

NOTES

Degradable Copolymers of Hindered Amine Light Stabilizer Derivatives and Their Stabilizing Efficiency in Polypropylene

INTRODUCTION

The optimum efficiency of additives to polymers (mainly polyolefins) is usually a compromise of opposite requirements.¹ Besides suitable chemical structure for proper functioning, an additive must fulfil additional parameters. For example:

1. Processing stability, that is, ability to preserve high activity during thermal processing;
2. Long-term stability, that is, ability to remain in a particular polymer for a long time in an active form.

Fulfillment of these requirements might be at least partially reached by:

1. Decreasing the volatility;
2. Improving the compatibility;
3. Decreasing the washability.

Improvement of the specified parameters is possible by increasing the molecular mass of the additive or its binding to the polymeric substrate. In both cases it is necessary to functionalize the additive. Polymerization, copolymerization, or grafting might be used for increasing the molecular mass of the additive. A serious disadvantage of this approach, mainly for grafting, is that molecular mass of the additive prepared in this way is seldom in the range proper to its application.

Ways to optimize additive function with respect to molecular mass have not been elaborated upon, neither experimentally nor theoretically. Moreover, the experimental optimization of a particular additive-polymer pair, is rather time consuming. On the other hand, theoretical approaches lack suitable models. An alternative approach to solving this problem has therefore been sought.

In this short preliminary communication we propose an alternative method of optimizing the molar mass of the long term stabilizing additive during its stabilizing action. In this approach, the additive is so modified that it contains light sensitive units to secure degradability of the additive. In the course of the stabilization action, the

molar mass decreases and the mobility and compatibility increase. Unfortunately, the washability of the stabilizing fragments increases as well.

EXPERIMENTAL

2,2,6,6-Tetramethyl-4-piperidyl acrylate (TMA), melting point (m.p.) 53–56°C and *n*-octadecyl acrylate (ODA) were the same as previously described.² 1-Phenyl-2-propanone (PVK) was prepared by dehydrochlorination of 1-phenyl-3-chloropropanone-1 and used immediately after preparation. Terpolymers were prepared by radical copolymerization of a monomer mixture under nitrogen at 60°C using AIBN as initiator. During the preparation of terpolymer the ratio TMA : ODA was 1 : 1, and the addition of PVK was 4.6 and 16 mol %, that is, 2.3 and 8.7 mass %, respectively. Conversion was 45%. The content of the carbonyl groups was determined spectrophotometrically using ($31,000 \text{ cm}^{-1}$) $\epsilon = 83 \text{ L/mol cm}$ for 1-phenyl-3-chloropropanone-1 in chloroform. The limiting viscosity number was determined in benzene at 30°C. The average number molar mass was determined osmotically in chlorobenzene.

The samples for irradiation were prepared by mixing 0.2 mass % of additive with polypropylene (Tatren HPF, Slovnaft s.e., Bratislava, Czechoslovakia) in a Plastograph Brabender at 190°C for 5 min. Films (thickness 0.2 mm) were exposed to filtered (glass) radiation of 125 W mercury arc (Tesla s.e., Holešovice, Czechoslovakia) at 30°C. Absorption in the 1700–1750 cm^{-1} region was monitored as elsewhere.²

RESULTS AND DISCUSSION

Terpolymers were slightly yellowish rubbery materials. The copolymer TMA/ODA was a white powder. The stabilizing action derives from the TMA unit having a sterically hindered amine structure (HALS, Hindered Amine Light Stabilizer). The presence of a long alkyl chain in ODA secures better compatibility with a nonpolar stabilized polymer and raises the efficiency of the TMA units as has been shown earlier.² The third comonomer—PVK—represents the light-sensitive unit. IR spectra unequivocally confirmed the presence of PVK structural

units in terpolymer. This is evident from the presence of carbonyl vibrations at 1680 cm^{-1} . This band cannot be used for quantitative determination of the carbonyl content since it is overlapped by the ester band. The content of PVK structural units was therefore determined by UV spectrometry. The $n - \pi^*$ band was used for the determination. The extinction coefficient at $31,000\text{ cm}^{-1}$ equal to 83 L/mol cm is based upon the model compound 1-phenyl-3-chloropropanone-1. The content of PVK for both terpolymers was higher (4.0 and 11.6 mass %) than expected from the polymerization mixture (2.3 and 8.7 mass % respectively). This confirms the high reactivity of vinyl ketone type monomer observed previously on different occasions.³ Since the conversion was rather high (33 and 47%), terpolymers are not completely statistical. This conclusion can be drawn from irradiation of benzene solutions of terpolymers with filtered radiation of 125 W RVC mercury arc. The irradiation of the copolymer TMA/ODA does not change the viscosity (Fig. 1). The irradiation of terpolymer solutions showed the greatest changes at the beginning (first 10 min); curves were nearly the same for both terpolymers. This indicates that the chemical composition of both terpolymers is rather inhomogeneous. The initial molar mass of terpolymers is different. It is lower for terpolymer of higher PVK content. Assuming the same relationship between the molar mass and the viscosity for both terpolymers, the fractions of lower molar mass for the terpolymer of higher PVK content are responsible for higher stabilizing efficiency though the course of degradation of both terpolymers in solution is similar (Fig. 1). We assume that the degradation proceeds as the Norrish Type II Reaction.³ Quantitative evaluation is, however, not possible because the Mark-Houwink coefficients are not known for these terpolymers.

Figure 2 shows the course of the accumulation of oxidation products during irradiation of polypropylene films. The copolymer TMA/ODA of rather high molar mass determined by osmometry (450,000, chlorobenzene) did not exhibit any efficiency. This molar mass is too high to

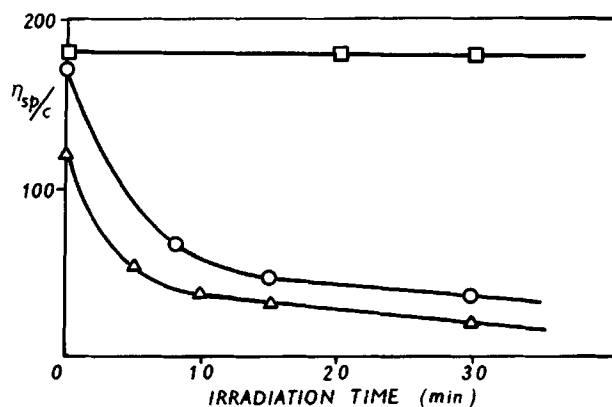


Figure 1 Photolysis of copolymer TMA/ODA (□), terpolymer TMA/ODA/PVK (4.0 wt %) (○), and TMA/ODA/PVK (11.6 wt %) (△) in benzene solution.

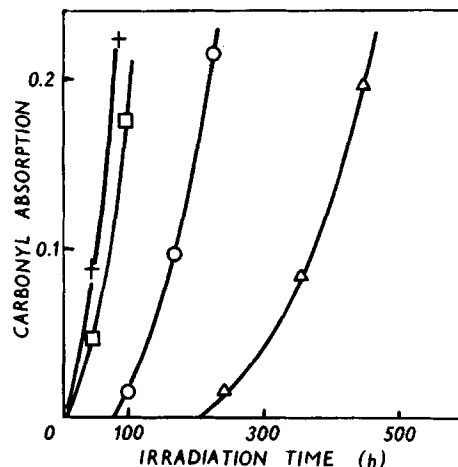


Figure 2 Photooxidation of polypropylene films (0.2 mm) with no stabilizer (+); copolymer TMA/ODA (□); terpolymer TMA/ODA/PVK (4.0 wt %) (○); terpolymer TMA/ODA/PVK (11.6 wt %) (△). Concentration of additives 0.2 wt %.

enable any mobility of the stabilizer and, consequently, any inhibition efficiency: the stabilizer is fixed in the polymeric substrate. The terpolymer of similar molar mass, 420,000 but with 4.0 mass % PVK content, shows doubled efficiency. This is due to degradation fragments with lower molecular mass, which are more mobile in the polymer substrate. This is better demonstrated with the terpolymer of 11.6 mass % concentration of PVK. The initial molar mass is, however, lower (330,000). The efficiency is 4 times higher. The comparison of the time scales in Figures 1 and 2 shows that the fragmentation of terpolymers occurred before the start of polymer degradation, despite the fact that fragmentation was carried out in solution and polymer degradation in film. The quantum yield of the photolysis is only 2–3 times higher in solution than in film for copolymers containing PVK.³

These data indicate some possibilities to regulate molar mass of additives in the course of degradation and its transformation in a more active form with respect to its molar mass. On the other hand, suitable properties are preserved during storage before irradiation. No migration of stabilizer is possible. We are aware that molar masses of polymeric stabilizers are rather high, beyond the range used in applications. Further optimization of the initial molar mass as well, as the content of the light sensitive structural unit, is needed.

SUMMARY

To achieve the optimum stabilizing efficiency of additives to polymers, it is necessary to fulfil several requirements, which might be related to some physicochemical parameters. These parameters usually exhibit various functional dependence on molecular mass. For optimal efficiency it

would consequently be necessary to vary molecular mass, depending upon the step in the processing and application of an additive in a particular polymer. This can be achieved by the so-called "degradable additives." Application of a terpolymer of 2,2,6,6-tetramethyl-4-piperidyl acrylate/*n*-octadecyl acrylate/1-phenyl-2-propenone in photostabilization of PP films demonstrates advantages and limitations of this approach.

References

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Š. CHMELA
P. HRDLOVIČ

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

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