

Functionalization of isotactic polypropylene with maleic anhydride by reactive extrusion: mechanism of melt grafting

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Abstract

In this work, chemical structures and molecular parameters of grafted materials of PP-g-MAH prepared by melt reactive extrusion were studied by using electrospray ionization-mass spectrometer and gel permeation chromatography. It was found that the initial radicals, due to homolytic scission of dicumyl peroxide could be combined with maleic anhydride (MAH) monomers as well as polypropylene (PP) molecular chains. The homopolymerization of MAH cannot occur and the MAH radicals undergo a dismutational reaction under the processing condition (180–190°C). A modified mechanism of melt grafting MAH onto PP has been proposed tentatively on the basis of our experimental results and other experimental findings published in the literature. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Functionalization; Polypropylene; Mechanism

1. Introduction

The functionalization of polypropylene (PP) through grafting unsaturated monomers such as maleic anhydride (MAH), acrylic acid and its derivatives, in the presence of an organic peroxide as an initiator, has received much attention over the past decades. Functionalized PP has been prepared successfully by using solution [1], melt [2–4] and solid state routes [5,6]. The modified PP has been used extensively for compatibilization of immiscible polypropylene–polyamide and polypropylene–polyester blends, as well as to improve the interfacial adhesion of PP with glass and carbon fibers, and even as a processing aid for degradable plastics [7,8]. In spite of the commercial success of functionalized polyolefins, the precise nature of the chemical paths involved in the functionalization process is not completely clear. It is generally accepted that chain scission occurs during the peroxide initiated functionalization of PP [4].

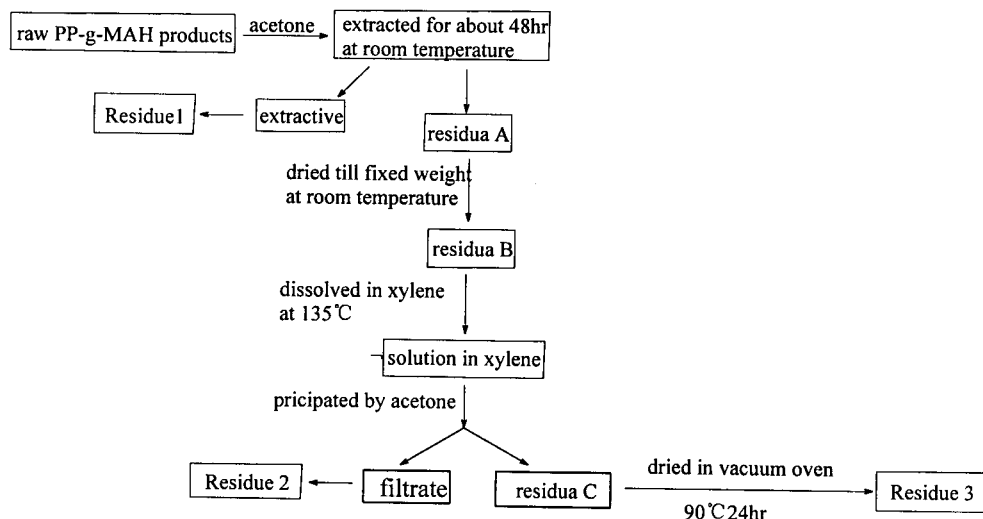
In an earlier study using a solution grafting process, Minoura et al. [1] proposed that the graft reaction involved mainly the appending of MAH to tertiary carbons along the PP backbone. Gaylord and Mishra [4] studied the grafting

reaction by means of melt grafting process. They suggested that MAH might be appended to tertiary site along the PP backbone as a single ring or as short branches that were attributed to homopolymerization of MAH. More recently, Roover et al. [9] also reported that homopolymerization of MAH can take place during the processing. However, Heinen et al. [10] and Russell et al. [11] have pointed out that according to the ceiling temperature, there is no possibility for the homopolymerization of MAH to occur under the melt grafting process conditions (190°C). ¹³C NMR analysis carried out by Rengarajan et al. [5] indicated that the grafted MAH might also introduce cross-links between the PP chains. Constable and Adur [12] suggested that PP-g-MAH materials they have obtained consisted of single anhydride rings connected to the PP chain ends.

From the aforementioned studies, it can be noted that the grafting reaction mechanisms of PP-g-MAH proposed by several authors are somehow controversial. Thus, further experimental evidence can be useful to understand completely the overall reaction, which takes place during the functionalization. In the previous studies, all PP-g-MAH samples used for investigating the grafting mechanism were obtained with the following procedure: dissolution of the grafted samples in hot xylene, precipitation with acetone and drying of the precipitated polymers in a vacuum oven. The molecular weights of the dried precipitates are usually

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Scheme 1. Procedures of preparing the MS samples.

very high. Only a few solvents such as xylene and trichlorobenzene can dissolve them at over 80°C. So it is quite difficult to study the grafting reaction mechanism through the characterization of their chemical structure.

It is well known that during melt grafting process of PP with MAH degradation reactions occur. A part of PP-g-MAH materials with low molecular weights are produced, which remain in the solution when the above purification process was adopted to obtain purified PP-g-MAH samples. To our knowledge no attention has been devoted so far, to the PP-g-MAH material kept in the mother liquor. It seems reasonable to assume that the same grafting reaction mechanism takes place for both PP-g-MAH materials with high and low molecular weights. Furthermore, it will be much easier to investigate the chemical structure of PP-g-MAH with low molecular weight, from which grafting reaction mechanism of PP-g-MAH can be deduced.

We report here on the chemical structure of PP-g-MAH samples with very low molecular weights determined by using electrospray ionization-mass spectrometer (ESI-MS). Some interesting results were obtained, which would give us some suggestions to understand the grafting mechanism. On the basis of the ESI-MS data, of the results obtained by gel permeation chromatography (GPC) as well as of other experiments previously published [10,11,15], a modified melt grafting reaction mechanism of PP-g-MAH is tentatively proposed.

2. Experimental

2.1. Materials

Isotactic PP (commercial code 2401) with MFR = 7.9 g/10 min (ASTM D569-90) was supplied by Beijing Yanshan Petrochemical Co. China. Taichang Special Agent Factory,

China, kindly offered Dicumyl peroxide (DCP) reagent grade. MAH purchased from Beijing Hongxin Chemical Factory, China as well as xylene, acetone and alcohol were all reagent grades and used without any further purification.

2.2. Preparation of PP-g-MAH

PP-g-MAH samples were prepared by using a home made co-rotating twin-screw extruder. The diameter of the screws is 30 mm and the ratio of length to diameter, L/D , is 44. L/D of reactive zone is 24 and 16 for melting zone. The maximum torque of screw was 2×147 NM. The maximum operating temperature that can be achieved is 360°C and the fluctuation of temperature is within $\pm 5^\circ\text{C}$. The barrel of extruder is divided into 11 segments and each segment is heated independently. The Dicumyl peroxide was dried at room temperature under 0.02 MPa, and MAH was ground into powder before mixing with the PP powder. The MAH, DCP and PP powder were premixed in a rotating mixer before adding into the hopper of the extruder. Rotating rates of the feeder screw and the main screw were 19 and 120 rpm, respectively. Under these conditions, the residence time is about 2 min. The temperature of the feeding zone, the mixing zone, the reacting zone and the exit die were 175, 190, 190, and 180°C, respectively. In order to study the oxidation effect on the graft reaction, we also did a plain experiment with only MAH/PP and pure PP. Here we named the sample with DCP/MAH/PP as Sample 1, MAH/PP as Sample 2 and that with pure PP as Sample 0.

2.3. Purification and fractionation

Several grams of raw grafted PP material (after reactive extrusion) were pressed into thin films, with thickness lower than 0.1 mm by using a hot press at 190–200°C. The raw grafted PP films obtained thus were extracted for at least 24 h with acetone at room temperature. Unreacted MAH

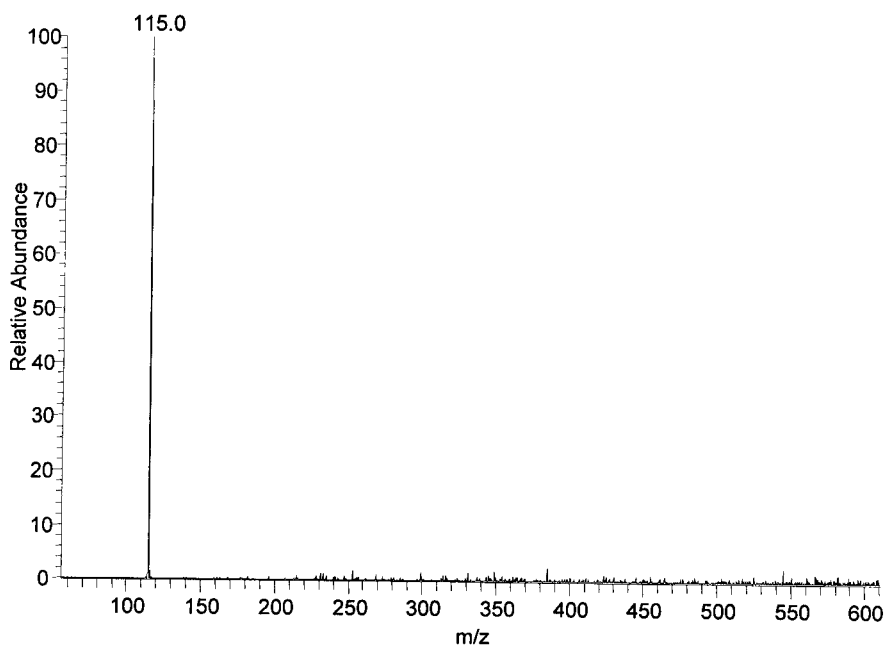


Fig. 1. MS spectra of Residue 1 (Sample 1).

monomer or MAH oligomers (if formed during extrusion), which will be referred as Residue 1 would remain in acetone and can be isolated after evaporation of acetone.

About 1 g of the acetone insoluble grafted PP material thus obtained was dissolved in 100 ml xylene at 130°C and the resulting solution was added slowly into acetone. Most of grafted PP with high molecular weight was precipitated. And a little amount of grafted PP with very low molecular weight, which would be referred as Residue 2, was kept in the mother liquor and was recovered by removing the mixture of acetone and xylene under 0.02 MPa in a vacuum oven. The precipitated grafted PP material, which will be referred as Residue 3, was dried in a vacuum oven at 90°C for 24 h. The overall procedure is represented in Scheme 1.

2.4. Determination of grafting degree of Residue 3

A small amount (1 g) of dried Residue 3 was dissolved in 100 ml of boiling xylene in a conical flask and a few drops of water were added to hydrolyze all anhydride functions. Afterwards, 10 ml of 0.05N potassium hydroxide solution in methanol was added into the flask. The formed solution was back titrated with 0.03 N trichloroacetic solution in xylene using cresol red as the indicator. A blank test for PP was carried out by the same method. Grafting degree of Residue 3 was calculated from Eq. (1):

$$G (\%wt) = \frac{(V_0 - V_1) \times N}{2 \times W \times 1000} \times 98 \times 100\%, \quad (1)$$

where, G (%wt) is the grafting degree of MAH, on PP-*g*-MAH, V_0 (ml) the acid volume used in the blank test, V_1 (ml) is the acid volume used in the test with the sample, N is the

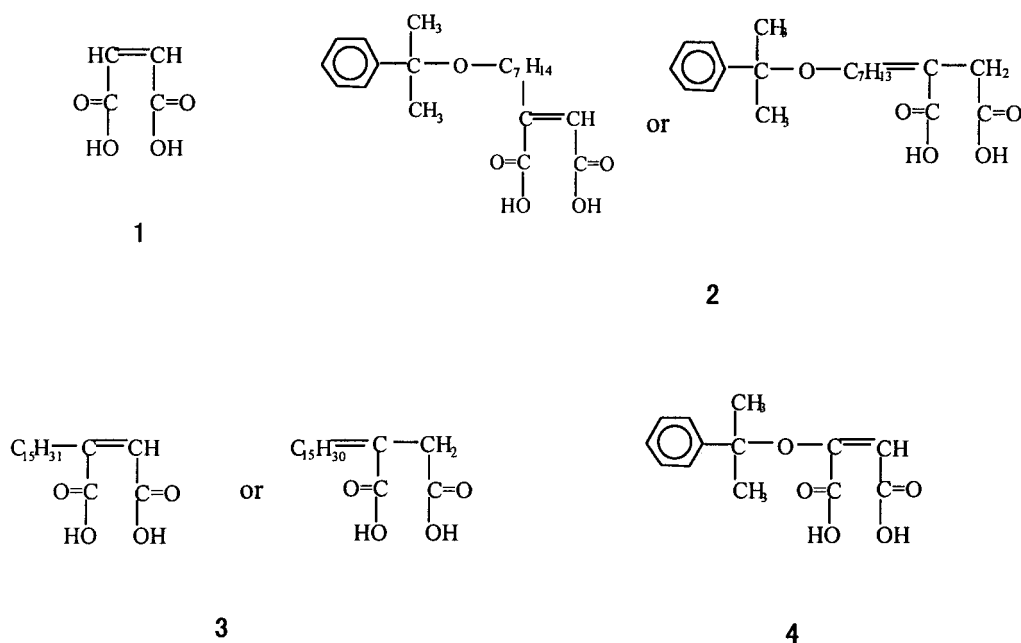
acid concentration (mol/l) and W is the weight of the sample (g). The M_w of MAH is 98.

2.5. ESI-MS Measurements

A LCQ ESI-MS (Finnigan MAT) was used to investigate the chemical composition and structure of Residues 1 and 2. The spray potential was 3.5 kV. Full scan spectra were acquired in the ion peak centroid over the mass charge range of 50–1000 at 1.2–2.0 s. The mass spectra were obtained by flow injection method with a flowing rate of 3 μ l/min. The ion abundance (%) was normalized on the base of one of the peaks assumed as a reference (100%) in each spectrum. Data analysis was controlled by a DEC 2100 data system. In order to open all the anhydride rings, a small amount of water was added to both Residues 1 and 2.

2.6. GPC Experiments

The characterization of molecular parameters of Residue 3 was carried out by high temperature GPC. Polymer Laboratories GPC-220 equipped with 3 Mixed-D columns was used in this work. A differential refractometer detector coupled with a “chromatography data station” provided by Digital was used for recording and analyzing the signal. 1,2,4-Trichlorobenzene stabilized with 0.025% BHT was used as the eluent. Samples were dissolved in 1,2,4-trichlorobenzene at 150°C and the concentrations of the solutions were in the range of 6–8 mg/ml. The injected volume was 200 μ l and the eluent flow rate was 1.0 ml/min. The measuring system was maintained at 135°C during the analysis.



Scheme 2. Chemical structures of Residue 1 and Residue 2 of Sample 1 determined by ESI-MS.

3. Results

Fig. 1 is the MS spectrum of Residue 1 of Sample 1. The peak 115.0 m/z represents the maleic acid, referred as structure 1, derived from the hydrolyzed unreacted MAH in Scheme 2. We did not find any dimer, trimer or oligomer of MAH in Residue 1.

Fig. 2 shows the MS spectrum of Residue 2 of Sample 1 (grafting degree 1.1 wt%). The molecular ion peak 249.1 m/z represented the structure 4 of Scheme 2. The peak 325.2 and 339.2 m/z represented the structure 3 and its homologous

structure in Scheme 2. The other series peaks seen in Fig. 2 such as 409.3, 423.3, 437.3, 451.3, 465.3, 479.3, 493.3, 507.2 and 521.3 m/z can be assigned to all the homologous compounds of structure 3 in Scheme 2. Their difference is due to one or more $-\text{CH}_2-$ groups in a sequence that results from the different ways in scission. The two peaks at 347.2 and 361.1 are related to the homologous compounds indicated as structure 2 in Scheme 2.

Figs. 3 and 4 are the ESI-MS spectra of Residue 2 of Sample 0 and Sample 2, respectively. It can be found in this figure that there is the oxidation effect during the

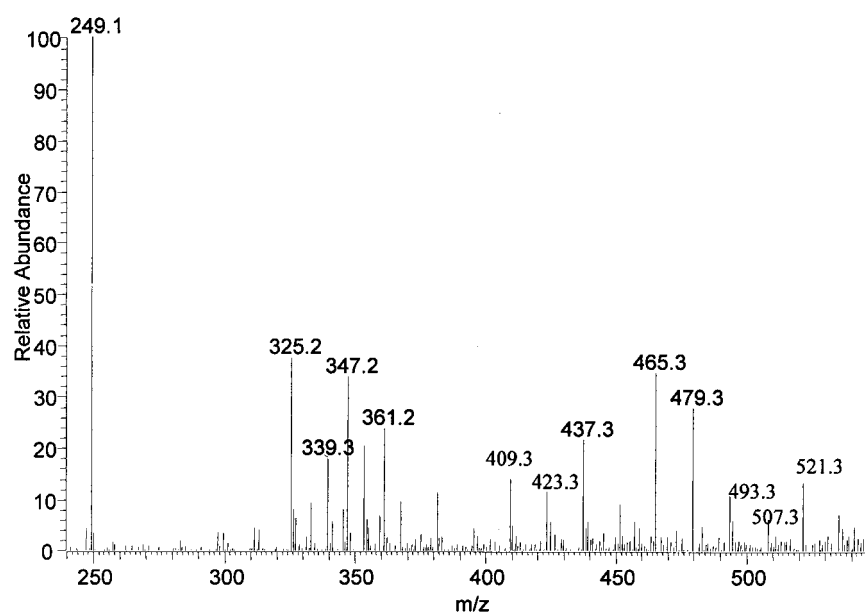


Fig. 2. MS spectra of Residue 2 (Sample 1).

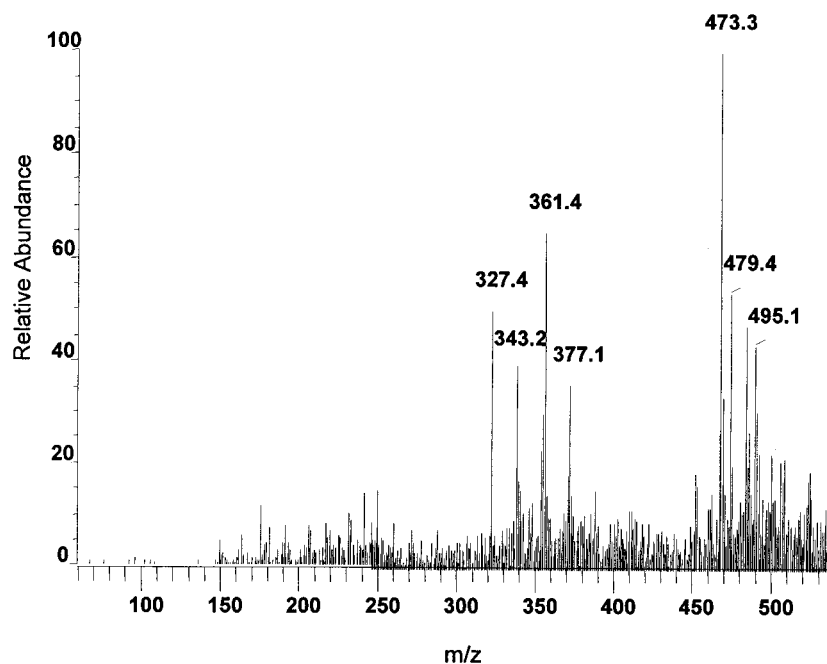


Fig. 3. MS spectra of Residue 2 (Sample 0).

extrusion. The ion peak groups 327.3, 343.3; 361.4, 377.3; 479.3, 495.2, which with a margin of 16 in each group, must be coming from the effect of oxidation. But as the oxidation reaction of PP is very complicated [16,17], it will lead to the formation of oxygen-containing groups such as carbonyl, carboxyl, epoxy and hydroperoxide groups. So it is very difficult to define the definite structure of each peak. Here only one possible structure of each peak is listed in Scheme 3.

Comparing Figs. 3 and 4, it is found that the ion peaks existing in the two figures are almost the same. This indicates that the oxidation has very little effect on the grafting reaction during reactive extrusion. As shown in Fig. 2, all ion peaks in Figs. 3 and 4 are depressed sharply except 361.3 and 479.3, which happen to be superposed at the same position as that from structure 2 and structure 3 in Scheme 2. It means that the oxidation degradation of PP

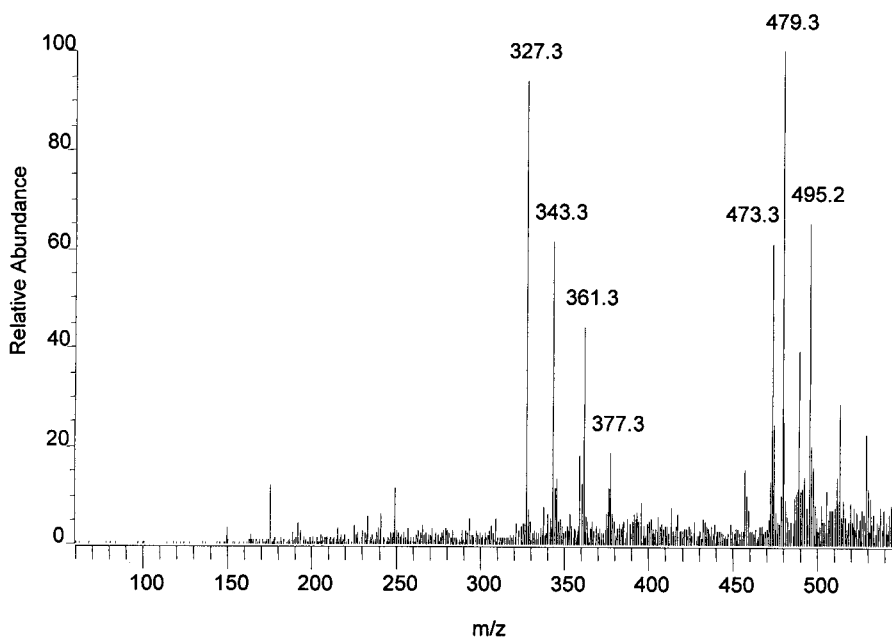
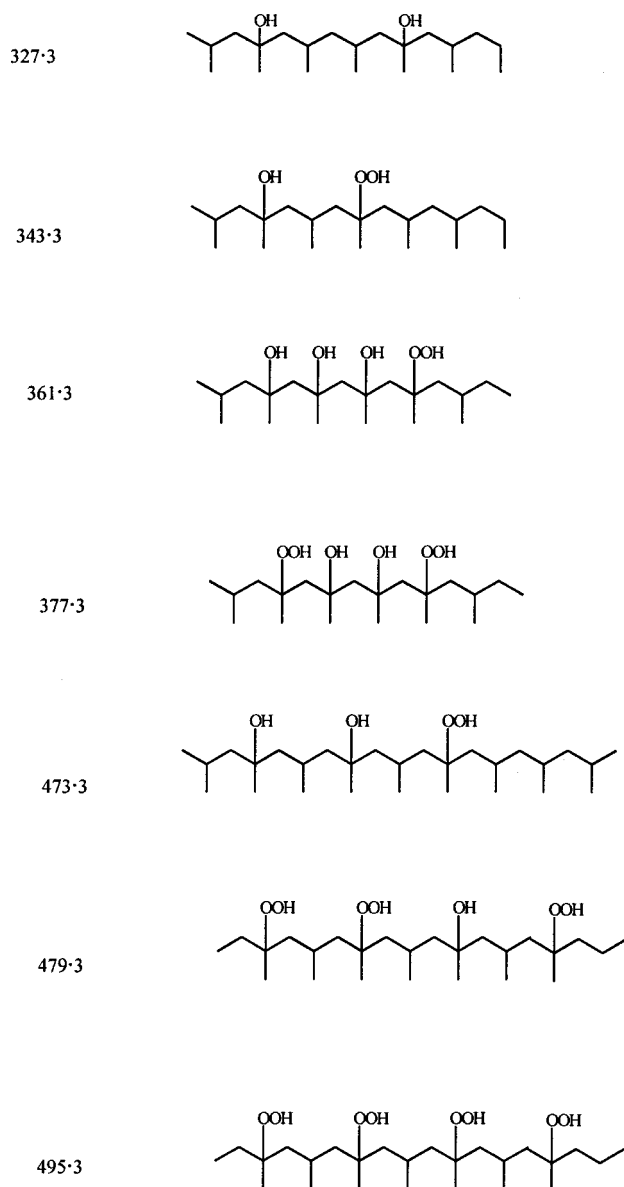


Fig. 4. MS spectra of Residue 2 (Sample 2).



Scheme 3. Chemical structure of Residue 2 of Sample 0 and Sample 2 determined by ESI-MS.

during the graft processing through extrusion is very small compared to that of peroxide initiator and so the oxidation effect here can be ignored.

From the above experimental results, the following conclusions can be drawn for the reactive extrusion of DCP/MAH/PP system:

1. there are no MAH oligomers or MAH homopolymers in Residue 1;
2. the MAH radicals can only dismutationally terminate and always keep double bonds with them after terminating;
3. the presence of structure 4 in Residue 2 suggests that peroxide radicals coupled with MAH molecules during the grafting process are primarily present. This could

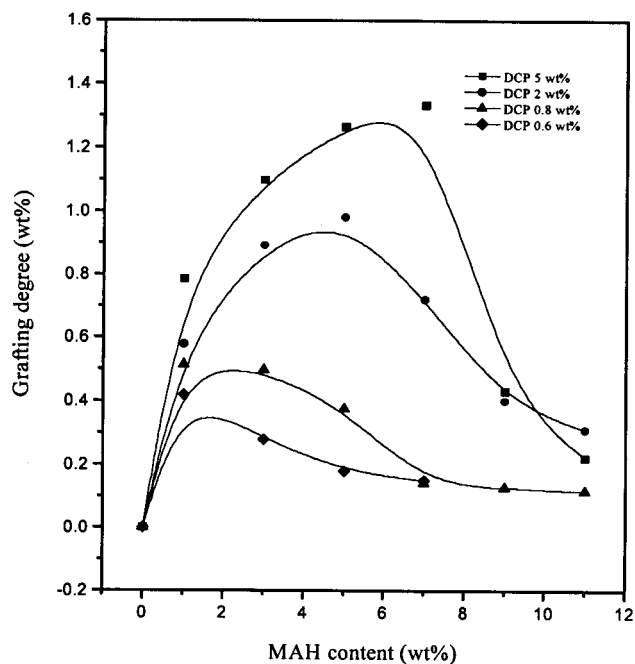


Fig. 5. Grafting degree of PP-g-MAH as a function of loading concentration of MAH monomer.

consume a part of the grafting monomers and of the initial peroxides;

4. the oxidation effect can be ignored during the processing.

Grafting degrees of PP-g-MAH as a function of concentration of the added MAH monomer is shown in Fig. 5. It can be seen that by increasing the amount of MAH monomer different maxims of grafting degree of PP-g-MAH are obtained, depending on the initiator (DCP) level. The higher the loading level of DCP, the higher the peak value of grafting degree of PP-g-MAH and the more the position of the maximum shifts towards the high MAH concentration.

The molecular weights of PP-g-MAH samples (Residue 3) are collected in Table 1. From these data it is evident that a reduction of the M_w occurs when the grafting degree increases. However, the rate of molecular weight decrease depends on the grafting degree; in fact, when the grafting degree is higher than 0.38 wt%, the decreasing rate becomes lower.

By using Eq. (2) [13] we calculated the maximum radical concentration generated during grafting, which is lower than the total reactive center content, B ($\mu\text{mol/g}$), as determined by the grafting degree and is shown in Table 1.

$$A = \frac{1}{2}N = \frac{1}{2}10^6 \times \left(\frac{1}{M_n} - \frac{1}{M_n^0} \right), \quad (2)$$

where M_n is the number average molecular weight of PP after grafting (g/mol), M_n^0 is the number average molecular weight of PP before grafting (g/mol), N is the concentration of new polymer chain ends created during grafting ($\mu\text{mol/g}$) and A is the concentration of active radical sites ($\mu\text{mol/g}$).

Table 1
Grafting degree, molecular weight, distribution of molecular weights and concentrations of active radical sites, *A* calculated by Eq. (2), and *B* determined by grafting degree for PP-*g*-MAH samples

Grafting degree (wt%)	Molecular weight $\times 10^4$	M_w/M_n	<i>A</i> ($\mu\text{mol/g}$)	<i>B</i> ($\mu\text{mol/g}$)
0	6.5	4.2	0	0
0.12	5.0	4.2	2.35	12.24
0.13	4.9	3.8	2.57	13.27
0.38	3.5	2.6	6.65	38.77
0.51	3.2	2.5	7.67	52.04
0.78	2.9	2.3	9.69	79.59
1.1	2.4	2.3	13.28	112.2
1.26	2.4	2.3	13.54	128.6
1.33	2.1	2.5	15.97	135.7

4. Discussions

On the basis of the above results and other experimental findings reported in some previous publications [9–11,15], an improved grafting mechanism of PP with MAH by means of melt reactive processing is tentatively proposed, as shown in Scheme 4. Here, it has been assumed that in Residue 3 structures similar to structure **2** and structure **3** of Residue 2 (shown in Scheme 2) are present in Residue 3. This new modified mechanism can be used to explain our experimental results perfectly as well as those obtained by other research groups [11,15].

The experimental results shown in Fig. 5 can be explained as follows. At a given concentration of DCP, both reaction A and reaction C as well as D in Scheme 4 would consume initial radicals originated from DCP. When the loading concentration of the MAH monomer is low, there are enough initial radicals to combine with the MAH monomer and to initiate PP macroradicals. Therefore, the grafting degree of PP would increase with increasing concentrations of MAH. But with a further increase in the MAH concentration, more and more initial radicals would be consumed in reaction A. The number of initial radicals to induce reaction C and D would then decrease consistently. Therefore, the grafting degree of PP-*g*-MAH would decrease and a maximum of grafting degree of PP-*g*-MAH appears.

Independent of the initial concentration of the MAH monomer, the grafting degree of PP-*g*-MAH increases with increasing the loading level of DCP, at least in the range of 0.6–5 wt%. The higher the concentration of DCP, the higher the grafting degree of PP-*g*-MAH and the more the peak value shifts towards high MAH concentrations. On the other hand, for a given amount of MAH monomer, by increasing the DCP concentration the grafting degree increases, although its absolute value decreases when MAH is sufficiently high. Similar explanation based on the proposed grafting mechanism can account for these results. When the initial concentration of MAH monomer is below the value corresponding to the peak (Fig. 5), with increasing DCP content, reaction A would consume some

MAH monomer. But if the remaining MAH content is enough to react with the macroradicals, which would result in increasing grafting degree, the graft degree of PP increases. However, if the MAH left is not enough to react with macroradicals, which can occur at high amounts of MAH, the grafting degree of PP will be lower.

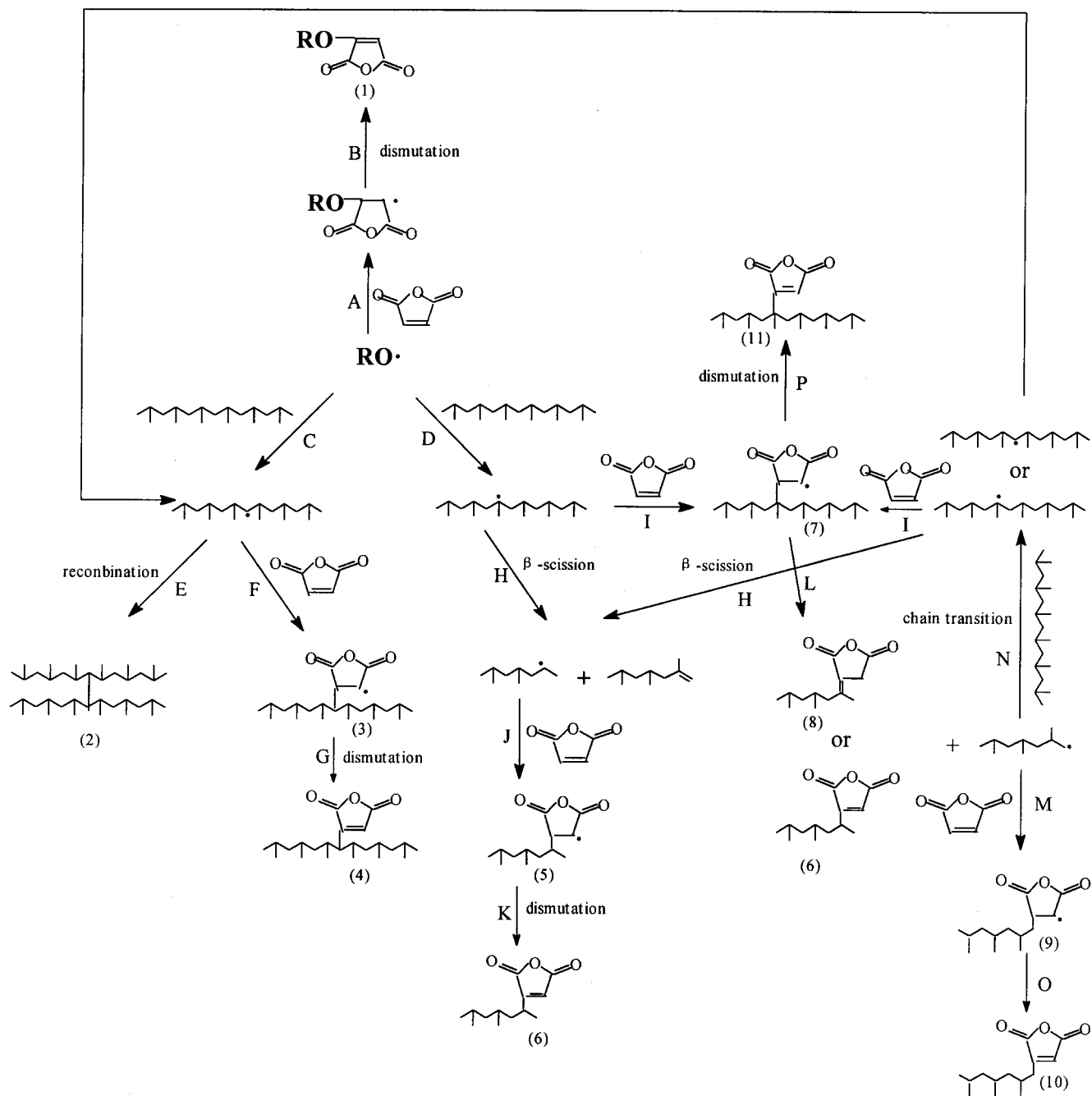
The proposed grafting mechanism can also be used satisfactorily to explain the experimental results in Table 1. When the molecular weight of PP is high, its melt viscosity should be high. As PP is immiscible with MAH, it can be very difficult for the MAH monomers to diffuse into the PP molecular chains. Reaction F and I would then be inhibited, thus decreasing the grafting degree. Furthermore, if the molecular weight of PP was low there would be easier for MAH monomers to interact with PP molecular chains and then to react with the macroradicals on PP chains. Reaction F and I would be favored, which induces increasing of the grafting degree of PP-*g*-MAH. On the other hand, Reaction E and H would be largely inhibited. Since the ratio of the tertiary and secondary radicals could be considered as constant [14], the final grafting degree would be simply related to the final molecular weight at the same processing conditions.

Not all the tertiary macroradicals could be involved in the β -scission, which lead to the degradation of the polymer, and not all the secondary macroradicals could be involved in combinations, which lead to the increase of the molecular weight. Part of tertiary and secondary macroradicals would become the grafting sites of the MAH, as shown in reaction I and G of Scheme 4, respectively. Therefore, the total reactive center B was larger than the calculated value A as shown in Table 1.

The proposed grafting mechanism of PP-*g*-MAH could be also used to explain the experimental results obtained by Ho et al. [15]. They found out that at low concentrations of DCP and MAH, the existence of MAH could enhance the degradation of PP during the processing, but the PP degradation can be also reduced at higher MAH concentrations. This could be explained as follows: when both concentrations of DCP and MAH were very low, reaction A could be neglected. Initial radicals that originated from DCP would be used to induce the PP macroradicals. A small quantity of MAH could act as a chain transfer agent. Reaction H would become more important. So, the degradation of PP molecular chains would be enhanced. But with increasing MAH content, reaction A could be strengthened and the number of the effective radicals that initiate the macromolecular chain would be reduced; therefore the degradation of PP would decrease.

5. Conclusions

ESI-MS, GPC and chemical titration method were used to study the grafting mechanism of PP with MAH prepared by means of reactive extruding method. A modified grafting



Scheme 4. Proposed grafting mechanism of PP-g-MAH by means of reactive extrusion method.

mechanism was proposed and from the overall results the following conclusions can be drawn:

1. the initial radicals that were formed by DCP homolytic scission can combine with MAH monomers as well as with the PP molecular chains;
2. the Homopolymerization of MAH does not take place under the conditions used in this reactive extrusion process;
3. the MAH radicals could be dismutationally terminated or acted as a chain transfer agent;
4. not all the tertiary macroradicals can be involved in the β -scission that leads to the degradation of the polymer, and not all the secondary macroradicals can be involved in combination that leads to the increase of the molecular weight;
5. structures **4**, **6**, **8**, **10** and **11** as shown in Scheme 4 were formed during melt reactive grafting of PP with MAH. The only path to increase the grafting degree of PP-g-MAH was to strengthen reactions F and I;
6. the oxidation effect could be neglected during the processing.

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