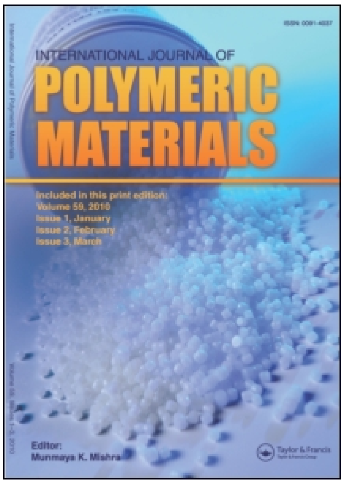

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Pavol Hrdlovič[a]; Štefan Chmela[a]
[a] Polymer Institute, Centre of Chemical Research, Slovak Academy of Sciences, Bratislava, Czechoslovakia

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Oligomeric Stabilizers of HALS Type; Influence of Polarity and Molecular Mass on Efficiency

PAVOL HRDLOVIČ and ŠTEFAN CHMELA

Polymer Institute, Centre of Chemical Research, Slovak Academy of Sciences, Dúbravská cesta 9, CS-842 36 Bratislava, Czechoslovakia

The optimal performance of the polymer additives is usually a compromise of several often contradictory requirements. The high efficiency of a given additive whose activity is determined by its chemical structure must be supported by good compatibility and high mobility of additive in the polymer substrate and low volatility and washability during processing and service.

The improvement of physico-chemical parameters can be achieved by increasing the molecular mass (at least above 10^3) of the low molecular mass additive. In this case the compatibility of the system polymer—oligomeric additives begins to play a pivotal role. The compatibility of this system is good when the polarity of its component is similar. To estimate the polarity of oligomeric stabilizers, the ratio of the intensity of two vibrational bands I_3/I_1 of monomer fluorescence of pyrene was used. Chimasorb 944 was found to be the least polar oligomeric HALS stabilizer under study.

It was found that copolymers 2,2,6,6-tetramethyl-4-piperidyl acrylate with *n*-octadecyl acrylate in the range of molecular mass between 10^3 and 10^5 exhibit the same polarity. The efficiency of these polymeric stabilizers in the inhibition of unoriented polypropylene films photooxidation decreases according to the relationship

$$E_r = aM_n^{-b}$$

where E_r is the relative efficiency, M_n is the number average molecular mass of the oligomeric stabilizer, a and b are constants. The value of b is 0.25 which is within the range of the dependence of any rate constant on the molecular mass.

KEYWORDS: Stabilizers of HALS type, efficiency, structure, molecular mass, stabilization, mechanism

INTRODUCTION

The additives must fulfil several requirements to achieve high performance. First of all they must have suitable chemical structure for a given task. Moreover, it is often neccessary to modify the basic structure for application in a given polymer. For any additives applied to a polymer it is necessary to secure;

1. Processing stability that is the ability to perform correctly after introducing into polymer. For thermoplasts it means the thermal stability during processing.
2. Service stability that is the long persistence in polymer substrate during service lifetime.

Each type of additive has its specific features but the efficiency is based on chemical reactivity for most of them. On the other hand, to fulfil the two above conditions means to give up the high chemical reactivity as a result of decreased mobility.

Physico-chemical parameters can be improved in some extent by increasing the molecular mass.[1,2] This can be achieved in several ways:

1. By functionalization. This means introducing functional groups into the parent structure which are capable of polymerization or polykondensation reactions and preparation of the homopolymer or copolymer in the given range of molecular masses.

2. By copolymerization of the functionalized additive with the monomers of large scale productions.

3. By chemical modification of the given polymer with the functionalized additive.

The last two routes, however, are not good because the final molecular mass is determined by the required properties (mainly mechanical) of the final product and is not optimized in respect to a given additive. At present the first route has led up to commerically successful products mainly in the class of light stabilizers, antistatic agents and in lesser extent in technological stabilizers and dyes.

A very important parameter in the system polymer—low molecular mass or oligomeric stabilizer is the compatibility. Similar compounds generally mix better than the different ones. In addition to the other factors, the compatibility of the system is determined by the polarity of its components. According to empirical scale of polarity, the hydrocarbons are considered as non-polar on one edge and water as polar on the other edge of this scale. There were many attempts to quantify this qualitative empirical scale. Kalyanasundaram and Thomas[3] have recently used the sensitivity of the vibrational structure of monomer fluorescence of pyrene to estimate the polarity of micelles. Similar approach can be applied to estimate the polarity of oligomeric stabilizers or polymers in the solid phase.

In literature there is a large amount of papers devoted to evaluation of the efficiency of light stabilizers. The conditions of the evaluation are, however, very different (for example: sources of irradation, temperature or climatic conditions, polymeric substrates, stabilization systems etc.) so that it is rather difficult to obtain meaningful data to make any conclusions concerning the effect of physical parameters on efficiency. Several authors[1,4] on the basis of data taken from literature and their own ones tried to make conclusions concerning the effect of molecular mass on physical parameters as:

-distribution of stabilizer in the polymer;

-compatibility and solubility of stabilizers in polymers;

-washability of stabilizers with polar and non polar solvents from polymers.

The range of molecular masses of stabilizers was limited to 10^3 only. Polyethylene was often used as polymer matrix for these studies.[1,4] Reasonable dependence on molecular mass was found for some physical parameters. These dependences do not allow to make any general dependence of the overall efficiency on molecular mass of the stabilizer. Only one short report on the influence of molecular mass on overall efficiency has so far appeared. Gugumus[5] reported that the dependence of the efficiency of poly(1,2,2,6,6-pentamethyl-4-piperidyl acrylates) goes through maximum at molecular mass 2000 and then decreases.

In this paper we investigate the influence of different ways of increasing the molecular mass on efficiency of stabilizers of HALS type. We explore the possibilities of estimating the polarity of oligomeric stabilizers spectroscopically.

EXPERIMENTAL

Synthesis of parent HALS stabilizers and some radicals derived from them, monomers, homopolymers and copolymers have been described previously.[6–10] *n*-Octadecyl acrylate used as non-polar comonomer was the same reported elsewhere.[8] Copolymers of 2,2,6,6-tetramethyl-4-piperidyl acrylate with *n*-octadecyl acrylate were prepared by radical polymerization in solution (benzene or toluene) initiated by AIBN. Chain transfer agent—dodecyl mercaptane—was used for the preparation of copolymers of molecular mass 3590 and 5140. Copolymers were purified by precipitation of benzene solution into methanol. Molecular masses of the samples were determined by vapour pressure osmometry (Dr. Knauer, Berlin, F.R.G.).

The additives were introduced into polyporpylene (Tatren HPF, Slovnaft n.e., Bratislava, Czechoslovakia) by mixing in a Brabender plastograph at 200°C. Other ways of doping polymers were occasionally used as well. Polymer films (thickness 0.15 mm) were exposed in merry go round irradiation devices to the full spectrum of the 125 W RVC medium pressure mercury arc (Tesla n.e., Holešovice, Prague, Czechoslovakia). The course of photoxidation is monitored by the increase of absorption of valence vibration of carbonyl band at 1710–1730 cm^{-1}. Typical photooxidation curves are shown on Figure 1. The relative efficiency is defined as a ratio of the time to reach carbonyl absorbance 0.2 with and without stabilizer.

Emission spectra were taken on an instrument composed of commercially available optical and electronic parts.[11–13] Polymer films of oligomeric stabilizers and some polymers were prepared by casting from chloroform solutions onto silica slides of 25 × 35 mm dimensions. The thickness of the films was between 20–100 μm. Spectra from films were taken frontally under 20° angle. The value of the ratio I_3/I_1 was determined by direct measurement of the height of the respective band from base-line. The reproducibility of R for films was not as good as for solutions.[3] It is probably caused by the way of film preparation. The critical step might be the slow evaporation of the solvent which is poorly controlled. Error at determination of the ratio of intensity is about ±0.1.

The lifetime measurements of monomer fluorescence of pyrene doped in polymer films were performed on LIF-200 (Zentrum fur wissenschaftlichen Geratebau der AdW der DDR, Rudower Chaussee 6, DDR-1199 Berlin)

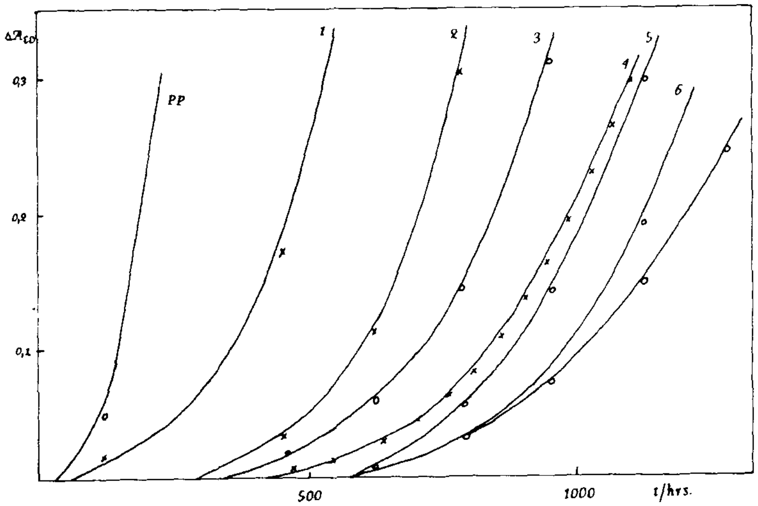

FIGURE 1 Typical course of photooxidation of polypropylene (0) stabilized by copolymer 2,2,6,6-tetramethyl-4-piperidyl arylate/*n*-octadecyl 116 000 (1), 78 000 (2), 13 100 (3), 12 300 (4), 5 164 (6), 3 590 (7) and Chimasorb 944 (5).

attached to microcomputer ZX Spectrum+, (Sinclair, England) and printer K 6313 (VEB Robotron, Dresden, DDR) according to Ref. 14.

Pyrene (zon. ref.) was obtained from Lachema n.e., Brno, Czechoslovakia and chloroform was analytical reagent. Poly(alkyl methacrylates) were products of Rohm & Haas, (Darmstadt, F.R.G.), polycarbonate was product of General Electric Co. (Schenectady, New York, U.S.A), and poly(vinyl acetate) was product Duslo n.e. (Šala, Czechoslovakia). These polymers were used without purification. Other polymers and solvents were the same as elsewhere.[13]

RESULTS AND DISCUSSION

Spectral measurements

Spectrum of monomeric fluorescence of pyrene in different polymer matrices is well vibrationally resolved (Figure 2). The values of ratio R equal to $I_3(0-2)/I_1(0-0)$ are given in Table I for some polymers and oligomeric stabilizers of HALS. The range of values varies between 0.7 for polar poly(vinyl acetate) and 2.0 for polyethylene. The highest value of R was exhibited by Chimasorb 994 from oligomeric HALS stabilizers (Figure 3). This value was difficult to reproduce. The film of Chimasorb 944 was often rather hazy. The oligomers based on esters of acrylic or methacrylic acid were more polar than Chimasorb 944. Their polarity was similar to that of Tinuvin 622. The polarity of copolymers 2,2,6,6-tetramethyl-4-piperidyl acrylate with *n*-octadecyl acrylate did not much differ from that of homopolymer. The following conclusions can be made:

1. The polarity of copolymers of 2,2,6,6-tetramethyl-4-piperidyl acrylate with *n*-octadecyl acrylate of different molecular mass is nearly the same. Therefore the

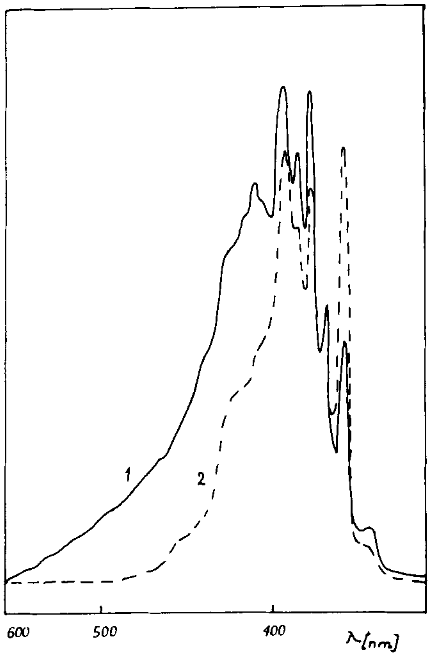

FIGURE 2 Monomer fluorescence of pyrene doped in polyethylene (1) and copolymer 2,2,6,6-tetramethyl-4-piperidyl acrylate *n*-octadecyl acrylate (2).

TABLE I

Ratio of intensity of different bands I_3/I_1 and I_e/I_m of pyrene fluorescence doped in polymer films

Polymer	I_3/I_1	I_e/I_m	T_g
Poly(vinyl acetate)	0.71		
Poly(methyl methacrylate)	0.83	0.04	378
Poly(ethyl methacrylate)	0.84	0.02	338
Poly(hexyl methacrylate)	1.01	0.02	268
Poly(dodecyl methacrylate)	1.27	0.32	208
Polystyrene	1.19		373
Polycarbonate	1.28		
Polyethylene	2.04		148
Polypropylene atactic	1.95	0.1	253
Chimasorb 944	1.27	0.02	
Tinuvin 622	0.87	0.01	
Spinuvex A 36	1.01		
Poly(2,2,6,6-tetramethyl-4-piperidyl acrylate)	0.83		
Poly(2,2,6,6-tetramethyl-4-piperidyl acrylate-co-*n*-octadecyl acryalte), 1:2	0.94		
Copolymer as above, 1:1	0.91		

[a] Film thickness 100 m. Pyrene concentration 4.8×10^{-2} mol. kg^{-1}.
[b] Ref. 17.

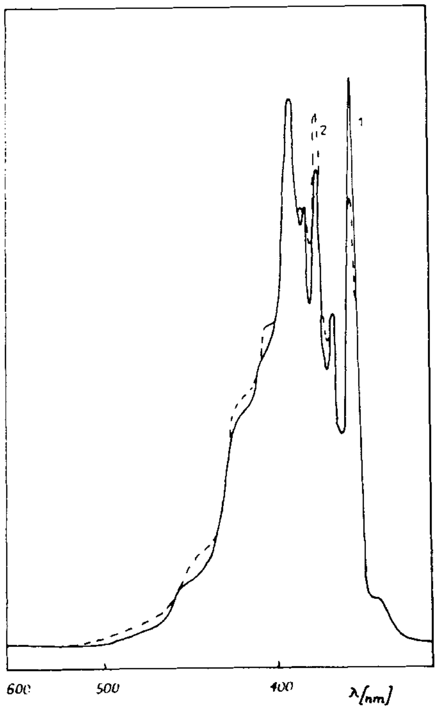

FIGURE 3 Monomer fluorescence of pyrene doped in poly(2,2,6,6-tetramethyl-4-piperidyl) acrylate) (1) and Chimasorb 944 (2).

most probable reason for different stabilization efficiency is different mobility of copolymers due to different molecular mass.

2. Pyrene seems to be a large molecule to probe the micro-environment of copolymers.

At the concentration of 4.8×10^{-3} mol . kg^{-1} of pyrene in film of polymers with T_g above room temperature the ratio of I_e/I_m is low under 0.05. It means that monomer emission prevails. Broad excimer emission at 460 nm appears at the same pyrene concentration for polymers with T_g under room temperature (Figure 4). Monomer fluorescence of pyrene decays in solution monoexponentially (cyclohexane 20 ns and methanol 15 ns). The decay of pyrene monomer fluorescence does not follow monoexponential law in polymer films like poly(methyl methacrylate). It means that there is some aggregation of pyrene doped in polymer films even at low concentration which brings about more complex decay.

THE EFFICIENCY OF BONDED STABILIZERS

The physico-chemical parameters of the system polymer-stalizer are difficult to judge separately. Usually one change causes changes of several other parameters. In the system polypropylene–monomer–homopolymer–copolymer based on

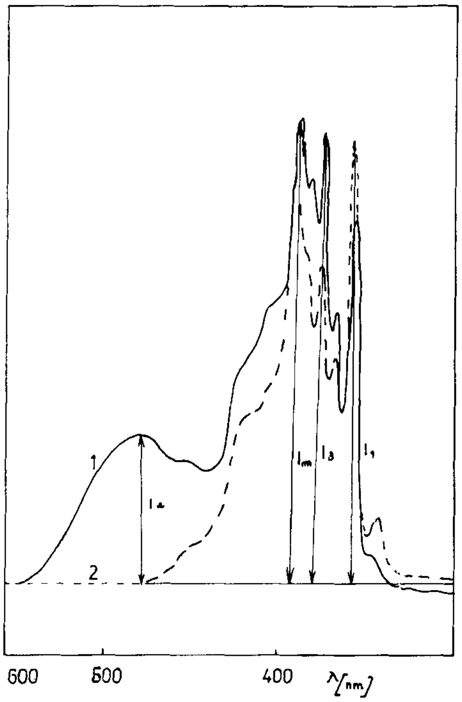

FIGURE 4 Monomer and excimer fluorescence of pyrene doped in poly(dodecyl methacrylate) (1) and poly(vinyl acetate) (2).

TABLE II

The efficiency of free and bonded stabilizers at polypropylene photooxidation

Stabilizer	E_r[d]	E_r[e]
Without	1.00[f]	1.00[g]
Monomer[a]	2.50	3.88
Homopolymer	1.88	2.13
Copolymer/DMA[b]	5.00	9.88
Copolymer/ODA[c]	6.18	12.31
Tinuvin 622	7.82	11.50

[a] 1,2,2,6,6-Pentamethyl-4-piperidyl methacrylate.

[b] Dodecyl methacrylate.

[c] *n*-Octadecyl acrylate.

[d] Relative efficiency expressed as the ratio of the times with and without stabilizer needed to reach $\Delta A_{co} = 0.2$ at isotactic polypropylene photooxidation.

[e] Relative efficiency after washing with alkaline detergent.

[f] Time for $\Delta A_{co} = 0.2$ is 170 hrs.

[g] Time for $\Delta A_{co} = 0.2$ after washing is 85 hrs.

TABLE III

The efficiency of free and bonded stabilizers in polystyrene

Stabilizer	M_n	E_r[b]	E_r[c]
Without		1.00[d]	1.00[e]
Monomer[a]	223.33	1.86	1.89
Monomer N—O	239.33	1.26	1.27
Polymer	6.70×10^3	1.29	1.13
Copolymer	1.04×10^5	1.23	1.20

[a] 2,2,6,6-Tetramethyl-4-piperidyl methacrylamide.

[b] Relative efficiency for radiation with $\lambda > 313$ nm (glass filter).

[c] Relative efficiency for radiation with $\lambda = 366$ nm (combination of glass and liquid filters).

[d] Time to reach $\Delta A_\infty = 0.2$ is 525 hrs.

[e] Time to reach $\Delta A_\infty = 0.2$ is 1 960 hrs.

2,2,6,6-tetramethyl-4-piperidyl acrylate or methacrylate, we demonstrated that copolymer exhibits the highest efficiency.[5] Table II shows that monomer and homopolymer are distinctly less efficient. After washing with alkaline detergent, the relative efficiency of homopolymer slightly increases while that of copolymer rises substantially. Similar results were obtained with Tinuvin 622. These results indicate that the higher efficiency of copolymer is due to its better compatibility with polypropylene in comparison with monomer and homopolymer. Moreover, polar monomer and homopolymer are more easily washed out of polypropylene film. The increased relative efficiency is partially due to the fact that the stability of films without light stabilizer is remarkably decreased. Washing of the rest of processing stabilizer has detrimental effect on the long term stability of polypropylene.

Similar approach using polystyrene as polymer brings about different results. Table III shows that the relative efficiency is lower for polystyrene than for polypropylene. It was observed with several systems that the monomer stabilizer is more effective than homopolymer or copolymer. Binding monomer into homopolymer or into copolymer with styrene decreases the mobility of active structural unit. No great difference between efficiency of homopolymer and copolymer is seen through the difference in molecular masses is one order of magnitude. The distribution of active structural units in statistical copolymer HALS-styrene (molecular mass 10^5) is probably the same as when homopolymer with molecular mass 10^4 is added. The overall efficiency is similar.

INFLUENCE OF MOLECULAR MASS

The study of the efficiency of several systems monomer (low molecular mass stabilizer)–homopolymer–copolymer[8,9] demonstrated that it is not possible to make any conclusions about correlation efficiency–molecular mass when more parameters like polarity, mobility, compatibility and washability are changed. To study correlation efficiency–molecular mass we have chosen copolymer 2,2,6,6,-tetramethyl-4-piperidyl acrylate with *n*-octyl acrylate in the region of molecular

TABLE IV

Dependence of efficiency on molecular mass for copolymer 2,2,6,6-tetramethyl-4-piperidyl acrylate/*n*-octadecyl acrylate

	Stabilizer M_n	$\log M_n$	t^c hrs	E_r	$\log E_r$
	Without		185	1.00	0.000
1	116 000	5.064	470	2.54	0.405
2	78 000	4.892	710	3.84	0.504
3	13 100	4.117	850	4.59	0.662
4	12 300	4.089	1 000	5.41	0.733
5	10 060	4.003	965	5.22	0.717
6	9 150	3.961	835	4.51	0.655
7	5 140	3.711	1 135	6.14	0.788
8	4 200	3.623	1 085	5.86	0.768
9	3 590	3.555	1 215	6.57	0.817

[a] Time to reach $\Delta A_{co} = 0.2$ at polypropylene photooxidation.

masses 10^3–10^5 (Table IV). Although the number of experimental points is limited, the linear correlation $\log E_r$ on M_n is evident (Figure 5). The slope of the correlation is 0.25 ± 0.03 and correlation coefficient 0.97.

The relative efficiency is rather complex kinetic quantity composed of several elementary steps with factors different weight. Few data about elementary processes have been reported in the literature. For example, the slope of correlation diffusion of antioxidants on molecular mass in polyethylene is 1.33.[1] On the other hand, the dependence of volatility on molecular mass yield slope 0.02–0.01[1,4] for different additives. These data determine the range 0–1.15 in which the slope of such dependence can be expected.

For more precise estimation of the slope of this type of dependence, the knowledge of molecular mass dependence of some elementary process would be desirable, Such measurements were mainly performed in solution. For instance,

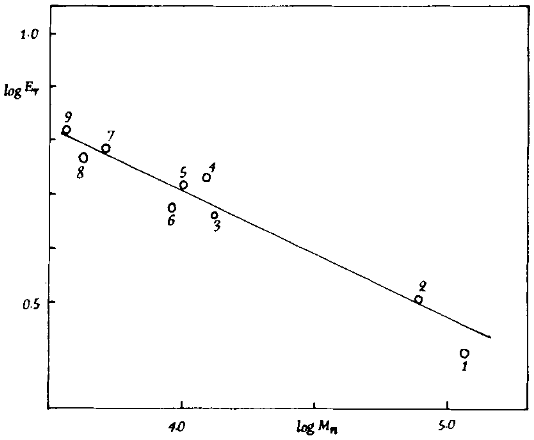

FIGURE 5 The dependence of $\log E_r$ on M_n for system isotactic polypropylene-copolymer 2,2,6,6-tetramethyl-4-piperidine/*n*-octadecyl acrylate of different molecular mass (number according to Table 4).

Horie and Mita[15] investigated influence of molecular mass on the diffusion controlled quenching in the system benzil—anthracene. The chromophores were bound on polystyrene of narrow molecular mass distribution. The authors found the value of 0.3 as a slope of this dependence in benzene solution. This value agrees quite well with that determined by us. Another elementary process is end-to-end cyclisation of polymers. It was shown by Horie and coworkers[16] that the dependence of the rate constant of end-to-end cyclization exhibits the slope -1 in good solvent (benzene) and even larger slope in theta solvent -1.5 (cyclo-hexane). It means that the decrease of rate constant for end-to-end cyclization with the increase of molecular mass is even steeper than for quenching.

The rough estimate of the slope between 0.1 and 1.5 seems to be reasonable but for more precise value additional measurements on different systems will be needed. Moreover, the optimization of the system polymer–stabilizer cannot be performed solely with respect on molecular mass.

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