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New combined hindered phenol/hindered amine stabilizers for polymers based on diphenylmethane-4,4′-diisocyanate

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Dedicated to Professor Dr. K. Schwetlick on the occasion of his 70th birthday.

Abstract

A new type of combined stabilizer based on hindered phenols and Hindered Amine Stabilizers (HAS) were synthesized and tested as light stabilizers. 2,4-Di-*tert*-butylphenol (**I**) and 2-*tert*-butyl-4-methylphenol (**II**) were coupled with 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP), 4-hydroxy-1,2,2,6,6-pentamethylpiperidine (PMP), 4-amino-2,2,6,6-tetramethylpiperidine (ATP), 4-*N*-butylamino-2,2,6,6-tetramethylpiperidine (BATP) or 4-hydroxy-2,2,6,6-tetra-methyl-piperidin-*N*-oxyl (*N*-oxyl) through the reaction with diphenylmethane-4,4′-diisocyanate. The structure and purity of the synthesized compounds were proved by conventional analytical methods. They were tested as light stabilizers in polypropylene films. Stabilizing efficiency depends on the structure of the phenol as well as on the structure of the HAS. Derivatives of phenol **I** exhibited better efficiency compared with phenol **II** for all HAS used. Concerning the structure of HAS stabilizing activity increased in the following order ATP < BATP < N-oxyl < TMP = PMP. Much higher stabilizing performance of combined phenol **I** and **II** with TMP in comparison with the performance of their physical mixtures shows the quite strong synergistic effect arising from chemical bonding of both types of stabilizers in one molecule.

Keywords: Stabilization; Photooxidation; Combined stabilizers; Phenols; Hindered amines; Polypropylene

1. Introduction

The commercially used polyolefin materials contain a number of additives to improve both their processability and final properties. The main part of these additives are stabilizers, which protect the polymer materials during their processing and against the influence of atmospheric conditions such as heat and sunshine.

A small quantity of processing stabilizers is usually added to prevent the oxidative degradation of polyolefins caused by combined action of shear, heat and oxygen during their melt processing. Sterically hindered phenols, which act as scavengers of oxygen centred alkoxy and peroxy radicals, are widely used as primary stabilizers [1,2]. On the other hand, they are not able to provide a sufficient long-term light and heat stability.

In the late 1960s the class of Hindered Amine Stabilizers (HAS) was found to be highly effective inhibitors of polypropylene photooxidation [3]. Beside the stabilization of polyolefins they found wide application in the protection of various polymer systems of commercial interest [3]. Recently, the hindered amine stabilizers are the most effective long-term light and partially heat stabilizers [4,5]. They act by a multifunctional mechanism.

The addition of mixtures of processing stabilizer (phenol and phosphite type) and long-term stabilizer (HAS type) to the polymer is frequently used to prevent the polymer against degradation. Disadvantages of using mixtures of low molecular weight stabilizers are mainly their physical loss, uneven distribution in the polymer matrix and poor compatibilization. One way to solve this problem is to use multifunctional additives with higher molecular weight prepared by connection of two or more stabilizing structures in one molecule. This combination is expected to improve the stabilizing activity by synergistic effects [6]. An elegant method to connect hindered phenol type antioxidants with hin-

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dered amines resulting in higher molecular weight multifunctional stabilizers is their stepwise reaction with di-(or poly-)isocyanates [7–9].

In this work we describe the synthesis and stabilizing efficiency of two series of combined phenol/HAS stabilizers derived from 2,4-di-*tert*-butylphenol and 2-*tert*-butyl-4-methylphenol and several hindered amines linked by reaction with diphenylmethane-4,4′-diisocyanate.

2. Experimental

2.1. Materials

Diphenylmethane-4,4′-diisocyanate (DMDI), 4-hydroxy-2,2,6,6-tetramethyl piperidine (TMP), 4-hydroxy-1,2,2,6,6-pentamethylpiperidine (PMP), 4-amino-2,2,6,6-tetramethylpiperidine (ATP), 4-N-butyl-amino-2,2,6,6-tetramethylpiperidine (BATP) and 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl (*N*-oxyl) were supplied by Hüls and 1,4-diazabicyclo[2.2.2]octane (DABCO) 2,4-di-*tert*-butylphenol (**I**) and 2-*tert*-butyl-4-methylphenol (**II**) were obtained from Merck. Polypropylene powder—Tatren HPF—(MFI = 10 g/10 min) containing no commercial additives was supplied by Slovnaft (Bratislava, Slovak Republic).

2.2. Synthesis

Two series of multifunctional polymer stabilizers containing different phenols were synthesized using the following general procedure. The phenol (0.01 mol) was added to a solution of diphenylmethane-4,4′-diisocyanate (MDI) (0.01 mol) and 0.1 g of DABCO (as a catalyst) in dry cyclohexane at 80 °C. The HAS (ATP, BATP, TMP, PMP or *N*-oyl) (0.01 mol) was added when the isocyanate absorption reduced to half of its initial intensity in the FTIR spectrum and no further change was observed. This reaction was also monitored by FTIR spectroscopy and was finished after the disappearance of the isocyanate absorption in the IR spectrum. The crude product, which precipitated from the solution at ambient temperature, was filtered out, washed with cyclohexane and purified by column chromatography using methylene chloride and ethyl acetate as eluents. The reaction conditions, yields of the purified products and the melting points for each compound are presented in Table 1.

2.3. Analysis

Infrared (IR) spectra were recorded on a Nicolet FT-IR 400 spectrometer. Elemental analysis for carbon, hydrogen and nitrogen was performed with a CHN-S elemental analyser 1108 (Carlo Erba). ^{1}H NMR spectra were recorded on a Bruker 300 NMR spectrometer. MALDI-TOF measurements were performed on Kratos Kompact MALDI-TOF **II** (Shimadzu) using 1,8,9-trihydroxyanthracene as the matrix.

2.4. Sample preparation

All the additives (0.2 wt.%, of combined hindered phenol/HAS or the mixture of equimolar amounts of starting phenols and HAS–TMP) were solvent blended into the polymer powder using dichloromethane as solvent. After evaporation of the solvent under stirring the impregnated polymer powders were mixed and homogenized in a Brabender Plastograph (Duisburg, Germany) at 190 °C for 5 min in air at 40 rpm. The bulk polymer was then pressed into ca. 0.1 mm thin films in an electrically heated laboratory press (Fontune, Vlaardingen, Netherlands) at 190 °C for 1 min.

2.5. Photooxidation

The photooxidation was performed on a merry-go-round type set up, using a medium pressure 250 W mercury arc with luminophore envelope (RVL, Tesla Holešovice, Czech Republic) as the source of irradiation. The temperature of photooxidation was 30 °C. The course of photooxidation was followed by IR

Table 1
Reaction conditions, yields and melting points of new combined phenol–HAS stabilizers using MDI as a linker

Code name	Phenol	HAS	Temp. (°C)	Reaction time (h)	Yield (%)	Melting point (°C)
IA	**I**	TMP	80 + 80	4 + 3	55	106–108
IB	**I**	PMP	80 + 80	3 + 3	64	104–107
IC	**I**	ATP	80 + 50	4 + 3	66	141–143
ID	**I**	BATP	80 + 50	4 + 1[a]	63	111–113
IE	**I**	N-oxy	80 + 50	4 + 3	29	86–88
IIA	**II**	TMP	80 + 80	4 + 3	70	104–107
IIB	**II**	PMP	80 + 80	4 + 3	50	109–111
IIC	**II**	ATP	80 + 80	4 + 3	75	139–142
IID	**II**	BATP	80 + 80	4 + 1[a]	65	192–197
II/E	**II**	N-oxy	80 + 50	4 + 3	19	64–67

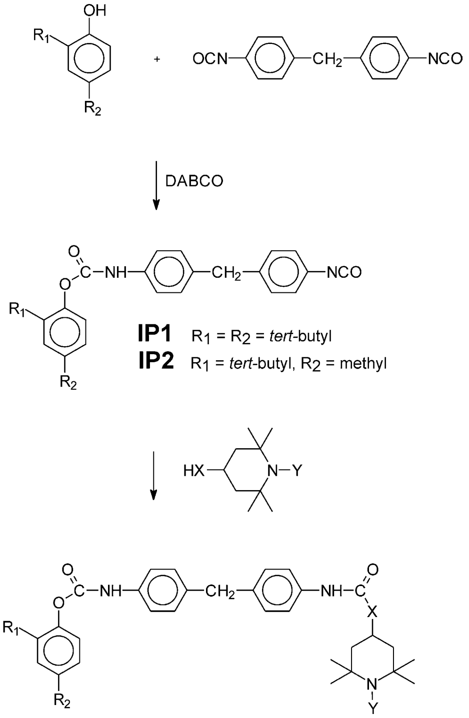
[a] Product precipitated 1 min after addition of BATP.

spectroscopy monitoring the increase of carbonyl absorption between 1700 and 1740 cm^{-1}, caused by oxidation products.

3. Results and discussion

The diphenylmethane-4,4′-diisocyanate (DMDI) chosen for our investigation contains two isocyanate groups with the same reactivity, in contrast to isophorone diisocyanate investigated previously [8,9]. Although the isocyanate group is reported to be highly reactive with simple primary alcohols and amines, the reaction with phenols and some HAS required catalytic conditions [10–13].

In our experiments we used 1,4-diazabicyclo[2.2.2]octane (DABCO) as a catalyst for the stepwise reaction of DMDI with 2,4-di-*tert*-butylphenol (**I**) or 2-*tert*-butyl-4-methylphenol (**II**) and several HAS. The reactions were performed as a one-pot process without isolation of an intermediate product **IP1** or **IP2** (Scheme 1). The reaction of sterically hindered phenols with DMDI and 4-hydroxypiperidines (TMP and PMP) with intermediates **IP1** or **IP2** besides using the catalyst, also required stronger reaction conditions, i.e. using a higher temperature and longer reaction time. On the other hand, the reaction of 4-amino or 4-butyliminopiperidine (ATP and BATP) with the intermediates **IP1** or **IP2** is faster and probably could be performed at lower temperature and without catalyst too. This fact was confirmed by our previous experiments [8], which showed, that the reactivity of ATP and BATP with isocyanates is higher in comparison with 4-hydroxypiperidines (TMP and PMP). Actually the reaction is exothermic and very fast without catalyst and without heating.



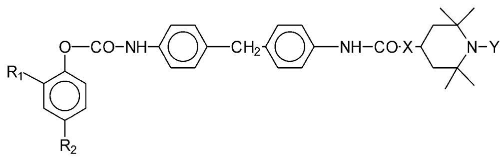
Scheme 1.

The synthesized compounds were analysed by elemental analysis, ^1H NMR and FTIR spectroscopy and MALDI-TOF mass spectrometry. The results are given in Table 2.

The course of the reaction can be monitored very conveniently by IR spectroscopy. For the intermediates **IP1** and **IP2** (Scheme 1) the characteristic absorption band of isocyanate groups around 2270 cm^{-1} decreased to half of the original value. The reactions were finished at a complete extinction of isocyanate group absorption. The formation of new absorption bands of carbamates and/or ureas, depending on the type of the piperidine derivatives, can be seen at 1650–1730 cm^{-1}. ^1H NMR spectra are described in detail in Table 2. They showed typical peaks for the piperidine ring as well as for the aromatic one in the correct ratio. MALDI-TOF mass spectra showed an expected molecular peak for each stabilizer.

All synthesized compounds were tested as light stabilizers in polypropylene (PP) films. The additive concentration was 0.2 wt.%, which is the most often used value for real applications. Usually when one wants to compare efficiency of different additives the same molar concentration is used. But in this case we could use the same wt% concentration because the difference between molar masses of the derivatives of phenol **I** and **II** are very small. The molar concentrations of phenol **I** derivatives are 5% higher compared with derivatives of phenol **II**. Besides the synthesized compounds, the equimolar mixtures of TMP with phenol **I** and **II** were also tested. The stabilizers were mixed with polymer powder in Brabender Plastograph to reach the best homogeneous dispersion of additive in the polymer film despite some possibilities of their thermal decomposition or partial evaporation due to the higher processing temperature (190 °C).

The courses of photooxidation are shown in Figs. 1 and 2 In both cases the efficiency depends on the structure of HAS. Derivatives **C** and **D** (Scheme 2) of 4-aminopiperidines (ATP) and 4-butylaminopiperidines (BATP) exhibited much lower stabilization effect in



IA $R_1=R_2$ = *tert*-butyl, X = O, Y = H
IB $R_1=R_2$ = *tert*-butyl, X = O, Y = CH_3
IC $R_1=R_2$ = *tert*-butyl, X = NH, Y = H
ID $R_1=R_2$ = *tert*-butyl, X = NBu, Y = H
IE $R_1=R_2$ = *tert*-butyl, X = O, Y = O·
IIA R_1= *tert*-butyl, R_2 = CH_3, X = O, Y = H
IIB R_1= *tert*-butyl, R_2 = CH_3, X = O, Y = CH_3
IIC R_1= *tert*-butyl, R_2 = CH_3, X = NH, Y = H
IID R_1= *tert*-butyl, R_2 = CH_3, X = NBu, Y = H
IIE R_1= *tert*-butyl, R_2 = CH_3, X = O, Y = O·

Scheme 2.

Table 2
Analysis of prepared compounds

Code name	IR changes cm^{-1}		Elemental analysis		MALDI-TOF MS	NMR (ppm)
	Reactants	Products	Theoret.	Exp.		
IA	2270 (–NCO)	1730 (Carbamate) 3250–3500 (NH)	**C**: 74.38 **H**: 8.3 **N**: 6.85	75.37 8.46 6.80	614	1.08; 1.19 (2*s, 2*6H, C-$\underline{CH_3}$), 1.24; 1.3 (2*s, 2*9H, C-$\underline{CH_3}$ *tert*.-butyl), 1.5; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 3.8 (s, 2H, Ph- $\underline{CH_2}$-Ph), 5.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.4 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$- arom.)
IB	2270 (–NCO)	1730 (Carbamate) 3250–3500 (NH)	**C**: 74.64 **H**: 8.45 **N**: 6.698	74.16 8.79 6.675	628	1.08; 1.17 (2*s, 2*6H, C-$\underline{CH_3}$), 1.3; 1.36 (2*s, 2*9H, C-$\underline{CH_3}$ *tert*.-butyl), 1.5; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 2.35 (s, 3H, N-$\underline{CH_3}$) 3.8 (s, 2H, Ph-$\underline{CH_2}$-Ph), 5.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.4 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$- arom.)
IC	2270 (–NCO)	1650 (NH–CO–NH) 3250–3500 (NH)	**C**: 74.51 **H**: 8.496 **N**: 9.15	75.23 9.45 8.65	613	1.1; 1.25 (2*s, 2*6H, C-$\underline{CH_3}$), 1.3; 1.35 (2*s, 2*9H, C-$\underline{CH_3}$ *tert*.-butyl), 0.9; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 3.9 (s, 2H, Ph- $\underline{CH_2}$-Ph), 4.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.2 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$- arom.)
ID	2270 (–NCO)	1650 (NH–CO–NH) 3250–3500 (NH)	**C**: 75.45 **H**: 8.98 **N**: 8.38	75.03 10.09 8.11	669	1.1; 1.25 (2*s, 2*6H, C-$\underline{CH_3}$), 1.3; 1.35 (2*s, 2*9H, C-$\underline{CH_3}$ *tert*.-butyl), 0.9; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 3.1 (m, 2H,-$\underline{CH_2}$-, n-butyl) 3.9 (s, 2H, Ph- $\underline{CH_2}$-Ph), 4.7 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.2 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$- arom.)
IE	2270 (–NCO)	1730 (Carbamate) 3250–3500 (NH)	**C**: 72.61 **H**: 7.96 **N**: 6.69	70.27 8.96 8.08	629	
IIA	2270 (–NCO)	1730 (Carbamate) 3250–3500 (NH)	**C**:73.55 **H**: 7.88 **N**: 7.35	70.68 8.0 7.1	571	1.1; 1.19 (2*s, 2*6H, C-$\underline{CH_3}$), 1.29 (s, 9H, C-$\underline{CH_3}$ *tert*.-butyl), 1.4; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 2.25 (s, 3H, Ph-$\underline{CH_3}$) 3.8 (s, 2H, Ph- $\underline{CH_2}$-Ph), 5.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.4 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$-arom.)
IIB	2270 (–NCO)	1730 (Carbamate) 3250–3500 (NH)	**C**: 73.85 **H**: 8.03 **N**: 7.18	73.5 8.18 7.16	585	1.1; 1.15 (2*s, 2*6H, C-$\underline{CH_3}$), 1.29 (s, 9H, C-$\underline{CH_3}$ *tert*.-butyl), 1.4; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 2.25 (s, 3H, Ph-$\underline{CH_3}$), 2.35 (s, 3H, N-$\underline{CH_3}$) 3.8 (s, 2H, Ph- $\underline{CH_2}$-Ph), 5.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.4 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$- arom.)
IIC	2270 (−NCO)	1650 (NH–CO–NH) 3250–3500 (NH)	**C**: 73.68 **H**: 8.07 **N**: 9.82	73.9 8.75 9.72	571	1.1; 1.19 (2*s, 2*6H, C-$\underline{CH_3}$), 1.35 (s, 9H, C-$\underline{CH_3}$ *tert*.-butyl), 0.85; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 2.35 (s, 3H, Ph-$\underline{CH_3}$) 3.9 (s, 2H, Ph- $\underline{CH_2}$-Ph), 4.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.3 (m, 1H,-$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$-arom.)
IID	2270 (–NCO)	1650 (NH–CO–NH) 3250–3500 (NH)	**C**: 74.76 **H**: 8.63 **N**: 8.95	73.5 8.9 8.06	628	1.1; 1.19 (2*s, 2*6H, C-$\underline{CH_3}$), 1.35 (s, 9H, C-$\underline{CH_3}$ *tert*.-butyl), 0.85; 1.9 (2*m, 2*2H, C-$\underline{CH_2}$-CH), 2.35 (s, 3H, Ph-$\underline{CH_3}$), 3.1 (m, 2H,-$\underline{CH_2}$- n-butyl) 3.9 (s, 2H, Ph- $\underline{CH_2}$-Ph), 4.1 (m, 1H, O-$\underline{CH}$-CH$_2$), 6.3 (m, 1H, -$\underline{NH}$-CO), 6.8-7.5 (m, 11H,-$\underline{CH}$- arom.)
IIE	2270 (–NCO)	1730 (Carbamate) 3250–3500 (NH)	**C**: 71.67 **H**: 7.51 **N**: 7.17	67.5 8.6 7.6	587	

comparison with 4-hydroxypiperidine ones (TMP, PMP) **A** and **B** for both phenols used. For quantification of this effect we can use the time when the carbonyl absorption reached the value 0.2. This value is roughly related to the loss of 50% of initial tensile strength. For the derivatives of phenol **I** it is 1200 h for **IC** (ATP), 1750 h for **ID** (BATP), 2600 h for **IA** (TMP) and 3000 h for **IB** (PMP). The values for derivatives of phenol **II** are as follows **IIC** (ATP) 900 h, **IID** (BATP) 1600 h, **IIA** (TMP) and **IIB** (PMP) 2200 h. The efficiency of the 4-aminopiperidines (ATP) **IC** and **IIC** is much lower compared with the very similar 4-butylaminopiperidines (BATP) **ID** and **IID**. The presence of the *n*-butyl group in **ID** and **IID** is responsible for this increase. This not very long alkyl chain seems to play an important role, most probably in increasing the compatibility and/or miscibility of these derivatives with the polymer.

Concerning the phenol structure it can be seen that the different substituent in the *para* position of the phenyl ring has considerable effect on the stabilizing performance. Derivatives of phenol **I** with *tert*-butyl in *para* position showed much better photo stabilizing

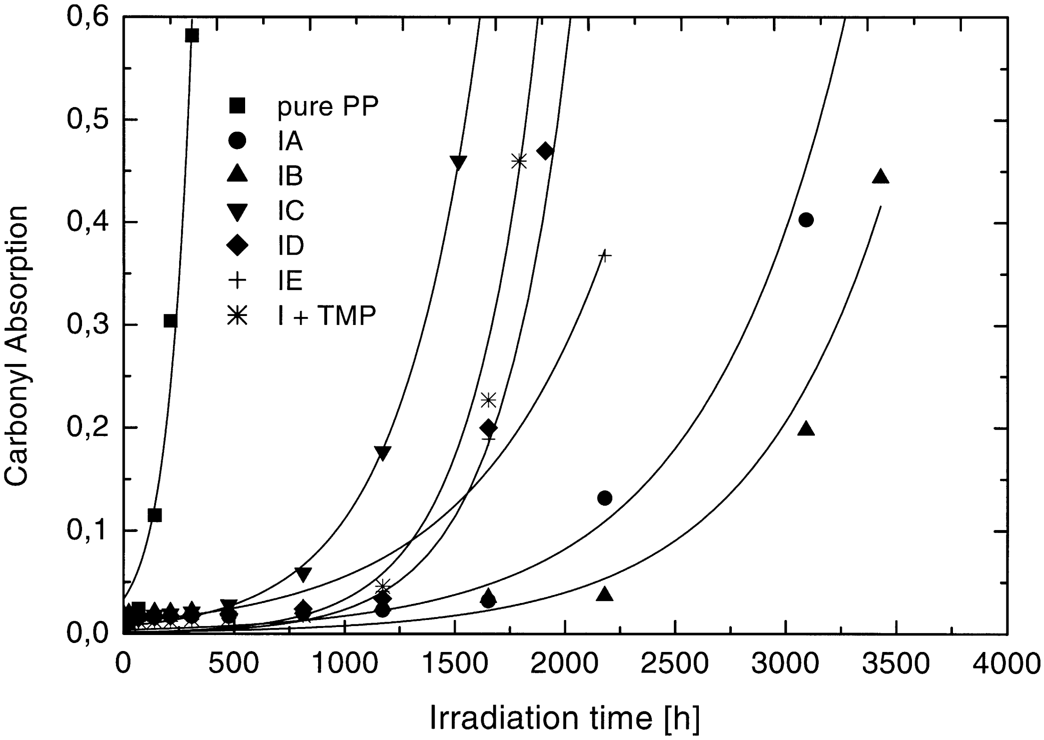


Fig. 1. Rates of photooxidation of polypropylene films (ca. 0.1 mm) containing derivatives of phenol **I**. Additive's concentration 0.2 wt.%. Molar concentration of the active parts in the mixture **PhI** + TMP is the same as in **IA**.

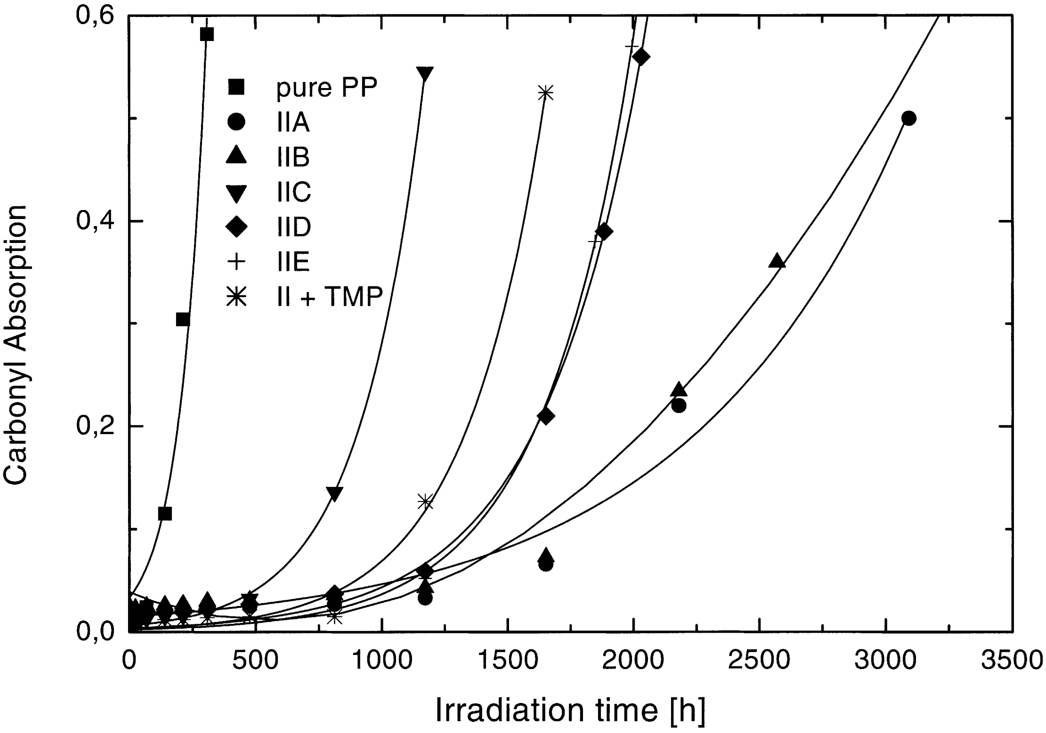


Fig. 2. Rates of photooxidation of polypropylene films (ca. 0.1 mm) containing derivatives of phenol **II**. Additives concentration 0.2 wt.%. Molar concentration of the active parts in the mixture **PhII** + TMP is the same as in **IIA**.

efficiency than derivatives of phenol **II** with methyl in *para* position. The difference also depends on the structure of HAS. If we take again the time to reach carbonyl absorption = 0.2 the increasing for ATP derivatives **IC** is 300 hours compared with **IIC**. For BATP i.e. **ID**/**IID** it is 150 h, for TMP **IA**/**IIA** 400 h and for PMP **IB**/**IIB** it is 900 h.

Surprisingly the stabilizing efficiency of the stable nitroxyl radicals **IE** and **IIE** derived from corresponding parent amines **IA** and **IIA** is much lower in both cases. Usually the stabilizing effect of the parent amine and its corresponding nitroxyl radical are very similar. At this moment we do not have any explanation for this pronounced difference.

Sterically hindered phenols are generally used as a primary processing stabilizers. The mechanism generally used to explain their effectiveness is based on the abstraction of the weakly bound H atom by oxygen centred alkoxy or peroxy radicals [14]. The synthesized compounds do not contain phenolic hydroxyl group. Thus they actually are not able to protect polymer in processing by H donation as a free phenol. Despite this drawback the effectiveness of combined phenol/HAS derivatives **IA** and **IIA** is much higher when compared with effectiveness of a physical mixtures of phenol **I** and **II** with TMP at the same molar concentration. This increase represents, ca. 1000 h to reach a carbonyl absorption 0.2 for both phenols. For **IA** it is decreased from 2600 h to 1500 h for the physical mixture of phenol **I** + TMP and for **IIA** from 2300 h to 1300 h for the mixture of phenol **II** + TMP. These values refer to the pronounced synergistic effect of combined phenol/HAS synthesized compounds. To find the possible explanation for the synergistic effect of the combined phenol/HASes is very difficult. As it has been mentioned, we have the phenol in combined molecules in the form of carbamates. They do not posses the free –OH group that is essential for the generally accepted stabilizing mechanism of phenols. One possibility for the free phenol formation is during processing. The combined molecule may break down at the carbamate link to release free phenol in the form of phenoxy radical, which can abstract a proton from the polymer chain with production of phenol. But the probability for this reaction is very low because the phenoxy radical is much more readily converted to a quinone structure [15]. We measured the changes of UV spectra of PP films containing starting free phenol **I**, mixture of free phenol **I** and 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP) and phenol I in combined molecule—**IA** during photooxidation. Changes of UV spectra are shown on Figs. 3–5. Free phenol **I** (Fig 3) showed two spectral bands at 280 and 220 nm after compounding in non-irradiated PP film. Combined molecule **IA** (Fig 5) showed new strong and broad absorption band with the maximum at ca. 250 nm. This band is result of the presence of absorbing 4,4′-disubstituted diphenylmethane coupling structure in combined molecule. The absorption band at 280 nm is just a shoulder and it is difficult to use it for calculation.

Comparison of UV spectra of non irradiated films containing free phenol **I** and a physical mixture of phenol **I** and TMP (Fig 4) showed that the concentration of phenol **I** is about 30% higher in the film containing the physical mixture than in the film with phenol **I** only (A_{280} = 0.066 and 0.044, respectively). The probability of physical loss during processing is the same in the both cases. So the lower consumption of phenol **I** in the mixture with TMP is most probably the result of the protecting action of TMP during processing. On the other hand physical loss of combined additive **IA** during processing is negligible due to the much higher molecular mass.

The kinetics of additive consumption as well as oxidation products formation during photooxidation are shown in Fig. 6. Free phenol **I** is consumed slower in the presence of TMP than it is in the case when PP contains just phenol I only. Time to reach Aco = 0.2 is ca. 400 h for phenol **I** and 1250 h for the mixture of phenol **I** + TMP. This time value for TMP is ca. 800 h (not shown). These times do not reflect either antagonistic or synergistic effects. The overall stabilizing efficiency for the physical mixture is the sum of contribution of individual additives. An entirely different situation is in the case when these molecules are coupled in one molecule as in additive **IA**. The kinetics of decomposition or consumption is the slowest and the time to reach Aco = 0.2 is double that for the physical mixture of phenol **I** + TMP. Chemical linking of sterically hindered phenol with HAS by DMDI improves the photo-stabilization efficiency.

As in the case of combined phenol/HASes coupled through toluene-2,4-diisocyanate [16] photooxidation starts after complete consumption of absorbing species. This means that the possible release of non-absorbing active HAS moieties and their stabilizing action is not effective after consumption of absorbing groups from phenol and diphenylmethane coupling structure. However, it does not exclude HAS release from the combined structure before this time during induction period.

4. Conclusions

Coupling of hindered phenols and HAS through the reaction with diphenylmethane-4,4′-diisocyanate is a very convenient method for preparation of combined stabilizers with a higher molecular mass. The reaction is very easily monitored by IR spectroscopy. Purification of the crude products is quite simple offering high yield (55–57%) of final products (exceptions are free nitroxyl radicals with much lower yields). The synthesized com-

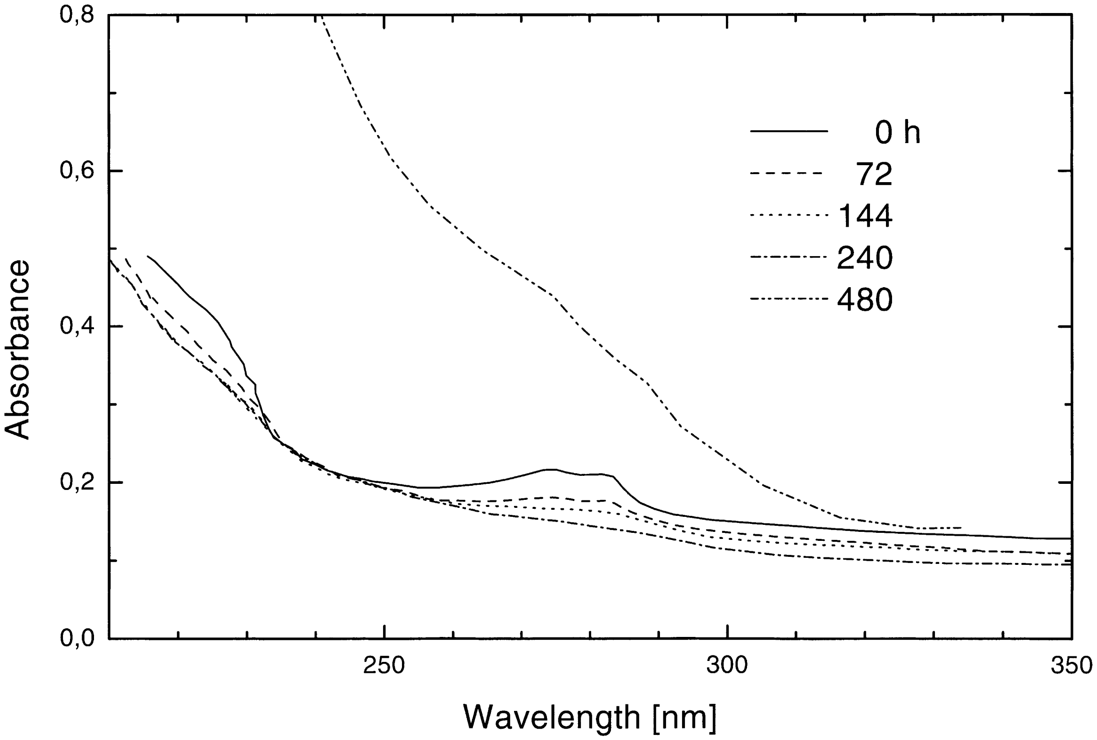


Fig. 3. Changes of UV spectra of PP film (ca. 0.1 mm) containing phenol **I** during photooxidation. Additive concentration 3.3×10^{-3} mol/kg.

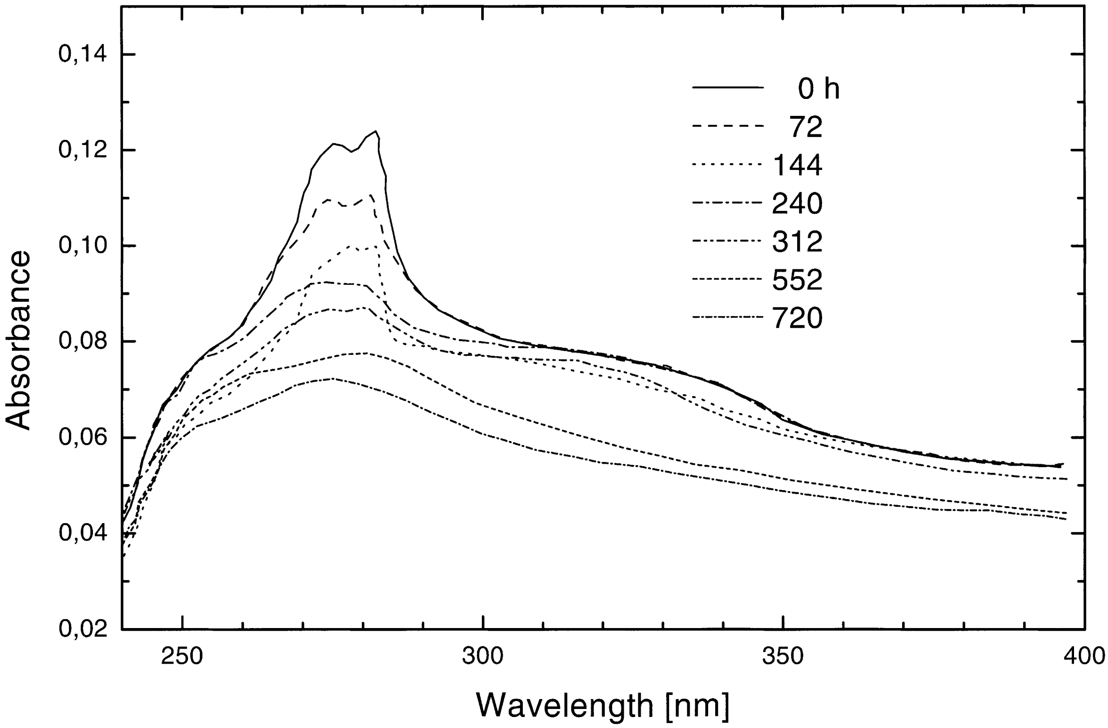


Fig. 4. Changes of UV spectra of PP film (ca. 0.1 mm) containing mixture of free phenol **I** and 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP) during photooxidation. Additives concentration 0.2 wt.% = 3.3×10^{-3} mol/kg.

pounds used as a light stabilizers in PP films revealed reasonably high stabilization efficiency. There is a strong influence of HAS as well as phenol structure on the stabilizing activity. Additives containing phenol **I** are more efficient than that ones containing phenol **II** for all HAS used. Concerning the influence of HAS structure, derivatives coupled through carbamate (TMP and PMP) are better than those linked through a urea

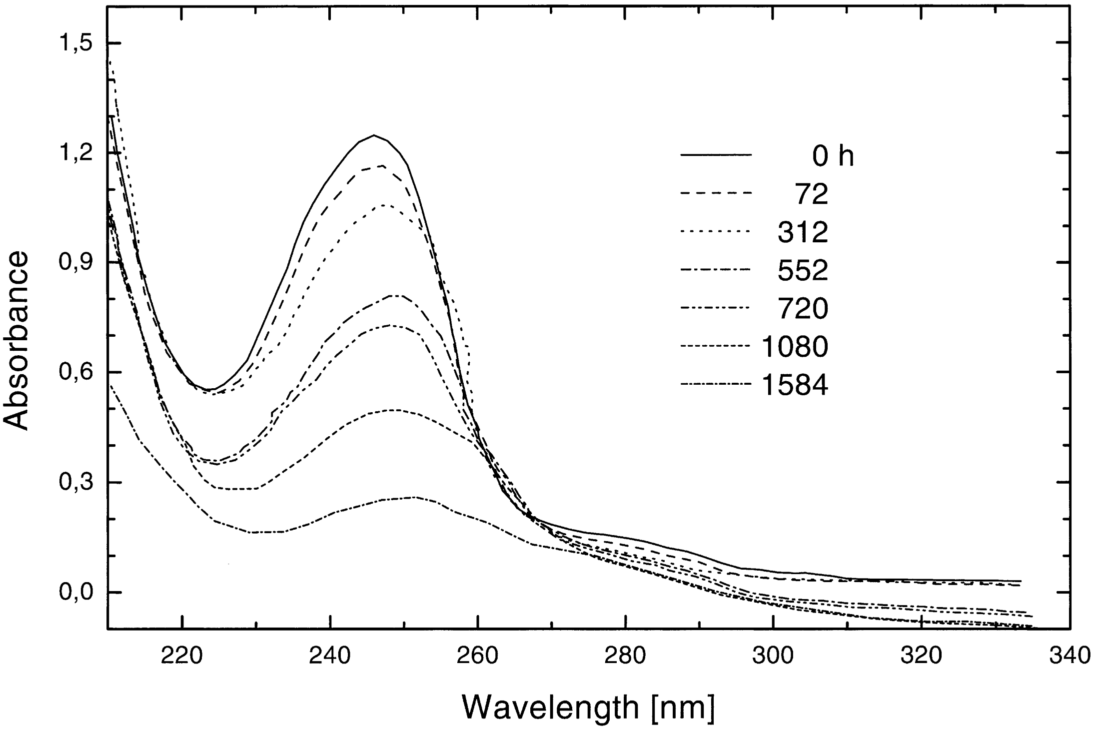


Fig. 5. Changes of UV spectra of PP film (ca. 0.1 mm) containing combine additive **IA** during photooxidation. Additive concentration 0.2 wt.% = 3.3×10^{-3} mol/kg.

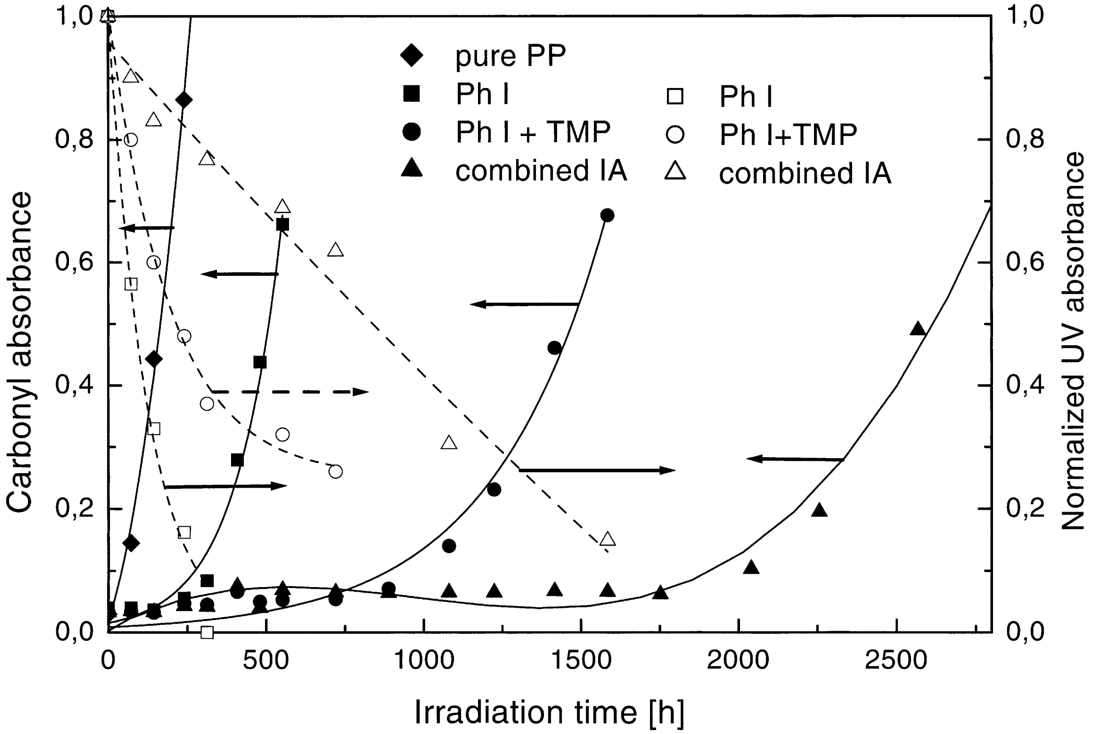


Fig. 6. Comparison of kinetics of additives consumption (empty points) in PP film (ca. 0.1 mm) measured by UV spectroscopy for phenol **I**, mixture of free phenol **I** + 4-hydroxy-2,2,6,6-tetramethylpiperidine (TMP) and combined additive **IA** and rates of photooxidation (full points). Additives concentration 3.3×10^{-3} mol/kg.

structure (ATP and BATP). Binding of phenol and HAS in combined molecule increases their efficiency in comparison with the efficiency of their physical mixture.

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