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# Brominated Polyethylene. Synthesis, Photooxidation and Use as the Intermediate for the Preparation of New Polymeric Stabilizers

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# BROMINATED POLYETHYLENE. SYNTHESIS, PHOTOOXIDATION AND USE AS THE INTERMEDIATE FOR THE PREPARATION OF NEW POLYMERIC STABILIZERS

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## ABSTRACT

The hydrobromination of polyoctenamer was performed using concentrated hydrogen bromide chloroform solutions. The conditions for the total hydrobromination of polyoctenamer were established. The photoageing of the resulting brominated polyethylene was analyzed and compared with those of pure polyethylene and chlorinated homologues. The brominated polyethylene has been used as an intermediate for the synthesis of a new polymeric hindered amine stabilizer. Nucleophilic substitution of bromine atoms was performed by 4-amino-2,2,6,6-tetramethylpiperidine and resulted in a partial grafting of 2,2,6,6-tetramethylpiperidine groups on the polymer chain. Using 2,2,6,6-tetramethyl and 1,2,2,6,6-pentamethyl-4-piperidinol in the presence of NaH or their sodium salts as the nucleophilic agents did not lead to any grafting under the experimental conditions used.

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This new additive resulted in good stabilizing properties upon the photo- and the thermooxidation of elastomers as EPDM and poly-octenamer.

## INTRODUCTION

The chemical modification of polymers is one of the simplest and cheapest ways to significantly change the polymer structure and to improve specific properties as impact resistance, flame retardancy [1]. Surface properties as adhesion, oxygen impermeability or friction coefficient can also be largely modified particularly in the case of elastomers [2, 3]. Quite a few modificating agents are available however, the use of halogen derivatives is largely developed and is involved in several industrial applications. Chlorinated polyethylenes, PVC or rubbers, are for example, are commercially available. Brominated polymers are not as developed, however, brominated derivatives are often used as fire retardant additives. Moreover, bromine substituents can be easily exchanged with other functional groups by nucleophilic substitution and have to be considered as potential intermediates for polymer modification.

From the literature, it appears that direct bromination of rubbers can be performed from aqueous solution of bromine or potassium bromide [4, 5] or in hexane solutions of bromine. Additions (trans), as well as substitutions and cyclization reactions are involved. The direct hydrobromination of unsaturated polymers is also a possible way but, here again, the reaction is accompanied by side reactions such as cyclisations and eliminitations. Therefore, to carry out the specific hydrobromination of polybutadiene and polyisoprene, a two-step synthesis was suggested [5, 6]. The first step was a hydroboration followed with a bromination of the resulting poly-meric organoborane. According to $^1$H-NMR analysis, the hydrobromination was quantitative. A partially hydrobrominated polybutadiene was also prepared in the presence of $FeCl_3$ [7] but NMR characterization was not done. The synthesis of an hydrobrominated polypentenamer is also described [8], the polymer being characterized by bromine content only.

The present paper reports on the hydrobromination of polyoctenamer by using the reaction of gaseous hydrogen bromide and on the use of this brominated polyethylene as a support for the grafting of piperidine groups to achieve the synthesis of a new polymeric stabilizer. The photochemical properties of both brominated and aminated polymers will be also analyzed.

Both low and high molecular weight stabilizers are currently used in polymer stabilization; usually low molecular weight compounds are very efficient at low temperature (outdoor ageing) while high molecular weight homologues act efficiently at higher temperature but generally with a significant decrease of the compatibility with the host polymer [9-11]. The use of an elastomer as primary support for the grafting of hindered amine groups allows to anticipate a certain compatibility with elastomers and to expect a good efficiency of this kind of stabilization.

## EXPERIMENTAL

### Chemicals

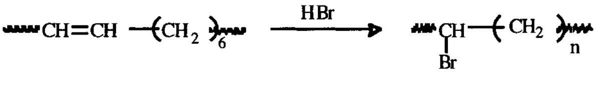
Polyoctenamer (VES) (Vestenamer, Hüls, Germany) was three times precipitated from chloroform solution into methanol before use. Low density polyethylene - LDPE (Hostalen, Hoechst, Germany), chlorinated polyethylene with 25 (PECl 25), and 48 wt% (PECl 48) of chlorine (Scientific Polymer Products, Ontario, USA), di(2,2,6,6-tetramethyl-4-piperidinyl) 1,10-decanedicarboxylate (Tinuvin 770, Ciba, Switzerland), 4-amino-2,2,6,6-tetramethyl piperidine (aTMP) (Fluka), gaseous HBr (Aldrich), bromooctadecane (Aldrich), 3-bromopentane (Aldrich) and $SF_4$ (Fluka) were used as received.

### Analysis

IR, UV, and NMR spectra and DSC curves were recorded on a Nicolet Impact 400, Shimadzu UV 160, Bruker AC400 and Mettler TA800, respectively. Films (*ca* 0.1 mm) were prepared by pressing in an electrically heated laboratory press or by casting from a chloroform solution.

For photoageing tests, all the spectra were normalized for a 0.1 mm thickness by using suitable band. The films were irradiated with medium pressure mercury arc (Mazda MA400, $\lambda \geq 300$ nm) at 35°C in merry-go-round apparatus described earlier [12]. Thermal ageing was performed in an oven ventilated by natural convection at 80°C. In few cases, the contribution of carboxylic acids in the broad carbonyl absorption band was determined by treating oxidized films with sulfur tetrafluoride. This derivatization reaction converts carboxylic acids into acid fluorides absorbing in the range 1800-1850 $cm^{-1}$ [13].

### Synthesis of Hydrobrominated Polyoctenamer (VESTHBr, PEBr)



$$\sim CH=CH-(CH_2)_6\sim \xrightarrow{HBr} \sim \underset{Br}{CH}-(CH_2)_n\sim$$

n = 6, 7 or 8

Gaseous HBr was introduced at -15/-25°C through a porous glass frit till saturation into a chloroform solution of VES (3.2 g into 60 ml). The vessel was closed and stored at +8°C overnight. Progress of the reaction was followed by FTIR spectroscopy (disappearance of the absorption of the double bond at 960 cm$^{-1}$). The procedure was repeated several times up to complete disappearance of double bonds.

Elemental analysis: Calcd. for $C_8H_{15}Br$: C, 50.27; H, 7.91; Br, 41.82%. Found: C, 50.36; H, 7.98 ; Br, 41.66%.

FTIR: C-Br bands at 540 and 620 cm$^{-1}$

$^1$H-NMR ($CDCl_3$): 1.2-1.7 (m, 10 H, $CH_2$ in β, γ, and δ position); 1.7-1.9 (m, 4H, $CH_2\alpha$); 3.95-4.10 (m, 1H, $CH$Br).

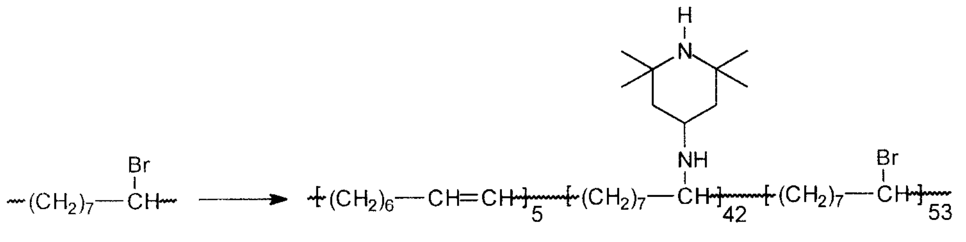
$^{13}$C-NMR ($CDCl_3$): 27.3 ($2C_\beta$) ; 28.5 ($2C_\gamma$); 29.4 ($C_\delta$) ; 39.2 ($2C\alpha$); 59.0 (CBr)

**Substitution of Bromine by 4-Amino-2,2,6,6-tetramethypiperidine (VESHAS)**

VESTHBr (1.72 g; 9 mmol) was dissolved into 4-amino,2,2,6,6-tetramethyl piperidine (aTMP, 3.55 g; 22.7 mmol) at 70°C under nitrogen. In the dark, the solution was magnetically stirred at 70°C for three days; then, the temperature was raised to *ca* 80° for two days. Excess of amine was removed by washing the crude oily viscous product with methanol (2 x 50 ml). The mixture (*ca* 1.5 g) was twice precipitated from THF solution (*ca* 10 ml) into water. The resulting product was dried under vacuum to give 1.4 g of the desired polymer.

Both FTIR and $^1$H-NMR spectra reveal a significant substitution of bromine atom (42%) beside a partial elimination (5%).

FTIR: decrease of C-Br bands at 540 and 620 cm$^{-1}$ and appearance of TMP bands at 1367 and 1377 cm$^{-1}$ - doublet $\delta_s$.



$^1$H NMR ($CDCl_3$): 0.75-0.95 (m, 2H of $CH_2$ of the piperidine ring), 1.05-1.25 (m, 12H, $CH_3$-), 1.25-1.60 (m, ~$CH_2$ CH(NH-)$CH_2$~ and other -$CH_2$- of the chain), 1.70-1.90 (m, 4H, -$CH_2$ CHBr $CH_2$- and 2H of -$CH_2$ of piperidine ring), 1.90-2.00 (m, 4H, -$CH_2$ CH=CH$CH_2$), 2.60-2.70 (m, 1H, ~$CH$(NH-)~), 2.90-3.00 (m, 1H, -$CH$- of piperidine ring), 3.95-4.05 (m, 1H, -$CH$Br-),5.30-5.40 (m, 2H, -$CH$=$CH$-).

Assignment of chemical shifts and $^1H$-$^1H$ connections were obtained by a COSY spectrum. From the integrals, it was possible to measure the molar ratio of different units observed: ~C*H*(NH-)~ and -C*H*- of the piperidine ring resulting from expected substitution (42%), C*H*Br for unreacted functions (53%) and -C*H*=C*H*- unsaturation (5%) coming from elimination reactions.

### Substitution of Bromine by 2,2,6,6-Tetramethyl-4-piperidinol

VESTHBr (1 g, 5.2 mmol) was dissolved in dry toluene (20 ml). Solution of sodium salt of 2,2,6,6-tetramethyl-4-piperidinol (1.06 g, 5.9 mmol) in 10 ml of toluene and 50 mg of KI were added at room temperature. The mixture was refluxed for 100 hours. After partial evaporation of toluene, the polymer was precipitated into methanol yielding after drying in vacuum 0.82 g of slightly yellow polymer.

$^1H$-NMR spectrum was identical as for starting material (VESTHBr).

### 4-Octadecyloxy-2,2,6,6-tetramethylpiperidine

To a solution of sodium salt of 2,2,6,6-tetramethyl-4-piperidinol (1.32 g, 7.4 mmol) in dry toluene (15 ml) was added 1-bromoctadecane (2.1 g, 6.3 mmol) and KI (50 mg). The mixture was refluxed for 24 hours. The precipitated NaBr was filtered and the toluene was evaporated. The residue was dissolved in ether and washed twice with diluted $NaHCO_3$ water solution then with water to remove starting alcohol. After evaporation of the ether, the crude product was purified by column chromatography (silica gel, hexane:acetone = 1:1) to give the desired product as white powder (m.t. = 30-31°C). The yield was 40%.

FTIR ($CCl_4$): 2927 $cm^{-1}$ (s) $\nu_{as}$ ($CH_2$); 2854 $cm^{-1}$ (m) $\nu_s$ ($CH_2$); 1377+1365 $cm^{-1}$ (m) doublet $\nu_s$ (CH3); 1099 $cm^{-1}$ (s) $\nu_{as}$(C-O-C).

$^1H$-NMR ($CDCl_3$) δ: 0.9 (t, J=7 Hz, 3H, C$H_3$ octadecyl); 1.01 (t, J=12, 2H, C$H_2$ of the ring) 1.08 (s, 6H, C$H_3$ of the ring); 1.21 (s, 6H, C$H_3$ of the ring); 1.25 (m, 30H, $(CH_2)_{15}$ octadecyl); 1.56 (m, 3H, O-C-C$H_2$ and N*H*); 1.95 (dd: J=12 and J=4, 2H, $CH_2$ of the ring); 3.48 (t, J=7, 2H, O-C$H_2$-); 3.65 (m, 1H, >C*H*-O). Chemical shift non equivalence of the methyl groups is frequently observed in these series based on substituted piperidine backbone. Note that a similar effect can be pointed out for the two protons of two $CH_2$ of the ring (Δδ=0.8 ppm). Each of these resonances can be considered as A and M parts of AMS spectra.

### 4-Octadecyloxy-1,2,2,6,6-pentamethylpiperidine

To a solution of 1,2,2,6,6-pentamethyl-4-piperidinol (1 g, 5.8 mmol) in dry tetrahydrofuran (20 ml) under $N_2$ atmosphere was added sodium hydride (0.4 g, 9

TABLE 1. Glass Transition and Melting Temperature of the Studied Polymers

| Polymer | Tg | Tm |
|---|---|---|
| VESTHBr | -45 | no |
| PECl 25 | -27 | 130 |
| PECl 36 | -22 | 130 |
| PECl 48 | -9 (broad) | no |
| LDPE | - | 132 |

mmol) and 1-bromo-octadecane (1.93 g, 5.8 mmol). The mixture was stirred at room temperature for 1 hour and then refluxed for 12 hours. After cooling water was added dropwise to destroy the excess sodium hydride and THF was evaporated. The product was extracted with chloroform and concentrated. The crude residue (slightly yellow oil) was chromatographed on silica gel using chloroform then a mixture of $CHCl_3$:MeOH saturated with $NH_3$ =20:1 as eluent. Collected fraction afforded 1.3 g (45%) of transparent oil which solidified on standing (m.t.=29-30°C).

FTIR ($CCl_4$): 2927 $cm^{-1}$ (s) $\nu_{as}$ ($CH_2$); 2854 $cm^{-1}$ (m) $\nu_s$ ($CH_2$); 2812+2792 $cm^{-1}$ doublet (w) $\nu_s$ (N-$CH_3$); 1377+1362 $cm^{-1}$ doublet (m) $\delta_s$ ($CH_3$); 1310 $cm^{-1}$ (w) ((C-N); 1099 $cm^{-1}$ (s) $\nu_{as}$ (C-O-C).

$^1$H-NMR ($CDCl_3$) $\delta$: 0.85 (t, J=7 Hz, 3H, $CH_3$ octadecyl); 1.05 (s, 6H, $CH_3$ of the ring); 1.15 (s, 6H, $CH_3$ of the ring); 1.25 (m, 30H, $(CH_2)_{15}$ octadecyl); 1.4 (t, J=12, 2H, $CH_2$ of the ring); 1.55 (m, 2H, O-C-$CH_2$ octadecyl); 1.85 (dd: J=12 and J=4, 2H, $CH_2$ of the ring); 2.22 (s, 3H, N-$CH_3$); 3.40 (t, J=7, 2H, O-$CH_2$-); 3.50 (m, 1H, >$CH$-O).

## Differential Scanning Calorimetry (DSC)

The fully hydrobrominated polyoctenamer (VESTHBr) was characterized by a low glass transition temperature and the absence of a marked melting point (elastomer behavior). This contrasts with the behavior of chlorinated polyethylene or conventional linear low density polyethylene (Table 1) which presents a certain degree of crystallinity (the melting point, Tm, was measured at the maximum of the peak for the melting endotherm).

## RESULTS AND DISCUSSION

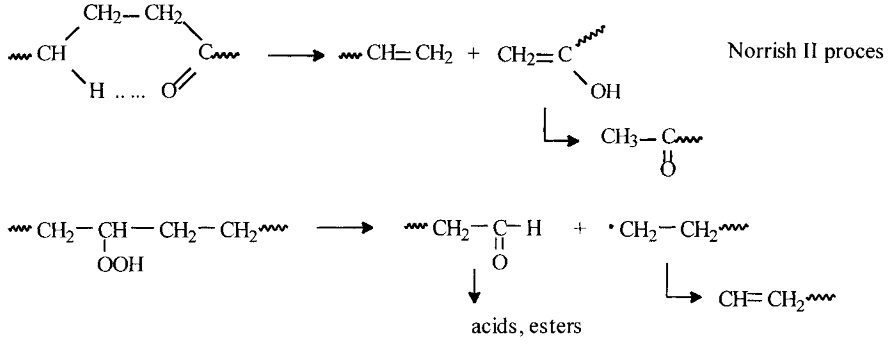
The addition of HBr at low temperature (-15/-25°C) allows us to significantly increase the gas concentration in the reaction mixture. Then, performing the reaction at higher temperature (+8°C) allows to reach high conversion yield for the hydrobromination reaction. A similar procedure was described for the hydrochlorination of 1,4-polyisoprene [14]. The significant changes revealed by IR and NMR spectroscopy showed complete disappearance of double bonds at 960 cm$^{-1}$ (IR), *ca* 5.4 ppm ($^1$H-NMR) and 130 ppm ($^{13}$C-NMR) as a consequence of total hydrobromination (confirmed by elemental analysis).

It could be pointed out that, conversely to conventional organic chemistry where the final products can be isolated, only the total conversion leads to a well defined compound in the case of polymer modification. Then, fully hydrobrominated polyoctenamer is identical to a brominated polyethylene or to an alternate cyclohexene/vinyl bromide copolymer. Such a polymer can be compared with conventional chlorinated polyethylenes even if in this case, the chlorination location is not clearly identified.

### Photoageing of Brominated Polyethylene and Comparison with Polyethylene and Its Chlorinated Homologues

The resistance of polymeric materials to photoageing can be easily performed by controlling the evolution of oxidized products (alcohols, carbonyls,...) by a non-destructive method as FTIR spectroscopy.

The carbonyl region of IR spectra for a family of oxidized polymers showed no important differences in the spectra shapes excepted the development of unsaturations at 1640 cm$^{-1}$ in the case of the quite long photoageing of polyethylene. These unsaturations are essentially associated with vinyl 909 and 990 cm$^{-1}$ (and in a smaller extent with vinylene 965 cm$^{-1}$ groups deriving from ketone or secondary hydroperoxide photolysis [15-17].



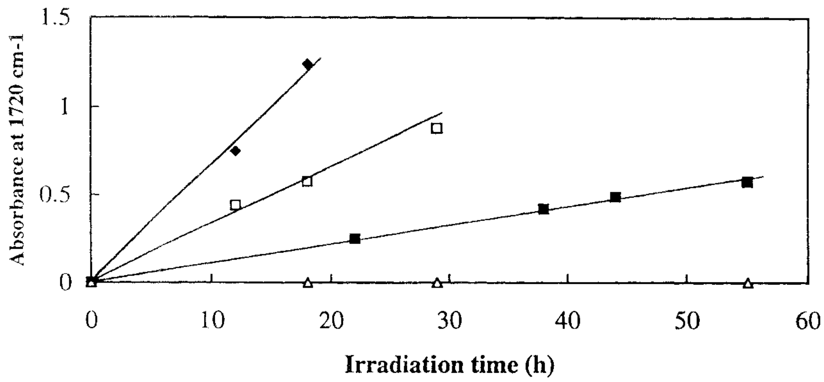
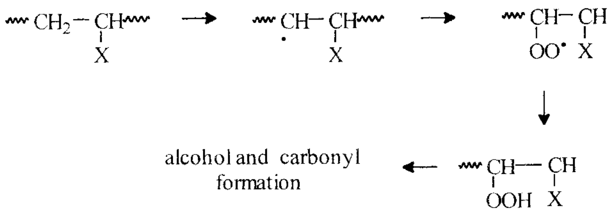


**Figure 1.** Photooxidation rates of PE (Δ); PEBr (□) (VESTHBr); PECl 25 (◆); and PECl48 (■); (measured in the carbonyl region of IR spectra).

Surprisingly, the ketones formed in the case of halogenated polymers do not seem to be photolyzed significantly. Moreover, the loss of halogenated acid (HBr or HCl) by deshydrohalogenation, often reported in PVC or chlorinated PE [1, 18-20], is not revealed in our experimental conditions (no double bonds formation and no change in the C-Br bands at 520 and 610 cm$^{-1}$). The carbonyl groups are mainly carboxylic acids and ketones overlapping near 1720 cm$^{-1}$. High absorbing species as esters and γ-lactones are also observed at 1732 and 1774 cm$^{-1}$ respectively. The relative contribution of ketones and acids can be derived from a treatment by $SF_4$ (conversion of carboxylic acids into acid fluorides). Assuming conventional absorption coefficients, the contribution of ketones/acids can be assumed to be 45/55 respectively. Both band positions and relative contribution of acids and ketones are very similar to those expected for pure polyethylene [15].

In spite of numerous similarities on the nature of photoproducts detected by IR spectroscopy, halogenated polyethylenes are much less resistant to photoageing than pure polyethylene (see Figure 1). The phenomenum is probably connected with the presence of labile hydrogen atoms in α position of the halogen group and (or) with the decrease of polymer crystallinity (see DSC results).



Some differences are also revealed between halogenated polyethylenes. If we consider that PEBr contains a similar halogen molar content to PECl 25, the brominated polymer seems to be more stable than its chlorinated homologue. However, the polymer structure is probably different (fully alternated) in PEBr. The increase of stability when the chlorine content increases (see PECl 48) may be due to a significant decrease of oxygen permeability.

According to the literature, polar solvents as alcohols are generally recommended to perform the bromine substitution. However, a complete reaction was reported in the case of benzyl bromide/amine in benzene [21]. Because of the poor solubility of brominated polyethylene in polar solvents, we chose to perform the nucleophilic substitution directly in the amine (aTMP), the temperature being maintained at 80°C. The resulting good efficiency of grafting makes this polymer a potential stabilizing agent (one piperidine unit per 519 g against one piperidine unit per 239 g for the conventionnal Tinuvin 770).

The effort to use the presence of bromine on polyethylene chain as a leaving group for nucleophilic substitution by sodium salts of 2,2,6,6-tetramethyl or 1,2,2,6,6-pentamethyl-4-piperidinol for ether formatin was not successful. The conversion of starting alcohols to sodium salts by reaction with Na in dry toluene under reflux was checked by FTIR (disappearence of -OH band at 3600 $cm^{-1}$ for both alcohol and formation of new bands at 1093 $cm^{-1}$ for 2,2,6,6-tetramethyl and at 1091 $cm^{-1}$ for 1,2,2,6,6-pentamethyl-4-piperidinol as proof of >C-O-Na formation). A very long reaction time (100 hours) did not lead to any substitution, and starting brominated Vestenamer only was received after precipitation. The use of more polar solvent (THF instead of toluene) did not bring any progress concerning ether formation, just a partial dehydrobromination happened ($^1$H-NMR). Similar products were obtained when 2,2,6,6-tetramethyl or 1,2,2,6,6-pentamethyl-4-piperidinol was allowed to react with NaH in THF and solution of VESTHBr was added. The polymeric nature of the brominated product is not the reason for this lack of reactivity. Also, low molecular 3-bromopentane did not react. A combination of secondary alcohol with secondary bromide seems to be the main reason for the failure of Williamson's ether synthesis in these cases. Even the reaction of low molecular secondary bromides with sodium salts of primary alcohols leads mainly to olefin production (more than 90%), while the reaction of primary bromides results in more than 90% of ether formation [22]. As an example, reaction of low molecular primary substrate 1-bromooctadecane with 2,2,6,6-tetramethyl or 1,2,2,6,6-pentamethyl-4-piperidinol gave *ca*. 50% yield of desirable ether (see Experimental section).

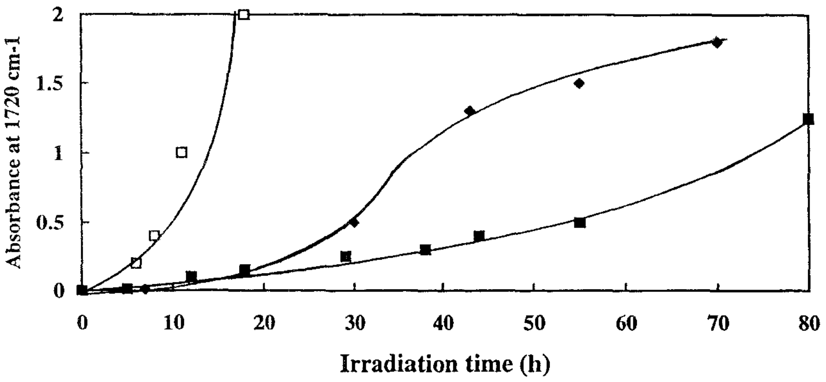


**Figure 2.** Effect of Tinuvin 770 and VESHAS on the photooxidation of polyoctenamer (carbonyl index). □: control; ◆: 8.3 mmol.Kg$^{-1}$ of VESHAS; ■: 8.3 mmol.Kg$^{-1}$ of Tinuvin 770.

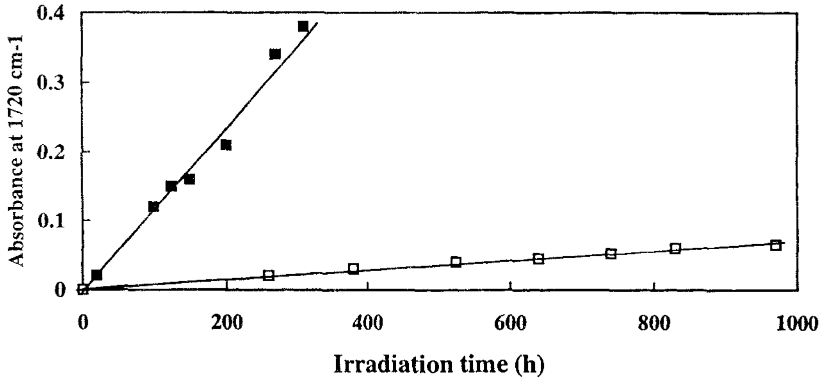


**Figure 3.** Effect of VESHAS on the thermal oxidation of EPDM at 80°C. ■: control; □: 0.3 wt% of VESHAS.

The stabilizing effect of VESHAS was tested in polyoctenamer and EPDM by following the carbonyl index at 1720 cm$^{-1}$. Tinuvin 770 was also tested for comparison. Figure 2. shows the effect of both Tinuvin 770 and VESHAS in polyoctenamer. To avoid concentration effects, the same content in piperidine moities was introduced (equivalent to 2000 ppm of Tinuvin 770). Both additives show a positive effect, however, Tinuvin 770 is better. Such differences between low and high molecular weight additives are often observed in the photooxidation of thin films and the expected relative photoinstability of VESHAS is probably not the reason. In addition, no significant band was detected at 1650 cm$^{-1}$.

The thermal oxidation was tested in EPDM containing a high content in ENB and consequently, very sensitive to oxidation. VESHAS behaves like a powerful stabilizer; Tinuvin 770 (not shown) has practically no effect at 80°C due to its volatility (Figure 3).

## CONCLUSION

The total hydrobromination of polyoctenamer is possible by using hydrogen bromide in specific conditions (dissolution of the gas at low temperature in the chloroform solution of the polymer and further reaction at +8°C). The resulting polymer can be considered as a brominated polyethylene with a precise location of bromine atom (similar to alternated co-(cycloalkene-vinyl bromide)). This polymer is completely amorphous and presents a photoageing resistance comparable to a chlorinated polyethylene having the same molar content. However, this resistance to photoageing is very low compared to that of a pure semi-crystalline polyethylene. In spite of this large difference in oxidation rates, the stoichiometry of the reaction seems very similar except for a significant increase of vinyl groups formation in the case of pure polyethylene.

The direct nucleophilic substitution of bromine by an amino piperidine is a quite efficient process with a substitution level above to 40%. A side-reaction is dehydrobromination (5%) but the resulting double bond can play a positive role in the case of the vulcanization process (elastomer) as an interpenetrated network (IPN) between the additive and the host polymer which could be expected. Using 2,2,6,6-tetramethyl and 1,2,2,6,6-pentamethyl-4-piperidinol in the presence of NaH or their sodium salts, as the nucleophilic agents did not lead to any grafting under the experimental conditions used.

The brominated polyethylene grafted HAS is reasonably stable to oxidation and plays a positive role in the stabilization of elastomers as polyoctenamer and EPDM-ENB particularly in thermal oxidation.

## ACKNOWLEDGEMENT

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