Melt functionalization of polypropylene with methyl esters of itaconic acid

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Abstract

Polypropylene (pp) was functionalized in the melt phase by grafting with itaconic acid derivatives. 2,5-dimethyl-2,5-bis(*tert*-buthyl-peroxy) hexane (lupersol 101) was used as radical initiator. A Brabender Plasticorder was used for all the experiments. The optimum conditions for the grafting reaction were 190°C, 75 rpm and 6 min. The itaconic acid derivatives used in this work were mono- and dimethyl esters. When dimethyl itaconate (DMI) was used as functional polar monomer, a maximum of 1.5% of grafting was reached. A similar value was found for grafting of monomethyl itaconate (MMI) where a maximum of 1.6% by weight of this monomer was incorporated in pp. The existence of grafted MMI and/or DMI in pp was confirmed by FT-IR spectroscopy. Carbonyl absorption bands from either MMI and/or DMI were observed in the FT-IR spectrum of the modified pp. The percentage of grafting attained was also followed by FT-IR analysis, where the amount of monomer incorporated in pp was estimated from a calibration curve established for the monomers used in this work. A systematic study of the reaction variables allowed the optimization of the grafting process. It was found that the percentage of grafting attained depends on the initial concentration of both monomer and initiator used in the reaction. Some properties of the modified pps were evaluated by employing dilute solution viscosity and differential scanning calorimetric (DSC) measurements. It was found that the molecular weight of the grafted polymer decreased with increasing percentage of grafting. DSC measurements indicated that functionalized pp samples have slightly higher crystallinity but show the same melting temperature as pp. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polypropylene; Functionalization; Itaconic acid

1. Introduction

Functionalization of polyolefins has been the subject of intense research works during the last two decades with the aim of introducing functional polar groups in their non-polar olefinic chains. Polypropylene (pp) has gained an important position among other polyolefins due to its versatile and broad range of applications. However, the application of pp in some technologically important fields seems to be limited due to its lack of polar functional groups as well as its inherent incompatibility with additives and other polar polymers [1–4].

The grafting of polar monomers onto pp via free radical reactions has gained wide industrial application and attracted scientific interest. A large number of works deal with the functionalization of pp with maleic anhydride, which is performed in solution [5–8], in the solid state [9,10] or in the pp melt phase [3,4,11–18]. Other polar monomers such as unsaturated carboxylic derivatives and vinyl or acrylic substances containing more than one functional group have also been investigated [3,7,14,18–31]. Our research group has been working on the functionalization of pp through solution free radical grafting reaction with itaconic acid and its dimethylester where reasonable percentages of grafting were achieved [7,14].

Modified pps with polar monomers have found wide applications in polymer blends in which the second component of the mixture is a polar polymer such as polyamides, polyesters, etc. It has been possible to compatibilize a large number of polar polymers by blending with functionalized polyolefins in order to improve the properties of the final products [32–47].

In this paper we present the results obtained from the functionalization of pp with itaconic acid derivatives in the melt phase. Some properties of modified pp are also reported.

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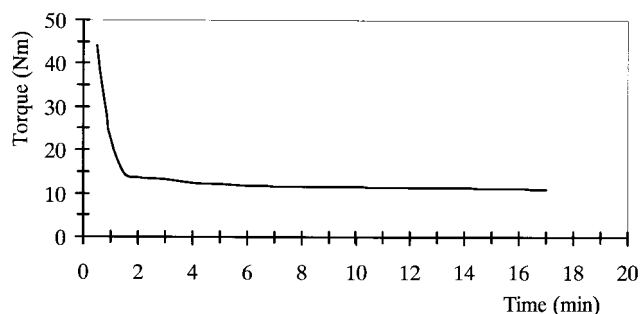 *E-mail address:* myazdani@ll.ciq.uchile.cl (M. Yazdani-Pedram).

Fig. 1. Variation of the melt viscosity of pp measured as a torque.

2. Experimental

A commercial sample of pp (MFI = 7.5 g/10 min; 230°C; 2.16 kg) in powder form was used in the grafting reactions. Itaconic acid was purchased from Aldrich. Monomethyl itaconate (MMI) and dimethyl itaconate (DMI) were synthesized by esterification of itaconic acid with methanol and their purity was checked by ¹H NMR spectroscopy. 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (lupersol 101) from Akzo was used as radical initiator. This organic peroxide has a half-life of 36 s at 190°C.

The grafting reactions were carried out in a mixing head of a Brabender-Plasticorder under a nitrogen stream at 190°C for 6 min and with a mixing speed of 75 rpm. Polypropylene was mixed with a predetermined amount of monomer and initiator before melt mixing. At the end of reaction the product was dissolved in hot xylene and was precipitated into acetone. The unreacted monomer, initiator and the possible homopolymer that could eventually form during grafting reaction was separated from grafted pp by exhaustive extraction of the sample in a Soxhlet for 24 h. Chloroform was used in the case of DMI and methanol in the case of MMI as solvents for the extraction. The extracted samples were dried under reduced pressure before their analysis.

The evidence of grafting as well as its extent, expressed as weight percent of grafting, was determined by FT-IR spectroscopy. FT-IR spectra were recorded on a Bruker IFS-28 spectrometer from 4000 to 400 cm^{-1}. Films of 600 μm thickness from pp and grafted samples were
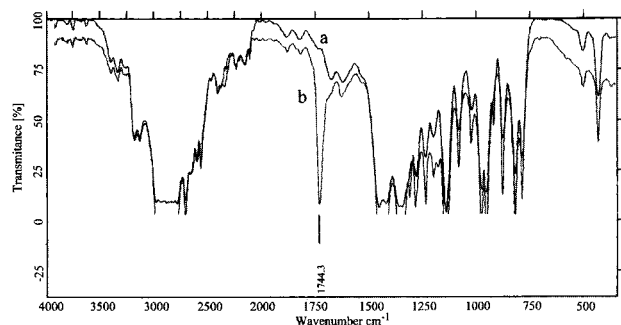

Fig. 2. (a) FT-IR spectrum of pp; and (b) pp grafted with DMI.

obtained by compression molding between steel plates covered with thin aluminum sheets at 190°C for 1 min.

The molecular weights of pp and functionalized pp samples were determined by dilute solution viscosity measurements using decalin as solvent at 135°C. An Ubbelhode dilution type viscometer was used. The viscometer was checked for kinetic energy correction by measuring the flow time for water at 20, 25, 30, 35 and 40°C before use. The concentrations of polymer samples was recalculated at 135°C by considering the volume correction factor for decalin at 135°C and by using the relation $C = 100M/1.07V$, where M is the mass of the polymer, V is the solvent volume in ml at 25°C and 1.07 is the volume correction factor. The intrinsic viscosity values $[\eta]$ of the samples were determined by single point method and the viscosity average molecular weights were calculated by employing the Kuhn–Mark–Houwink–Sakurada relation ($[\eta] = KM^a$) for pp in decalin with $a = 0.80$ and $K = 1.1 \times 10^{-4}$ dl/g.

3. Results and discussion

3.1. Determination of reaction conditions

pp was functionalized at 190°C in the melt phase either with DMI or MMI in a Brabender mixing chamber with a fixed mixing speed of 75 rpm during 6 min. The preliminary reactions carried out under the above conditions showed that the extent of grafting reached its maximum value for a determined amount of monomer and the initiator used for a particular reaction. Fig. 1 shows how the melt viscosity, measured as a torque, changes with the mixing time. It is seen from this figure that after 6 min of mixing at 190°C, the viscosity of molten pp reaches a constant value. The decay at the beginning is due to the plasticization of the pp at the initial state reaching a constant value with subsequent melting of the polymer.

3.2. Evidence of grafting

The existence of grafted MMI and/or DMI in pp was confirmed by FT-IR spectroscopy. Fig. 2 shows the FT-IR of pp grafted with DMI. The absorption band observed at 1745 cm^{-1} is due to the carboxyl group of the ester linkage of DMI and confirms the incorporation of this monomer in pp chains. The intensity of this band was compared with that of methyl group from pp centred at 1167 cm^{-1}. The 1745/1167 cm^{-1} band ratio was defined as the carbonyl index (I_{cE}). This can be considered as a measure of the extent of grafting of the monomer in pp either as single units and or poly(DMI) chains. The extent of grafting was converted into the incorporated weight percent (G_{DMI} in wt.%) of the monomer by using a calibration curve obtained from FT-IR analysis of the physical mixtures of pp with different amounts of DMI as shown in Fig. 3. These mixtures were obtained by melt mixing of pp and DMI in a Brabender mixing chamber
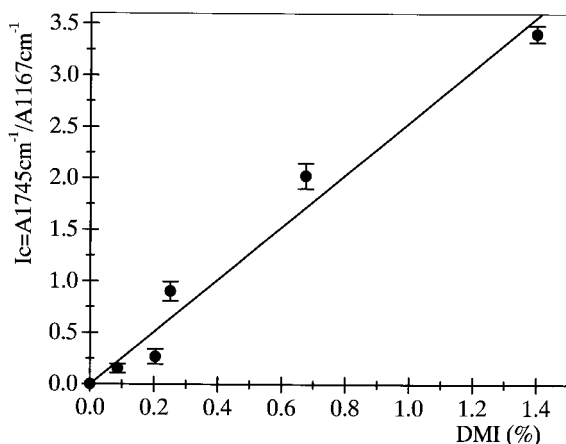
Fig. 3. FT-IR calibration curve for determining the weight percentage of grafted DMI onto pp.

at 190°C under nitrogen stream for 6 min. The percentage of grafting can be calculated using the relation:

$$G_{DMI} = 0.393 \frac{A1745 \text{ cm}^{-1}}{A1167 \text{ cm}^{-1}} = 0.393 I_{cE} \qquad (1)$$

In the case of MMI, the FT-IR spectrum of the modified pp with this monomer showed three absorption bands in the carbonyl region that are absent in the spectrum of unmodified pp (Fig. 4). The absorption bands at 1745 and 1710 cm^{-1} are due to stretching vibrations of the carbonyl groups of the ester and carboxylic acid of the monomer, respectively. The third absorption band centered at 1781 cm^{-1} was assigned to a carbonyl group from a five-member anhydride ring. The formation of five, six or even seven-member anhydrides through dehydration/de-esterification reactions of the monoesters of itaconic acid has been reported by Cowie and his co-workers [48,49] in their thermal stability studies of polymonoesters of itaconic acid. They came to the conclusion that the dehydration/de-esterification reactions were either inter- or intramolecular in nature. In order to quantify the amount of MMI incorporated in pp, two calibration curves were established. The first calibration curve was obtained by mixing different amounts of the monomer with pp. These physical mixtures of MMI and pp were prepared following the same
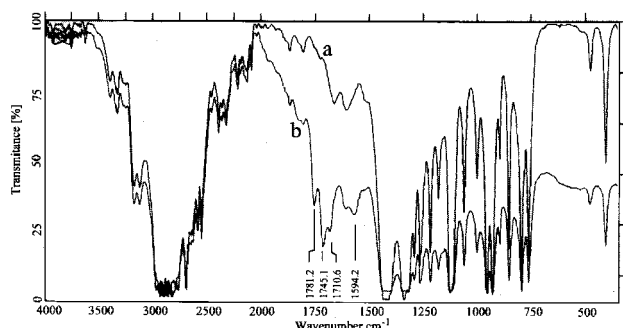

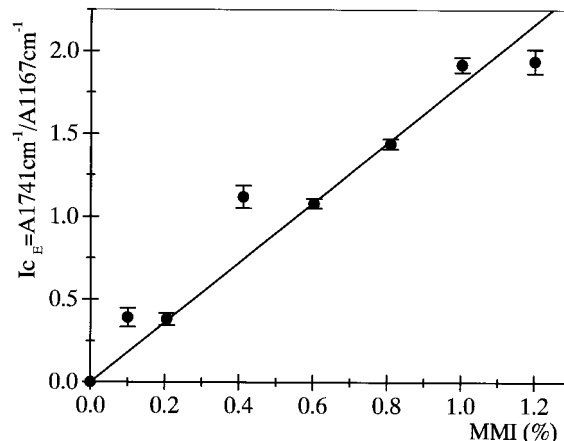Fig. 4. (a) FT-IR spectrum of pp; and (b) pp grafted with MMI.

Fig. 5. FT-IR calibration curve for determining the weight percentage of grafted MMI, in its monoester form, onto pp.

procedure used in the case of DMI, as already mentioned. The intensity of the sum of the absorption bands at 1710 and 1745 cm^{-1} was compared with that of methyl group from pp centered at 1167 cm^{-1}. This band ratio was defined as the carbonyl index, corresponding to the incorporation of the monomer as monoester (I_{cE}). The I_{cE} values were converted into the incorporated weight percent (G_{MMI} in wt.%) of the monomer by using a calibration curve obtained from FT-IR analysis of the physical mixtures of pp with different amounts of MMI as shown in Fig. 5.

Similarly, the intensity of the absorption band at 1781 cm^{-1} was compared with that of methyl group form pp centered at 1167 cm^{-1}. This band ratio was defined as the carbonyl index (I_{cA}) corresponding to the incorporation of the monomer in its cyclic anhydride form. To quantify the contribution of the MMI grafted in its cyclic form, a commercial anhydride namely 2-dodecene-1-il-succinic anhydride (DSA), was used as model compound. The physical mixtures of pp and DSA were prepared by melt mixing of pp with this compound at 190°C. The I_{cA} values were converted into the incorporated weight percent of the monomer ($G_{Anh.}$ in wt.%) by using a calibration curve. This calibration curve was obtained by FT-IR analysis of the physical mixtures of pp with different amounts of DSA as shown in Fig. 6.

The total percentage of the monomer grafted in the form of both ester and anhydride can be calculated from the two established calibration curves through the relation:

$$G_{MMI} = 0.554 \left[\frac{A1741 \text{ cm}^{-1}}{A1167 \text{ cm}^{-1}} \right] + 0.339 \left[\frac{A1788 \text{ cm}^{-1}}{A1167 \text{ cm}^{-1}} \right]$$

$$= 0.554 I_{cE} + 0.339 I_{cA}$$

$$(2)$$

However, an additional absorption band centered at 1594 cm^{-1} was identified by close examination of the FT-IR spectrum of the functionalized pp with MMI. This band
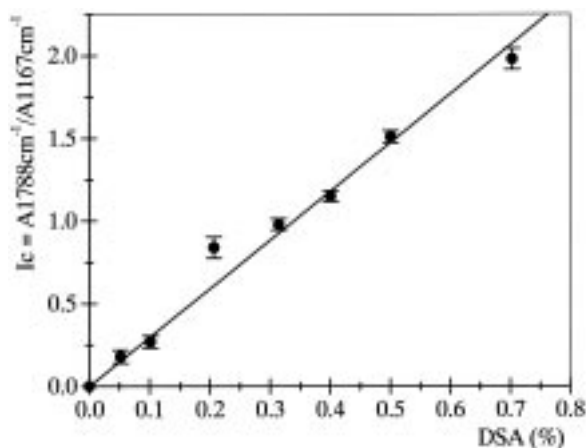
Fig. 6. FT-IR calibration curve for determining the weight percentage of grafted MMI, in its anhydride form, onto pp using DSA as model compound.

is absent in the FT-IR spectrum of the unmodified pp. The relative intensity of this band increases with increasing the initial concentration of MMI used in the grafting reaction. Although we have no clear explanation at this stage, it could be attributed to a product generated from decomposition of MMI. This decomposition product seems to be linked to pp chains since it was not possible to remove it by the extraction procedure used in this work.

3.3. Study of the reaction variables

3.3.1. Grafting with DMI

The influence of monomer and initiator concentrations on percentage of grafting of DMI attained is shown in Fig. 7. It is seen from this figure that the percentage of grafting (G_{DMI} in wt.%) increases with increasing amount of the monomer for a fixed concentration of the initiator. This could be explained by taking into account the number of pp macro-radicals that can be generated for a determined amount of the initiator used initially in the grafting reaction. The percentage of DMI grafted onto pp reaches its maximum value when the initial concentration of the monomer is
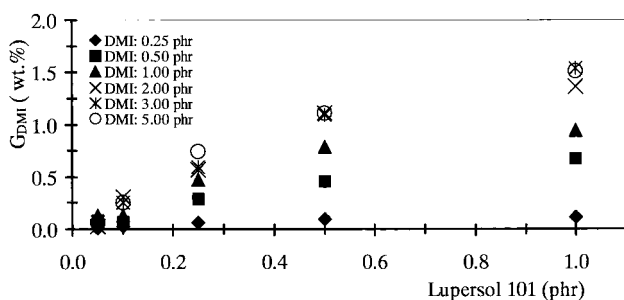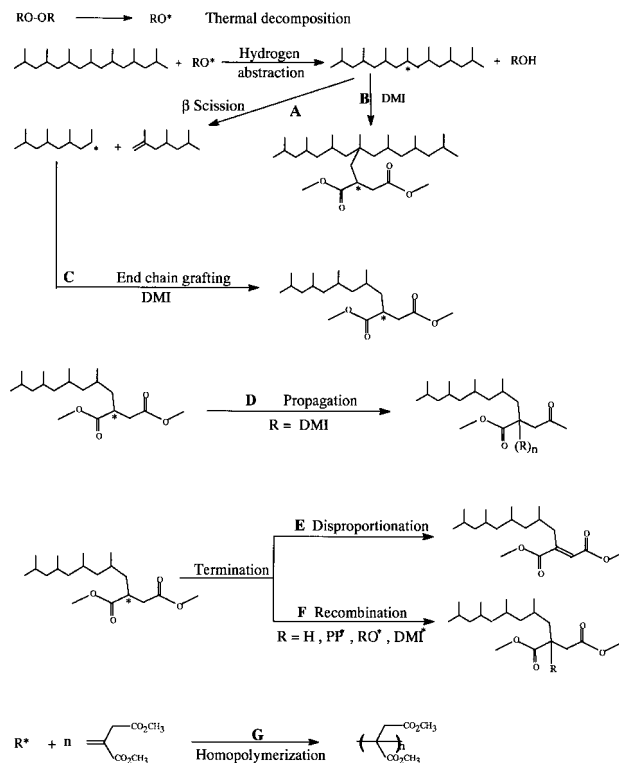

Fig. 7. Influence of the initial DMI and initiator concentrations on the percentage of grafted DMI onto pp at 190°C and for a reaction time of 6 min.

Scheme 1.

3 phr. However, the incorporation of DMI in pp does not increase further by increasing its concentration for a determined amount of the initiator used initially in the grafting reaction. This could be due to the partial homopolymerization of the monomer, since it has been shown [7,14,48,49] that itaconic acid esters polymerizes under reaction conditions used in this work, although it was not possible to isolate the homopolymer from the residue left after solvent extraction of the functionalized pp.

The sequence of reactions leading to grafting and possible homopolymerization of the monomer could be postulated by considering that organic peroxide used as initiator in grafting reactions undergoes homolytic rupture generating the primary radicals as shown in Scheme 1. The radicals generated by thermal decomposition of the peroxide could abstract the tertiary hydrogen atoms from pp chains leading to the formation of pp macroradicals as has been shown by De Roover et al. and Sclavons et al. [50,51]. The resulting macro-radicals could then undergo a process called β-scission where two new pp chains of lower molecular weights are generated. Consequently, one pp chain ended with a radical site is generated as the result of each β-scission event together with a second pp chain ended with a double bond. This has been discussed by De Roover et al. and Sclavons et al. when they studied the mechanism of melt functionalization of pp with maleic anhydride [50,51]. They stated that the β-scission is a fast intra-molecular reaction, taking place predominantly in the presence of organic peroxides in the melt phase. By analogy
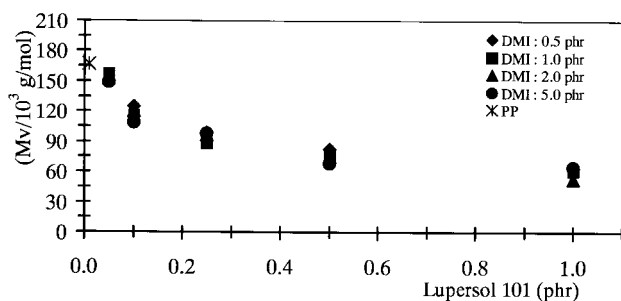
Fig. 8. Dependence of the viscosity average molecular weight of functionalized pp with DMI as function of the initial monomer and initiator concentrations used in grafting reactions.

Fig. 10. Relation between the amounts of grafted DMI onto pp and the amount of generated pp macroradicals (N).

to the case of maleic anhydride, a possible reaction mechanism for grafting of itaconic acid esters onto pp is shown in Scheme 1.

Considering that the monomer molecules can be grafted either as the chain end or along the pp backbone, the analysis of the amount of generated pp macroradicals, as the consequence of β-scission of the pp chains, should give information on the most probable grafting sites. This can be determined by measuring the molecular weight of functionalized pp samples with different initial amounts of the monomer and initiator used in the grafting reactions. Fig. 8 shows the variation of molecular weight of modified pp determined by dilute solution viscosity measurement as a function of monomer and initiator concentrations.

It can be seen from this figure that although the molecular weight of the modified pp decreases with the increasing concentration of the peroxide, no appreciable change in molecular weight is observed with the amount of monomer used initially in the reaction and for a determined concentration of the initiator. This could indicate that the grafting reaction takes place as chain end grafting, after β-scission, rather than along the pp backbone and that the monomer did not protect the pp from chain rupture. This can be further demonstrated by calculating the amount of pp macroradicals (N) created during grafting. This approach has been employed already by De Roover and Scalvons where $N =$
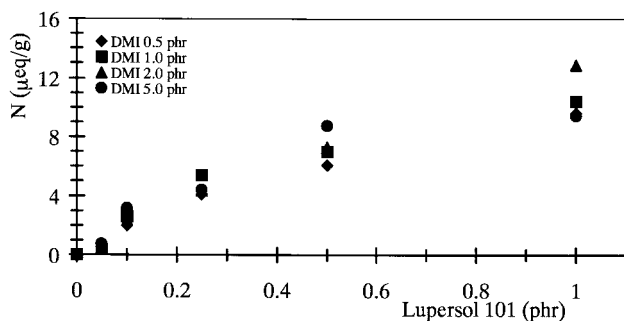

Fig. 9. Dependence of the amount of generated pp macroradicals (N) as function of the concentration of peroxide (lupersol 101) initially used in grafting reactions with DMI.
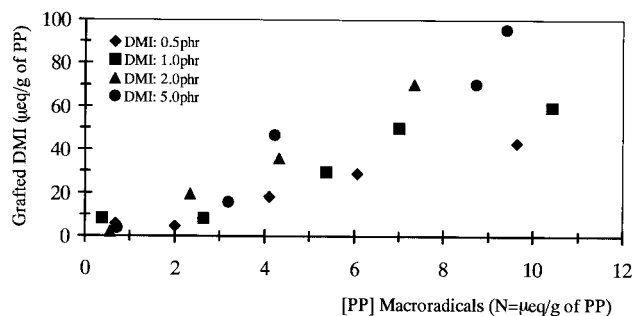
10^6 $(1/M_n - 1/M_n^\circ)$ was defined as the amount of pp macroradicals generated, in μeq/g of pp, by peroxide. In this relation M_n is the number average molecular weight of the pp after grafting (mol/g) and M_n° is the number average molecular weight of the pp before grafting (mol/g). If each primary radical generated from initiator decomposition induces one β-scission (Scheme 1), then the difference between the molecular weight of the pp after and before grafting represents the amount of the pp macroradicals produced as consequence of β-scission. This procedure was used in this work in order to obtain information on the possible grafting sites of DMI in pp chains. This was done by calculating the amount of grafted DMI expressed in mol/g of pp (G_{DMI} in wt.%/$M_{DMI} \times 100$) as well as the amount of pp macroradicals, assuming that β-scission takes place before the monomer is grafted. As can be seen in Scheme 1, thermal decomposition of the peroxide generates free radicals capable of abstracting the tertiary hydrogen atoms from pp chains and thus generating macroradicals. These macroradicals preferentially undergo β-scission, before grafting take place, since it has been shown that β-scission is a very fast intramolecular reaction [50,51].

Fig. 9 shows the amount of pp macroradicals generated ($[N]$/μeq per g of pp) as function of the initial concentration of the peroxide and for different amounts of the monomer used initially in grafting reactions. It is seen from this figure that pp suffers β-scission independent from the amount of monomer used initially in the reaction and that the amount of generated pp macroradicals increases with increasing peroxide concentration. On the other hand, if the amount of monomer that has been grafted onto P, ([DMI]/μeq per g of pp) is plotted against the amount of generated pp macroradicals, the results shown in Fig. 10 is obtained. It can be seen from this figure that the number of grafted DMI molecules are more than unity for any initial monomer concentration used in the grafting reaction. This indicates that DMI is grafted as short polymeric chains rather than as monomeric units, reaching a maximum of 10 monomer units in length. Similar result was obtained by Pan et al. [31] in their study on solid-phase grafting of glycidyl methacrylate onto pp, where they demonstrated that the monomer
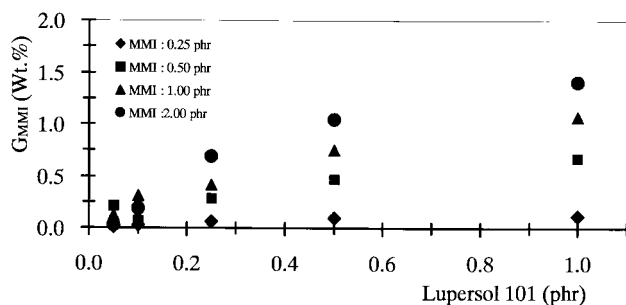
Fig. 11. Influence of the initial MMI and initiator concentrations on the percentage of grafted MMI onto pp at 190°C and for a reaction time of

Fig. 13. Dependence of the amount of generated pp macroradicals (*N*) as function of the concentration of peroxide (lupersol 101) initially used in grafting reactions with MMI.

was grafted as polymeric chains of different length rather than as single monomeric units.

3.3.2. Grafting with MMI

The effect of monomer and initiator concentrations on the extent of grafting attained with MMI is shown in Fig. 11. It can be seen from this figure that the amount of MMI incorporated in pp increases with monomer concentration for a determined amount of the initiator used in the grafting reaction. This behavior is expected since at higher monomer concentrations, more monomer is available for grafting onto a determined number of active sites that can be generated by a fixed amount of the initiator used initially in the reaction.

The extent of pp chain degradation was also determined in this case by measuring the viscosity average molecular weights of the modified samples. The molecular weight of MMI grafted pp samples as function of the monomer and initiator concentrations are shown in Fig. 12. The same tendency as in the case of grafting DMI is observed with the difference that, when 5 phr of monomer was initially used for grafting, less molecular weight breakdown was observed. This indicates that again grafting occurs mainly as chain end grafting and that the monomer did not protect the pp from β-scission. Although apparently the modified pp samples show less reduction in molecular weight, this could be attributed to the possible slight gelling of the modified pp

resulting from reaction of the polymer with products generated from decomposition of the monomer. Undoubtedly, the presence of even small amount of gelled polymer increases the solution viscosity. This in turn give rise to overestimate the molecular weights of functionalized pp samples as was determined through dilute solution viscosity measurements. This suggests that again the monomer is not grafted along the pp chains and therefore not protecting the polymer from chain scission. The latter can be demonstrated by applying the same analysis used in the case of DMI. Therefore, also in this case, the amount of pp chains generated ([*N*]/µeq per g of pp) as function of the initial concentration of the peroxide and for different amounts of the MMI initially used in the grafting reaction was calculated. The results obtained are shown in Fig. 13. It is seen from this figure that again pp suffers β-scission independent from the amount of monomer used initially in the reaction and that the amount of generated pp macroradicals increases with increasing peroxide concentration. If the amount of monomer that has been grafted onto pp, ([MMI]/µeq per g of pp), is plotted against the amount of the generated pp macroradicals, ([*N*]/µeq per g of pp), the results shown in Fig. 14 are obtained. This figure shows that more than one monomer unit has been incorporated in each pp macroradical and that the number of grafted monomer molecules is more than unity
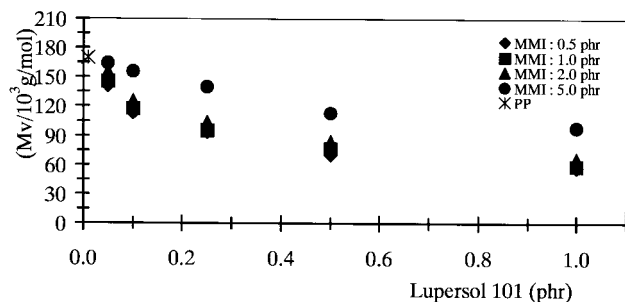

Fig. 12. Dependence of the viscosity average molecular weight of functionalized pp with MMI as function of the initial monomer and initiator concentrations used in grafting reactions.
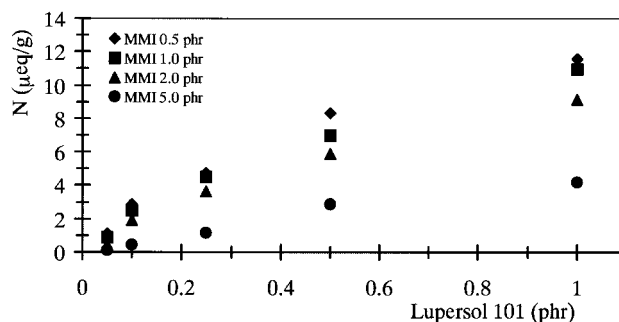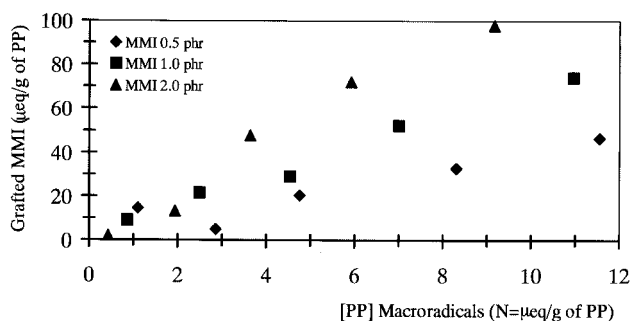

Fig. 14. Relation between the amount of grafted MMI and the amount of generated pp macroradicals (*N*).

for any initial concentration of MMI used in the grafting reaction.

3.4. Thermal analysis

Differential scanning calorimetry (DSC) was used to determine the melting temperatures of pp and functionalized pp samples. The thermal analysis of purified samples was conducted under a nitrogen stream with heating and cooling rates of 10°C/min. The temperature corresponding to the maximum in the melting endotherm was taken, after second heating run, as melting temperature (T_m). It was found that the grafting process did not affect the melting temperature of functionalized pp samples. The values obtained for heat of fusion, from DSC measurements, for pp and functionalized pp samples were used to estimate the percentage of crystallinity (x_c). This was done by using the value for enthalpy of fusion (ΔH_f) of 100% crystalline pp as 198 J/g. It was found that x_c increases by increasing the percentage of grafting from 45.7% for pp to 50.3% for sample with 1.5% of grafting. The increase in x_c values is also associated with the decrease in molecular weight of modified pp which is not unusual for crystalline polymers.

4. Conclusions

PP was functionalized at 190°C in the melt phase by grafting with MMI and DMI and by using lupersol 101 as free radical initiator. It was found that the percentage of grafting depends on both, monomer and initiator concentrations. A maximum of 1.5% by weight of grafting was reached when DMI was used as functional polar monomer. A similar value was found for grafting of MMI where a maximum of 1.6% by weight of this monomer was incorporated in pp. It was found that the molecular weight of the grafted polymer decreased with increasing percentage of grafting. The degradation of pp was attributed to the well-known β-scission process, induced by the peroxide used as radical initiator. It was concluded that MMI and/or DMI were grafted onto pp as short polymeric chains and that the chain end grafting could take place. Thermal properties of the modified pp samples, as measured by DSC, indicated slightly higher crystallinity of the functionalized polymers but having the same melting temperatures as pp.

Acknowledgements

References

[1] Mukherjee AK, Gupta BD. J Macromol Sci, Chem 1983;A19:1069.

[2] Grecco R, Maglio J, Musto PV. J Appl Polym Sci 1987;33:2513.

[3] Xu G, Lin S. J Macromol Sci-Rev Macromol Chem Phys 1994;C34:555.

[4] Naqvi MK, Choudhary MS. J Macromol Sci-Rev Macromol Chem Phys 1996;C36:601.

[5] Minoura Y, Ueda M, Mizunuma S, Oba M. J Appl Polym Sci 1969;13:1625.

[6] Weihua L, Jingyuan W, Yaoxian L, Yuwei L, Xinyi T. J Polym Engng 1995;15:271.

[7] Yazdani-Pedram M, Vega H, Quijada R. Macromol Rapid Commun 1996;17:577.

[8] Xie HQ, Feng DS, Guo JS. J Appl Polym Sci 1997;64:329.

[9] Lazár M, Hrckova L, Fiedlerová A, Borsig E, Ratzch M, Hesse A. Angew Makromol Chem 1996;243:57.

[10] Rätzsch M, Bucka H, Hesse A, Arnold M. J Macromol Sci Pure Appl Chem 1996;A33:913.

[11] Ho RM, Su AC, Wu CH, Chen SI. Polymer 1993;34(15):3264.

[12] De Roover B, Scalvons M, Carlier V, Devaux J, Legras R, Momtaz A. J Polym Sci, Part A: Polym Chem 1995;33:829.

[13] Hormehie AR, Hashemi SA, Meldurm IG, Waters DN. Polym Int 1997;42:117.

[14] Yazdani-Pedram M, Vega H, Quijada R. Macromol Chem Phys 1998;199:2495.

[15] Lin CW, Lee WL. J Appl Polym Sci 1998;70(2):383.

[16] Garcíamartinez JM, Laguna O, Areso S, Collar EP. J Appl Polym Sci 1998;70(4):689.

[17] Thompson MR, Tzogankis C, Rempel GL. J Appl Polym Sci 1999;71(3):503.

[18] Nachtigall SMB, Stedile FC, Felix AHO, Mauler RS. J Appl Polym Sci 1999;72(10):1313.

[19] Sun YJ, Hu GH, Lambla M. Angew Makromol Chem 1995;229:1.

[20] Rao GSS, Choudhary MS, Naqvi MK, Rao KV. Eur Polym J 1996;32:695.

[21] Beenen W, van der Wal DJ, Jansen LBM, Buijtenhuijs AB, Hogt AH. Macromol Symp 1996;102:255.

[22] Ciardelli F, Aglietto M, Ruggery G, Passaglia E, Castelvetro V. Macromol Symp 1997;118:311.

[23] Shearer G, Tzoganakis C. J Appl Polym Sci 1997;65:439.

[24] Wong B, Baker WE. Polymer 1997;38:2781.

[25] Vocke C, Anttila U, Heino M, Hietaoja P, Seppala J. J Appl Polym Sci 1998;70(10):1923.

[26] Demjen Z, Pukanszky B, Nagy J. Polymer 1999;40(7):1763.

[27] Anttila U, Vocke C, Seppala J. J Appl Polym Sci 1999;72(7):877.

[28] Garcíamartinez JM, Areso S, Laguna O, Collar EP. J Appl Polym Sci 1998;69(5):931.

[29] Plessier C, Gupta B, Chapiro A. J Appl Polym Sci 1998;69(7):1343.

[30] Hho YC, Kwon OH, Ryu HJ, Jung HC, Shin DS, Kim JS. J Appl Polym Sci 1998;70(12):2323.

[31] Pan Y, Ruan J, Zhou D. J Appl Polym Sci 1997;65:1905.

[32] Tang T, Li H, Huang B. Macromol Chem Phys 1994;195:2931.

[33] Bidaux JE, Smith GD, Bernet N, Mänson JAE, Hilborn J. Polymer 1996;37:1129.

[34] Sun YJ, Hu GH, Lambla M, Kotlar HK. Polymer 1996;37:4119.

[35] Rösch J, Mülhaupt R, Michler GH. Macromol Symp 1996;112:141.

[36] Kim S, Kim JK, Park CE. Polymer 1997;38:1809.

[37] Tjong SC, Meng Y. Polym Int 1997;42:209.

[38] Miller MM, Cowie JMG, Brydon DL, Mather RR. Polymer 1997;38:1565.

[39] Tjong SC, Chen SX, Li RKY. J Appl Polym Sci 1997;64:707.

[40] Sek D, Kaczmarczuk B. Polymer 1997;38:2925.

[41] Zhihui Y, Yajie Z, Xiaomin Z, Jinghua Y. Polymer 1998;39:547.

[42] Demarquette NR, Kamal MR. J Appl Polym Sci 1998;70(1):75.

[43] Bidaux JE, Smith GD, Mänson JAE, Plummer CJG. Polymer 1998;39:5939.

[44] Plummer CJG, Kausch HH, Creton C, Kalb F, Leger L. Macromolecules 1998;31(18):6164.

[45] Zhang XM, Yin JG. Macromol Chem Phys 1998;199(12):2631.

[46] Mehrabzadeh M, Nia KH. J Appl Polym Sci 1999;72(10):1257.

[47] Zhang XM, Yin ZH, Song YX, Yin JH, Chinese. J Polym Sci 1999;17(3):237.

[48] Cowie JMG. Pure Appl Chem 1979;51:2331.

[49] Cowie JMG, Haq Z. Br Polym J 1977;9:246.

[50] De Roover B, Sclavons M, Carlier V, Devaux J, Legras R, Momtaz A. J Polym Sci, Part A: Polym Chem 1995;33:829.

[51] Sclavons M, Carlier V, De Roover B, Franquinet P, Devaux J, Legras R. J Appl Polym Sci 1996;62:1205.