

Effect of polyolefin structure on maleic anhydride grafting

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Abstract

A series of polyolefins with different ethene/propene ratios was grafted with maleic anhydride (MA) both in the melt and in solution. The MA graft content and the degree of branching/crosslinking or degradation were determined by FT-IR and rheometry, respectively. The MA graft content is low for polyolefins with high propene content, increases as the propene content decreases and reaches a plateau at propene levels below 50 wt.%. Branching/crosslinking occurs for polyolefins with low propene content, while degradation is the main side reaction for polyolefins with a high propene content. A detailed chemical mechanism is proposed to explain these results. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Considerable efforts have been made in producing new polymer materials with an improved performance/costs balance. This can be achieved by (co)polymerisation of new monomers or by modification or blending of existing polymers. From a research and development point of view, the latter routes are usually more efficient and less expensive [1,2]. Free radical grafting of monomers is one of the most attractive ways for the chemical modification of 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 [1,2]. Such reactions can be performed in solution, yielding a relatively homogeneous medium because the reactants are easily mixed and the polymer and monomer are usually soluble. However, carrying out these reactions in the melt, i.e. via reactive extrusion, has economic advantages, as the modification is very fast and the need for solvent recovery is avoided.

Free radical grafting of maleic anhydride (MA) onto polyolefins has gained wide industrial application. MA modified polyolefins are an essential part of many plastics formulations. They are used as chemical coupling agents, impact modifiers, and compatibilisers for blends and filler

reinforced systems [1–3]. Despite the large number of studies on MA grafting and the commercial success of MA grafted polyolefins, the chemical mechanism involved in the functionalisation process is not fully understood. Several studies have shown that the reaction pathways depend on the polyolefin molecular structure. When a peroxide is used as initiator, crosslinking or chain scission may occur simultaneously with the grafting reaction. The dominant side reaction for polyethylene (PE) is crosslinking [4–12], for polypropene (PP) is chain scission [13–17] and in the case of ethene/propene rubber (EPM) both crosslinking and chain scission may occur [18–24]. Grafting levels of PE are substantially higher than those of EPM and PP [25,26]. More subtle effects have been demonstrated. For example, Avella et al. [27] and Martinez et al. [20] showed that tacticity is also an important parameter and they found that the grafting level for atactic polypropene (aPP) was significantly higher than that of isotactic polypropene (iPP). Recently, considerable progress has been made in elucidating the structure of MA grafted polyolefins. It was shown unambiguously that the MA graft structure consists of single saturated MA units [27]. Grafting occurs on secondary and/or tertiary carbons depending on the polyolefin composition. When long methylene sequences are present, grafting occurs mainly on secondary carbons. Actually, MA units seem to be attached to the polyolefin chain in close proximity to each other [28]. Despite the progress that has been made, the effect of the polyolefin composition on MA grafting is still not fully understood, due to the lack of true

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Table 1
Characteristics of the polyolefins used

| Polyolefin | Grade | Propene (wt.%) | Dynamic viscosity (7×10^{-3} Hz at 200°C) (Pa s) |
|------------|---|-----------------|--|
| HDPE1 | DSM Stamylan HD 2H280 | 0 | 4.3×10^2 |
| HDPE2 | DSM Stamylex 7359 | 0 | 2.0×10^2 |
| LDPE | DSM Stamylan LD 1922T | 0 | 4.4×10^2 |
| LLDPE1 | DSM Stamylex LL 09-258 | 10 ^a | 3.5×10^2 |
| LLDPE2 | DEX Plastomers Exact 2M009 | 28 ^a | 7.4×10^2 |
| EPM1 | Exxon PE 805 | 22 | 3.5×10^4 |
| EPM2 | Exxon EPM X1703 F2 | 27 | 1.2×10^4 |
| EPM3 | DSM Keltan 740 | 40 | 2.0×10^5 |
| EPM4 | Exxon VA 404 | 55 | 4.5×10^4 |
| EPM5 | Shell non-commercial hydrogenated polyisoprene | 60 | 2.5×10^3 |
| EPM6 | DSM Stamylan P 83E10 | 90 | 3.6×10^4 |
| EPM7 | DSM Stamylan P RA12MN40 | 95 | 8.4×10^2 |
| iPP | DSM Stamylan P 13E10 | 100 | 1.7×10^4 |
| aPP | Borealis non-commercial product | 100 | 5 |
| sPP | R&D sample DSM | 100 | 6.0×10^3 |

^a Octene instead of propene.

insight into the reaction mechanism. Actually, most grafting studies have been carried out using different grafting recipes (type and amount of peroxide and MA content) and different processing conditions (type of reactor, screw speed and temperature). As a result, a fair comparison of the experimental data in order to establish the true effect of the structure on grafting and crosslinking or degradation can not be made. This work aims at investigating the effect of the polyolefin structure on grafting and crosslinking or degradation both in the melt and in solution. A series of polyolefins with different ethene/propene ratios was modified with MA under similar conditions. The grafting yield was determined by FT-IR and the extent of crosslinking/degradation by dynamic rheological measurements.

2. Experimental procedure

2.1. Materials

The materials used together with their main characteristics are listed in Table 1. Maleic anhydride (MA) from Aldrich, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (DHBP) from Akzo Nobel and biphenyl from Acros were used as monomer, initiator and solvent, respectively. The recipe used (5 phr of MA and 1 phr of peroxide) was identical in all the experiments.

2.2. Modification

Modification of the polyolefins was carried out both in the melt and in solution. Melt grafting was carried out in a modular Leistritz LSM 30.34 intermeshing corotating twin-screw extruder [29]. The screw configuration adopted,

with three mixing zones consisting of sequences of kneading blocks and/or left hand elements, ensures efficient melting and homogenisation. In all experiments, the barrel set temperature was 200°C, the screw speed 75 r.p.m. and the throughput 5 kg/h. The premixed materials were fed in the hopper. In order to collect small amounts of material during processing, six sampling devices were inserted in the barrel of the machine (for more details see Ref. [29]). The evolution of grafting along the extruder could, therefore, be carried out and is reported separately [30]. Since the present study involves a significant number of polymers, material sampling from the extruder was only done at the first kneading zone and extrudate. Consequently, samples collected from the freshly molten material at the first kneading zone and from the extrudate were quenched in liquid nitrogen in order to prevent further reaction. In the case of aPP and syndiotactic polypropylene (sPP), melt modification was done in a Haake (Rheocord 90 equipped with a Rheomix 600) batch kneader under similar conditions, since only limited amounts of material were available.

Solution modification was performed in a glass reactor heated in an oil bath (180°C). Polymer, solvent and MA were added simultaneously in a 10/90/0.5 (w/w/w) ratio and the flask was purged with nitrogen. The materials were mixed with a glass stirrer until a clear solution was obtained. Then, the peroxide was added to start the grafting reaction. After 20 min (approximately 35 times the half life time of DHBP) the hot solution was precipitated in acetone (1/10; v/v) and the polymer was recovered for further characterisation.

2.3. Characterisation

The materials modified in the melt were dissolved in

Table 2

MA graft content (E/f) and dynamic viscosity (7×10^{-3} Hz at 200°C) of the various polyolefins after melt and solution modification (a, could not be determined due to extensive crosslinking; data in parenthesis are for products grafted in a batch kneader)

| Polyolefin | Melt modification | | | | Solution modification | |
|------------------|------------------------------|-------------------|------------------------------|-------------------|------------------------------|-------------------|
| | Kneading zone | | Extrudate | | E/f (1×10^{-3}) | Viscosity (Pa s) |
| | E/f (1×10^{-3}) | Viscosity (Pa s) | E/f (1×10^{-3}) | Viscosity (Pa s) | | |
| HDPE1 | 3 | 1.5×10^5 | 18 | 1.2×10^5 | 14 | 1.5×10^5 |
| HDPE2 | 6 | 1.1×10^5 | 21 | 9.3×10^4 | 13 | 5.1×10^4 |
| LDPE | 7 | 3.2×10^4 | 12 | 5.0×10^4 | 18 | 2.2×10^4 |
| LLDPE1 | 12 | 5.3×10^4 | 18 | 6.0×10^4 | 15 | 5.0×10^4 |
| LLDPE2 | 9 | 1.0×10^5 | 17 | 1.5×10^5 | 18 | 4.1×10^4 |
| EPM1 | a | 2.1×10^5 | a | 4.5×10^5 | – | – |
| EPM2 | 13 | 4.0×10^5 | 20 | 3.0×10^5 | 17 | 1.4×10^5 |
| EPM3 | a | 2.0×10^5 | a | 1.8×10^5 | 12 | 1.5×10^5 |
| EPM4 | 8 | 1.3×10^5 | 20 | 1.7×10^4 | 13 | 8.2×10^3 |
| EPM5 | 14 | 1.2×10^4 | 23 | 1.9×10^4 | 18 | 1.2×10^4 |
| EPM6 | 1 | 1.1×10^4 | 7 | 3.9×10^3 | 9 | 3.9×10^3 |
| EPM7 | 1 | 230 | 4 | 150 | 6 | 70 |
| iPP | 1 | 3.7×10^3 | 3(3) | 25 | 4 | 20 |
| aPP | | | (3) | | 5 | – |
| sPP | | | (3) | | 6 | 4.2×10^2 |
| EPM3/iPP (50/50) | 4 | 1.9×10^4 | 6 | 4.5×10^3 | 8 | 1.9×10^3 |

toluene (PE and EPM) or xylene (PP) under reflux until a clear solution was obtained. These solutions were then precipitated in acetone and filtered in order to obtain the purified products. The precipitated products obtained in the melt and in solution were dried in a vacuum oven for 1 h at 180°C. Thin films were prepared by compression-moulding and FT-IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. The grafted MA content is expressed as the extinction of the anhydride peak at 1785 cm^{-1} normalised by the film thickness (E/f).

For rheological measurements, the original and modified polyolefins were compression-moulded as discs of 4 cm in diameter and 2 mm in thickness for 10 min, at 200°C, under a pressure of 30 ton. Oscillatory measurements were carried out in a TA Instruments Weissenberg rotational rheometer with parallel-plate geometry. The gap and diameter of the plates was 1.8 mm and 4.0 cm, respectively. The linear viscoelastic material's response was measured at 200°C, imposing a constant strain of 0.01, and carrying out a frequency sweep from 4×10^{-3} to 40 Hz.

3. Results

The MA graft content and the dynamic viscosity (at constant frequency) of the different polyolefins modified in the melt and in solution are presented in Table 2. Data for melt modification for both the material collected from inside the extruder and from the extrudate are included. At the first kneading zone the conversion of the grafting reaction is significant, viz. 15–70% of the final conversion of the extrudate. The dynamic viscosity of the samples collected at the kneading zone is quite similar to that taken from the

extrudate. Thus, a considerable part of the various modification reactions occurs already in the first kneading zone, i.e. upon melting. The evolution of the reactions along the extruder axis will be discussed in a separate paper (Ref. [30]).

MA graft contents of the modified polyolefins both in the melt and in solution clearly depend on the initial polyolefin structure (Table 2 and Fig. 1), which is in agreement with the results of Hogt et al. and Avela et al. [25,26]. The MA content has a constant level until ~50 wt.% propene, it decreases to $E/f \sim 0.020$ – 0.015 as the propene content is increased further, and is low ($E/f \sim 0.004$) for polymers with a high propene content. PPs with different tacticity (iPP, aPP and sPP) show similar values of grafted MA, which is in contrast with the results obtained by Martinez et al. [20].

Within the experimental error (ca. 10% of the measured value), the MA graft contents acquired both in the melt and in solution are similar. As shown in Fig. 1 all the experimental values are contained within a range, except for EPM5, which has a somewhat higher MA graft content. For HDPE variation of the molecular weight does not have a significant effect on the degree of grafting. For EPM3/iPP blend MA grafted content levels are determined, which fall in the band.

Fig. 2 shows the change of viscosity as a function of propene content. Since the rheology of the modified polyolefins should be not only dependent on the chemical reaction but also on the rheology of the original polymer, the ratio of the two seems more relevant. The modified polymers with low propene content (less than 20 wt.%) have a high viscosity. The viscosity decreases significantly when the propene content is approximately 50 wt.% and the

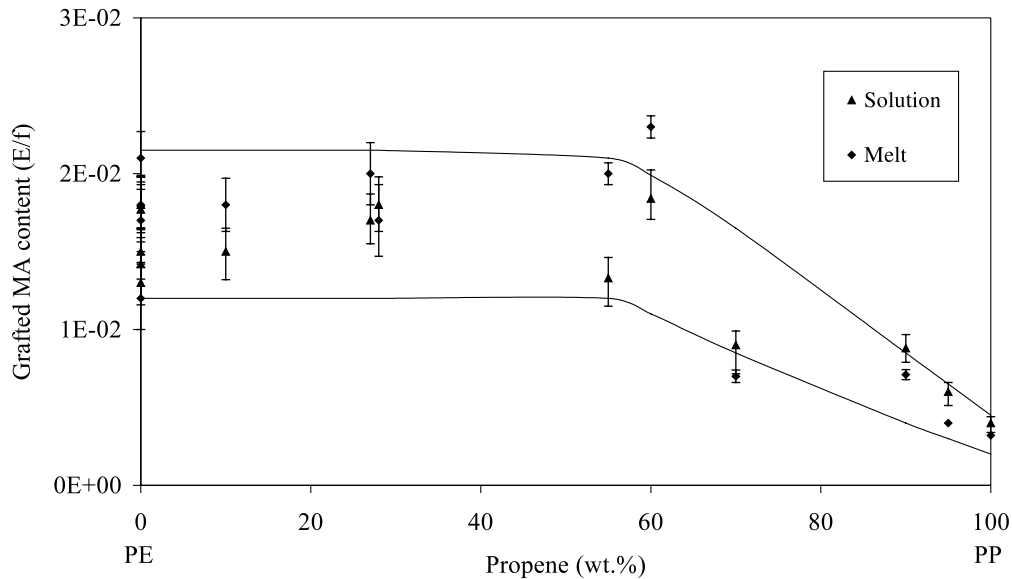


Fig. 1. Maleic anhydride graft level expressed as FT-IR extinction of anhydride band at 1785 cm^{-1} normalise to film thickness (E/f) as a function of propene content.

lowest viscosity is observed for PP (100 wt.% propene). Thus, branching/crosslinking dominates at low propene contents and degradation at high propene contents.

The variation of the ratio of the dynamic viscosities with the MA graft content is given in Fig. 3. A relationship between these two parameters is observed, viz. low MA graft contents are associated with low viscosities.

4. Discussion

The above results will be discussed on the basis of a mechanism for the free radical grafting of unsaturated

monomers onto polyolefins (Fig. 4). Although this mechanism is not proven in a truly scientific way, it is an adapted version of the free radical polymerisation mechanism and is generally accepted and used [1–3]. Graft copolymerisation is initiated by the generation of free radical species, for instance, by the thermal decomposition of a peroxide, ROOR, into primary alkoxy radicals RO' , which may subsequently decompose to secondary radicals. A peroxide derived radical abstracts a H-atom from the polyolefin backbone, producing a macromolecular radical P' . Next, a first monomer (M) adds to the polymer radical forming $\text{P}-\text{M}'$ which, depending on the structure of the monomer and/or the experimental conditions, may be followed by

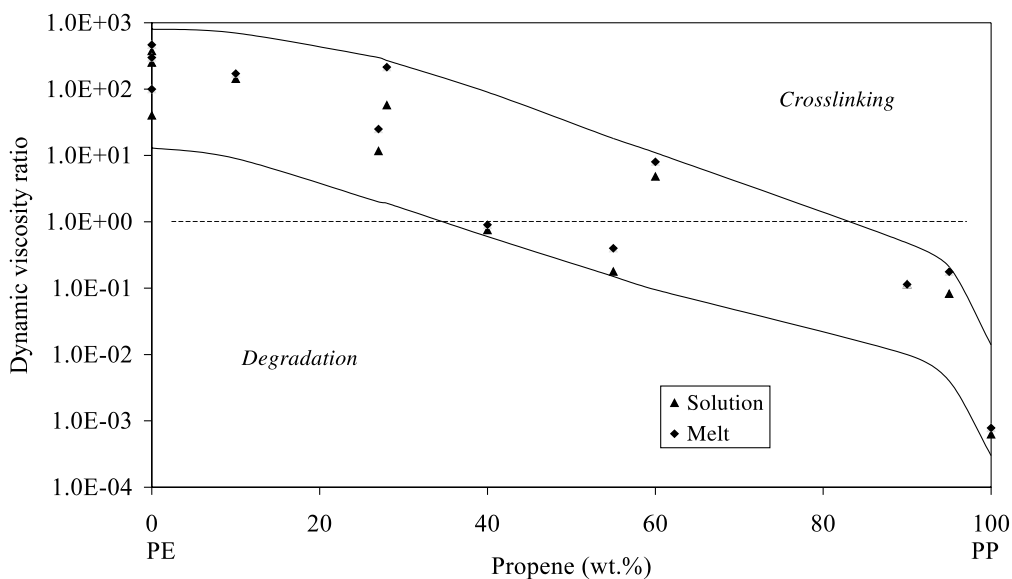


Fig. 2. Ratio of dynamic viscosities (7×10^{-3} Hz) of modified and original polyolefins as a function of propene content.

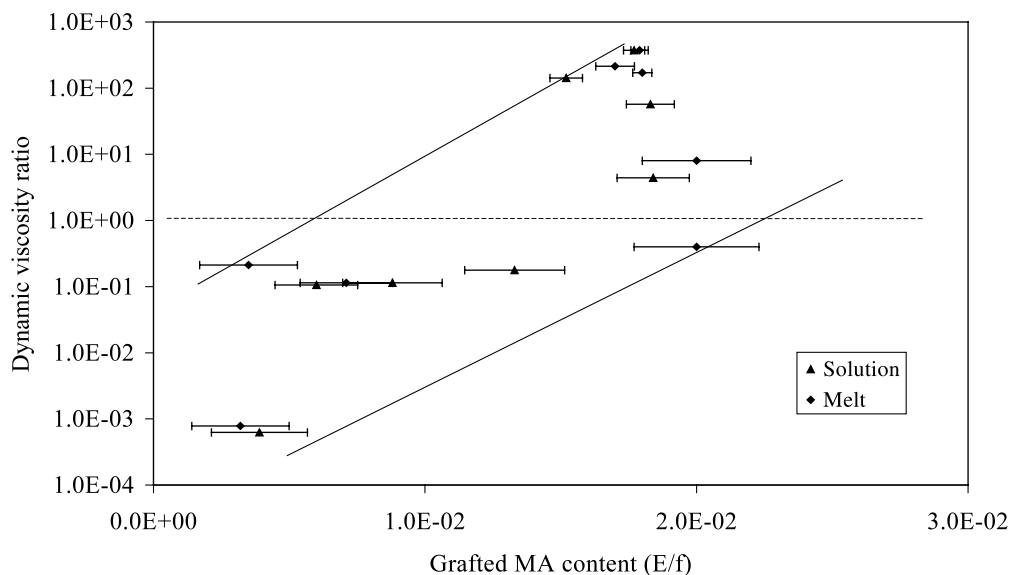


Fig. 3. Ratio of dynamic viscosities (7×10^{-3} Hz) of modified and original polyolefins as a function of the maleic anhydride graft level.

propagation to $P-(M)_n$. When H-transfer occurs, the final graft structure is obtained $P-(M)_n-H$ and a new polymer radical is formed, which may start up a new grafting cycle. Propagation usually does not occur for MA, hence $P-MA-H$ is the final graft structure [27]. It has been shown that substantial intramolecular H-transfer occurs for MA, yielding multiple MA grafts in close proximity [28]. Polymerisation of the monomer can be initiated not only by the macromolecular radical, but also by a peroxide derived radical, which will eventually result in the formation of free polymer. For MA it is believed that free oligomers are only formed when the MA added is not fully dissolved in the polymer melt or in the solvent. Termination of the various free radical species may in principle occur via combination to $P-P$ or disproportionation to $P'^{''}$ and $P'-H$. The polymer radical may also undergo degradation via β -scission, yielding $P''^{''}$ and P''' . Termination products derived from $P-MA$ are not formed [27].

In our study it was shown that the presence of a very large amount of biphenyl neither affects the degree of MA grafting nor the rheological properties of the modified polyolefin. Biphenyl only contains aromatic H-atoms, which in comparison to aliphatic H-atoms present in the polyolefins, are hardly susceptible for H-abstraction. As a result, H-abstraction in a polyolefin solution in biphenyl will only yield polyolefin radicals and, thus, grafting only occurs on the polyolefin. Obviously, when a solvent with more labile H-atoms is used, such as an alkane, the solvent will also be grafted, resulting in a decrease of the polymer MA graft content. This is supported by the demonstration of grafting onto n -alkanes, which are used as low molecular models for polyolefins [28].

The alkyl radicals obtained by H-abstraction from polyolefins will have a planar structure and there will be hardly any preference for the monomer to approach the carbon

centered radical either from above or below the plane. Whether starting with iPP, aPP or sPP, after H-abstraction the tacticity is lost and grafting will proceed independently of the original tacticity. Therefore, the degree of grafting of iPP, aPP and sPP should be equal as it was shown for both grafting in the melt and in solution. The effects of tacticity as observed by Martinez et al. [20] cannot be explained.

PE termination clearly occurs via combination of two P' radicals. Branched or even crosslinked PE is formed during processing of PE in the presence of peroxides both in the absence [31–35] or in presence of MA (Table 2; [4–12]). It is well established that in the presence of peroxides, n -alkanes form dimers [36]. It is assumed that the structure of peroxide crosslinked PE is similar, i.e. that linkages exist between tertiary C-atoms, as was demonstrated with Solid

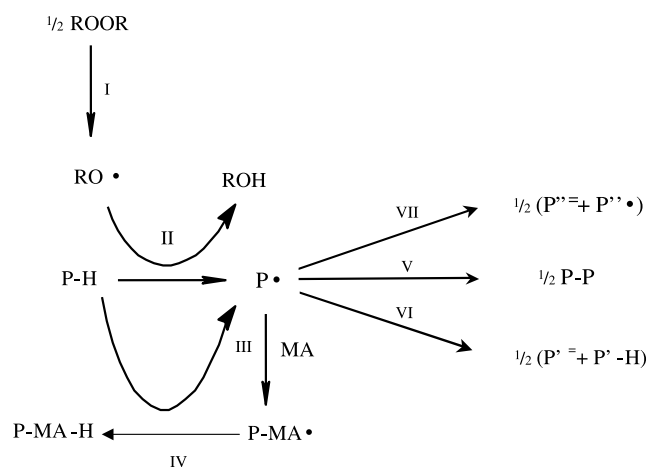


Fig. 4. Simplified mechanism of maleic anhydride free radical grafting. I, peroxide decomposition; II, H-abstraction; III, monomer addition; IV, H-transfer to polyolefin; V, combination; VI, disproportionation and VII, β -scission.

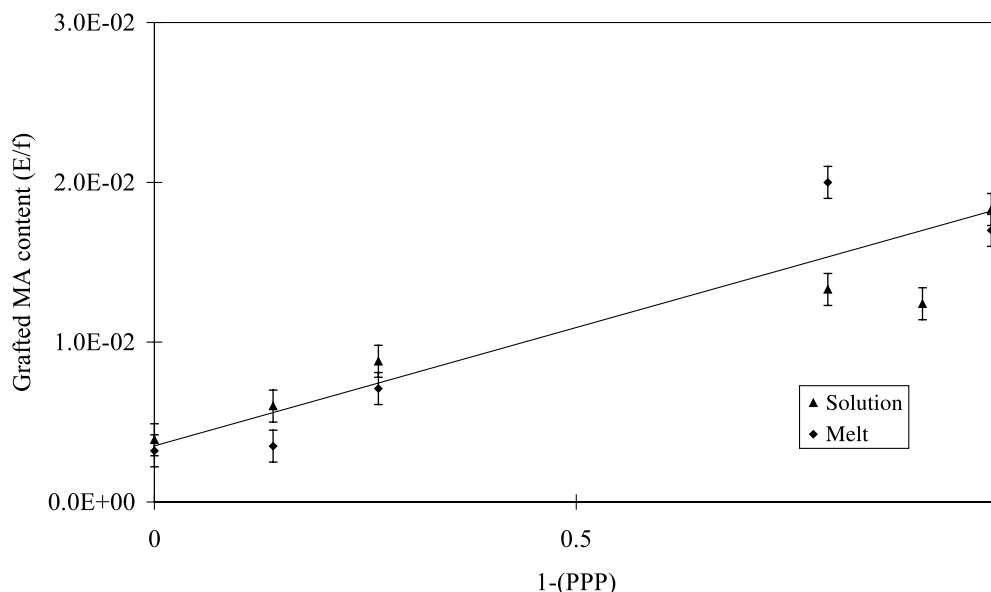


Fig. 5. Maleic anhydride graft level as a function of calculated fraction of non-PPP triads (1-[PPP]).

state ^{13}C NMR for PE crosslinked via radiation [37]. It is noted that crosslinking does not occur via combination of P^{\cdot} with $\text{P}-\text{MA}^{\cdot}$ radicals or of two $\text{P}-\text{MA}^{\cdot}$ radicals [27]. The competition between the propagation and combination reactions determines the number of propagation cycles and, thus, is one of the main parameters determining the graft efficiency. Assuming a peroxide efficiency of 50%, one can calculate from the MA graft content usually obtained for PE (~ 1 wt.%) and from the amount of peroxide usually applied, that the number of propagation cycles is in the order of magnitude of ~ 10 mol MA grafted per 0.5 mol of peroxide.

In the case of PP, degradation via β -scission of P^{\cdot} radicals occurs. This is used on a commercial scale for producing controlled rheology PP [1,38–40]. It has been stated that the relatively low degree of grafting for PP is the result of β -scission. However, this is an oversimplification, since β -scission is not a termination reaction, but produces an equivalent of secondary P'^{\cdot} radicals. MA grafts derived from P'^{\cdot} radicals have not been identified [27], which indicates that for some reason the P'^{\cdot} radicals terminate relatively rapidly. The latter, in combination with a rate of β -scission of P^{\cdot} radicals slightly above that of the addition of MA to P^{\cdot} radicals, probably explains why the MA graft content of PP is lower than that of PE. Typical PP grafting studies involve a peroxide range from 0.23 to 1.25 wt.% and results in 0.15–1.08 wt.% MA grafted. The order of magnitude for the number of grafting cycles for PP is calculated to be about 3.

One would anticipate that EPMS will have a behaviour between those of PE and PP. However, the MA graft level of EPM with up to 50 wt.% propene is more or less similar to that of PE. Only when the propene content is above

50 wt.%, the MA graft content starts to decrease with minimum levels for PP. At closer inspection of Fig. 2, it seems that both in the melt and in solution, the MA graft content of EPM5 (hydrogenated polyisoprene) is slightly above that of random EPMS. This suggests a specific effect of the ethene/propene sequence distribution. If the MA graft content is plotted not against the propene content (Fig. 1), but against the calculated number of propene centred triads different from the PPP sequence, i.e. 1-[PPP], a linear correlation is obtained (Fig. 5). For EPM5, 1-[PPP] is zero and, thus, equal to that of PE. The MA content of EPM5 is indeed close to those determined for HDPE and LDPE. In addition, it was shown that grafting of MA onto EPM5 occurs on methylene C-atoms only [27], which again demonstrates that EPM5 behaves similarly to PE. It is not clear why the presence of PPP-triads is decisive for the MA graft content. Probably, β -scission of a PPP sequence is faster than that of EPP or EPE sequences, since in the former case always P'^{\cdot} with a dialkyl-substituted and, thus, a relatively stable unsaturation, is formed. The dynamic viscosity ratio depends on the propene content over the whole propene range from PE to PP (Fig. 2) and does not level off like the MA graft content. Since the logarithm of the dynamic viscosity is proportional to the molecular weight, the actual number of chain scissions per chain is exponentially increasing with the propene content and eventually may produce an improved correlation with 1-[PPP].

5. Conclusions

Significant differences in MA grafting and rheological behaviour were obtained depending on the original

polyolefin structure. The MA graft content was low for polyolefins with high propene content and high when the propene content was below 50 wt.%. The degree of grafting was independent of the method used, i.e. solution or melt grafting. A decrease of the propene content of the polyolefin results in a transition from degradation to branching/cross-linking. The experimental data can be explained by using a general scheme for free radical grafting onto polyolefins.

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