ELSEVIER

Polymer 43 (2002) 1573–1579

polymer

www.elsevier.com/locate/polymer

New synergists for hindered amine light stabilizers

Pieter Gijsman*

DSM Research BV, P.O. Box 18, 6160 MD Geleen, The Netherlands

Received 14 October 2001; accepted 20 October 2001

Abstract

The development of hindered amine light stabilizers (HALS) in the seventies led to a tremendous increase in the outdoor use of polyolefins. Although since that time a great deal of insight has been gained into the UV-degradation mechanism of polyolefins and the mechanism of action of HALS, no new UV-stabilization chemistry has been discovered. In this paper, the most recent thoughts about the UV-degradation mechanism of polyolefins (initiation of photo-oxidation by polymer oxygen charge transfer complexes (CTCs)) and new insights into the mechanism of action of HALS stabilizers (quenching of these CTCs) are explored as a basis for designing new UV-stabilizers. A mechanism is proposed that explains the action of HALS as a quencher. Based on this mechanism several other possible quenchers (bridged amines) have been suggested. It is shown that these bridged amines are active as UV-stabilizers in films and plaques and that they show a synergism with HALS stabilizers. These new stabilizers are the most effective when they are present at concentrations higher than 0.1% and at higher concentrations of HALS. In such cases the addition of these synergists to a HALS stabilized system can lead to an improvement of a factor of 2–3. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: UV-stability; Bridged amines; HALS

1. Introduction

It is generally accepted that the degradation of polyolefins in sunlight is due to a free radical auto-oxidation mechanism [1–6]. For polypropylene (PP) the majority of the reactions in this mechanism are well described. However there is still no consensus about the initiation reaction, which is crucial in this mechanism [7,8]. In 1965 it was suggested that the initiation of the oxidation could be due to charge transfer complexes (CTCs) between PP and oxygen [9]. Later this reaction was dismissed as being irrelevant because of the expected weak absorption of this CTC above 290 nm [2]. The initiation was ascribed to hydroperoxides or ketones formed during polymerization, storage or processing [2,6]. In 1989 it was reported that the addition of low molecular weight hydroperoxides or ketones to polyethylene (PE) has only a small influence on the photo degradation rate in PE [10,11], which led to the suggestion that other species must be responsible for the initiation. The argument that the absorption of PP–oxygen CTCs above 290 nm is too weak to be relevant was refuted with the argument that the lifetime of (well stabilized) polymers is so long that even a very small absorption can cause a big effect [8]. Although there is still no direct proof that CTC initiation is important for UV-degradation in polyolefins, it was necessary to assume its importance to explain the results of oxygen uptake and IR measurements in UV-degradation experiments on unstabilized and hindered amine light stabilizers (HALS) stabilized PE and PP [12,13], accelerated versus outdoor weathering [14,15] of PE and the influence of temperature and oxygen pressure on UV-degradation in polyolefins [16].

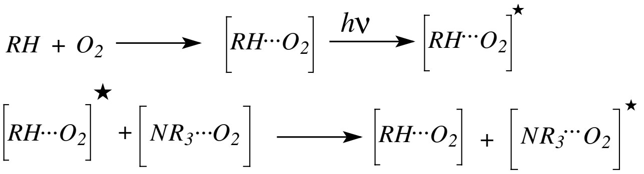
HALS are the best UV-stabilizers for polyolefins that are available. Many researchers have studied its mechanism of action [4,5,12,17–29]. The majority of these studies ascribe the function of HALS to radical scavenging by the nitroxide that can be formed by the oxidation of the HALS. According to Gugumus [11] the main function of HALS is to prevent initiation by quenching the initiating excited polymer–oxygen CTCs. To explain the results of oxygen uptake and IR measurements in UV-degradation experiments on unstabilized and HALS stabilized PE and PP [12,13], it was assumed that both mechanisms are important and that the high effectiveness of HALS is due to its quenching and radical scavenging ability.

The radical scavenging mechanism is well known and well described. The quenching mechanism is not. For quenching, UV-absorption with a wavelength higher than that of the energy donor is necessary. Aliphatic amines do not have such absorptions, but different amines show a contact CTC with oxygen that has UV-absorptions above

---

* Tel.: +31-46-476-1538; fax: +31-46-476-0503.
E-mail address: pieter.gijsman@dsm.com (P. Gijsman).

PII: S0032-3861(01)00708-X



$$RH + O_2 \longrightarrow \left[RH\cdots O_2\right] \xrightarrow{h\nu} \left[RH\cdots O_2\right]^{\star}$$

$$\left[RH\cdots O_2\right]^{\star} + \left[NR_3\cdots O_2\right] \longrightarrow \left[RH\cdots O_2\right] + \left[NR_3\cdots O_2\right]^{\star}$$

Scheme 1.

300 nm [30,31]. Excitation of these CTCs leads to an excited state with the same configuration as the CTC complex of the amine with singlet oxygen [30]. It has been postulated that amine oxygen CTCs are able to quench polymer oxygen CTCs [12,13]. In this way, excited amine oxygen CTCs are formed and polymer–oxygen CTCs are deactivated (Scheme 1, schematic representation of the stabilization of amines through the quenching of excited polymer oxygen CTCs).

In this paper a mechanism is proposed that explains the action of HALS as a quencher. Based on this mechanism other possible quenchers are suggested and it is shown that these molecules are active as UV-stabilizers in PP films and plaques.

2. Experimental

2.1. Materials

The PP used was a high impact copolymer containing 21% ethylene (M_n 65,000, M_w 310,000).

2.2. Additives

The HALS stabilizer used was bis(2,2,6,6,-tetra-methyl-4-piperidinyl)-decanedioate (Tinuvin® 770 from Ciba SC). For chemical structure see Scheme 2 (chemical structures of the HALS and bridged amines used).

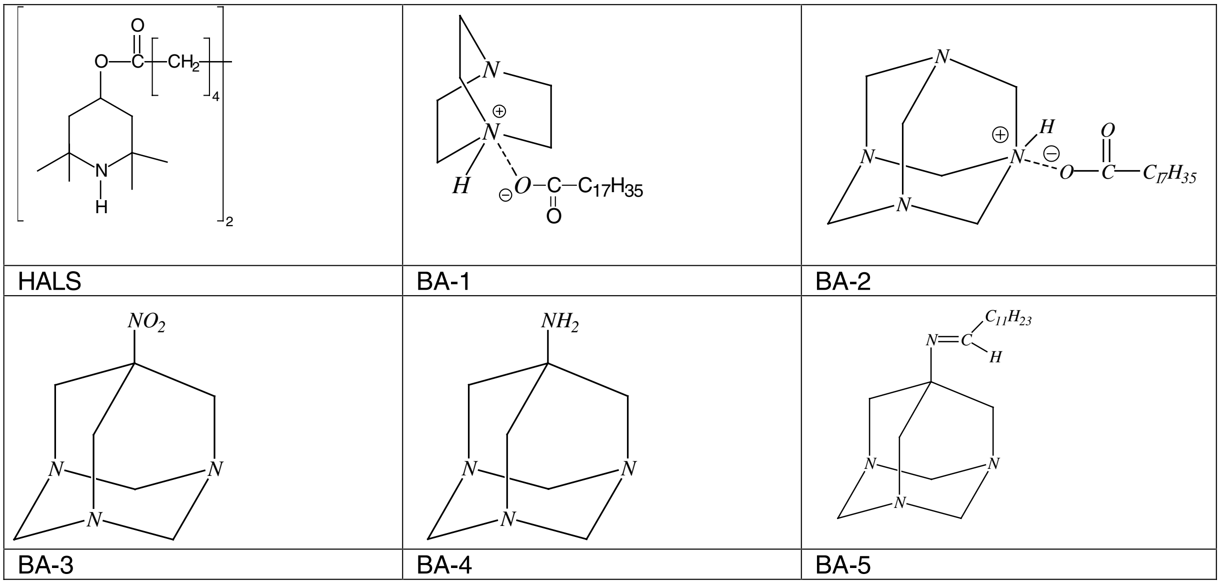
Synthesis of bridged amines. Different bridged amines were synthesized. The chemical structures of these products are shown in Scheme 2.

Stearic acid salt of di-azo-bicyclo-octane (BA-1) and hexamethylenetetramine (BA-2). To a solution of diazo-bi-cyclo-octane or hexa-methylene-tetramine (HMTA) in ethanol, a molar equivalent amount of stearic acid in ethanol was added dropwise. The ethanol was evaporated in a rotating evaporator. The products were identified with FT-IR and NMR.

7-Nitro-1,3,5-triaza-adamantane [32] *(BA-3)*. HMTA was dissolved in ethanol. During refluxing a mixture of formic acid and nitromethane was added dropwise, followed by 4 h refluxing. The reaction product was cooled to 0 °C, filtered and washed with water and ethanol. The mixture was purified by recrystallization from hot water. The chemical structure was verified with FT-IR, Mass Spectrometry, ^{1}H and ^{13}C NMR, the purity was checked with gas chromatography.

7-Amino-1,3,5-triaza-adamantane. (BA-4). A solution of 7-nitro-1,3,5-triaza-adamantane in methanol was hydrogenated with Raney Cobalt (75 °C, 80 bars of hydrogen) for 30 min. After cooling and flushing with nitrogen, the solution was filtered to remove the Raney Cobalt. The methanol was evaporated in a rotating evaporator. The remaining solid was dried in dry toluene on molecular sieve 4A. The chemical structure was verified with the aid of FT-IR, ^{1}H and ^{13}C NMR, the purity was checked gas chromatographically.

7-Dodecyl imino-1,3,5-triaza-adamantane (BA-5). This product was synthesized according to the procedure mentioned in Ref. [33]. The chemical structure was verified with the aid of FT-IR and Mass Spectrometry, the purity was checked gas chromatographically.



Scheme 2.

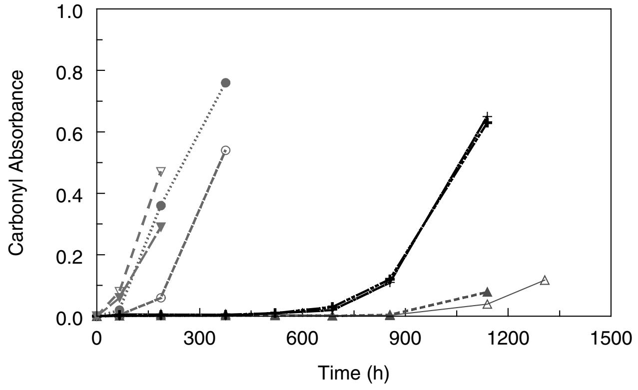


Fig. 1. Absorbance at 1713 cm^{-1} minus absorbance at 1860 cm^{-1} versus photo-oxidation time in PP films containing HALS-1 and/or BA-1 in duplicate (unstabilized (▽, ▼), 0.15% BA-1 (○, ●), 0.1% HALS-1 (+, +); 0.1% HALS-1 + 0.15% BA-1 (△, ▲).

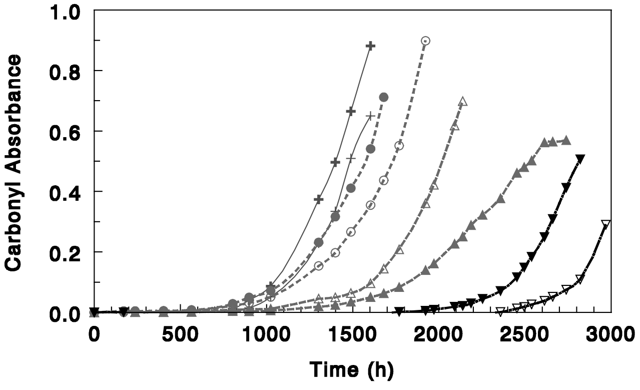


Fig. 2. Absorbance at 1713 cm^{-1} minus absorbance at 1860 cm^{-1} versus photo-oxidation time for PP films containing 0.2% HALS-1 and different amounts of BA-1 in duplicate (without BA-1 (+, +); 0.1% (○, ●); 0.2%: (△, ▲); 0.5%:(▽, ▼).

2.3. Film/plaque preparation

Solvent blending of a solution of the stabilizers with the polymer powder was used to prepare the different mixtures. These mixtures were dried in a vacuum oven. From the resulting compounds, films with thicknesses of about 150 μm and plaques with a thickness of 1 mm were pressed (5 min at 190 °C followed by cooling under a pressure of 100–120 kN).

2.4. UV ageing

The UV-degradations were performed in a Weather-Ometer Ci 65 (Atlas Material Testing Technology) with a filtered (boro-borosilicate) Xenon lamp at a black panel temperature of 63 °C, an intensity of 0.35 $W/m^2/nm$ (at 340 nm), a relative humidity of 55% and a dry/wet cycle: 18 min rain/102 min dry.

2.5. Carbonyl measurements

The degradation rate was determined with FT-IR. As an indicator of degradation the absorption at 1713 cm^{-1} was used; this absorption was base line corrected by subtracting the absorption at 1860 cm^{-1} (carbonyl absorbance). This corrected carbonyl absorbance was measured as a function of degradation time. The degradation criterion used was the time that elapsed until the carbonyl absorbance became 0.1 (for the films) or 0.5 (for the plaques).

3. Results

The influence of different HALS-1 concentrations and different concentrations of several bridged amines (BA1-5) on the UV-stability of PP films and plaques was determined. In Fig. 1 the increase in carbonyl absorbance versus photo-oxidation time is shown in duplicate for PP films containing HALS-1 and/or BA-1. The reproducibility of the results is reasonable. UV aging of unstabilized PP leads to a fast increase in carbonyl absorbance. Within 200 h a carbonyl absorbance of 0.5 is reached. The PP containing only BA-1 is only marginally better. HALS-1 is a well known stabilizer for PP and shows quite a big improvement in stability. The combination of HALS-1 and BA-1 shows by far the best performance. Thus, without HALS-1 the bridged amine is hardly effective, while in the presence of HALS-1 it is quite effective.

The increase in carbonyl absorbance during UV aging was also measured for several PP films containing 0.2% HALS-1 and different concentrations of BA-1. These results are shown in Fig. 2. The development of the carbonyl absorbances at different concentrations of BA-1 only is not shown in Fig. 2, but the stability of the films containing BA-1 only was comparable to that of the unstabilized film, as is shown in Fig. 1. So, this bridged amine alone is not effective. In the polymer containing HALS-1 only, the carbonyl absorbance starts to increase after about 1000 h; the addition of 0.1% of BA-1 had only a small effect. At higher BA-1 concentrations the UV-stabilization effect was larger. The combination of 0.2% HALS-1 and 0.5% BA-1 shows an increase in carbonyl absorbance after more than 2000 h. So especially at higher concentrations of the bridged amine there is a synergism with HALS-1.

The plot of the carbonyl absorbance versus the UV-degradation time was used to calculate the time until a carbonyl absorbance increase of 0.1 was reached. These times were plotted versus the concentration of BA-1 in combination with 0.1 and 0.2% HALS-1 (Fig. 3). In the presence of 0.1% HALS-1 the influence of the addition of BA-1 is much smaller than in the presence of 0.2% HALS-1. With 0.1% HALS-1 the addition of 0.5% of BA-1 causes an increase in the time needed to reach a carbonyl absorbance of 0.1: from 700 to 900 h. In the presence of 0.2% HALS-1 the influence of the concentration of the synergist is much larger. In this case the addition of 0.5% of BA-1 caused an increase from 1050 to more than 2600 h. For both HALS-1

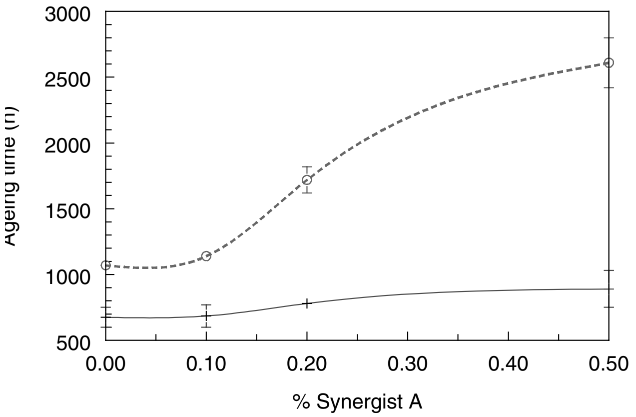


Fig. 3. Influence of the concentration of BA-1 on the aging time causing a carbonyl absorbance increase of 0.1 in PP films containing 0.1% (+) and 0.2% (○) HALS-1. Bars show standard deviation.

concentrations there seems to be a critical synergist concentration. Below 0.1% the effect of the synergist is marginal.

The influence of the concentration of BA-2 on the UV-stability is comparable to that of BA-1 (Fig. 4). Without HALS-1, BA-2 does not contribute to the UV-stability of the PP film. At a low HALS-1 concentration (0.05%) the influence of BA-2 is negligible. At higher HALS-1 concentrations, the influence of BA-2 becomes obvious. For this synergist the influence already becomes noticeable at a HALS-1 concentration as low as 0.1%. The compounds containing 0.2% HALS-1 and 0.5% BA-2 did not reach a carbonyl absorbance of 0.1 even after 4600 h.

A comparison of the results of Figs. 3 and 4 shows that BA-2 seems to be more effective than BA-1. For BA-5 a comparable effect was found (Fig. 5). At a low HALS-1 concentration (0.05%) the addition of BA-5 did not contribute to the UV-stability. At higher HALS-1 concentrations of (0.1 and 0.2%) an increase in UV-stability was found only for higher BA-5 concentrations (0.2% and higher). This bridged amine is less effective than BA-2.

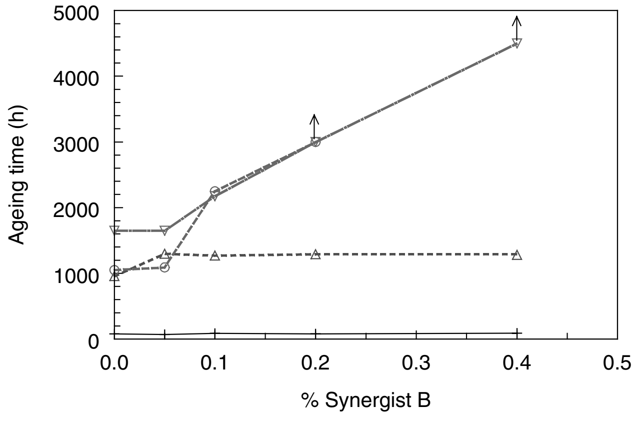


Fig. 4. Influence of the concentration of BA-2 on the aging time causing a carbonyl absorbance increase of 0.1 in PP films containing no (+), 0.05% (△), 0.1% (○) and 0.2% (▽) HALS-1 (arrows indicate that the carbonyl absorbance of these samples had not reached 0.1 yet at the indicated time).

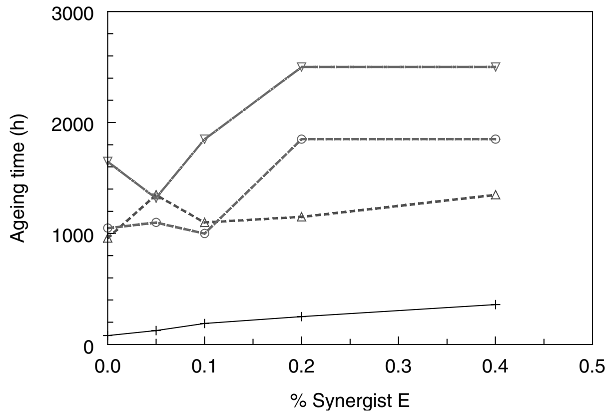


Fig. 5. Influence of the concentration of BA-5 on the aging time causing a carbonyl absorbance increase of 0.1 in PP films containing no (+), 0.05% (△), 0.1% (○) and 0.2% (▽) HALS-1.

The increase in carbonyl absorbance during UV aging was also measured for several PP plaques (1 mm) containing 0.1% HALS-1 and 0.2% BA 1, 2, 3 and 4 (Fig. 6).

In plaques containing only 0.1% HALS-1 the carbonyl absorbance increased after about 1500 h. The addition of 0.2% BA 1, 2, 3 or 4 resulted in an increase in UV-stability. In the plaques containing 0.1% HALS-1 and 0.2% BA 2 or 3, the increase in carbonyl absorbance was found after 3500 h, and in the plaques with HALS-1 and BA 1 or 4 after 4500 h. Clearly, just as in the films, the addition of bridged amines caused a big increase in UV-stability. However, there are some differences. In the plaques, BA-1 has a big influence at a HALS-1 concentration of only 0.1%, while in the films higher HALS-1 concentrations were necessary to obtain the same effect. In the films BA-2 is more effective than BA-1, while in the plaques this is the other way around.

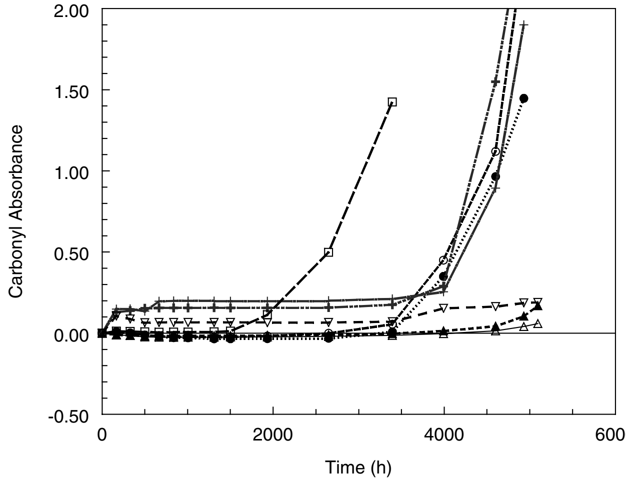
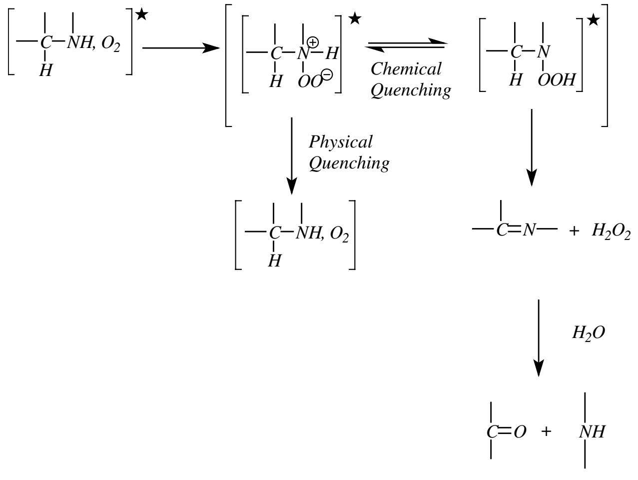


Fig. 6. Absorbance at 1713 cm^{-1} minus absorbance at 1860 cm^{-1} versus photo-oxidation time for PP plaques containing 0.1% HALS-1 without (□), with 0.2% of BA-1 (△, ▲), BA-2 (○, ●), BA-3 (+, +) and BA-4 (▽).



Scheme 3.

4. Discussion

It has been shown that the evaluated bridged amines alone are not effective as UV-stabilizers, but they can show a synergism with HALS. Addition of these amines to HALS stabilized PP can result in a 2–3 times longer lifetime.

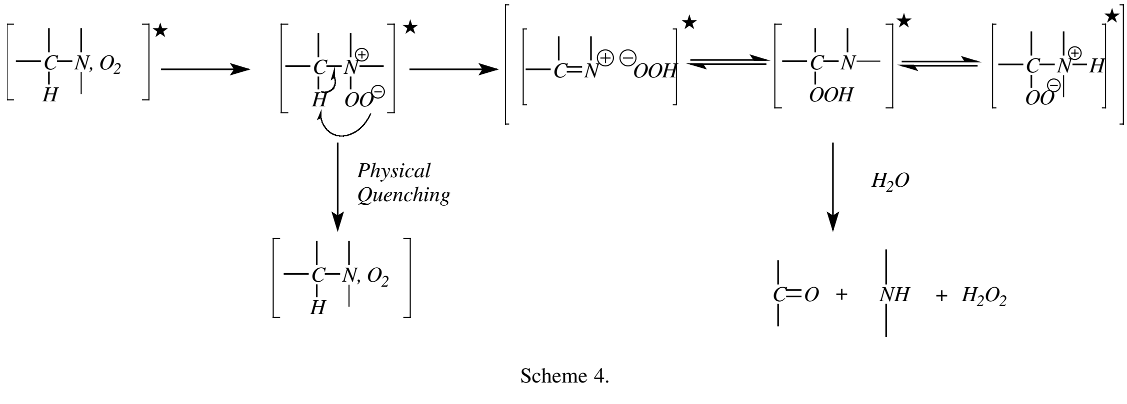
It is well known that acids can deactivate HALS [34]. The bridged amines used are basic and can also react with acids. However, a mechanism in which the bridged amines react with acids formed by oxidation and in this way prevent the HALS from being deactivated cannot explain the results. According to this explanation, the highest effectiveness of the bridged amines is expected for the lowest HALS concentration, which is not the case. The bridged amines are not effective at a concentration of 0.05% HALS-1, so deactivation of acids formed by oxidation cannot explain the activity of the bridged amines.

It is postulated that HALS-oxygen CTCs can act as quenchers for excited polymer–oxygen CTCs. This reaction leads to an excited amine oxygen CTC (see Scheme 1). According to Davidson excited amine–oxygen CTCs show the same configuration as the CTC complex of the amine with singlet oxygen [30]. Deactivation of this excited state is chemical or physical, which depends on the chemical structure of the amine. On the analogy of singlet oxygen quenching [35], a mechanism is postulated for the quenching of polymer–oxygen CTCs by primary, secondary and tertiary amine–oxygen CTCs (see Schemes 3 and 4, proposed mechanism for the deactivation of excited tertiary amine oxygen CTCs).

According to these mechanisms, chemical quenching will lead to the destruction of the amine and the formation of hydrogen peroxide. Hydrogen peroxide can initiate the oxidation of PP, so this mechanism does not lead to stabilization. According to this mechanism, chemical quenching will be found for primary and secondary amines containing an α-hydrogen. HALS does not contain an α-hydrogen and will therefore act mainly as a physical quencher.

In tertiary amines the first reaction leads to a double bond (Scheme 3, proposed mechanism for the deactivation of excited primary and secondary amine oxygen CTCs). In further reactions, the tertiary amine is converted into a secondary amine and hydrogen peroxide is formed too. Again it is not expected that chemical quenching lead to stabilization. However, in the case of tertiary amines that cannot form such a double bond, physical quenching can be expected. According to Bredt's rule, amines with nitrogen in a bridge-head position cannot form a C=N bond [35,36], which means that these types of molecules will act mainly by physical quenching. From these mechanisms, it can be concluded that the deactivation of excited oxygen-HALS and oxygen-bridged amines CTCs will mainly be physical and can lead to stabilization of the polymer.

Initiation by CTCs only is important if the amount of radicals formed by the decomposition of hydroperoxides is very small. Thus, as long as hydroperoxides are formed, initiation by CTCs can be neglected. In the absence of HALS this will be the case and hydroperoxides will initiate the photo-oxidation. In this case, CTC initiation is not important and it can be expected that quenching of CTCs will not lead to a UV-stability increase. This explains why the bridged amines alone are not effective. At high concentrations of HALS, it can be expected that the amount of hydroperoxides that will be formed can be neglected. In this case initiation of CTCs becomes important and quenching



Scheme 4.

of CTCs can lead to an increase in UV-stability. Indeed it is found that the bridged amines are mainly effective at high concentrations of HALS. For films it was found that at a HALS concentration of 0.05% the bridged amines are not effective, probably because at this low HALS concentration enough hydroperoxides are still formed to initiate the photo-oxidation and in this way reduce the importance of initiation and thus the quenching of CTCs.

The stability of the plaques with 0.1% HALS-1 is higher than that of the films with the same concentration of HALS-1, which is ascribed to the fact that the 'reservoir' of stabilizer in the plaque is larger than that in the film [37]. The higher stability of the plaques also implies that HALS starts to be effective at lower concentrations, as a result of which BAs also start to active these HALS concentrations.

Dipole–dipole energy transfer can occur when an excited donor molecule can transfer its energy to an acceptor molecule over distances much larger than the collisional diameters (long range quenching). In this case quenching over distances of 5–10 nm has been reported [30,38]. The molecular weight of BA 1, 2 and 5 is between 300 and 500. Assuming a homogeneous distribution of the BA, a 5–10 nm distance between the molecules corresponds to a concentration of about 0.1%(w/w). This is equal to the minimum concentration of quencher necessary to be effective. Thus, the quenching is probably due to long range dipole–dipole interactions.

The importance of CTC initiation for the photo-oxidation of polyolefins has long been debated [2,7–9]; this mechanism has not yet been proven. The idea behind the mechanism of action of bridged amines was quenching of excited CTCs. For this mechanism there is no proof either, but it is clearly shown that these molecules can increase the UV stability. Although there is no direct proof, in my opinion there is enough circumstantial evidence to accept that CTC initiation can be important for UV-degradation in polyolefins and that it is possible to increase UV-stability by quenching excited CTCs.

5. Conclusions

A mechanism has been proposed that explains how HALS can act as a quencher. Based on this mechanism several other possible quenchers (bridged amines) for the excited polymer–oxygen CTCs have been suggested. It has been shown that these bridged amines act as UV-stabilizers in films and plaques and that they show a synergism with HALS stabilizers. Although there is no direct proof, it seems that in HALS stabilized polyolefins initiation by CTCs is important and that it is possible to quench these excited CTCs. The effectiveness of these new quenchers is most pronounced at higher concentrations of HALS and synergist. In such cases the addition of the synergist to a HALS stabilized system can lead to an improvement of a factor of 2–3.

This new development might lead to a new class of stabilizers and might make PP applicable in new areas.

Acknowledgements

The author would like to thank Magali Gitton, Guido Meijers, Arnold Schaafsma, Daan Tummers and Giacomo Vitarelli for their assistance in the preparation and evaluation of the different stabilizers and Jacques Sampers for useful discussions.

References

[1] Cicchetti O. Adv Polym Sci 1970;7:70.
[2] Carlsson DJ, Wiles DM. J Macromol Sci Rev, Macromol Chem 1976;C14(1):65.
[3] Gugumus F. Angew Makromol Chem 1990;176/177:27.
[4] Gugumus F. In: Pospisil J, Klemchuk PP. (Eds.), Oxidation inhibition in organic materials, vol. II. Boca Raton, FL: CRC Press, 1990. p. 29–163.
[5] Rabek JF. Photostabilization of polymers. London: Elsevier, 1990.
[6] Scott G. In: Scott G, editor. Atmospheric oxidation and antioxidants, vol. II. Amsterdam: Elsevier, 1993. Chapter 8.
[7] Scott G. Polym Degrad Stab 1998;60:215–6.
[8] Gijsman P. Polym Degrad Stab 1998;60:217–9.
[9] Chien JCW. J Phys Chem 1965;69:4317.
[10] Gugumus F. Makromol Chem Makromol Symp 1989;27:25.
[11] Gugumus F. Angew Makromol Chem 1990;176/177:241.
[12] Gijsman P, Hennekens J, Tummers D. Polym Degrad Stab 1993;39:225–33.
[13] Gijsman P, Dozeman A. Polym Degrad Stab 1996;53:45.
[14] Gijsman P, Hennekens J, Janssen K. In: Clough RL, Billingham NC, Gillen KT, editors. Polymer durability, degradation, stabilization and lifetime prediction, Advances in chemistry series 249. Washington DC: American Chemical Society, 1996. p. 621–49.
[15] Gijsman P, Hennekens J, Janssen K. Polym Degrad Stab 1994;46:63–74.
[16] Gijsman P, Sampers J. Polym Degrad Stab 1997;58:55–9.
[17] Sedlar J, Petruy J, Pak J, Navratil M. Polymer 1980;21:5.
[18] Carlsson DJ, Chan KH, Wiles DM. In: Pappas SR, Winslow FH, editors. Photodegradation and photostabilisation of coatings, American Chemical Society Symposium Series No. 151. 1981. p. 51–63.
[19] Geuskens G, Nedelkos G. Polym Degrad Stab 1987;19:365.
[20] Toda T, Mori E, Murayama K. Bull Chem Soc Jpn 1972;45:1904.
[21] Felder BN. In: Klemchuk PP, editor. Polymer stabilization and degradation, American Chemical Society Symposium Series No. 280. 1985. p. 69–90.
[22] Zahradnickova A, Sedlar J, Dastych D. Polym Degrad Stab 1991;32:155.
[23] Chakraborty KB, Scott G. Polymer 1980;21:252.
[24] Klemchuck PP, Gande ME. Polym Degrad Stab 1988;22:241.
[25] Denisov ET. Polym Degrad Stab 1989;25:209.
[26] Denisov ET. Preprints of 12th International Conference on Advances in the Stabilization and Controlled Degradation of Polymers, Luzern, Switzerland, 1990. p. 77–82.
[27] Step EN, Turro J, Gande ME, Klemchuck PP. J Photochem Photobiol A:Chem 1993;74:203.
[28] Step EN, Turro J, Gande ME, Klemchuck PP. Macromolecules 1994;27:2529.
[29] Step EN, Turro J, Gande ME, Klemchuck PP. Polym Preprints 1993;34(2):231.
[30] Davidson RS. In: Foster R, editor. Molecular association. New York: Academic Press, 1975. p. 216–334.

[31] Tsubomura H, Mulliken RS. J Am Chem Soc 1960;82:5966.
[32] Collection Czechoslov. Chem Commun 1975;40:2179.
[33] Hoechst AG. Patent DE, 2637193, 1978.
[34] Zhang C, Carlsson DJ, Wiles DM. J Polym Sci:Part C: Polym Lett 1986;24:453.
[35] Bellus D. In: Ranby B, Rabek JF, editors. Singlet oxygen, reactions with organic compounds and polymers. New York: Wiley, 1978. p. 61–110.
[36] Keese R. Angew Chem 1975;87:568.
[37] Gugumus F. Polym Degrad Stab 1999;66:133.
[38] Rabek JF. Photodegradation of polymers. Berlin, Heidelberg: Springer, 1996.