

Modification of poly(propylene) through grafting with dimethyl itaconate in solution

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SUMMARY: Functionalization of isotactic poly(propylene) (PP) with dimethyl itaconate (DMI) as functional polar monomer using 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (L101) as radical initiator was carried out in both boiling xylene and decalin as solvent media. The effect of DMI and the initiator concentration on the extent of grafting was studied by varying reaction time and temperature. It was found that temperature affects the percentage of DMI grafted onto PP, which is slightly higher for reactions carried out in xylene than in decalin. The results also show that the amount of DMI incorporated is proportional to the initial DMI and initiator concentrations used in the grafting reaction up to certain concentrations, and thereafter a decrease in the percentage of grafting (*G* in wt.-%) was found. The maximum value of grafting obtained was 0.7 wt.-%. The melt flow index (*MFI*) values increase with increasing initial amount of initiator used in the grafting reaction. The degradation of the PP chain is higher when xylene is used as solvent. *MFI* values of 20–100 were found for modified PP compared with 11.4 for the unmodified polymer.

Introduction

The modification of polymeric materials, especially polyolefins, with functional monomers has been the subject of extensive studies during recent years with the aim of obtaining advanced materials with improved technological properties. Several studies dealing with the homo- and copolymerization of olefins with functional monomers and/or modification of preformed polymers by grafting polar monomers have been published^{1–6}.

Poly(propylene) (PP) has gained an important position among other polymers due to its low cost and its versatile properties for commercial applications. It is well known that great scientific and technological efforts have been made to create new technologies for developing special poly(propylene)s, such as the use of metallocene catalysts to obtain new homo- and copolymers based on the propylene monomer, but having specific structures and properties⁵. However, the application of PP in various technologically important fields seems to be limited due to its lack of polar functional groups and its inherent incompatibility with additives and other polar polymers. Hence, it is necessary to functionalize this polyolefin either by copolymerization of propylene with polar monomers or by means of grafting reactions in which an organic peroxide initiator is used with an unsaturated polar monomer.

The grafting of polar monomers onto PP via free radical reactions has gained wide industrial applications and attracted scientific interest. The most studied modification of PP is that with maleic anhydride^{1,3–12}, which is performed either in solution^{7,10,11,13}, in the solid state^{14,15}

or in the PP melt phase^{3,4,8,9,12}. Other polar monomers such as unsaturated carboxylic derivatives and vinyl or acrylic substances containing more than one functionality have also been investigated^{3,13,16–22}.

It has been possible to compatibilize a large number of polymers by blending with functionalized polyolefins in order to improve the properties and stability of the final products. Within the modified polyolefins, PP is one of the polymers that show great commercial interest, since through its blending with other polar polymers some properties of ordinary PP, such as toughness, adhesion, dyeability, compatibility, etc., can be improved^{23–32}.

Our research group has been working on the grafting reaction of itaconic acid and its derivatives on PP chains. Results obtained from the functionalization of PP with itaconic acid using xylene and decalin as solvents have already been published¹³. The aim of this study is to approximate the reaction conditions to the real processing conditions of this polymer in an extruder. It was found that PP can be functionalized with itaconic acid in a homogeneous medium with short reaction times at reaction temperatures as high as 190 °C and with reproducible proportions of incorporated monomer. Preliminary results related to the modification of PP with itaconic acid derivatives have been reported recently²².

In this paper we present the results obtained from the functionalization of PP with itaconic acid derivatives, namely dimethyl itaconate (DMI), in solution, by using 2,5-dimethyl-2,5-bis(*tert*-butylperoxy)hexane (L101) as initiator and xylene and decalin as solvents. The functio-

nalized PP was characterized by FT-IR spectroscopy and melt flow index (*MFI*) measurements.

Experimental part

A commercial sample of PP (*MFI*: 11.4 g/10 min; 230 °C; 2.16 kg) in pellet or powder form was used in the grafting reactions. Dimethyl itaconate (dimethyl 2-methylenesuccinate) was prepared by direct esterification of itaconic acid (Aldrich) and its purity was checked by ¹H NMR spectroscopy. The peroxide used as radical initiator (L101) was obtained from Akzo and was used as received. This organic peroxide [(CH₃)₃C—O—O—C(CH₃)₂—CH₂—CH₂—(CH₃)₂C—O—O—C(CH₃)₃] is characterized by having a half life of 100 min at 132 °C, and 36 s at 190 °C. All solvents used were analytical grade from E. Merck (Darmstadt).

The grafting reactions were carried out in cylindrical glass reactors of 0.5 L capacity under a nitrogen stream in order to prevent oxidation of the PP. 10–15 g of PP were first dissolved in 200 mL of xylene and/or decalin by heating the mixture and stirring at 200 r.p.m. until complete dissolution was attained. Monomer and initiator were then added to the dissolved PP in that order. To calculate the amount of monomer and/or initiator necessary for a particular reaction, the total mass of PP to be modified was taken as 100 parts. Therefore, the monomer and initiator concentration were calculated as parts per hundred parts of PP (phr). After the reaction was finished, the reactor was cooled to 80 °C and the product isolated by precipitation in cold acetone, dried under reduced pressure and finally subjected to Soxhlet extraction with chloroform during 24 h to eliminate unreacted monomer and initiator, and to isolate the homopolymer from dimethyl itaconate that could eventually form during the grafting reaction.

The functionalized PP was characterized by FT-IR using a Bruker model IFS-28 FT-IR spectrometer. The extent of incorporation of DMI in PP was evaluated from the relation between the area of the carbonyl absorption band of grafted PP at 1745 cm⁻¹ and the absorption band of the methyl group of PP at 1167 cm⁻¹. This was defined as the carbonyl index (*I_c*) and can be considered as a measure of the extent of grafting. The percentage of grafting was determined by a calibration curve method based on FT-IR analysis of the mixtures of PP with different amounts of DMI obtained through melt mixing in a Brabender internal mixer.

Good reproducibility was found for all the grafting reactions. Average values of the percentage of grafting were taken from at least three different samples, and the mean values are presented in the corresponding figures.

Results and discussion

Evidence of grafting

The PP was functionalized by reacting the dissolved polymer either at 132 °C (boiling xylene) or at 182–192 °C (boiling decalin) with dimethyl itaconate using L101 as radical initiator. The existence of grafted dimethyl itaconate in PP was confirmed by FT-IR spectroscopy.

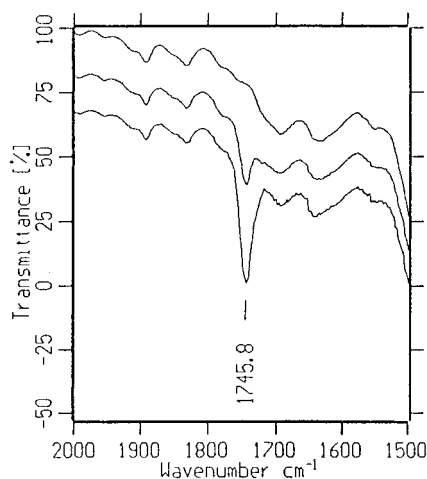


Fig. 1. FT-IR spectrum of PP (upper curve) and PP grafted with dimethyl itaconate with 0.2 wt.-% grafting (middle curve) and 0.7 wt.-% grafting (bottom curve)

Fig. 1 shows the FT-IR spectra for different amounts of monomer incorporated in the PP chains. It is possible to distinguish the carbonyl absorption band at 1745 cm⁻¹ due to the presence of the polar carboxyl group in the dimethyl itaconate molecule. The intensity of this band was compared with that of the methyl group from PP centered at 1167 cm⁻¹. The 1745 cm⁻¹/1167 cm⁻¹ band ratio, defined as the carbonyl index (*I_c*), can be considered to be a measure of the extent of grafting. Fig. 1 shows clear evidence of the grafting with different initial concentrations of dimethyl itaconate used in the grafting reaction. The extent of grafting was converted into the incorporated weight percent (*G* 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. 2. These mixtures were obtained through melt mixing of PP and DMI in a Brabender mixing chamber at 190 °C.

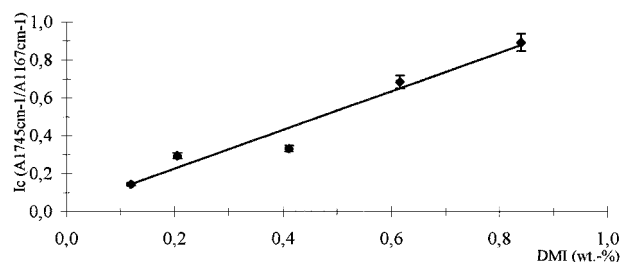
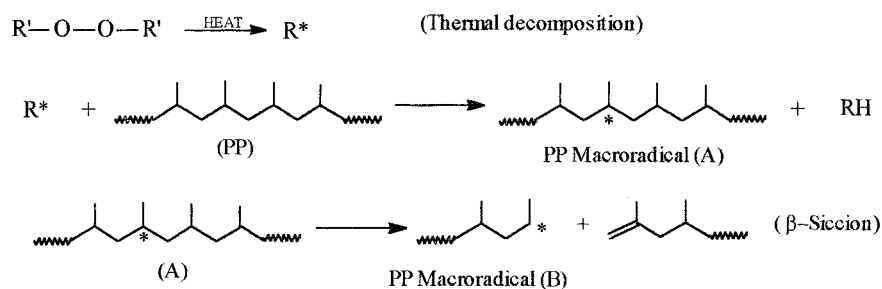


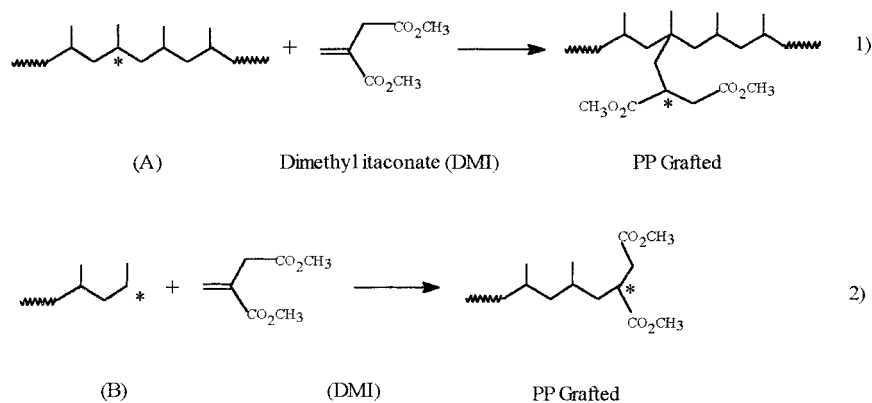
Fig. 2. FT-IR calibration curve for determining the grafting percentage of DMI

In analogy to the case of itaconic acid, a probable mechanism for the grafting of dimethyl itaconate onto PP is shown in Scheme 1¹³.

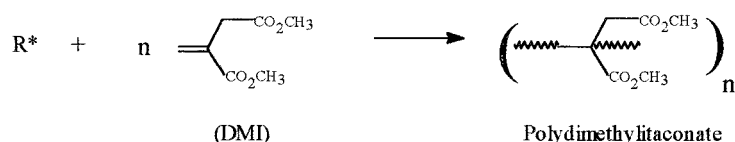
Scheme 1:



Two possible way to chain extention or chain termination



Homopolymerization of DMI



Reaction parameters

Reaction time and initiator concentration

The first parameter studied was the influence of reaction time and varying initiator concentrations on the percentage of grafting for a constant monomer concentration of 10 phr with xylene as solvent. The results obtained are presented in Fig. 3. From this study it is seen that the percentage of grafting depends initially on the reaction time up to about 90 min for initial peroxide concentrations lower than or equal to 1.0 phr. Thereafter the amount of grafted monomer does not increase substantially. A possible explanation for this behavior could result from: (a) a decay of PP macroradicals following β -scission, due to coupling reactions with the primary radicals from the

initiator decomposition, and (b) a limited amount of monomer remaining for grafting. Taking into account the half life of the initiator at 132 °C, which is about 100 min, the percentage of grafting does not increase markedly with reaction time beyond 90 min when most of the initiator has been consumed. When the initiator concentration was 3.0 phr, the tendency for reaching a maximum attainable grafting was shifted to higher reaction times.

As expected, the incorporation of DMI in PP increases with increasing concentration of the initiator from 1 to 3 phr (Fig. 3). This is most probably due to the increasing number of active sites formed in PP leading to a higher percentage of grafting. However, the amount of monomer incorporated practically reaches a constant value in each case. This behavior could be due to: (a) a reduced availability of the active radical sites for grafting on PP chains,

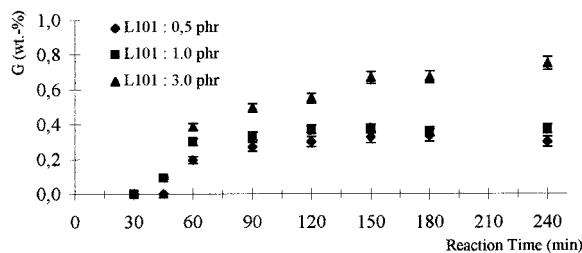


Fig. 3. Influence of reaction time and initiator concentration on the grafting percentage of DMI onto PP using xylene as solvent. Xylene was used at its boiling temperature (132 °C); monomer concentration 10 phr

(b) a decreasing efficiency of the initiator due to recombination reactions of the primary radicals produced by its decomposition, and (c) an increasing probability of the reactions of PP macroradicals with primary radicals from the initiator.

Monomer concentration

The effect of the initial monomer concentration on the percentage of grafting was studied for a constant reaction time of 60 min in xylene as the solvent, in order to reproduce the results obtained when the effect of the reaction time was studied. A reaction time of 60 min was chosen because the degree of grafting attained by that time was considered to be sufficient in terms of obtaining an acceptable amount of grafting and also a modified polymer with a low extent of degradation and *MFI* values close to those of unmodified PP. The results obtained are shown in Fig. 4, demonstrating that the amount of monomer incorporated in the PP chains increases as the initial monomer concentration increases up to 20 phr. The percentage of monomer incorporated decreases when the initial concentration is higher than that value. This could be due to the tendency of DMI to homopolymerize, since it is well known that this monomer undergoes free radical polymerization, in contrast to maleic anhydride that does not homopolymerize under the reaction conditions used in this study. In fact, the amount of homopolymer obtained from DMI, isolated from the grafted PP by exhaustive solvent extraction, was greater for the higher initial concentrations of monomer used in the grafting reaction. This may indicate that DMI was grafted as short polymeric chains rather than as succinic derivative units. It is also possible that the number of active sites that can eventually form on the PP chains is determined by the initial concentration of the peroxide used in the grafting reaction. The value obtained for the maximum incorporation of DMI in PP, 0.7 wt.-% for reactions carried out in xylene, could indicate that chain end grafting of the monomer after β -scission of PP is the predominant mechanism of the functionalization reaction.

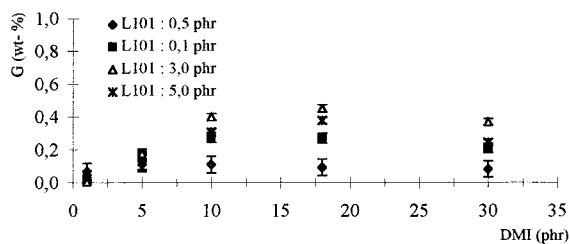


Fig. 4. Variation of DMI incorporated onto PP for different initial monomer and initiator (L101) concentrations and a constant reaction time of 60 min in xylene. Xylene was used at its boiling temperature (132 °C)

Temperature effect

In order to determine the effect of temperature, the grafting reactions were carried out in decalin as solvent. The results referring to the influence of reaction time against percentage of grafting for a constant monomer concentration of 10 phr and different initiator concentrations are shown in Fig. 5. Very similar trends to those obtained for reactions carried out in xylene were observed. The figure shows that at a higher reaction temperature (182–192 °C) the amount of dimethyl itaconate incorporated in the PP chains is lower for the whole range of initiator concentrations studied, with the difference that the percentage of grafting reaches an almost constant value in shorter reaction times for the three initiator concentrations used in these grafting reactions, as compared to the grafting reactions carried out in xylene.

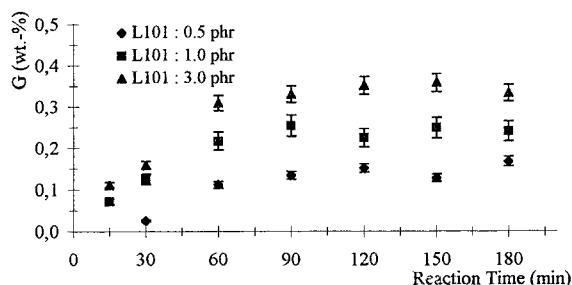


Fig. 5. Influence of reaction time and initiator concentration on the grafting percentage of DMI onto PP using decalin as solvent. Decalin was used at its boiling temperature (182–192 °C); monomer concentration 10 phr

The effect of the initial monomer concentration on the extent of its incorporation in PP was also studied in decalin as solvent. The results obtained for the percentage of grafted monomer corresponding to different initial concentrations of dimethyl itaconate are shown in Fig. 6. In our previous studies, a dependence of the degree of grafting on the initial monomer concentration was also observed when itaconic acid was used as the polar monomer for the functionalization of PP in xylene and/or decalin as solvents¹³. It can be seen from Fig. 6 that at a

Tab. 1. Comparison between percentage of grafting (G) and MFI values of PP grafted with DMI for reactions carried out in xylene and decalin, using 10 phr of DMI

Reaction time min	Initiator phr	G in wt.-% (Xylene)	G in wt.-% (Decalin)	$MFI^a)$ (Xylene)	$MFI^a)$ (Decalin)
60	0.5	0.19	0.11	37.1	49.9
90		0.27	0.13	40.5	–
120		0.30	0.15	48.9	32.9
150		0.33	0.13	54.2	20.2
180		0.34	0.17	59.4	46.8
60	1.0	0.38	0.22	84.6	–
90		0.33	0.25	95.1	25.2
120		0.37	0.19	>100	24.5
150		0.36	0.25	>100	–
180		0.37	0.21	>100	–
60	3.0	0.38	0.15	88.8	–
90		0.49	0.16	>100	>100
120		0.55	0.31	>100	–
150		0.67	0.30	>100	>100
180		0.67	0.35	>100	–

a) g/10 min, 230 °C, 2.16 kg.

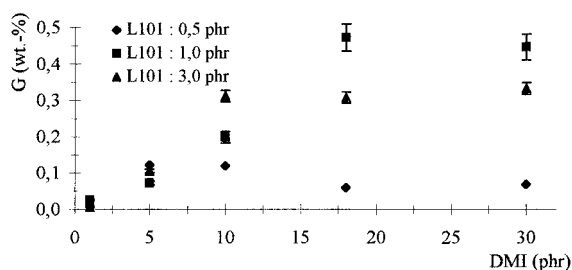


Fig. 6. Variation of DMI incorporated onto PP for different initial monomer and initiator (L101) concentrations and a constant reaction time of 60 min in decalin. Decalin was used at its boiling temperature (182–192 °C)

higher reaction temperature (182–192 °C) the incorporation is lower for all monomer concentrations studied. In this case, perhaps, the generation of primary radicals produced by thermal decomposition of the initiator is much faster, and therefore the generation of PP macroradicals is promoted due to a greater number of primary radicals produced as a result of the faster decomposition of the initiator. Consequently, the possibility for propagation of the grafted poly(dimethyl itaconate) chains is lowered, giving rise to a lower degree of grafting. It is also possible that the transfer reactions, which do not contribute to the grafting process, are promoted at higher temperatures. These includes transfer reactions to a polymer chain, a monomer, solvents, etc., as has been suggested by De Roover et al.⁹⁾ On the other hand, the available number of primary free radicals necessary for subsequent homopolymerization of the monomer is lowered. In fact, the

amount of homopolymer isolated from the reactions in decalin was lower compared with the grafting reactions carried out in xylene under the same reaction conditions.

Properties of modified poly(propylene)

As can be seen in the FT-IR spectra, there is no evidence of an oxidation of the polymer formed under the reaction conditions used in this study, since no carbonyl absorption band due to an oxidation of PP (1730 cm^{-1}) was detected. The degradation of PP during the grafting reactions was followed by MFI measurements. It was observed that the extent of chain degradation of the PP during the functionalization reaction was not significant, and was lower in decalin than in xylene used as solvent media. The MFI values of modified PPs with different degrees of grafting were in the range of 20–100, as compared to that of the unmodified polymer with $MFI = 11.4$. These results are presented in Tab. 1. The fact that the MFI values of the modified PP in decalin are lower than those obtained for reactions carried out in xylene may be due to a possible chain extension process of the grafted polymer. This means probable recombination reactions between PP macroradicals, peroxide radicals with PP macroradicals before β -scission, PP grafted with growing poly(dimethyl itaconate) macroradicals and PP macroradicals, and between two PP chains grafted with growing poly(dimethyl itaconate) macroradicals. The above assumptions could be explained considering that the half life of the initiator is much lower in decalin than in xylene, and therefore an important number of primary

radicals are generated from the thermal decomposition of the peroxide in decalin. Consequently, the probability of the above mentioned reactions increases.

It is concluded that PP can be functionalized with dimethyl itaconate in a homogeneous medium at reaction temperatures reaching as high as 192 °C and with a controllable percentage of incorporated monomer. The grafting reaction could be initiated by an organic peroxide. The percentage of grafting depends on the monomer and initiator concentrations as well as on the reaction temperature. A chain degradation of PP occurs during the functionalization reactions, most probably as a result of β -scission of the polymeric chains. The extent of PP degradation was found to have a direct relation with the peroxide concentration used in the grafting reaction. It is possible that DMI was grafted as poly(dimethyl itaconate), since the homopolymer from this monomer was separated from the grafted PP. At present we have not clear evidence for this. Since the functionalization of PP is usually carried out in the melt phase, our future aim is to approach this type of reaction to the reactive extrusion method in the molten state.

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