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Functionalization of low molecular weight atactic polypropylene
Part II. Thermal and molecular weight studies

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Summary

Number average molecular weight (M_n), intrinsic viscosity ([η]) and glass transition temperature (T_g) of low molecular weight atactic polypropylene (APP) grafted with 4-allyl-1,2-dimethoxybenzene (DMAB), 4-allyl-2-methoxyphenol (eugenol) and 4-propenylanisole (trans-anethole) in the presence of dicumyl peroxide (DCP) at 170°C were determined. The influences of reaction time, concentration and extent of grafting on M_n, [η] and T_g of APP were examined. The data were discussed with the mechanism of grafting reactions.

Introduction

Functionalization of polypropylene (PP) is a popular research area because of its limited applications (1-3). Functional modification of PP was studied by several workers by using various methods (4,5). Some of the studies cover the use of unsaturated compounds, which under the reaction conditions are usually unable to give propagation step up to an appreciable extent (6-10). The initiation in the functionalization of PP with such compounds in the presence of organic peroxides takes place by the decomposition of peroxide, which abstracts hydrogen from the polymer chain. However, formation of a radical on the used functional compound is also possible. Therefore, depending on the nature of the used compound, grafting reactions may follow an addition or a combination mechanism (6,7). The reaction of functional compound with primary (1°) and secondary (2°) polymer radicals generally is accepted to be more favored than with tertiary (3°) radicals due to steric reasons (8,11,12). However, the low stability of the unreacted 3° radicals lead to chain scission, hence decreases in molecular weight (MW) (9,11,13,14). PP mainly experiences chain scission during peroxide modification, which leads to a decrease in MW and MW distribution. This process is often accompanied by branching and crosslinking (13,15).

This second paper considers mainly the thermal and MW studies of the samples prepared in Part I (6). The influences of reaction time, concentration of functional compounds and DCP and extent of grafting on M_n, [η] and T_g of APP were discussed. The data were also correlated with the mechanism of grafting reactions.

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Experimental

Atactic polypropylene was first treated with boiling acetone in order to remove the low MW compounds and then with boiling benzene. The fraction soluble in benzene was used in the functionalization experiments (M_n=1.97 kg/mol, determined by cryoscopy). Reactions were carried under vacuum with several concentrations of functional compounds (5, 15, 25 and 35 wt.% w.r.t. APP) and DCP (8, 15 and 25 wt.% w.r.t. APP) at 170°C in melt, for different reaction times (20, 30, 40 and 60 min). Details of the applied functionalization and characterization techniques were already provided in Part I (6).

M_n of the samples in benzene was determined by cryoscopy. A vacuum jacketed system, equipped with a Beckmann thermometer was used. Cryoscopic constant was determined by using purified naphthalene. Reproducible freezing points were obtained by melting and freezing the solutions for several times. M_n values were calculated from the obtained linear $\Delta T/c$ vs. c curves.

$[\eta]$ of the samples in toluene were measured by means of an Ubbelhode viscometer at 25°C and was found by graphical extrapolation of the linear dependence of η_{sp}/c and η_r/c vs. c to zero concentration.

T_g of the samples were obtained from the inflexion points of the thermograms, which were calculated by the software of a Setaram. DSC 131 differential scanning calorimeter. Measurements were carried under nitrogen atmosphere with a heating rate of 3°C/min. Reproducible results were obtained by cooling and heating the samples for several times.

RESULTS and DISCUSSION

Effect of DCP on M_n, $[\eta]$ and T_g of APP

APP was reacted with DCP in similar conditions to functionalizations in order to differentiate the effects of DCP and grafting on M_n, $[\eta]$ and T_g of APP. Upon reaction with 8% DCP, products with M_n values slightly higher than the M_n of pure APP ($M_{n,APP}$) (1.97 kg/mol) were obtained (Table 1). $[\eta]$ of these products were observed to be varied around the $[\eta]$ of pure APP ($[\eta]_{APP}$) (0.136 dL/g). However, the obtained ca. 4-6°C increases in T_g values indicated formation of the products with higher MW and probably with low MW distributions. $[\eta]$ of the products increased with the increase in DCP concentration (0.155 and 0.175 dL/g at 15 and 25% DCP respectively). This result showed the increase in MW hence in crosslinking reactions. However, the slight increase in M_n at 15% DCP (from 2.34 to 2.90 kg/mol) and the followed slight reduction at 25% DCP (2.65 kg/mol), indicated a considerable increase in the chain scission reactions also. The observed decrease in T_g from -14.5 to -15.5°C and then to -16.9°C with the increase in DCP concentration also favored this conclusion. Low T_g of the products cannot only be attributed to the increased amount of low MW fractions due to chain scission reactions.

Table 1. Effect of DCP on M_n, $[\eta]$ and T_g of APP
Reaction temperature=170°C

		APP-8% DCP				APP-15% DCP	APP-25% DCP
	APP	20 min	30 min	40 min	60 min	40 min	40 min
M_n, kg/mol	1.97	2.50	3.20	2.34	2.84	2.90	2.65
$[\eta]$*10, dL/g	1.36	1.37	1.37	1.39	1.35	1.55	1.75
T_g, °C	-21.3	-16.6	-17.0	-14.5	-16.1	-15.5	-16.9

Comparing the values obtained, the unexpectedly low T_g of 8% DCP-30 min and 15 and 25% DCP products, with relatively high M_n and/or [η] also demonstrated possible branching of the products. Therefore, the absence of any order between T_g, M_n and [η], was possibly due to the variation in the extent of branching and MW distribution of the products.

Influence of Grafting on M_n, [η] and T_g of APP

The highest MW that should be obtained theoretically from the reactions due to bonded groups was about 2.70 kg/mol (calculated by assuming complete bonding of the used maximum amount of functional compound, i.e. 35%, on ca. 0.05 moles of APP). However, higher M_n values were obtained. In general, Mn, [η] and T_g of functionalization products were observed to be higher than the values of pure APP and APP-DCP products. This result demonstrated the enhancement in crosslinking reactions in most of the functionalizations.

Increases in M_n values, which indicated the decreases in chain scission, were observed in all cases with 8% DCP (except APP-35% eugenol) up to 30 min (Fig.1.a). Depending on the [η] values, it may be concluded that the crosslinking reactions slightly decreased for DMAB (decreasing [η]) but increased for eugenol and anethole (increasing [η]) (except 15% anethole) within the same reaction period (Fig. 1.b). The first sign of increase in chain scission reactions (decreasing M_n) was observed at 40 min in all cases. This result is also in agreement with the result of FTIR spectroscopic studies (6). The decrease in M_n at 40 min was accompanied with a slight increase in [η] for DMAB (except 35% DMAB-40 min) while [η] decreased for the others. Depression in M_n of eugenol and anethole grafted products (except 5% anethole-60 min) continued even at 60 min, of which demonstrated further increases in chain scission reactions. On the other hand, the unchanged or slightly increased [η] of APP-eugenol-60 min products indicated the predominance of crosslinking reactions. T_g values of eugenol and anethole bonded products (except APP-5% anethole-60 min) were also found to be lowered at 40 and 60 min, probably because of the increased content of low MW fractions (Fig. 1.c). However, the increase in M_n and [η] of the products obtained from the reactions carried with DMAB and 5% anethole for 60 min demonstrated the declined effects of chain scission within these reactions. Therefore, probably due to the depressed content of low MW fractions, T_g of these products generally were observed to be higher than the others.

At higher DCP concentrations (15 and 25%), products with higher M_n and [η] were obtained with DMAB and eugenol (Fig. 2.a-b). However, the limited increases in T_g of these products from -21.3°C up to ca. -11°C (Fig. 2.c) were probably due to the high extent of branching of the products. From the reactions carried with anethole, products with unexpectedly low [η] were obtained. Except for 5% anethole-25% DCP, the increase in DCP reduced [η] of APP-anethole products almost to $[\eta]_{APP}$. On the other hand, M_n of these products were 2-4 times higher than $M_{n,APP}$. This result may indicate the decrease in chain scission and also, in crosslinking reactions up to certain extents. On the contrary, considerably high T_g of APP-anethole-15 and 25% DCP products (-13.6,-12.1°C) demonstrated formation of the products with low branching and MW distributions.

Mechanism of Functionalization

Formation of an allylic radical on DMAB and eugenol was proposed previously (Scheme 1) (6). Combination of polymer and allylic radicals would result in the formation of an unsaturated group on the polymer chain, which probably acts as a crosslinking site in the reactions. Disappearance of the double bond peak at 1650 cm^{-1}, in the FTIR spectrum of certain products (6) also showed the consumption of these double bonds, probably through the crosslinking reactions.

Except the M_n (17.5 kg/mol) of APP-5% DMAB-25% DCP (Fig. 2.a), M_n of other DMAB grafted products were ca. 2.5-4.4 times higher than $M_{n,APP}$. This general trend of increase in M_n demonstrated the low extent of formation of chain scission (ß-scission), hence the low concentration of 3° polymer radicals in DMAB grafting. APP-DMAB products showed a considerable increase in T_g, from -21.3°C (T_g of pure APP, $T_{g,APP}$) up to -11.3°C (Fig. 2.c). However, variation of these values in a somewhat narrow range (-14.8,-11.3°C), may also be attributed to the low extent of chain scission reactions. Otherwise, higher extent of branching and MW distribution, hence greater variations in T_g

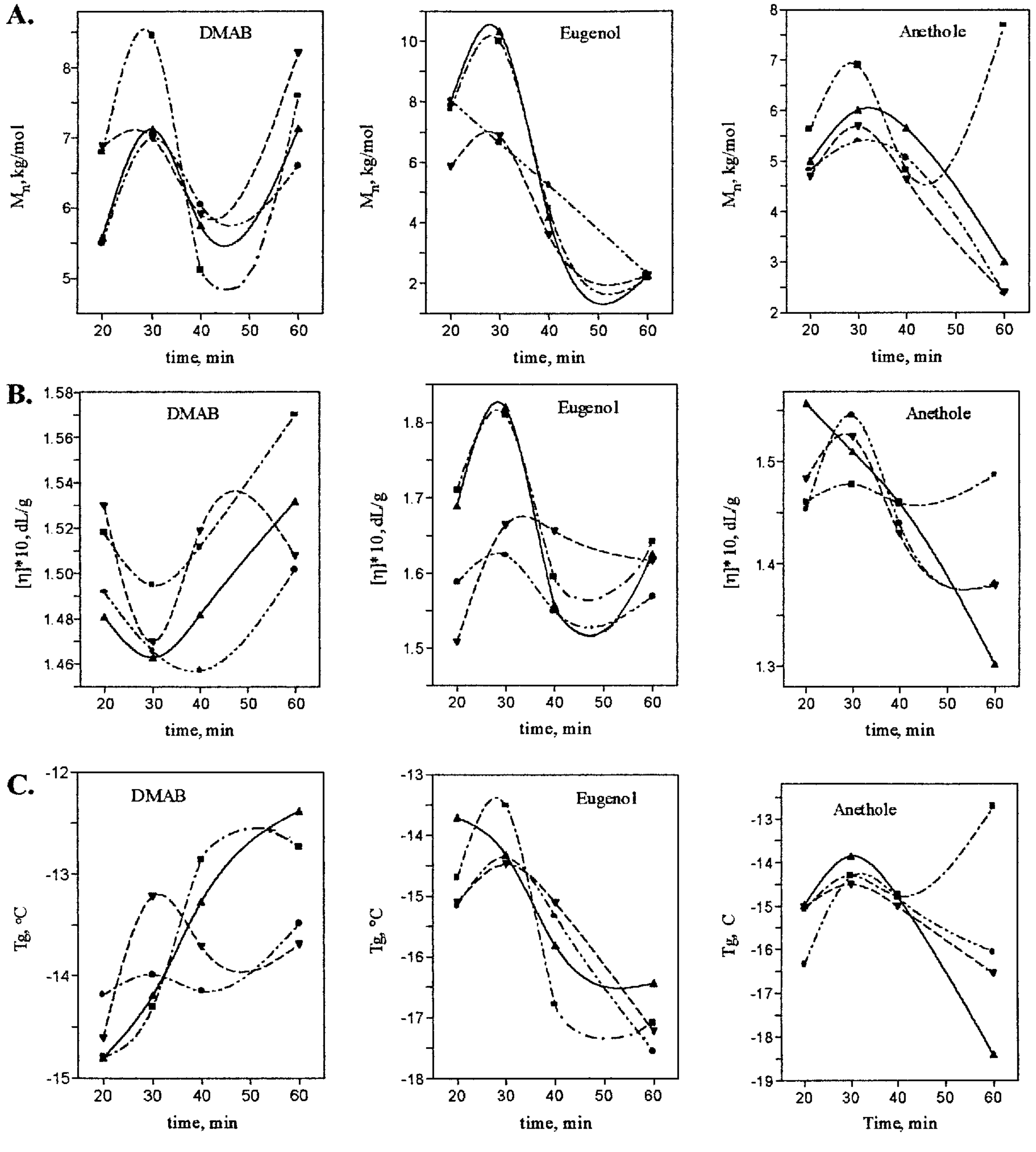


Figure 1. Effect of reaction time on **a)** M_n, **b)** [η] and **c)** T_g of APP
DCP=8 wt.%, reaction temperature=170°C
Compound concentration, wt.%= 5(--■--), 15(—▲—), 25(--▼--), 35(--●--)

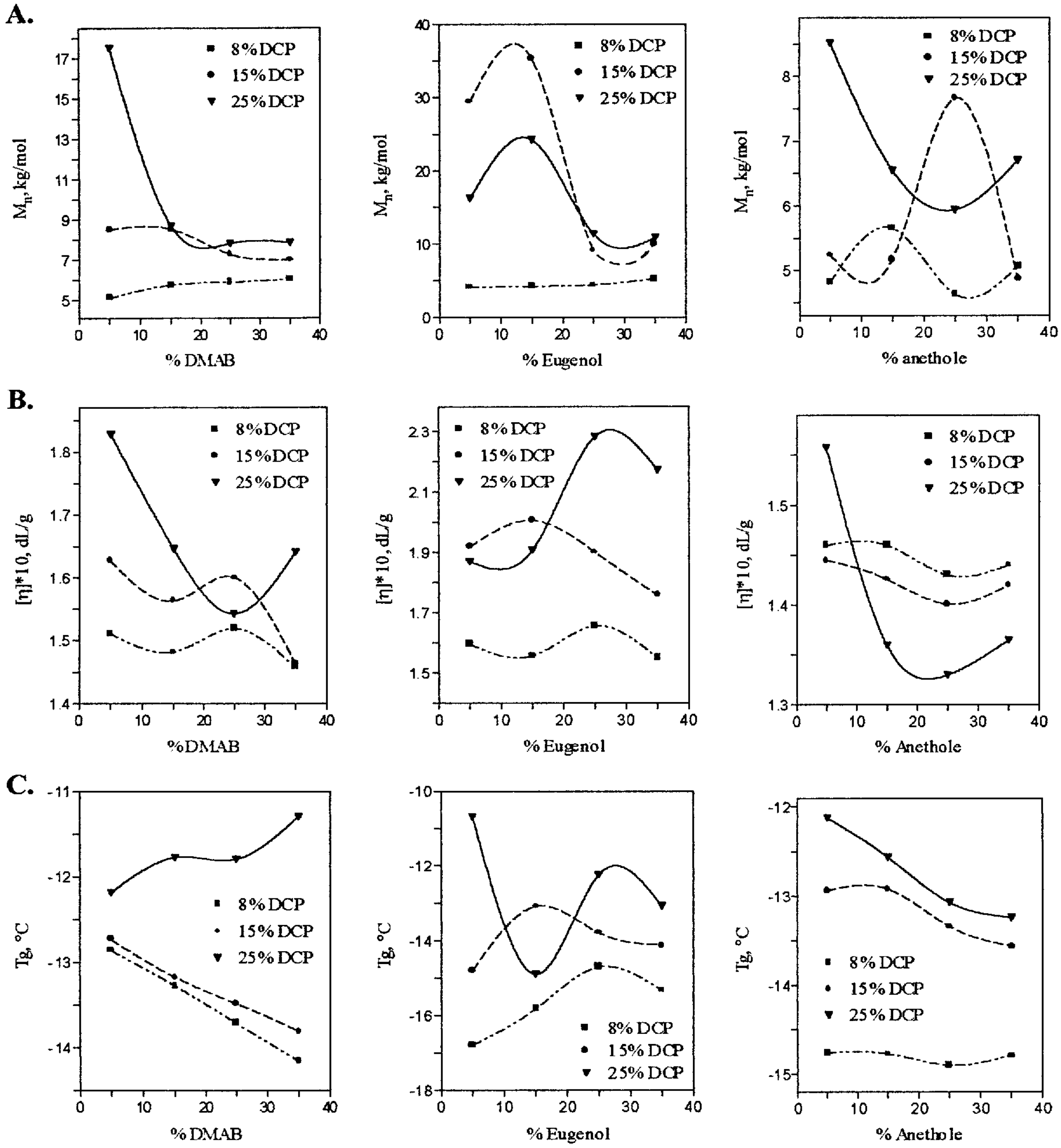
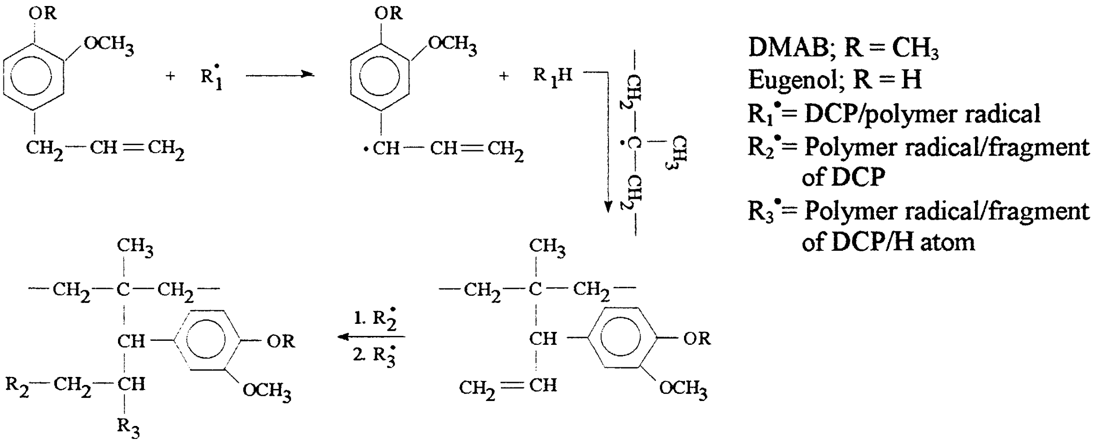


Figure 2. Effect of DCP concentration on **a)** M_n, **b)** [η] and **c)** T_g of APP
Reaction temperature=170°C, reaction time=40 min

(as in the case of eugenol) would be expected. Therefore, as the result of reductions in chain scission reactions slight increases in [η] (up to 1.3 times) were obtained. Thus, it may be concluded that, in case of functionalization with DMAB and probably with the other allyl compound eugenol, grafting reactions mainly proceed by the combination of 3° polymer radical with the formed allylic radical (Scheme 1).

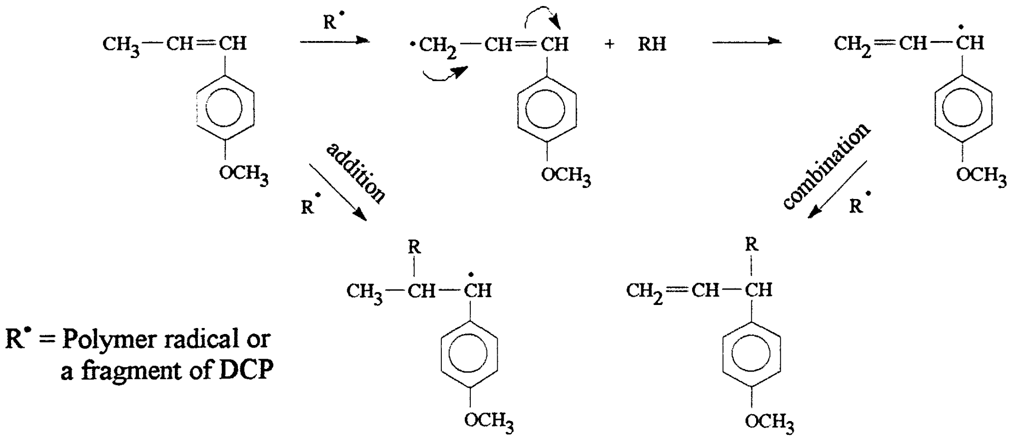
Eugenol differs than DMAB by containing a OH group. Either free or bonded, it may give rise to the formation of phenoxide radical. Therefore, the possibility of hydrogen abstraction of phenoxide radical from the polymer chain (inter- or intra-molecular) may increase the concentration of polymer radicals. M_n of APP-eugenol products, obtained from the reactions carried with 8% DCP for 20 and 30 min ($[3.0\text{-}5.3]^{*}M_{n,APP}$), were



Scheme 1. Mechanism of Functionalization

higher than the M_n of corresponding DMAB grafted products ($[2.8\text{-}4.3]^*M_{n,APP}$). However, the unexpected decreases in M_n at 40 (ca. $[2.0\text{-}2.5]^*M_{n,APP}$) and 60 min (almost equal to $M_{n,APP}$) (Fig. 1.a) indicated a considerable production of 3° radicals, probably due to enhancement of phenoxide radical. On the other hand, high $[\eta]$ of these products (slightly higher than the $[\eta]$ of corresponding DMAB grafted products) demonstrated the predominance of the crosslinking reactions. In addition, reductions by 1-3°C in T_g of these products (-15.8,-17.6°C), because of the increased amount of low MW fractions, were obtained as expected. In general, lower extent of grafting was obtained with eugenol than with DMAB (6). Therefore, high $[\eta]$ of APP-eugenol-8% DCP products cannot be attributed wholly to the reaction of polymer radicals with the unsaturated groups of eugenol molecules, which were bonded in low amounts. Thus, the probable hydrogen abstraction of phenoxide radicals may also cause to increase in the concentration of 2° polymer radicals. At higher DCP concentrations, APP-eugenol products with higher M_n ($[4.7\text{-}18.0]^*M_{n,APP}$) and $[\eta]$ ($[1.3\text{-}1.7]^*\ [\eta]_{APP}$) were obtained. It is probable that, because of the consumption of 3° radicals in grafting reactions, amount of these radicals remain well below the critical concentration at which the chain scission reactions start to compete with the crosslinking reactions. Consequently, higher increases in M_n and $[\eta]$ were seen. Although, the product with highest T_g (-10.7°C, i.e., $2^*T_{g,APP}$) was obtained with eugenol (5% eugenol-25% DCP) (Fig. 2.c), almost equal or lower T_g of APP-eugenol products than the corresponding APP-DMAB products demonstrated a higher degree of branching in APP-eugenol products.

Usually products with lower M_n (2.39-8.52 kg/mol) and $[\eta]$ (0.130-0.156 dL/g), than the products of DMAB and eugenol, were obtained with anethole. FTIR spectra of some APP-anethole products indicated the presence of double bond on APP due to bonded molecules. Therefore, formation of a methylene radical, which rearranges into an allylic radical and combination of this radical with a polymer radical was proposed previously (6) (Scheme 2). Considerably high $[\eta]$ of the products obtained from the reactions carried in the presence of 8% DCP with 5% anethole and from those carried up to 40 min, may indicate a grafting mechanism similar to that of DMAB and eugenol. However, at 8% DCP-40 min (Fig. 1), the obtained values remained almost constant (% grafting=2.1-2.3 wt.% (6), M_n=4.6-5.6 kg/mol, T_g=-14.7,-14.8°C) without indicating any dependence on the anethole concentration of the reaction mixtures. At 60 min, although approximately equal extent of grafting to 40 min was obtained, M_n (2.4-3.0 kg/mol) and



Scheme 2. Grafting reactions of anethole.

[η] (0.130-0.138 dL/g) of APP-anethole products (except 5% anethole) decreased to the values of pure APP (Fig. 1). T_g values also were observed to be decreased (-18.4,-16.1°C) with the decrease in MW (Fig. 1.c). The declined effects of crosslinking reactions may be attributed to the increase in addition reactions (Scheme 2). The possible consumption of 2° polymer radicals and loss of unsaturated groups on the bonded molecules in addition reactions probably decreases the crosslinking efficiency of APP. An increase in the concentration of 3° polymer radicals hence in chain scission reactions due to inter- or intra-molecular hydrogen abstraction of the radical formed on the molecule after an addition may also be expected.

At higher DCP concentrations, the reactions with anethole (except 5%) unexpectedly differed than those carried with DMAB and eugenol by showing decreases in [η] and slight increases in M_n (Fig. 2.a-b). Almost equal [η] of 15% DCP (0.140-0.145 dL/g) to those of 8% DCP-40 min (0.144-0.146 dL/g) may demonstrate the prevailing of combination reactions up to a certain extent. However, at 25% DCP, for the reactions carried with the concentrations of anethole higher than 5%, the possible cause of reductions in [η] (0.136-0.137 dL/g) to $[\eta]_{APP}$, may indicate predominance of the addition reactions. The absence of double bond peak at 1650 cm^{-1}, in the FTIR spectra of these products may also be attributed to the followed addition mechanism. Although the crosslinking reactions decreased tremendously at 25% DCP (except 5% anethole-25% DCP), slight increases in M_n (5.24-8.52 kg/mol) and almost equal T_g of the products (-13.2,-12.1°C) to the T_g of corresponding DMAB and eugenol products (Fig. 2.c), demonstrated a low degree of branching and a probable rearrangement in MW toward to low distribution.

Dependence of T_g and [η] on the Extent of Grafting

The effect of grafting on thermal properties of APP was followed by T_g. A gradual change from a non-polar to polar structure leading to greater secondary forces between chains, hence increases in T_g were expected with the introduction of functional compounds on APP. However, T_g of eugenol and anethole grafted products did not indicate any dependence on the amount of bonded groups. Therefore, it may be concluded that the T_g values were mainly affected by the MW and MW distribution of the products. In addition, the dependence of T_g on the extent of branching was observed in some cases. With DMAB, the observed certain linearity between T_g and amount of bonded groups (highest with 5% DMAB) showed the dependence of T_g on the degree of grafting up to a certain extent. This result may demonstrate the homogeneity of the reactions carried with DMAB. The other property that was expected to be affected with the increase in secondary forces is [η]. The obtained results did not clearly indicate any dependence of [η] on the content of grafted groups. Therefore, it may be concluded that the [η] values mainly biased to higher MW fractions of the products.

Conclusion

Products with higher M_n, [η] and Tg values than that of pure APP and APP-DCP products, were obtained upon grafting. Results of functionalizations carried with DMAB and eugenol indicated a combination mechanism, which enhances the crosslinking reactions. Unexpectedly low M_n and [η] of APP-anethole products were attributed to the competition between addition and combination reactions. At 8% DCP-60 min and 15-25% DCP reactions, predominance of the addition mechanism was proposed. In general, the increased extent of formation of disproportionation reactions at high DCP concentrations (6) may also be expected to be effective on further increases in MW. T_g of the products generally showed about 10°C increases at high DCP concentrations. T_g values varied with the changes in MW, MW distribution and degree of branching of the products.

Finally, the results indicated that the functionalization of PP with such compounds might be an important way of modifying the properties of PP without decreasing the MW.

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