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Functionalization of low molecular weight atactic polypropylene

Part I. Spectroscopic studies

Zeki Öktern[1], Sedat Çetin[2], Gudlsu Akin-Öktem[1,*]

[1] Department of Chemistry, Faculty of Arts and Sciences, Kirikkale University,
TR-71100 Yahşihan, Kirikkale, Turkey

[2] Department of Chemistry, Faculty of Arts and Sciences, Aban İzzet Baysal University,
TR-14280 Gölköy, Bolu, Turkey

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Summary

Low molecular weight atactic polypropylene (APP) was functionalized with 4-allyl-2-methoxyphenol (eugenol), 4-allyl-1,2-dimethoxybenzene (DMAB), 4-propenylanisole(trans-anethole), cis-2,4,5-trimethoxypropenylbenzene (β-asarone) and 4-allyl-2,6-dimethoxyphenol (ADMP) in the presence of dicumyl peroxide (DCP) at 170°C. Amount of grafted eugenol, DMAB and anethole on APP and characterization of the products were carried by UV-VIS and FTIR spectroscopies respectively. The effects of the reaction time, concentrations of the functional compounds and DCP on the extent of grafting were examined.

Introduction

Among the polyolefins, polypropylene (PP) is one of the widely used plastics with very suitable mechanical and chemical properties. However, its applications are limited due to inertness toward chemicals, poor hygroscopicity, sensitivity to photo or thermal oxidation, low dyeability, low melting point and sticking temperatures, inadequate compatibility with other synthetic polymers and no adhesion to metals or inorganic fillers. PP cannot be modified by polar groups via copolymerization of propylene with polar monomers because of the high sensitivity of Ziegler-Natta catalysts to heteroatoms present in the polar monomers. Therefore, an increase in the polarity of PP can only be obtained through additional functionalization processes (1,2). Halogenation (3,4) or substitutions of halogen containing groups and graft copolymerization of several vinyl monomers onto PP are widely used techniques in the functional modification of PP (5-11). Recently, in order to avoid formation of long side chains and marked changes in the mechanical properties of PP, monomers which are unable to give propagation step up to an appreciable extent under the reaction conditions have been used (9-12).

In this work, with regard to easier preparation of the reaction mixtures and to the characterization of the reaction products, APP was used in the functionalizations with several allyl and 1,2-disubstituted alkene compounds. Functionalizations with these compounds are similar to the graft copolymerizations in which the polymer radicals reacting with the compounds are obtained by using peroxides. The study covered the

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[*] Corresponding author

influence of the reaction time and the concentration of the functional compounds on the extent of grafting, as well as the mechanistic aspects of grafting reactions.

Experimental

Atactic polypropylene was supplied from Turkish Petrochemical Industry, PETKİM, Aliağa, TURKEY. It was first treated with boiling acetone in order to remove the low molecular weight compounds and then with boiling benzene. The fraction soluble in the last solvent was used in the functionalization experiments (M_n=1.97 kg/mol, determined by cryoscopy).

Chemicals, DMAB, ADMP, β-asarone and DCP were the products of Aldrich and eugenol and trans-anethole were purchased from Merck. Laboratory grade solvents and reagents were purified and dried by standard methods before used.

The functionalization mixtures were prepared by dissolving a calculated amount of DCP (8, 15 and 25 wt. % with respect to APP) in a benzene solution of a known weight of APP sample in a glass ampoule. After evaporating the solvent by freeze drying, a calculated amount of functional compound (5, 15, 25 and 35 wt. % with respect to APP) was added onto APP-DCP mixture. The reaction ampoules were evacuated and sealed under vacuum. The mixtures for the reactions between APP and DCP were also prepared in the similar way. The reactions were carried at 1.70°C for different reaction times (20, 30, 40 and 60 min) in melt. The products were twice dissolved in toluene and precipitated in methanol. In similar conditions, no precipitation was observed for the reactions carried between DCP and functional compounds in the absence of APP. This showed merely the precipitation of APP with bound groups from the functionalization mixtures.

Functionalizations of APP with DMAB, eugenol and anethole were studied in detail. Dependence of the content of bonded groups on the concentration of these compounds was examined with various concentrations of DCP at 170°C for different reaction times. Functionalizations carried with asarone and ADMP were studied in the presence of 8% DCP for 40 min and the products were only characterized by FTIR spectroscopy.

The contents of the bonded eugenol, anethole and DMAB groups onto APP were followed by a Shimadzu, UV-160 A UV-VIS spectrophotometer. Measurements were carried at λ_{max} values of the hydrogenated compounds as described previously (12). Hydrogenations were carried under hydrogen gas (1 atm) in the presence of platinum oxide and the obtained products were purified by vacuum distillation through a vigreux column (yield = 80-90%).

FTIR spectroscopic characterizations of the samples were carried with a Jasco FTIR-430 spectrometer by using films prepared on KBr pellets.

Results and Discussion

Extent of grafting

In functionalizations of APP with DMAB and anethole, in the presence of 8% DCP at 170°C, amount of the grafted groups onto APP increased with time and reached to a maximum at 40 min (Fig. 1). Nearly equal content of bondings at 40 and 60 min indicated the completion of bonding reactions approximately at 40 min. In addition, it was observed that in each set of functionalization (functionalizations carried out at the same reaction conditions) the amount of bonded DMAB and anethole groups increased to a

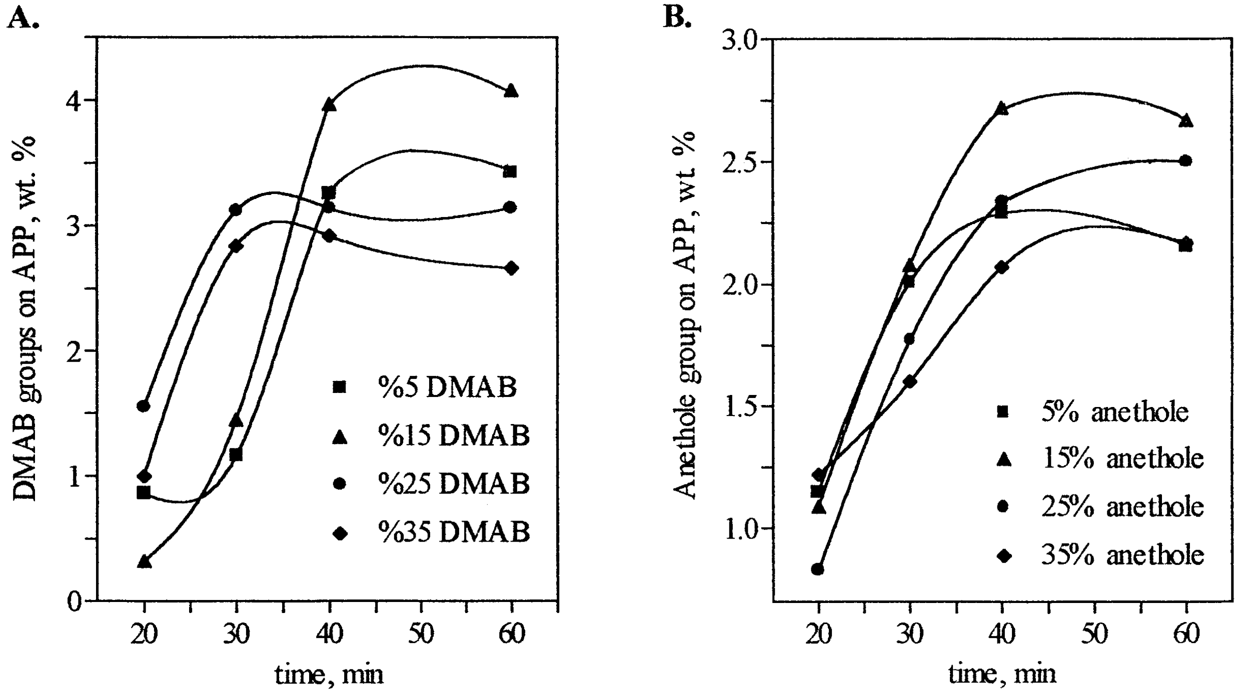


Fig. 1. Formation of **a)** DMAB and **b)** anethole groups on APP with time (DCP=8 wt. %, reaction temperature=170°C).

maximum value as the concentrations of the compounds increased in the reaction mixtures. However, a further increase in the concentration of compounds caused to decrease in the content of the bonded groups. These decreases may indicate that the direct reactions between peroxide radicals and free functional compounds start to compete remarkably with the formation of reactive radical sites on APP chains. Hence, the possibility of binding of DMAB and anethole groups onto APP decreases. A similar result with a maximum at 15% was also reported by Borsig and Brown(12) for the functionalization of atactic polypropylene with DMAB in the presence of 8% DCP at 170°C for 40 min.

In case of functionalization of APP with eugenol in the presence of 8% DCP extent of grafting was lower than those obtained with DMAB and anethole (Fig. 2). Differing from the functionalizations with previous compounds, the maximum amount of bonding was obtained from the mixtures containing the lowest eugenol concentration, i.e. 5%. Eugenol, which contains an OH group, may give rise to the formation of phenoxide radical. Formation of Phenoxide radical probably enhances direct reactions between peroxide radicals and free eugenol molecules.

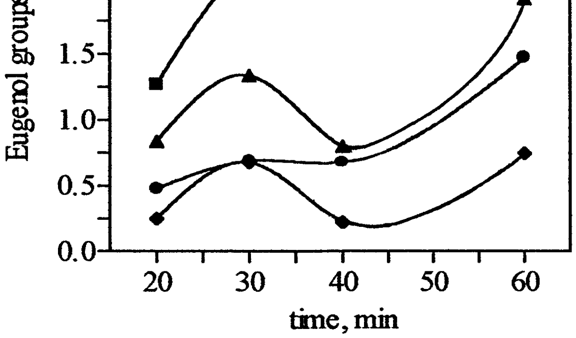


Fig. 2. Formation of eugenol groups on APP with time (DCP=8 wt. %, reaction temperature=170°C).

Therefore, the possibility of these direct reactions increases with eugenol content, since the possibility of finding eugenol molecules in the vicinity of a DCP radical becomes higher.

Effect of radical concentration

The effect of radical concentration on the content of the bonded groups was examined by increasing the concentration of DCP in the reaction mixtures. An increase in the content of the bonded groups was obtained in all cases with the increase in DCP concentration (Fig. 3). This indicated the increase in the possibility of formation of polymer radicals, which bound functional groups in the proceeding step.

When DCP concentration was increased from 8 to 25% the amount of bonded DMAB and anethole groups increased about 2-3 times (Fig 3). However, the increase in bonded eugenol groups was surprisingly much higher than DMAB and anethole (3 times for 5%, 10 times for 15 and 25% and 20 times for 35%). This result demonstrates that the radical concentration becomes high enough to react both with free eugenol molecules and APP chains to form more active centers when DCP concentration is increased.

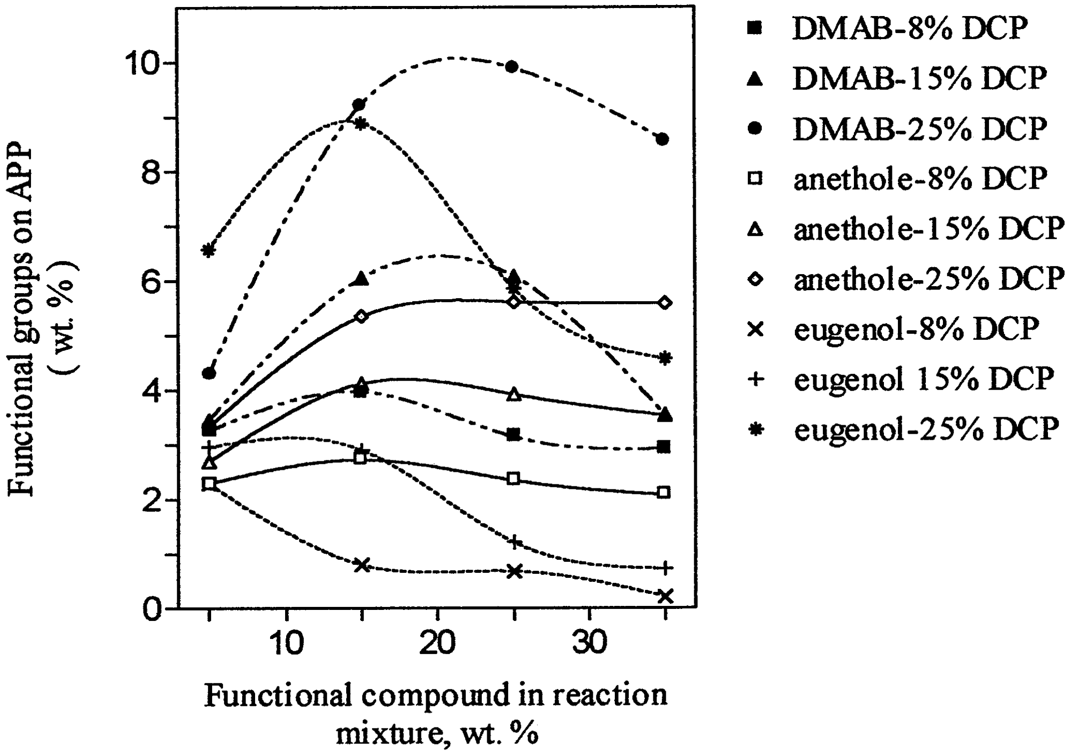
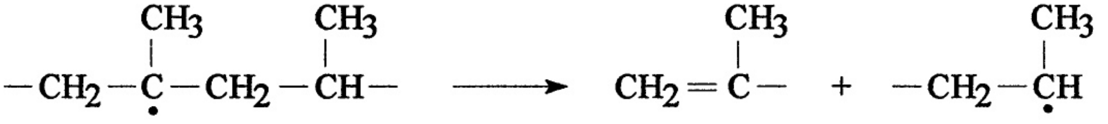


Fig. 3. Effect of DCP concentration on the formation of functional groups on APP (reaction temperature = 170°C, reaction time = 40 min), DMAB (–··–··–··); anethole (————); eugenol (--------).

Reaction between APP and DCP

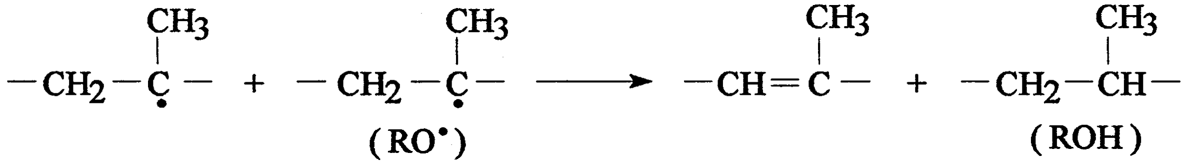
APP was reacted with DCP in reaction conditions similar to functionalizations. These reactions were followed by FTIR. The spectra of APP samples that were reacted with DCP in the ratios of 0.6-1.9 mmol DCP/mol APP at 170°C for 20-60 min, indicated the formation of two new bands at around 1642 and 1691 cm^{-1}. No any other significant change than the spectrum of pure APP was observed (Fig. 4).

The band at 1642 cm^{-1} is associated with the vibrational mode of the C-H bonds in a $=CH_2$ group. The formation of a product containing $=CH_2$ group is possible through the chain scission reaction as follows (eq. 1),



$$-CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\overset{CH_3}{\overset{|}{CH}}- \longrightarrow CH_2=\overset{CH_3}{\overset{|}{C}}- + -CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}H \qquad (1)$$

On the other hand, the band observed at 1691 cm^{-1} whose intensity increased with DCP concentration was due to the C-H bond in a -CH=C- group of a product. Formation of a double bond along the main chain is possible through a disproportionation process between a polymer radical and a DCP radical, $RO^\bullet$, or between two polymer radicals, as shown in eq. 2. The relative intensities of these bands indicated the increase in the extent of formation of disproportionation reactions with the increase in DCP concentration.



$$-CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}- + \underset{(RO^\bullet)}{-CH_2-\underset{\bullet}{\overset{CH_3}{\overset{|}{C}}}-} \longrightarrow -CH=\overset{CH_3}{\overset{|}{C}}- + \underset{(ROH)}{-CH_2-\overset{CH_3}{\overset{|}{CH}}-} \qquad (2)$$

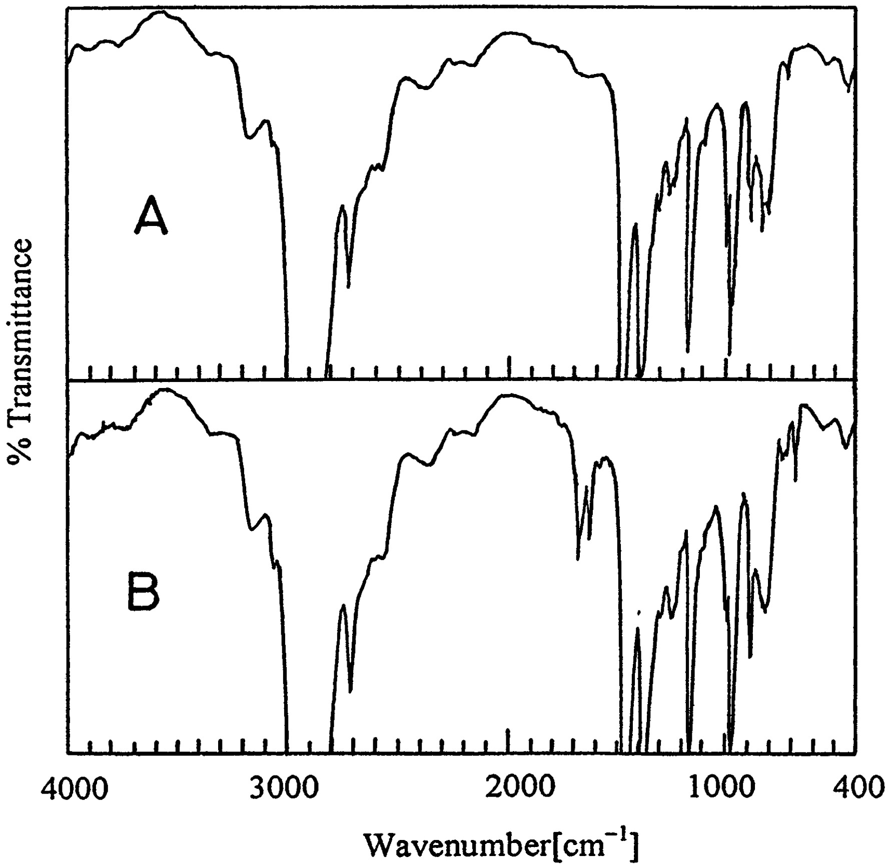
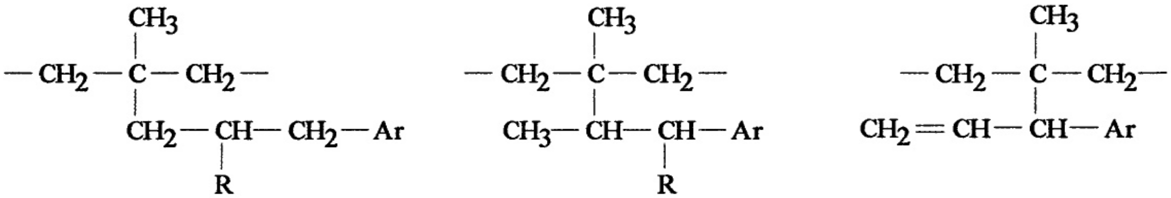


Figure 4. FTIR spectra of a) Pure APP, b) APP reacted with 25 % DCP (reaction temperature = 170°C, reaction time = 40 min).

Mechanism of functionalization

In the functionalizations carried by chain transfer reactions, the polymer radical formed by the hydrogen abstraction after decomposition of peroxides are important in the first stage of reactions. In these reactions, methine and then methylene hydrogens were generally assumed to be most reactive (1,4,12). In the following steps, polymer radicals may react with the functional compound or may be consumed in other reactions such as disproportionation, chain scission, cross-linking, etc. The reaction between polymer radical and functional compound generally follows two different reaction mechanisms;
i. The addition of polymer radical to the olefinic double bond of the functional compound, in which saturation of the olefinic double bond takes place (structures I and II in eq. 3 for the addition to allylic and disubstituted alkene compounds respectively), ii. The combination of polymer radical with the radical on the functional compound, which may form at the preceding transfer reaction of the functional compound with a primary radical of a peroxide or with a polymer radical. The most possible radical that may form on the used allyl compounds is an allylic radical, $(CH_2{=}\dot{C}H\text{-}CH\text{-}Ar)$, and on the used disubstituted alkene compounds is a methylene radical, $(\dot{C}H_2{-}CH{=}CH{-}Ar)$, which probably rearranges into an allylic radical. Therefore, formation of olefinic double bonds on APP due to the bonded groups is expected (structure III).



(3)

I II III

FTIR spectra of the products obtained from different stages of functionalization of APP with DMAB, anethole and asarone showed a peak at around 1650 cm^{-1}, which is attributed to the vibration of C-H bonds of the $=CH_2$ group. 'The presence of $=CH_2$ groups on the functionalized APP samples indicate a radical combination mechanism for the reactions between APP and allyl or 1,2-disubstituted alkene compounds (Fig. 5.a.II-5.c.II). The peak at 1650 cm^{-1} in the spectra of the products obtained from the functionalizations carried with asarone and ADMP in the presence of 8% DCP for 40 min demonstrated also a radical combination mechanism.

FTIR spectra of APP samples with bonded eugenol groups showed a band at around 3560 cm^{-1} due to unreacted OH groups (Fig. 5.c). Therefore, the possibility of formation of a combination reaction between a polymer and a phenoxide radical may expected to be low. This conclusion can also be extended to the functionalizations with ADMIP, since the FTIR spectra of the products showed the presence of unreacted OH groups on ADMP bonded APP samples.

The peaks of some products at about 1642 and 1692 cm^{-1} could be referred to the products of chain scission and disproportionation reactions, respectively. The spectra of the products of functionalizations carried with DMAB, eugenol and anethole up to 30 min indicated only the peak at 1650 cm^{-1}. M_n and $[\eta]$ values of these products increased also up to 30 min (13). However, this result does not show the complete absence of chain scission and disproportionation reactions. The extents of formation of these reactions are probably low up to this stage of reactions. The peak at 1642 cm^{-1}, which probably overlaps the peak at 1650 cm^{-1}, was first observed for the products of functionalizations carried for 40 min with low concentrations of compounds, i.e. 5% (Fig. 5.a.I-5.c.I). Decreases in M_n values of these products were also observed at 40 min (13). However, this peak (1642 cm^{-1}) was disappeared with the increase in the concentrations of functional compounds (Fig. 5.a.II-5.c.II). Similar behavior was also observed for the products of the functionalizations carried for 60 min.

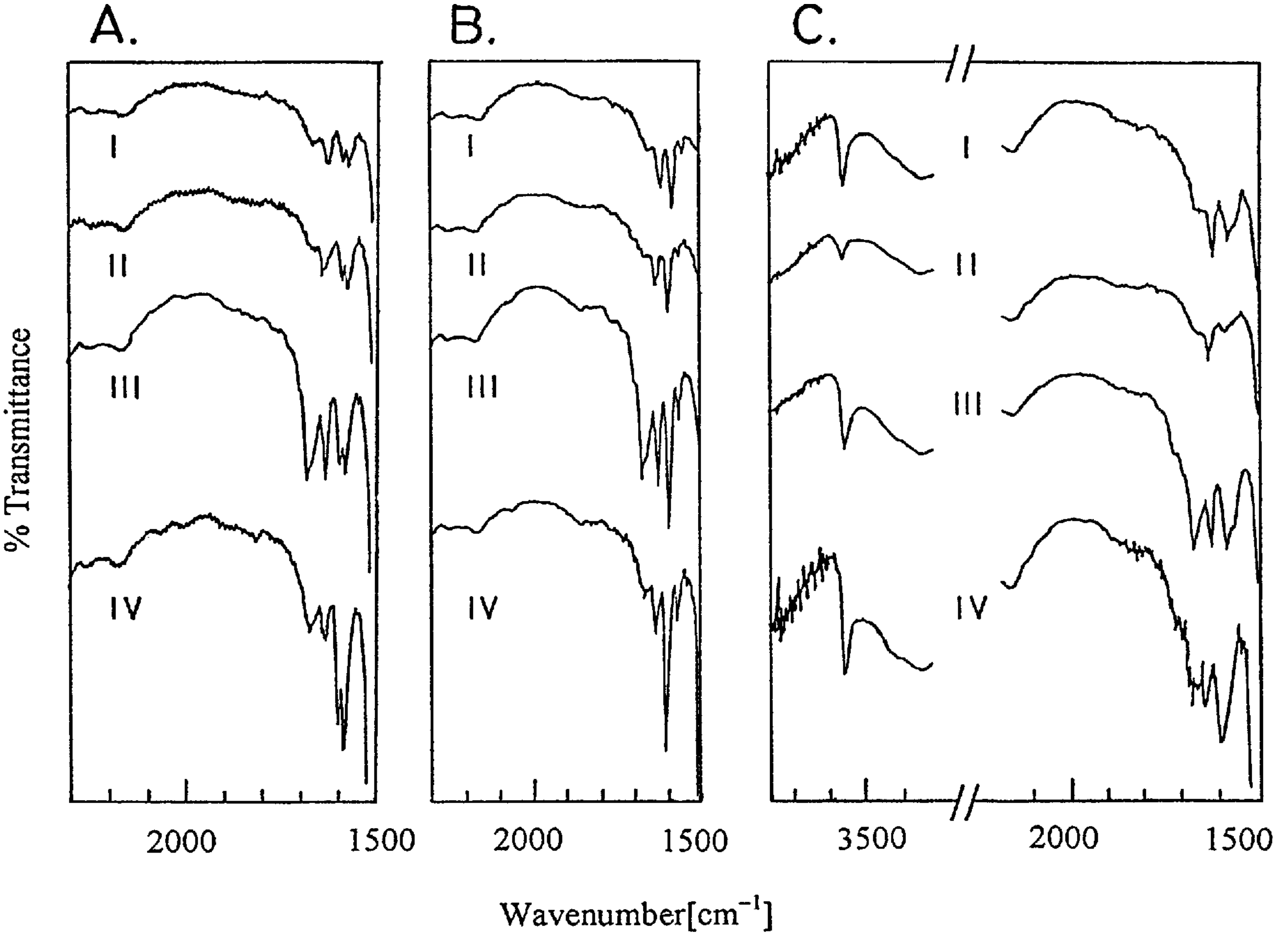


Figure 5. FTIR spectra of APP with bonded a) DMAB, b) anethole, c) eugenol groups. I. 5% (DMAB, eugenol, anethole)-8% DCP, II. 15% (DMAB, eugenol), 35% (anethole)-8% DCP, III. 5% (DMAB, eugenol, anethole)-25% DCP, IV. 25% (DMAB), 35% (eugenol, anethole)-25% DCP. (reaction temperature=170°C, reaction time=40 min)

Among the functionalizations of APP with asarone and ADMP (5-35%), which were only carried in the presence of 8% DCP for 40 min, the FTIR spectra of the ADMP bonded APP samples differed than the others by indicating only the presence of the band at 1650 cm^{-1}.

The spectra of the products of functionalizations carried with 5-15% DMAB and 5% eugenol in the presence of 15% DCP indicated also the formation of the bands at 1642 and 1691 cm^{-1} (less intense band). These peaks were disappeared with the increase in the concentrations of the compounds. However, they observed for all products obtained from the functionalizations carried with 5-35% anethole in the presence of 15% DCP. In the functionalizations carried with 25% DCP, although further increases in the contents of the bonded groups were obtained (Fig. 3), FTIR spectra of the products indicated also the formation of the peaks at 1642 and 1692 cm^{-1}. The relative intensities of these peaks with respect to the benzene peak at 1600 cm^{-1} were observed to be decreased with the increase in the concentration of functional compounds. The decrease in the intensity of 1692 cm^{-1} was higher than the decrease in 1642 cm^{-1} (Fig. 5.a.III-5.c.III and 5.a.IV-5.c.IV). The peak at 1650 cm^{-1} was clear only in the spectra of the product of reaction carried with 35% eugenol (Fig. 5.c.IV).

Conclusion

The nature of the functionalization of APP with several allyl and 1,2-disubstituted alkene compounds were studied by spectroscopic characterizations to clarify the bonding mechanism, the reactions occurring during functionalizations and the variations in the amount of grafted groups.

The studied compounds were attached to APP by the combination of radicals on APP chains and compounds. However, bonding of the compounds by the addition of radicals on APP to the olefinic double bonds of the compounds could also be expected up to certain extent as noted earlier (11, 12).

In the reactions between DCP and APP and in the functionalizations, extents of formation of chain scission and disproportionation reactions increase with the increase in concentration of DCP. However, the observed increases in M_n and $[\eta]$ values of the products with DCP concentration indicated the low influence of these reactions on the increase of molecular weights (13). An increase in the concentration of the functional compound mainly decreased the extent of formation of disproportionation then chain scission reaction. The effects of functionalization on the molecular weights and the thermal properties of functionalized APP samples will be discussed in the second part of the paper (13).

Acknowledgement

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