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Photografting on Ethylene/Propylene/5-Ethylidene-2-norbornene Rubber Initiated by Photogenerated Hydroperoxides

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ABSTRACT: Terpolymer ethylene/propylene/5-ethylidene-2-norbornene (EPDM) reacts with singlet oxygen leading to the production of polymeric pendant isolated and associated secondary hydroperoxides. Anthracene was used as a sensitizer for production of singlet oxygen under 365 nm irradiation. Irradiation ($\lambda > 300$ nm) of hydroperoxidized EPDM rubber (EPDM-OOH) in the presence of monomers grafted these monomers onto the rubber. Volatile monomers (methyl methacrylate, styrene, 2,2,6,6-tetramethyl-4-piperidyl acrylate) can be easily grafted on EPDM-OOH film by irradiation in their vapor. Nonvolatile as well as volatile monomers and some stable nitroxyl radicals were grafted onto EPDM-OOH films in methanol solution of monomers or nitroxyl radicals. Concentration of grafted monomers depends on the starting hydroperoxide concentration. Hydroperoxidation as well as grafting occurs in the films; it is not simply a surface process only.

Introduction

In a recent paper[1] we have shown that modification of terpolymer ethylene/propylene/ethylidenenorbornene (EPDM) can be easily performed with singlet oxygen. This modification leads to the production of polymeric pendant hydroperoxides. Anthracene was used as a sensitizer for production of singlet oxygen under irradiation with 365 nm light. This procedure has been first used by Geuskens at al.[2,3] for polymeric hydroperoxide formation of styrene−butadiene−styrene block copolymer. Moreover, thermal decomposition of these polymeric hydroperoxides in the presence of methacrylic acid initiated grafting, but the concentration of grafted methacrylic acid was not reported.

Duynstee and Mevis[4] photohydroperoxidized and reduced the ethylidene portion of EPDM rubber in solution using $\alpha,\beta,\gamma,\delta$-tetraphenylporphirine as the photosensitizer. Chemically produced singlet oxygen was used by DeRosa at al.[5] for the same reaction. Thermal decomposition of EPDM-hydroperoxides in the presence of either methyl methacrylate or 2-vinylpyridine free radically grafted these monomers to the rubber, but no quantitative results concerning the amount of grafted monomer were presented.

The aim of this work is modification of EPDM rubber by utilizing the pendant hydroperoxide groups as the initiator of grafting. We have tried to graft different monomers on EPDM-OOH in the solid state as well as in the solution. The selection of monomers has been made first with the aim of increasing the polarity (methyl methacrylate (MMA), acrylic acid) and second with groups representing mainly the polyolefin stabilizers of hindered amine type (HAS). By the grafting we increased the resistance against washing and blooming. In some cases stable nitroxyl radicals were used as radical-trapping agent instead of monomer. The conversion of hydroperoxides and the concentration of grafted monomer have been measured by IR spectroscopy in most cases.

Experimental Section

The polymer used is a terpolymer of ethylene/propylene/5-ethylidene-2-norbornene, Vistalon 7500 (Exxon, France). Initially the rubber was precipitated from toluene solution into methanol to remove possible additives. Preparation of hydroperoxides in the solid state (film) or in the solution is described in ref 1. Hydroperoxide concentration was measured from IR spectra directly or after derivatization reaction with gaseous NO and by iodometric analysis. IR spectra were measured on a Nicolet Impact 400 spectrometer and micro-IR spectra on Nicolet 800 spectrometer equipped with a NICPLAN microscope. Iodometry involved refluxing film samples in acetic acid/propan-2-ol with sodium iodide and measuring the I_3^- liberated by UV spectroscopy (Shimadzu UV 160) at 360 nm[6]; ^{1}H-NMR spectra were measured on a Bruker AC 400 spectrometer.

Grafting on the EPDM-OOH in the solid state was performed by three different ways. In the first case the EPDM-OOH film was irradiated (medium pressure mercury arc, Mazda 400 W, $\lambda > 300$ nm) in the vapor of monomer (MMA,

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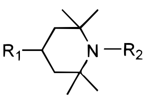
styrene, 1,2,2,6,6-pentamethyl-4-piperidyl acrylate) in the absence of oxygen. The second way involved the dipping of EPDM-OOH film into aqueous solution of methacrylic acid at 100 °C for different times. In the third way, the EPDM-OOH film was irradiated in methanol solution of monomer. Before irradiation, the monomer solution-containing film was bubbled with argon for ca. 5 min.The temperature during irradiation was 55 °C. After grafting the films were extracted in a Soxhlet extractor with suitable solvent for homopolymer.

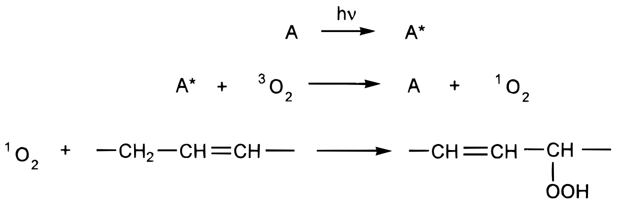
Grafting in solution was performed by irradiation of EPDM-OOH and monomer solution. Prior to the irradiation, the solution was bubbled with argon for 5 min. Monomers (methyl methacrylate and styrene; Prolabo) were distilled to remove inhibitors prior to grafting. Preparation of 2,2,6,6-tetramethyl-4-piperidyl acrylate (TPA) and methacrylate (TPM) and 1,2,2,6,6-pentamethyl-4-piperidyl acrylate (PPA) is described in ref 7. (Stearoyloxy)-2,2,6,6-tetramethyl-4-piperidyl-*N*-oxyl (St-NO•)was prepared by oxidation of parent amine with mCl-peroxobenzoic acid. 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) was obtained from Aldrich. Structures of HAS monomers and stable nitroxyl radicals are as follows:



	R_1	R_2
TEMPO	H	O·
St-NO·	$-O-CO-(CH_2)_{16}-CH_3$	O·
PPA	$-O-CO-CH=CH_2$	CH_3
TPA	$-O-CO-CH=CH_2$	H
TPM	$-O-CO-C(CH_3)=CH_2$	H

Results and Discussion

Characterization of Starting EPDM-OOH. Composition of EPDM was calculated from ^{1}H-NMR spectra measured in C_6D_6. Ethylene content was 60 mol % and 5-ethylidene-2-norbornane content 2.4 mol % on the base of ethylidene singlet at 5.44 ppm. This gives the concentration of double bonds as 0.76 mol/kg. The hydroperoxidation of EPDM in the solid state (film) and in the toluene solution is described in ref 1. The following reactions lead to the production of polymeric pendant hydroperoxide:



$$A \xrightarrow{h\nu} A^*$$

$$A^* + {}^3O_2 \longrightarrow A + {}^1O_2$$

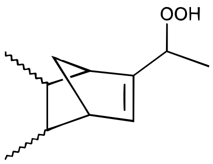
$${}^1O_2 + -CH_2-CH=CH- \longrightarrow -CH=CH-\underset{OOH}{\underset{|}{CH}}-$$

By changing the initial anthracene (A) concentration or irradiation time (365 nm), it is possible to receive different hydroperoxide concentrations. The residual anthracene and anthracene endoperoxide, which is a product of anthracene and singlet oxygen reaction, were removed by extraction with methanol (in the case of hydroperoxidation in the film) or precipitation into methanol (in the case of reaction in toluene solution).

Derivatization reaction of hydroperoxides with gaseous NO transforms hydroperoxides to nitrates:

$$ROOH + NO \rightarrow RONO_2$$

While IR spectra of primary, secondary, and tertiary hydroperoxides are very similar, the IR spectra of adequate nitrates are reasonably different in the 1260−1300 cm^{-1} region. After NO reaction it is possible to distinguish among primary, secondary, and tertiary hydroperoxides. EPDM-OOH film after reaction with NO revealed very sharp peak at 1276 cm^{-1}, and -OH absorption entirely disappeared. Position of this peak fits exactly with the position of the peak from the model secondary nitrate 2,6,8-trimethyl-4-nonyl nitrate.[8] There is no peak after NO treatment at 1300 cm^{-1}, which is typical for tertiary nitrates. It means the starting EPDM-OOH has the following structure:



Grafting on EPDM-OOH Film in the Vapor of Monomer. Irradiation of EPDM-OOH film ($\lambda > 300$ nm, 16 h (this time was checked to be sufficient for complete photolysis of the hydroperoxide groups), 35 °C, film thickness ca. 50 μm) in the MMA vapor resulted in grafted polymer with the pressure of MMA at 3 mmHg. At higher pressure (30 mmHg) considerable amount of ungrafted poly(MMA) has been produced. Concentration of grafted MMA depends on the initial hydroperoxide concentration. Change of the initial -OOH concentration from 0.05 to 0.08 M and finally to 0.16 M resulted in the grafted MMA concentrations 0.33, 0.38, and 0.42 M, respectively. It gives ca. 7, 4, and 3 MMA units/-OOH group. Grafted MMA concentration calculated from IR spectra using $\epsilon_{1732\text{cm}^{-1}} = 340$ L/mol•cm was in very good accord with the concentration determined from the methyl peak $-OCH_3$ at 3.7 ppm of ^{1}H-NMR spectra.

The same procedure in the presence of styrene gave grafted material with new peaks typical for styrene at 1600, 1494, 760, and 542 cm^{-1}. For an initial hydroperoxide concentration of 0.05 M, concentration of the grafted styrene reached the value 0.3 M (6 styrene units/-OOH group), and for 0.16 M, it was 1.82 M (11 styrene units/-OOH group). Concentration of grafted PPA was 0.3 M (5 mmHg). Starting hydroperoxide concentration was 0.1 M and it gave 3 PPA units/-OOH group (calculated on the basis of ester absorption at 1732 cm^{-1} and $\epsilon = 600$ L/mol·cm).

Micro-FTIR spectroscopy was used to monitor the depth dependence of the hydroperoxidation and grafting. This method involved the microtoming of a shawing of the film obtained in a plane to the axis of irradiation. The IR spectra of narrow areas (ca. 10 μm in width) are monitored by moving the sample along the axis of irradiation. Results for hydroperoxides and grafted MMA distributions are shown in Figure 1. The precision of hydroperoxide measurement was enhanced by their transformation to nitrates by NO treatment. The extinction coefficient for nitrate ($RONO_2$) at 1276 cm^{-1} is 9 times higher than for -OH at the 3000−3600 cm^{-1} region (660 and 70 L/mol•cm, respectively). Film thickness was 10 times larger in this experiment (ca. 500 μm). Figure 1a shows that hydroperoxidation is not a surface process. The highest concentration has been reached up to ca. 80 μm from both sides of the sample. After that, the concentration decreases to the middle of the film. In most cases our film thickness was ca. 100−150 μm. This means that hydroperoxides are uniformly distributed throughout the film. Distribution of

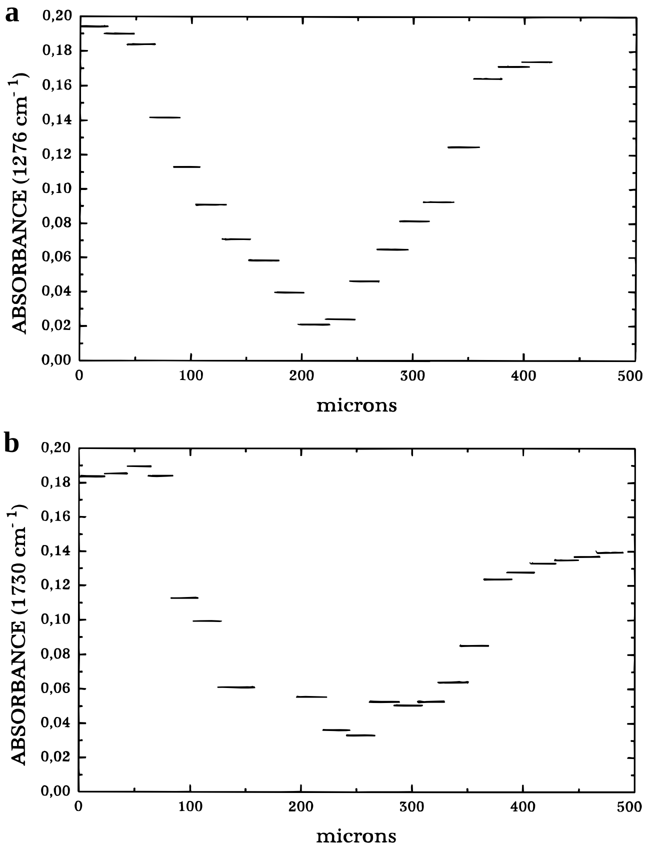


Figure 1. (a) Hydroperoxide distribution in EPDM-OOH film (measured as nitrate at 1276 cm^{-1} after NO treatment) determined by micro-FTIR spectroscopy. (b) Distribution of grafted MMA in EPDM film determined by micro-FTIR spectroscopy.

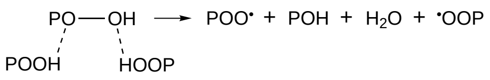
grafted MMA revealed exactly the same pattern, Figure 1b; so, grafting occurs in the film and not at the surface only.

Very small changes of the IR absorbance at 1732 cm^{-1} for MMA-grafted film and at 542 cm^{-1} for styrene-grafted film as well as at 1732 cm^{-1} for PPA-grafted film were detected when grafted films were washed with good solvents for homopolymers. This means that initiation of homopolymerization by hydroxyl radicals or transfer reaction to the monomer is negligible. Most probably hydroxyl radicals very quickly abstract allylic hydrogen from the polymer in such a way that only macroradicals remain.

$$\mathrm{POOH} \xrightarrow{h\nu} \mathrm{PO}^{\bullet} + {}^{\bullet}\mathrm{OH}$$

$$^{\bullet}\mathrm{OH} + \mathrm{PH} \rightarrow \mathrm{HOH} + \mathrm{P}^{\bullet}$$

In our previous paper[1] we have shown that the ratio of isolated to associated hydroperoxides was 1:3 on the basis of IR spectra. So, we have the starting material containing 75% of associated hydroperoxides. Geuskens at al.[9] suggested a concerted mechanism for decomposition of clustered hydroperoxides formed around sites initially occupied by anthracene molecules. This mechanism results in macroradicals exclusively and is thermodynamically more favorable than cleavage of isolated hydroperoxides.



$$\underset{\mathrm{POOH}}{\mathrm{PO}}\text{—}\underset{\mathrm{HOOP}}{\mathrm{OH}} \longrightarrow \mathrm{POO}^{\bullet} + \mathrm{POH} + \mathrm{H_2O} + {}^{\bullet}\mathrm{OOP}$$

Grafting in the monomer vapor is possible only with reasonably high-volatile monomers. Using nonvolatile monomers which were incorporated into EPDM-OOH film by sorption from methanol and then irradiated in vacuum did not result in sufficient grafting. We have done this experiment with TPA and TPM. The first possible reason to explain the low grafting yield is that the initial concentration of TPA and TPM in EPDM-OOH was very low (0.23 wt % for TPA and 0.34 wt % for TPM, on the basis of IR absorption at 1728 and 1720 cm^{-1}, respectively). A second possible reason might be insufficient mobility of monomers to reach the places where polymeric radicals are formed despite the fact that both monomers can be expected to be mainly in the proximity of -OOH groups. This follows from the comparison of concentrations of TPM and TPA which were reached by the sorption into EPDM-OOH and virgin EPDM. For TPM it was 0.34 wt % in EPDM-OOH and 0.1 wt % in EPDM and for TPA 0.21 wt % for EPDM-OOH and 0.027 wt % for EPDM. Hydrogen bonding of sterically hindered secondary amines in TPM or TPA to hydroperoxides is the most probable reason for the increasing solubility, as has been suggested by Carlsson et al.[10]

Grafting of Acrylic Acid in Aqueous Solution. As has been mentioned, Geuskens at al.[2,3] have shown that grafting of methacrylic acid from an aqueous solution onto a styrene−butadiene−styrene (SBS) block copolymer can be initiated by thermal decomposition of photogenerated hydroperoxides. Grafting was performed by dipping hydroperoxidized SBS film into aqueous solution of methacrylic acid at 100 °C for 1−10 min. The same procedure for EPDM-OOH film revealed only a very low amount of grafted acrylic acid even after a reaction time of 20 min. Film with initial hydroperoxide concentration of 0.13 M after 20 min of dipping in 10% water solution of acrylic acid at 100 °C revealed the new very small peak in the carbonyl region at 1710 cm^{-1}. If we assumed that all of this absorption is from grafted acrylic acid, we get the concentration of grafting of 0.003 M using $\epsilon = 600$ L/mol·cm, as was used in ref 3. At the same time, the peak at 3550 cm^{-1} which belongs to isolated hydroperoxide disappeared, and the broad peak of associated hydroperoxides at 3420 cm^{-1} shifted to 3380 cm^{-1} as a consequence of hydroperoxide conversion into alcohol. The resistance of acrylic acid to penetrate into film from water solution seems to be the reason for the very low yield of grafting.

Grafting on EPDM-OOH Film in Methanol Solution of Monomers. We have successfully employed this procedure for nonvolatile monomers. Polymeric radicals were produced by irradiation at 55 °C. To check the feasibility of this procedure, 10% MMA solution was used. Initial hydroperoxide concentration was 0.13 M. Grafting was very efficient, and after 60 min of irradiation and washing, the concentration of grafted MMA reached the value 0.44 M (on the basis of a new peak at 1732 cm^{-1}). At the same time, the peak at 3550 cm^{-1} which belongs to the isolated -OOH group decreased only by 20%. Change in the region of associated hydroperoxides was not informative because of overtone from the ester peak at 1732 cm^{-1}. The same procedure with original EPDM film did not lead to any MMA grafting.

Irradiation of EPDM-OOH film in 10% solution of acrylic acid in methanol for 19 h resulted in grafting. The concentration of grafted acrylic acid was 0.06 M (after washing in water at 50 °C for 2 h to remove

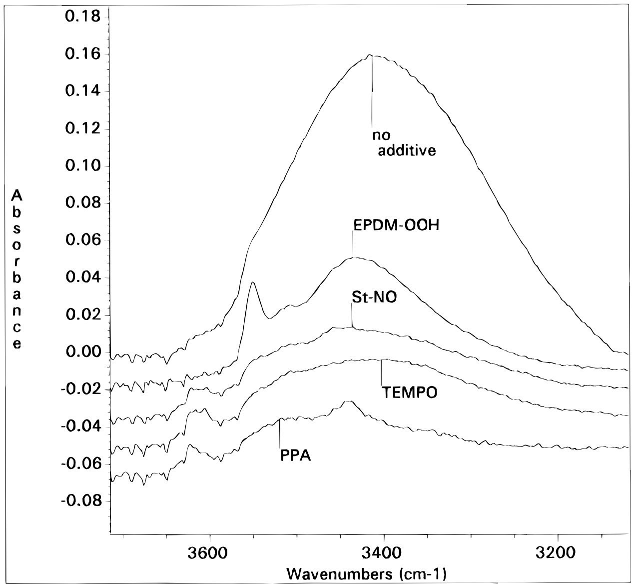


Figure 2. Changes of IR spectra of EPDM-OOH films after irradiation in methanol (no additive) and in methanol solution of St-NO$^•$, TEMPO, and PPA. Thickness of the films was 0.1 mm.

possible nongrafted homopolymer) calculated from the peak at 1710 cm^{-1}.

Grafting of PPA on EPDM-OOH was performed in 2% methanol solution. Irradiation time was 23 h. The IR spectrum of grafted film is shown in Figures 2 and 3 together with the IR spectra of initial EPDM-OOH film and films irradiated in methanol solution of St-NO$^•$ (2% sol) and TEMPO. Concentration of grafted PPA is 0.16 M calculated on the basis of the 1732 cm^{-1} peak using $\epsilon = 600$ L/mol·cm, Figure 3. Irradiation time of 23 h is sufficient to cleave all isolated hydroperoxide groups as revealed by disappearence of the peak at 3550 cm^{-1}, Figure 2. At the same time, a new peak at ca. 3620 cm^{-1} can be observed as a consequence of isolated alcohol production. But the intensity of this peak is much lower in comparison with the peak of isolated hydroperoxides.

Irradiation of EPDM-OOH film in MeOH without any additives resulted in remarkable increase of -OH absorption (Figure 2) as well as production of different carbonyl compounds (Figure 3). Part of hydroxy and carbonyl products resulted from hydroperoxyl radical termination reaction:

$$\mathrm{C{-}OO^\bullet + {}^\bullet OO{-}C \rightarrow C{=}O + O_2 + C{-}OH}$$

but this reaction can not explain the big increase in the -OH region and the high production of carbonyl compound. Grafting of methanol (through recombination of polymeric radical and $^\cdot$CH$_2$-OH radical formed from methanol by abstaction of proton) can explain the increased -OH absorption but can not explain the production of carbonyl compounds. Presence of a low oxygen concentration despite the bubbling with argon before irradiation is a more acceptable explanation. The photooxidation of EPDM-OOH film in methanol appears to produce typical products such as alcohol and hydroperoxide (3000−3600 cm^{-1}), ketone (1712 cm^{-1}), and ester (shoulder at 1738 cm^{-1}).

Presence of nitroxyl radicals (St-NO$^\cdot$ and TEMPO) inhibited this process. Nitroxyl radicals are generally accepted to be one of the most essential intermediates in the stabilization mechanism of HAS.[10,11] They are known to act as an alkyl radical-trapping agent, and this is how they are grafted on EPDM polymer chain.

$$\mathrm{R^\bullet + {}^\bullet ON{<} \rightarrow R{-}O{-}N{<}}$$

Reaction of peroxyl radicals with nitroxyl radical has recently been suggested[12].

$$\mathrm{C{-}OO^\bullet + {}^\bullet ON{<} \rightarrow C{-}OOO{-}N{<} \rightarrow C{-}O{-}N{<} + O_2}$$

In our case this reaction should lead to grafting nitroxyl radical too. Concentration of grafted St-NO$^\cdot$ reached the value 0.1 M. Presence of nitroxyl radicals did not completely stop the production of carbonyl products (seen in Figure 3 for TEMPO). This additive does not absorb in the carbonyl region. The broad peak can be assigned to ketone (1710 cm^{-1}) and ester (1740 cm^{-1}). The peak at 1685 cm^{-1} was proved to be carbonyl absorption of unsaturated acid on the basis of SF$_4$ treatment. This peak disappeared after SF$_4$ reaction, and a new peak was visible at 1800 cm^{-1} as a consequence of acid fluoride production. The same carbonyl products which are hidden by strong ester absorption can be expected in the case of St-NO$^\cdot$ and PPA.

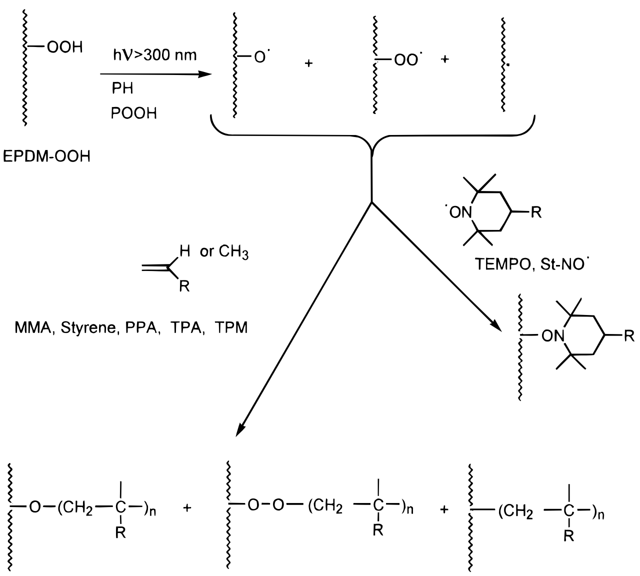
Oxidation process was inhibited by PPA, which is the parent amine. It is most probably due to partial oxidation of the parent amine to nitroxyl radical by hydroperoxide or peroxyl radical. Contrary to St-NO$^\cdot$, grafting of PPA happens mainly through the double bond as is in the MMA case. This leads to a higher concentration of grafted PPA (0.16 M) compared to St-NO$^\cdot$ (0.1 M).

Irradiation of EPDM-OOH film in methanol solution of TPA (same concentration as for PPA grafting experiment) did not result in grafting for an unknown reason. Presence of TPA just inhibited oxidation. The IR spectrum of the film after irradiation was almost the same as for the film irradiated in methanol solution of TEMPO.

Grafting in Solution of EPDM-OOH. In this procedure EPDM-OOH was dissolved in toluene or *n*-heptane. Irradiation of 2 wt % solution of EPDM-OOH in the presence of 2 wt % of monomer resulted in grafting, but at the same time, cross-linking and production of gel occurred. Irradiation of EPDM-OOH in *n*-heptane solution in the presence of MMA (24 h/room temperature) gave the cross-linked material. After washing with acetone and chloroform, the concentration of grafted MMA measured by attenuated total reflectance (ATR) IR spectroscopy revealed the value 1.66 M. Starting hydroperoxide concentration was 0.12 M and it gave ca. 14 MMA units/-OOH group. A similar result was obtained in toluene. The same procedure for TPA gave 0.92 M grafted TPA (8 TPA units/-OOH group). Efficiency of grafting is higher than in the previous procedure (MeOH solution of monomers), but production of gel makes this procedure questionable. It is interesting to note that irradiation of EPDM-OOH in *n*-heptane solution did not lead to any gel production.

Conclusion

Reaction of singlet oxygen with EPDM rubber is a convenient way to introduce pendant hydroperoxide groups. Their concentration can be regulated by changing of irradiation time (365 nm) or anthracene concentration. The residual anthracene (photosensitizer) and anthracene endoperoxide can be easily extracted from rubber. Photodecomposition (λ > 300 nm) of polymeric hydroperoxides initiates grafting of different monomers and stable nitroxyl radicals. The following scheme summarizes the mechanism of both grafting types, by radical polymerization or radical trapping:



Three possible initiations occur in the case of free radical polymerization, while in the grafting by nitroxyl radical, only poly-alkyl-substituted hydroxylamine is produced.

This way of grafting is very simple for volatile monomers. Grafting can be performed by irradiation of EPDM-OOH film in the vapor of monomer. Most ofthe monomers used can be grafted in their methanol solution. Concentration of grafted monomers can be regulated by initial hydroperoxide concentration. Work concerning the study of new properties due to the grafting is now in progress.

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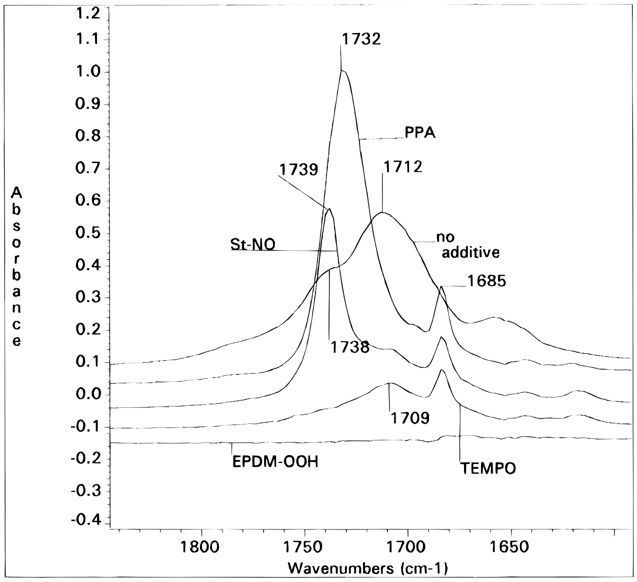

Figure 3. Changes in the carbonyl region of IR spectra of EPDM-OOH films irradiated in methanol (no additive) and in methanol solution of St-NO•, TEMPO and PPA. Thickness of the films was 0.1 mm.

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