruded under the same conditions used for the granular PP, and it was cleaned and dried in the same way as well.

Characterization of graft PP

The number of carboxylic acid groups substituted onto PP chains during the grafting reactions was determined by a standard titration method, in which 0.4 g of the polymer was dissolved in 100 mL of toluene in a conical flask and a few drops of water were added to hydrolyze all anhydride groups into carboxylic acid. The hot solution was titrated with 0.05N KOH (in methanol). Thymol blue dissolved in methanol (1% w/v) was added to the titration medium as an indicator. The reaction medium was continuously agitated to prevent the precipitation of PP. The titration was continued until the blue color appeared and stayed about 12 s. The polymer was completely soluble at the reflux temperature and did not precipitate during titration. The carboxylic acid content was determined with the following equation and converted into the MA content, and the grafting efficiency is presented as the grafted MA units in PP (wt %) in the rest of this article:

Carboxylic acid content(wt%)

$$= \frac{[(45 \times N \times V)]}{m} \times 100 \quad (1)$$

where N and V are the concentration (mol/L) and volume (mL) of the titrant (potassium hydroxide/methanol solution), respectively, and m (g) is the weight of the grafted PP.

The Fourier transform infrared (FTIR) spectra of the grafted polymers were recorded with an FTIR spectrometer (Shimadzu 800, Kyoto, Japan) in the range of 4000–400-cm⁻¹ range with a 4-cm⁻¹ resolution. From the FTIR spectrum, the carbonyl index (CI) was calculated with the following equation:

$$\text{CI} = A^{1792}/A^{1167} \quad (2)$$

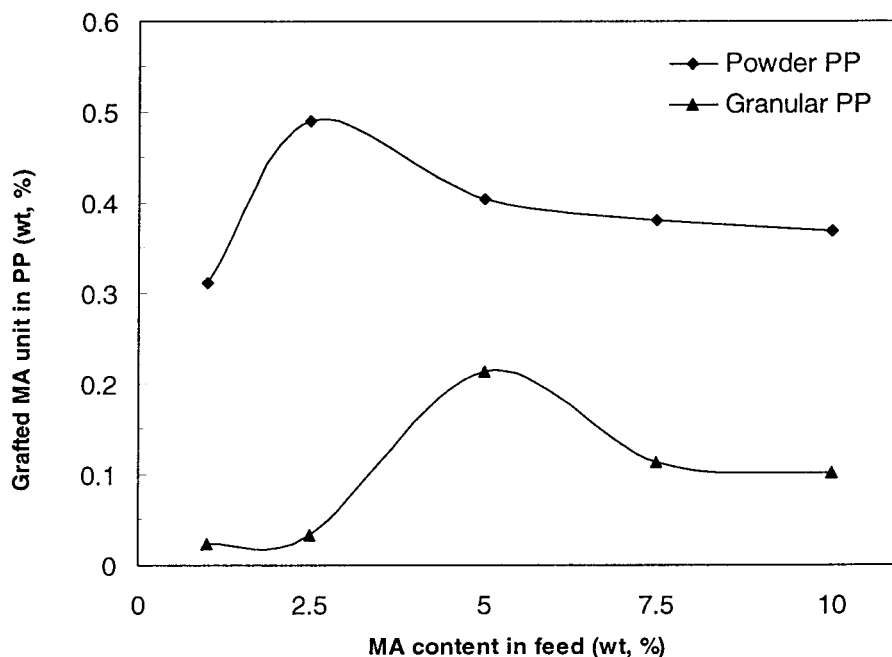


Figure 1 Effects of the MA content in the feed on grafting.

where A^{1792} is the absorbance 1792 cm^{-1} , characteristic of carbonyls from cyclic anhydrides with a five-member ring, and A^{1167} is the absorbance 1167 cm^{-1} , characteristic of CH_3 groups.²¹

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis of the grafted polymers were performed with a Thermal DSC-TGA-DTA analyzer (Setaram Labsys, Caluire, France) and Shimadzu DSC-50 analyzer under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The glass-transition temperature (T_g) and melting temperature (T_m) were read directly from the DSC scans within a wide temperature region of -50 to 200°C . The area under the melting peak was measured and was taken to be the melting enthalpy. The crystallinities of the polymers were determined with the following well-known equation:²²

$$\text{Crystallinity (\%)} = (\Delta H_f / \Delta H_f^0) \times 100 \quad (3)$$

where ΔH_f is the melting enthalpy of the polymer and ΔH_f^0 is the enthalpy of 100% crystalline PP ($\Delta H_f^0 = 209\text{ J/g}$).²³

X-ray powder diffraction (XRD) patterns of the synthesized polymers were recorded with a Philips manual spectrogoniometer (Almelo, The Netherlands) with $\text{Cu K}\alpha$ ($\lambda = 1.54184\text{ \AA}$) radiation over the range of $5^\circ \leq 2\theta \leq 50^\circ$. The χ_c values of the synthesized polymers were determined by the area ratio method with the following equation:²⁴

$$\chi_c = \frac{\int_0^\infty s^2 I_c(s) ds}{\int_0^\infty s^2 I(s) ds} \quad (4)$$

where s is the magnitude of the reciprocal-lattice vector, which is given by $s = (2 \sin \theta) / \lambda$ (θ is one-half the angle of derivation of the diffracted rays from the incident X-rays and λ is the wavelength); $I(s)$ and $I_c(s)$ are the intensities of coherent X-ray scatter from both the crystalline and amorphous regions and from only the crystalline region of the polymer sample, respectively; and d is the interplanar spacing.

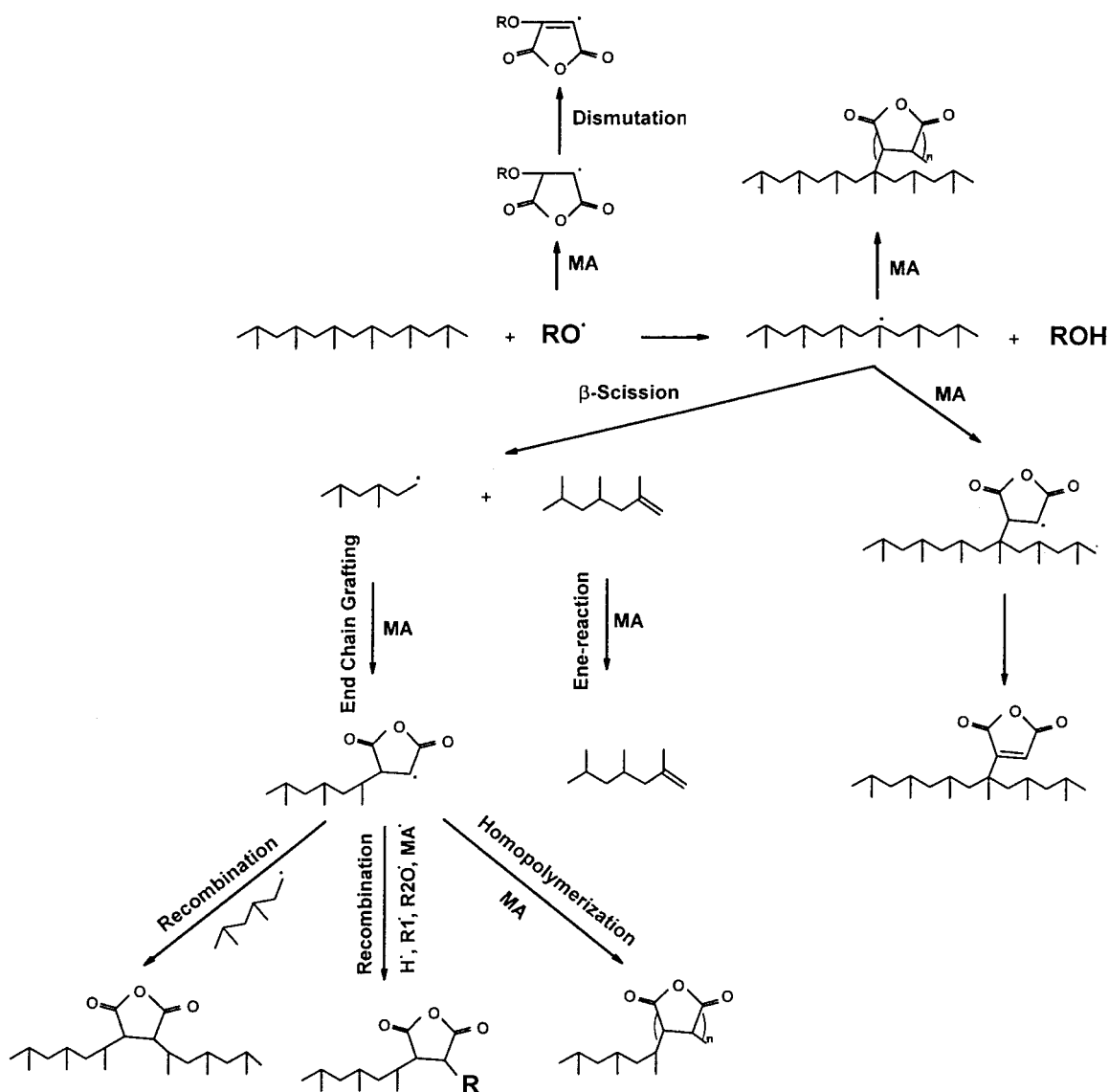
The melt-flow index (MFI) values of the polymers were obtained with an extrusion plastometer (ATS FAAR, Vignate, Italy) according to ASTM D 1238. The analyses were carried out twice under the following conditions because of the high MFI of most of the samples processed by extrusion: 230°C and 2.16 kg and 190°C and 2.16 kg .

RESULTS AND DISCUSSION

Effects of the MA content in the feed on grafting

In this group of experiments, the amount of the monomer (MA) used in the feed was varied over the range of 1–10 wt % at a constant initiator feed concentration of 1 wt %. The grafting efficiency, expressed as the grafted MA units in PP (wt %), was estimated for the

MA GRAFTING ON PP BY REACTIVE EXTRUSION



Scheme 1 Possible reactions of the grafting of PP with MA.

grafting reactions performed with different MA contents in the feed and is illustrated in Figure 1.

Figure 1 shows that the MA content of grafted PP is a function of the MA content in the feed, for both the granular and powder PP. Under the experimental conditions applied in this study, the grafted monomer unit content was varied from 0.023 to 0.5 mol %. Much higher values were observed for the granular PP. This was expected because of the much better mixing of MA and DCP with granular PP in the feed. Diffusion limitations in for the granular PP resulted lower grafting efficiencies.²⁵

For both types of PP, the effects of the MA feed content were similar: grafting increased first with

the MA content, reached a maximum value, and decreased afterward. The maximum MA grafting percentages achieved in powder and granular PP were about 2.5 and 5.0%, respectively. Similar behavior was observed by us in the solution grafting of PP and also by others.¹⁴ This behavior may be explained by several reactions that may occur during grafting (Scheme 1). The first reaction is the formation of radicals from the thermal decomposition (homolytic scission) of the initiator molecules, which can combine with the MA monomer (reaction I) as well as the PP backbone chains (reaction II). MA graft homopolymerization is one of the possible reactions (reaction III), but it normally does not take

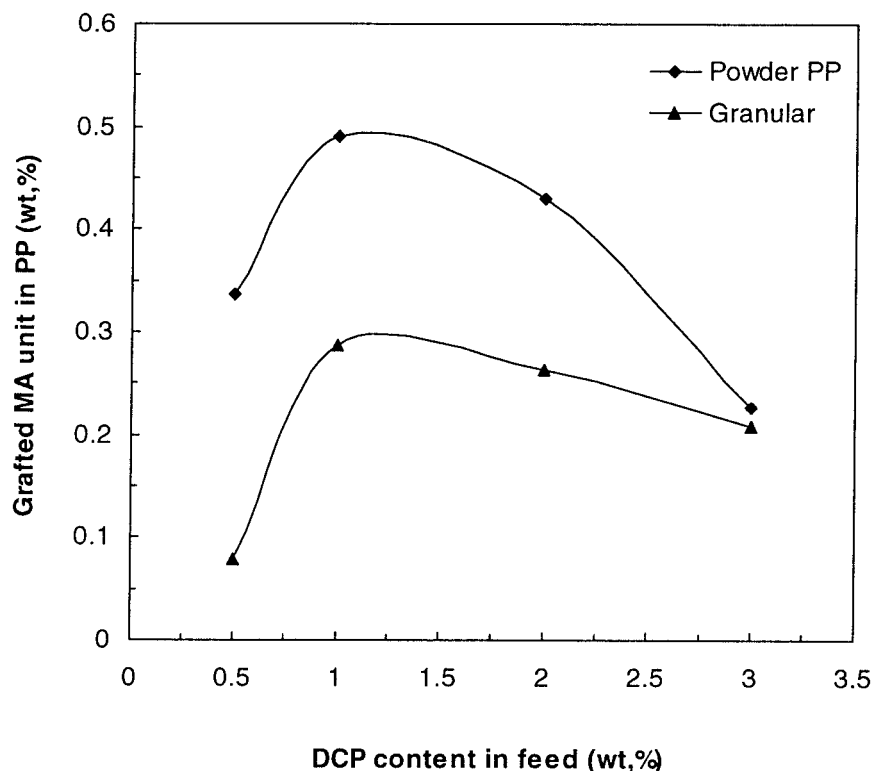


Figure 2 Effects of the DCP content in the feed on grafting.

place under the conditions that have been applied in this study. The MA radicals could be dismutationally terminated, this being the desired reaction in grafting (reaction IV). The macroradicals (the radicals on the PP backbone) may cause β scission, which, in turn, degrades the PP chains (a reduction in the molecular weights; reaction V). On the contrary, some of the macroradicals may combine with one another and lead to an increase in the molecular weight (reaction VI). Thermal oxidation may also be a possible cause of degradation of the PP chains (reaction VII). However, in our case, all the reactions were conducted under a pure nitrogen atmosphere; therefore, this side reaction could be neglected in solution grafting experiments. 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 MA content in the feed. However, with a further increase in the initial MA content, more and more radicals would be consumed in graft homopolymerization, and the effective radicals that initiate the macromolecular chain would be reduced. Therefore, the grafting degree of PP would decrease, and a maximum of grafting degree of PP would appear, as also seen in our results.

Effects of the initiator (DCP) content in the feed on grafting

In this group of experiments, the amount of the initiator (DCP) used in the feed was changed within the range of 0.5–3.0 wt % with constant concentrations of MA in the feed of 2.5 and 5 wt % for powder and granular PP, respectively. The grafting efficiency, expressed as the grafted MA units in PP (wt %), was estimated for the grafting reactions performed with different DCP contents in the feed and is given in Figure 1.

The type and amount of the initiator in the feed for MA grafting onto PP are among the most important parameters in grafting.^{10,17} As shown in Figure 2, grafting is also significantly affected by the DCP content in the feed for both powder and granular PP. At the same DCP content, grafting was higher for the powder PP feed because of the much better mixing in the feed, as discussed in the previous section. In general, grafting first increased with the initiator content in the feed, reached a maximum value, and then decreased. The maximum graftings were achieved with DCP concentrations in the feed of 0.5 and 0.22% for the powder and granular PP, respectively. This behavior may be explained as follows. The higher the peroxide concentration is in the reaction medium, the more primary radicals are formed and the higher the con-

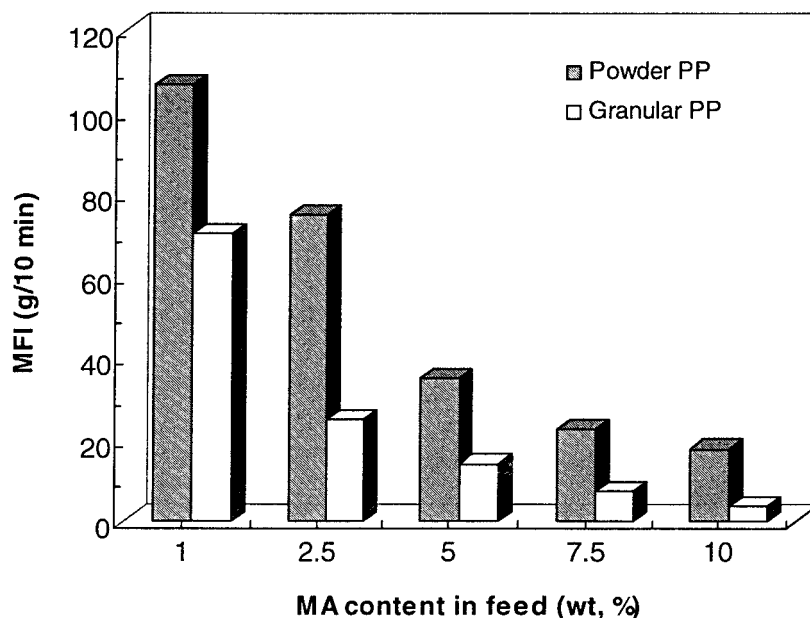


Figure 3 Changes in MFI with the MA content in the feed.

centration is of macroradicals available for the reaction with MA. When the peroxide concentration is very high; the extent of the side reaction of PP degradation increases. At a higher DCP content, the grafting degree decreases because of the faster termination rate of free radicals at higher free-radical concentrations.²¹

Changes in MFI

MFI depends on the molecular weight of the polymer, its branching, and its composition (in the case of copolymers), and it is very important in polymer processing. Here we have measured the MFI values of MA-grafted powder and granular PPs prepared with feeds with different amounts of MA. The results are given in Figure 3.

Figure 3 shows that MFI of modified PP is a function of the MA content, and it decreases very significantly when the MA content is increased. Most likely, this is due to chain scissions, which are more profound when the MA content of the medium is high because of the increased availability of MA molecules during the formation of macroradicals, which reduces MFI.

Structural peculiarities

The structure of MA-grafted PP was examined with FTIR transmission spectroscopy and XRD.

FTIR spectra

The presence of the MA groups grafted onto PP was confirmed with FTIR. Representative FTIR spectra of

the MA-grafted PPs are shown in Figure 4. As shown by the spectra of the anhydride-grafted polymers, the most significant difference in the spectral characteristics, in comparison with virgin PP spectra, corresponds to the carbonyl region ($1900\text{--}1700\text{ cm}^{-1}$),

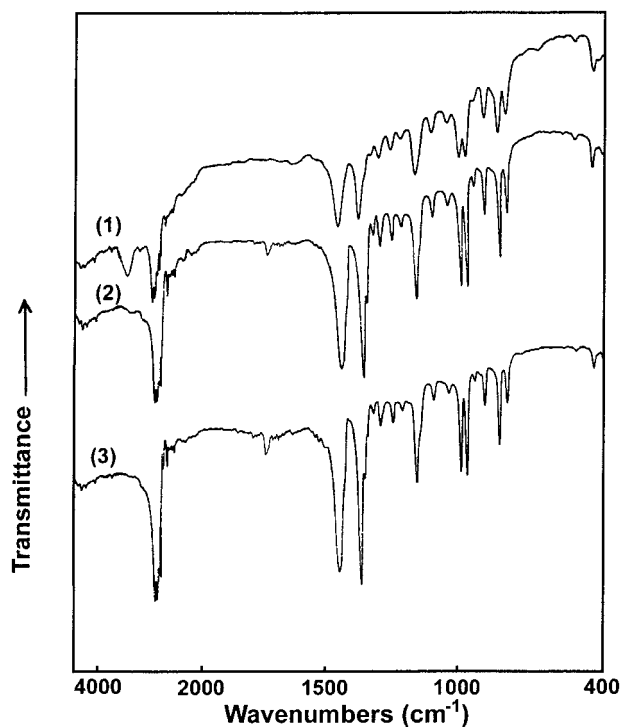


Figure 4 Representative FTIR spectra of (1) ungrafted (virgin) PP, (2) MA-grafted granular PP, and (3) MA-grafted powder PP.

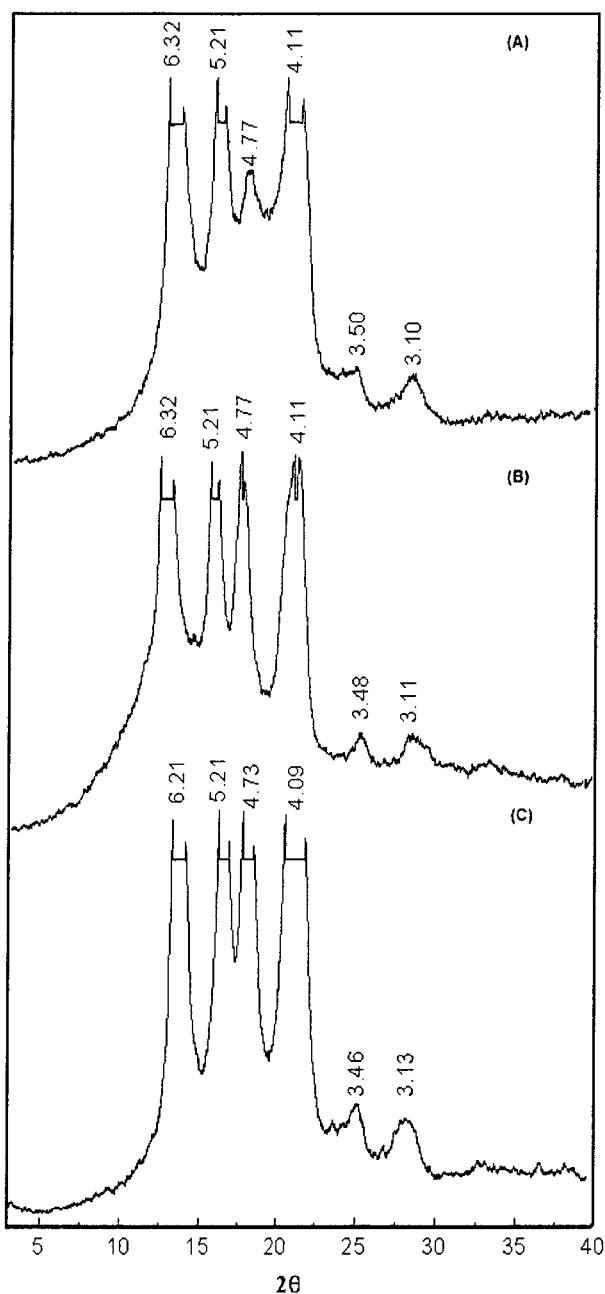


Figure 5 Representative XRD patterns of (A) ungrafted (virgin) PP, (B) MA-grafted granular PP, and (C) MA-grafted powder PP.

which contains new bands at 1835 (antisymmetric C=O stretching) and 1792 cm^{-1} (symmetric C=O stretching) for the grafted anhydride unit.^{26,27} A visible change in the intensity of the stretching and deformation bands for CH, CH₂, and CH₃ groups, which depend on the grafting degree, can also be observed. A comparative analysis of the spectra of virgin PP and grafted polymers for granular and powder PP feeds (Fig. 4) indicates an increase in the intensity of the

characteristic bands at 2961, 2923, 2874, and 2840 cm^{-1} (C—H stretching in CH, CH₂, and CH₃ groups), at 1470 and 1380 cm^{-1} (CH₂ and CH₃ deformations), and at 1162, 998, 974, 898, and 808 cm^{-1} , which are associated with various vibrations of the CH—CH₃ group conformation. The 998- cm^{-1} helix band characterizes the fraction of isotactic spirals in the PP structure and is caused by the interaction of CH₃ and CH₂ groups; the intensity of this band is usually used as a criterion of the regularity of iPP macrospirals. The 974- cm^{-1} band is assigned to the isotactic form of macromole-

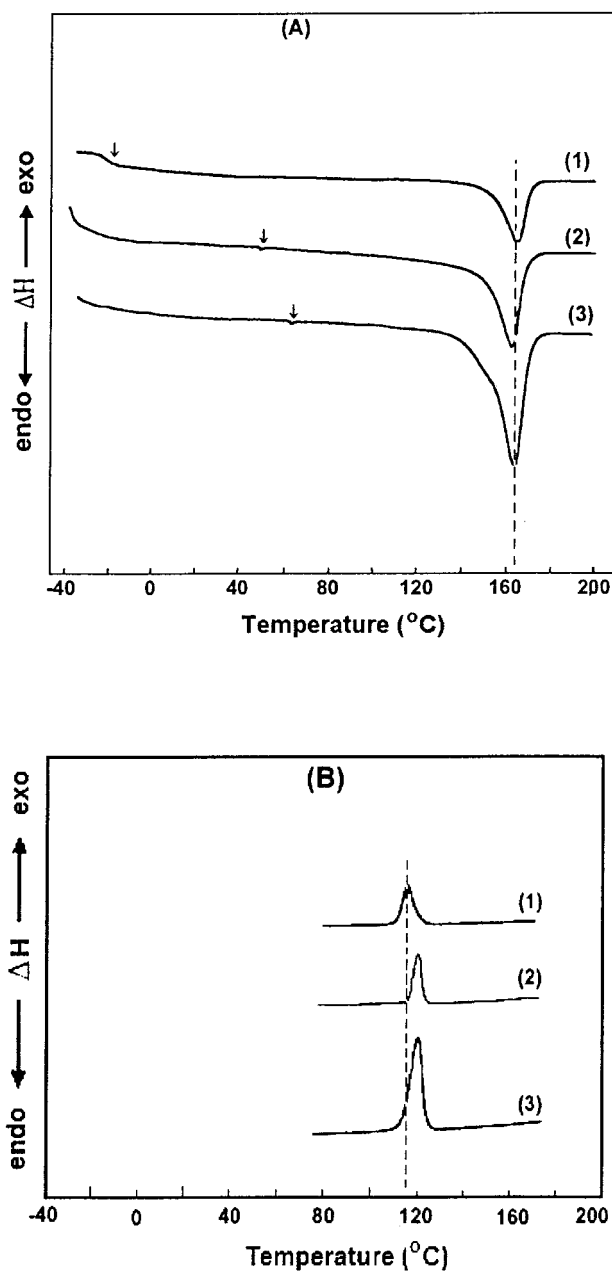


Figure 6 (A) DSC curves and (B) nonisothermal-crystallization DSC curves of (1) ungrafted (virgin) PP, (2) MA-grafted granular PP, and (3) MA-grafted powder PP.

TABLE I
Characteristics of Ungrafted PP and MA-Grafted PP with Different MA Contents

MA content in the feed (wt %)	Acid number (mg of KOH/g)	Grafted-MA content (mol %)	T_m (°C)	ΔH_m (J/g)	χ_c (%) by DSC
iPP	0.00	0.000	166.00	67.70	32.4
Powder PP feed					
1	3.58	0.319	163.90	107.70	51.5
2.5	5.61	0.500	165.19	111.23	53.2
5	4.63	0.413	164.91	110.30	52.8
7.5	4.35	0.388	164.64	110.13	52.7
10	4.21	0.375	164.20	109.00	52.2
Granular PP feed					
1	0.26	0.023	162.2	107.7	51.5
2.5	0.39	0.034	163.6	118.7	56.8
5	2.45	0.219	164.1	106.7	51.1
7.5	1.30	0.116	165.1	109.9	52.6
10	1.16	0.103	162.7	104.0	49.8

cules, the intensity of which visibly increases with an increasing content of grafted anhydridocarboxylic fragments in PP. The ratio of the absorbance values for these two bands (A^{998}/A^{974}) is used for the determination of the tacticity of the grafted PPs, the results of which are presented later in Table III. This is a well-known method for the determination of the tacticity of PP.²⁸

XRD analysis

The crystalline structure of grafted PPs was confirmed by XRD analysis, the results of which are illustrated in Figure 5. As evidenced from the recorded patterns, all the grafted polymers showed both amorphous and crystalline structures. The χ_c values of these polymers were determined by the area ratio method with the Bragg angles (2θ), the d values, and the relative intensities (I/I_0) of coherent X-ray scatter from the crystalline region.^{29–31}

As shown in Figure 5, the diffraction patterns of the MA-grafted PP show some differences in the 2θ positions in comparison with virgin PP. The peaks observed around 14, 17, 18.6, 21.5, 25.6, and 28.8° are common signals for all studied polymer systems. The intensity of the peak at 18.6° increased in all the grafted polymers synthesized. A visible increase in the intensity was also observed for the 25.6° position of the 2θ value.

Thermal properties of grafted PP

The effects of the composition and type of the PP feed on the thermal behavior, crystallization parameters, and crystallinity of synthesized functional PPs were determined with DSC, differential thermogravimetry, and XRD analysis. Figure 6 shows the DSC thermograms of virgin PP and its MA-grafted forms. The T_g , T_m , and melting enthalpy (ΔH_m) values for the MA-grafted polymers are presented in Tables I–III.

TABLE II
Characteristics of Ungrafted PP and MA-Grafted PP with Different DCP Contents

DCP content in the feed (wt %)	Grafted-MA unit content (mol %)	Acid number with titration (mg of KOH/g)	T_m (°C)	T_c (°C)	ΔH_m (J/g)	χ_c (%) by DSC
Powder PP feed						
0.5	0.344	3.86	165.27	121.3	107.14	51.4
1	0.500	5.61	165.19	122.3	111.23	53.2
2	0.437	4.90	163.07	118.7	109.25	52.3
Granular PP feed						
0.5	0.088	0.98	161.83	122.7	87.50	41.9
1	0.219	2.45	164.10	122.8	92.81	44.4
2	0.188	2.10	163.75	122.5	90.13	43.1

T_c = crystallization temperature.

TABLE III
Thermal and Crystallization Parameters of the Ungrafted and MA-Grafted PPs

Grafted iPP (1% DCP feed)	Grafted monomer linkage (mol %) by titration	CI (A^{1792}/A^{1167}) by FTIR	Tacticity (%) (A^{998}/A^{974}) by FTIR	DSC			χ_c (%)		T_d (°C) by TGA
				T_g (°C)	T_c (°C)	ΔH_c (J/g)	DSC	XRD	
Ungrafted PP	0.00	—	95.0	-28.3	115.5	96.3	32.4	33.6	379.3
PP-g-MA (powder PP feed)	0.50	0.355	95.5	60.7	122.3	104.7	53.2	52.9	405.3
PP-g-MA (granular PP feed)	0.22	0.190	97.7	50.71	122.8	93.2	49.7	45.5	395.0

T_c = crystallization temperature; T_d = decomposition temperature; (maximum values on the DTG peaks); ΔH_c = crystallization enthalpy.

T_m of the MA-grafted PP decreased significantly in comparison with those for the ungrafted PP in the powder and granular PP feeds. The grafted PP has a lower T_m than the ungrafted PP. This may be due to the grafting, which destroys the ordered structure of the PP crystals. The chain degradation of PP during grafting may also result in a reduction of T_m . The ΔH_m results show that the crystallinity of grafted PP is higher than that of virgin PP. This behavior may be due to the nucleation effect of the grafted monomer. The grafting caused an increase in the polarity of the medium, intensifying the interaction forces between the grafted PP molecules, and then increased the polymer crystallinity.

The TGA curves of the grafted PP are given in Figure 7. The results obtained by TGA indicate that the degradation reaction does not occur under the reaction conditions. The initial decomposition temperature and overall degradation values of all the grafted PPs changed very little in comparison with PP.

CONCLUSIONS

The graft copolymerization of PP in two forms (powder and granular) with MA was studied in the melt with a twin-screw extruder with DCP as a radical initiator. The effects of the MA and DCP concentrations on grafting were investigated. As a general be-

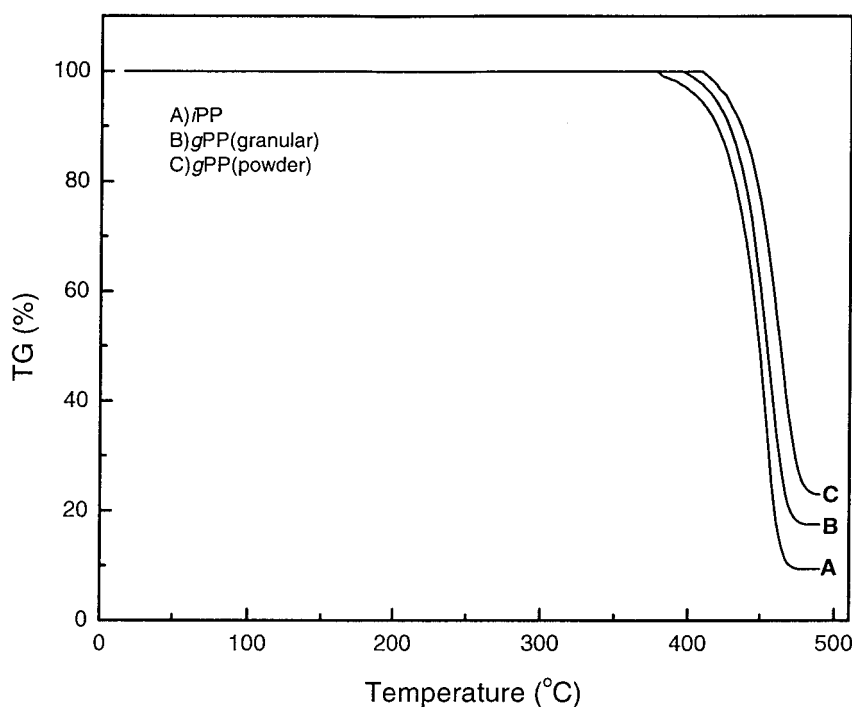


Figure 7 Representative TGA curves of (A) ungrafted (virgin) PP, (B) MA-grafted granular PP, and (C) MA-grafted powder PP.

havior, the grafting degree first increased with the MA or DCP content in the feed, then reached a maximum value, and finally decreased because of several possible reactions during the grafting. The grafting of powder PP was more successful because of better initial mixing and also less diffusional resistance during grafting. An increase in the MA content in the feed caused significant decreases in MFI of the graft copolymers.

The results obtained with FTIR, DSC, and XRD analyses indicated that the structure, macrotacticity, crystallinity, crystallization, and thermal behavior of the synthesized PP grafts depended on the grafting degree.

References

1. Mehta, I. K.; Kumar, S.; Chauhan, G. S.; Mishra, B. N. *J Appl Polym Sci* 1990, 41, 1771.
2. Srinivasa Rao, G. S.; Jain, R. C. *Polym-Plast Technol Eng* 2002, 41, 933.
3. Horak, H. *Macromol Chem Phys* 1994, 195, 3381.
4. Huang, H.; Zhu, C. Y.; Zhou, Z. F.; Liu, N. C. *React Funct Polym* 2001, 50, 49.
5. Chandranupap, P.; Bhattacharya, S. N. *J Appl Polym Sci* 2000, 78, 2405.
6. Rengarajan, R.; Parameswaran, V. R.; Lee, S.; Vicic, M.; Rinaldi, P. L. *Polymer* 1990, 31, 1703.
7. Machado, A. V.; Covas, J. A.; van Duin, M. *Polymer* 2001, 4, 3649.
8. Roove, D.; Slavovs, M.; Carlier, V.; Devaux, J.; Legras, R.; Momtaz, A. *J Polym Sci Part A: Polym Chem* 1995, 33, 829.
9. Gaylord, N. G.; Mehta, M. *J Polym Sci Polym Lett Ed* 1982, 20, 481.
10. Li, C.; Zhang, Y.; Zhang, Y. *Polym Test* 2003, 22, 191.
11. Betini, S. H. P.; Agnelli, J. A. M. *Polym Test* 2000, 19, 3.
12. Minoura, Y.; Ueda, M.; Mizunuma, S.; Oba, M. *J Appl Polym Sci* 1969, 13, 1625.
13. Ruggeri, G.; Aglietto, M.; Petraghani, A.; Ciardelli, F. *Eur Polym J* 1983, 19, 863.
14. Shi, D.; Yang, J.; Yao, Z.; Wanga, Y.; Huang, H.; Jing, W.; Yin, J.; Costa, G. *Polymer* 2001, 42, 5549.
15. Rengarajan, R.; Parameswaran, V. R.; Lee, S.; Vicic, M.; Rinaldi, P. L. *Polymer* 1990, 31, 1703.
16. Singh, R. P. *Surf Prog Polym Sci* 1992, 17, 251.
17. Moad, G. *Prog Polym Sci* 1999, 24, 81.
18. Patel, A. C.; Brahmabhatt, R. B.; Rao, P. V. C.; Rao, K. V.; Devi, S. *Eur Polym J* 2000, 36, 2477.
19. Lazar, M.; Hrcckova, L.; Fiedlerova, A.; Borging, E.; Ratzsch, M.; Hesse, A. *Angew Makromol Chem* 1996, 243, 57.
20. Russell, K. E. *Prog Polym Sci* 2002, 27, 1007.
21. Bettini, S. H. P.; Agnelli, J. A. M. *J Appl Polym Sci* 1999, 74, 247.
22. Gaylord, N. G.; Mishra, M. K. *J Polym Sci Polym Lett Ed* 1983, 21, 23.
23. Belofsky, H. *Plastics: Product Design and Process Engineering*; Hanser: Cincinnati, OH, 1995.
24. Rabek, J. F. *Experimental Methods in Polymer Chemistry*; Wiley: New York, 1980.
25. Moad, G. *Prog Polym Sci* 1999, 24, 81.
26. Triverdi, B. C.; Culbertson, B. M. *Maleic Anhydride*; Plenum: New York, 1982.
27. Slavovs, M.; Franquinet, P.; Carlier, V.; Verfaillie, G.; Fallais, I.; Legras, R.; Laurent, M.; Thyron, F. C. *Polymer* 2000, 41, 1989.
28. Dechant, J.; Danz, R.; Kimmer, W.; Schmolke, R. *Ultraspektroskopische Untersuchungen an Polymeren*; Akademie-Verlag: Berlin, 1972.
29. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiley: New York, 1989.
30. Feng, J.; Chen, M. *Polym Int* 2003, 52, 42.
31. Meille, S. V.; Bruickner, S.; Porzio, W. *Macromolecules* 1990, 23, 4114.