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INFLUENCE OF MALEIC ANHYDRIDE ON THE MOLECULAR WEIGHT OF ATACTIC POLYPROPYLENE AT THE FUNCTIONALIZATION REACTION

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ABSTRACT

The influence of maleic anhydride (MAN) on the molecular mass of atactic polypropylene in the functionalization reaction initiated by organic peroxide was studied. It was found that under certain reaction conditions MAN takes part in the radical degradation of polypropylene after it is grafted. From the results of the study, a mechanism of degradation reaction was suggested.

INTRODUCTION

The methods and the mechanism of functionalization of polypropylene (PP) or its copolymers with maleic anhydride (MAN) (or with its esters) using a radical reaction most frequently initiated by peroxides have been a focus of academic and industrial research for over two decades [1–13]. This is due to the fact that the reaction offers the possibility of binding highly polar groups to a completely nonpolar polyolefin chain. The advantage of binding MAN groups to PP, compared to other groups such as $-SO_3H$, $-Cl$, etc. is the higher thermal stability of the MAN-modified polymer. Polypropylene functionalized by maleic anhydride groups can be advantageously utilized for improving the compatibility of PP groups with other polar polymers or inorganic fillers [14–18].

There are also disadvantages to this radical reaction of binding MAN to PP such as a rather low ratio of bound MAN groups (2 mass% under the usual conditions) as well as a subsequent degradation reaction of the polymer [6, 7, 9, 12, 13].

This is why we have studied the degradation reaction of the polypropylene chain. At present the prevailing opinion is that in the case of radical grafting and functionalization of modified polypropylene and other polymers, the scale of the subsequent degradation reaction of modified polymer can be ascribed to the radical initiator (i.e., the concentration of radicals occurring under radical conditions) [9]. Gaylord and Mishra [7] found that for the functionalization of isotactic polypropylene in the presence of MAN, the value of the limiting viscosity number of MAN appeared to be lower than in the absence of MAN under the effect of an equal content of dicumyl peroxide and at the same temperature, 180°C. This result implies that a detailed study of the influence of the separate components of the reaction system of functionalization on the molecular weight of atactic polypropylene can contribute to the results of Gaylord and Mishra [7], and also to an explanation of the mechanism of degradation of the polypropylene.

EXPERIMENTAL

Chemicals

Atactic polypropylene (aPP) (Slovnaft, Bratislava, Slovak Republic) with a very low average molecular mass ($\overline{M}_w \approx 3000$ g/mol) was used as the starting material. By fractional precipitation of aPP from toluene solution with methanol, a fraction with a number-average molecular mass, $\overline{M}_n = 8100$ (determined by vapor pressure osmometry), was obtained and used in the functionalization reaction. Maleic anhydride p.a. (MAN, Lachema, Brno, Czech Republic) and *tert*-butyl perbenzoate (98%) (TBPB, Merck, Germany) were used.

Reaction of Maleic Anhydride with Atactic Polypropylene

A reaction mixture consisting of aPP, MAN, and TBPB with a total mass of 3 to 5 g (the contents of MAN and TBPB in separate samples are listed in Table 1) was prepared in a laboratory blender at 80°C. The reaction mixture was transferred to a glass tube, sealed under nitrogen, and then allowed to cure in an oil bath at 130°C. The period of curing at the required temperature corresponded to six half-lives of peroxide. Low-molecular reaction products were extracted from each sample by boiling water (three times with 20 mL water) with simultaneous mechanical mixing of the polymer. Samples of aPP with bound MAN were then dried in a vacuum oven at 80°C to constant weight.

Determination of Maleic Anhydride in Modified Atactic Polypropylene

The quantity of bound MAN in aPP after reaction and extraction was determined by using titrimetry as described by Gaylord [7]. We used about 0.5 g of the sample dissolved in water-saturated xylene, and the solution was titrated using 0.02 N KOH in *n*-butanol solution and taken to a phenolphthalein end point.

TABLE 1. Atactic Polypropylene Functionalization Reaction with Maleic Anhydride in the Presence of TBPB (concentration of TBPB = 3 wt%) in Bulk

Sample	Wt% of MAN in the reaction mixture	Wt% of bonded MAN to aPP	
		at 130°C	at 190°C
1	0	0	0
2	0.97	0.45	0.53
3	1.85	0.86	0.98
4	2.33	0.87	1.07
5	4.59	0.89	1.14
6	4.97	0.93	1.37
7	7.61	1.12	1.85

Molecular Weight Determination

The average molecular weight of the modified aPP was determined using a Knauer vapor pressure osmometer. Dried and distilled chloroform was used as solvent, and the measurement temperature was 37°C. Five solutions of different concentrations were used for each estimation.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between the concentration of MAN added to the reaction mixture and the molecular weight of functionalized aPP in the presence of *tert*-butyl perbenzoate (3 mass%) at 130 and 190°C. Amounts of MAN greater

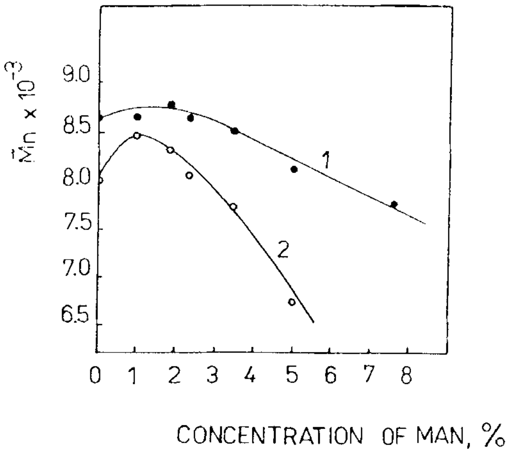


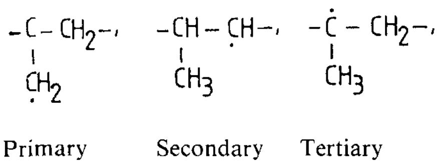
FIG. 1. The effect of MAN concentration on number-average molecular weight ($\overline{M}_n$) of aPP (3 wt% TBPB): (1) at 130°C, (2) at 190°C.

than 2% in the reaction mixture with aPP cause a gradual reduction of molecular mass. The molecular mass reduction in aPP for the MAN content in the reaction mixture is more notable at 190°C (Fig. 1, Curve 2) than at 130°C (Curve 1).

General knowledge about the effect of unsaturated monomers on the radical degradation of such polymers as polypropylene [19] leads us to expect that the presence of unsaturated monomer should slow down the degradation. It is expected that the addition of unsaturated monomers to the polymer radicals will diminish the source of the degradation process, but from the dependencies in Fig. 1 it seems that MAN influences the degradation reaction to some extent. We attempted to find an explanation for this observation.

Let us compare the behavior of free radicals in polypropylene, i.e., the precursors of the functionalization reaction, under the following circumstances.

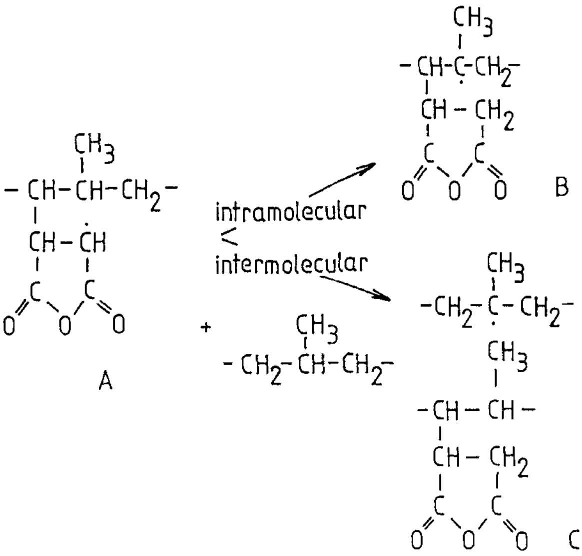
(a) In the presence of peroxide alone, the primary, secondary, and tertiary radicals are formed on the polypropylene chain in the known ratio 1:10:50 [19] (see Scheme 1):



$$-\underset{\dot{C}H_2}{\underset{|}{C}}-CH_2-, \quad -\underset{CH_3}{\underset{|}{CH}}-\dot{C}H-, \quad -\underset{CH_3}{\underset{|}{\dot{C}}}-CH_2- \qquad (1)$$

SCHEME 1.

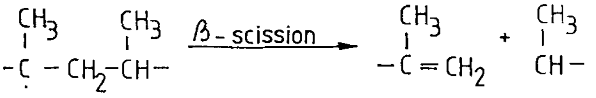
(b) In the presence of peroxide and MAN, free radicals formed on the PP chain will react with MAN. For steric reasons we can assume that MAN will react more quickly with primary and secondary radicals than with tertiary radicals. This assumption has been made by other authors as well [18]. When we follow the fate of the radical formed after addition of MAN to PP radicals, we see that they are converted with their own intermolecular or intramolecular products B or C, respectively, in Reaction (2).



(2)

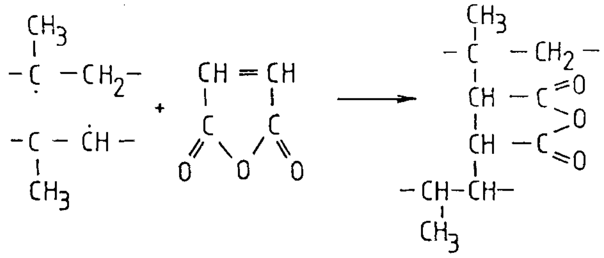
The tendency of this transfer to lead to the formation of tertiary polymer radicals is much higher than the transfer reaction of the oxyradicals formed from the decomposition of peroxide to PP chains. This means that as a result of this transfer of MAN radicals to PP chains, more tertiary radicals in relation to secondary and primary radicals will be formed than in the case of the transfer reaction of oxyradicals of peroxide with PP chains (see Scheme 1).

Under the assumption of such a course of transfer reactions it seems logical to expect that in the presence of MAN and with an equal concentration of radical initiators a higher concentration of tertiary radicals in the polypropylene will be formed than in the absence of MAN. Since the degradation reaction of polypropylene is caused by tertiary radicals [19] which undergo β-scission (Reaction 3), the presence of MAN will result in lower molecular weight aPP. This is represented by the dependencies shown in Fig. 1.



$$-\overset{CH_3}{\underset{\cdot}{C}}-CH_2-\overset{CH_3}{CH}- \xrightarrow{\beta\text{-scission}} -\overset{CH_3}{C}=CH_2 + \overset{CH_3}{CH}- \quad (3)$$

On the other hand, the dependency shown in Fig. 1 also illustrates that at small concentrations of MAN (approximately 2%), a certain increase of molecular mass of aPP is observed. It is quite probable that with low concentrations of MAN a proportional increase in the concentration of tertiary radicals cannot compete with the simultaneous reaction in which MAN forms a crosslink between PP chains, which generally proceeds as a side reaction. The extent of this reaction depends on the ratio of free radical concentration to MAN concentration (Reaction 4).



(4)

With an increasing ratio, the probability of the occurrence of Reaction (4) will also increase. On the other hand, with a decreasing ratio the extent of reactions (2) and (3) will increase. Reaction (4) will appear mainly in cases where the radicals in neighboring chains are so close to each other that additive and consequently recombining reactions are favored over transfer reactions. The distance between two radicals in the polymer melt depends on the reactivity of radicals of the peroxide initiators [19]. This consideration about the possibility of reactions between radical pairs in the polymer relative to the possibility of other reactions is very significant since we have to take into account the considerable viscosity of the melt and the course of reaction under static conditions.

Binding of MAN to aPP under the reaction conditions used for observation of the molecular weight is shown in Table 1. This observation leads to the conclusion that the greater rate of decay of peroxide at the higher temperature leads to a considerable increase of binding of MAN to the polymer chain only in the case of a higher MAN content.

It is interesting to compare the dependence of $\overline{M}_n$ on the reaction temperature at two different contents of MAN and a constant content of peroxide in the reaction mixture. In the case of 6 wt% MAN and 3 wt% TBPB, $\overline{M}_n$ decreases with increasing reaction temperature up to 160°C. Above 160°C, $\overline{M}_n$ begins to increase, and at 180 and 190°C the samples become quite crosslinked (Fig. 2).

If only 4 wt% MAN and 3 wt% TBPB are present in the reaction mixture, the dependence of $\overline{M}_n$ on the reaction temperature is quite different (Fig. 3). Increasing the temperature from 130°C leads to an increase in $\overline{M}_n$ up to 160°C where the maximum $\overline{M}_n$ is reached. Any further temperature increase has a negative influence on $\overline{M}_n$. Gel formation was not observed over the whole temperature range.

The differences in the course of both dependencies shown in Figs. 2 and 3 agree with the explanation based on the ratio of concentrations of free radicals to concentrations of MAN. The participation of MAN in the crosslinking reaction of polypropylene is not surprising since unsaturated compounds are generally used as crosslinking agents for radical crosslinking of saturated polymers [19]. MAN at 6 wt% can be considered to be above the "critical" amount of crosslinking agent at the peroxide concentration used. The presence of 4 wt% MAN and 3 wt% TBPB seems to be below the "critical" amount of crosslinking agent, and thus it is insufficient for crosslinking aPP at the reaction conditions used.

For large amounts of MAN (Fig. 2), the initial temperature increase speeds up Reactions (2) and (3). Because of the high MAN content, Reaction (4) starts to compete with Reactions (2) and (3) only at temperatures above 160°C, at which a higher decomposition rate for the peroxide results in a higher stationary concentra-

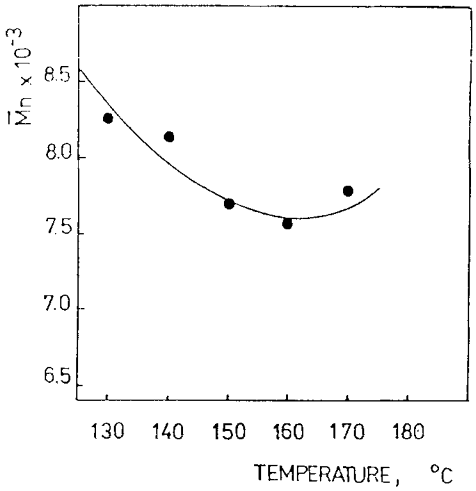


FIG. 2. The effect of temperature on number-average molecular weight ($\overline{M}_n$) of aPP (3 wt% TBPB, 6 wt% MAN).

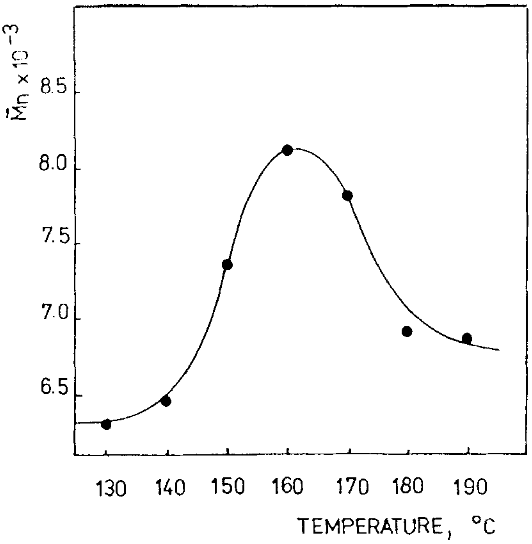


FIG. 3. The effect of temperature on $\overline{M}_n$ of aPP (3 wt% TBPB, 4 wt% MAN).

tion of radicals. This supports Reaction (4), i.e., the formation of crosslinks between polymer chains, which can lead to the formation of a polymer network.

At low amounts of MAN (4 wt%), Reactions (2) and (3) compete less favorably with Reaction (4). Reaction (4) prevails at high temperatures for the same reason as in the previous case—high radical concentration. The lower MAN content relative to the peroxide content explains the increase of $\overline{M}_n$ which is observed at 140°C (Fig. 3), but which is reached in the case of 6 wt% MAN only at 160°C (Fig. 2). On the other hand, increasing of temperature above 160°C leads to an increase of Reactions (2) and (mainly) (3) much more than of Reaction (4) because of the low content of MAN which causes a remarkable decrease of the curve above 160°C in Fig. 3.

CONCLUSIONS

The functionalization process of PP with MAN presents a complex reaction mechanism which consists of parallel reactions.

The binding reaction of MAN is followed by reactions leading to degradation or an increase in molecular mass. There are reaction conditions under which degradation due to the increasing molecular mass of PP prevailed.

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