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Mechanisms of antioxidant action: polymer-bound hindered amines by reactive processing, Part III Effect of reactive antioxidant structure*

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Bis-acryloyl HALS (hindered amine light stabilisers) react with polypropylene under reactive processing conditions to give initially a cross-linked product which rearranges under conditions of high shear and high temperature to give a homogeneous gel-free polymer graft which blends with normal polypropylene to give an effective polymer-bound photoantioxidant.

Monoacrylates and acrylamides and bis-methacryloyl HALS bind to polypropylene to a much lower extent under the same conditions and this is rationalised on the basis of the higher tendency of these monomers to homopolymerise.

1 INTRODUCTION

It was shown in an earlier paper[1] that the *O,N*-bis-acryloyl hindered amine light stabiliser (**I**, AATP) was capable of being completely bound to polypropylene by reactive processing and that the bound antioxidant so produced was an effective light stabiliser for this polymer. In order to understand fully the mechanism of this process and to explore the generality of the binding reaction other *O*- and *N*-disubstituted HALS have been investigated. Table 1 shows the compounds examined in the present study. Compounds **II** and **III** represent monoacrylates and monoacrylamides, respectively, and **IV** is an *O,N*-bis-methacryloyl HALS.

2 EXPERIMENTAL

2.1 Materials

Unstabilised polypropylene (HF-26) was supplied by ICI (Plastic Division) Ltd, 2,2,6,6,-tetramethyl-4-piperidinol was supplied by Ciba-Geigy, Switzerland. Methyl acrylate, myristoyl chloride, methyl myristate, acryloyl chloride, methacryloyl chloride, titanium(IV) isopropoxide (Tipox) were all ex-Aldrich Chemical and were used directly without further purification. Di-cumylperoxide (DCP), supplied by Akzo Chemical Ltd, was recrystallised from methanol.

2.2 Synthesis of antioxidants

1-Acryloyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine (AATP, **I**) was prepared by a known procedure described in an earlier paper.[1]

Preparation of compounds **II**, **III**, and **IV** were carried out by a similar method described in the patent literature[2–4] with minor modifications. In the case of 1-myristoyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine (MyATP, **II**), 15·7 g of 2,2,6,6-tetramethyl-4-piperidinol was continuously refluxed in dry benzene with 8·4 ml of methylacrylate and 3 ml Tipox under a nitrogen atmosphere for 24 h. The remaining Tipox was treated with aqueous sodium bicarbonate and the evaporated product was recrystallised in hexane. The purified product (21·1 g) and 14·6 ml of triethylamine were then dissolved in dry benzene. A solution of 23·1 ml of myristoyl chloride

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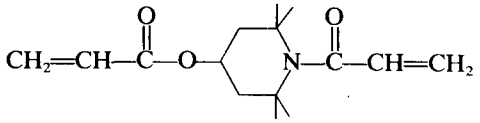
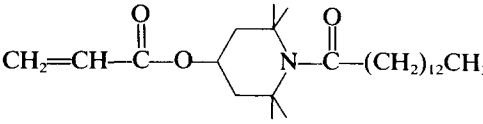
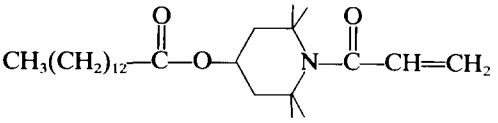
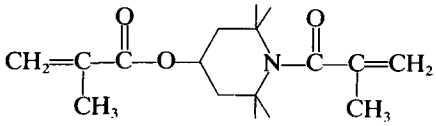
Table 1. Various acrylic and methacrylic ester and amide derivatives of hindered amines

Structure number	Chemical structure, name and molecular weight (MWt)	Abbreviation
I		AATP
	1-acryloyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine (MWt = 265)	
II		MyATP
	1-myristoyl-4-acryloyloxy-2,2,6,6-tetramethyl piperidine (MWt = 421)	
III		AMyTP
	1-acryloyl-4-myristoyloxy-2,2,6,6-tetramethyl piperidine (MWt = 421)	
IV		MMTP
	1-methacryloyl-4-methacryloyloxy-2,2,6,6-tetramethyl piperidine (MWt = 293)	

in dry benzene was added dropwise with constant stirring at a temperature below 10°C, and at room temperature for an additional 12 h. Solid triethylamine hydrochloride formed was filtered out. An oily product was obtained after vacuum evaporation from the neutralised filtrate: this was then washed with hexane. Elemental analysis: N = 3·3%; C = 74·3%; H = 11·2%, (Calculated). N = 3·4%; C = 72·8%; H = 12·8%, (Found). FTIR-analysis, (liquid film): ester >C=O, 1728 cm^{-1} (s); amide >C=O, 1706 cm^{-1} (s); unsaturation >C=C<, 1556 cm^{-1} (m). NMR analysis in $CDCl_3$ indicated proton peaks: unsaturation (CH_2=CH—) at 6·3 ppm (doublet), 6·1 ppm (quartet) and 5·7 ppm (doublet), myristyl group at 2·1, 1·9 and 1·2 ppm [—$(CH_2)_{12}$—], and 0·8 ppm (—CH_3, triplet), hindered piperidine ring, C_4 (—O—CH<) at 5·2 ppm (nine splits), C_3 (—CH_2—) at 1·9 ppm (doublet), CH_3-groups at 1·1 and 1·2 ppm (two singlets).

1-Acryloyl-4-myristoyloxy-2,2,6,6-tetramethyl-piperidine (AMyTP, **III**) was similarly prepared.[2-4] 2,2,6,6,-Tetramethyl-4-piperidinol (15.7 g), 20·9 ml of methyl myristate, and 3 ml of Tipox were refluxed in dry benzene as in the previous procedure. After purification 36·7 g of the oily product obtained and 14·6 ml of triethylamine were dissolved in dry benzene. A solution of 9·05 g acryloyl chloride in benzene was then added with stirring at a temperature below 10°C. A yellowish liquid was obtained after purification. Elemental analysis: N = 3·3%; C = 74·3%; H = 11·2%, (Calculated). N = 3·5%; C = 74·1%, H = 10·2%, (Found). FTIR-analysis (liquid film): ester >C=O, 1734 cm^{-1}(s); amide >C=O, 1651 cm^{-1}(s); unsaturation >C=C<, 1608 cm^{-1}(m). NMR analysis in $CDCl_3$ indicated proton signals: unsaturation (CH_2=CH—) at 6·3 ppm (doublet), 6·1 ppm (quartet) and 5·7 ppm (doublet), myristoyl group at 2·1 and 1·3 ppm [—$(CH_2)_{12}$—], 0·7 ppm (CH_3—, triplet), hindered piperidine ring, C_4 (—O—CH<) at 5.2 ppm (nine splits), C_3 (—CH_2—) at 1·9 ppm (doublet), CH_3-groups at 1·1 and 1·2 ppm (two singlets).

For synthesis of 1-methacryloyl-4-methacryloyloxy-2,2,6,6-tetramethyl piperidine (MMTP, **IV**), 15.7 g of 2,2,6,6-tetramethyl-4-piperidinol was also used and dissolved with 29·2 ml of triethylamine in dry benzene. A solution of 21·4 ml methacryloyl chloride in dry benzene was added dropwise at a temperature below 10°C with constant stirring, followed by additional 12-h stirring at room temperature (20–25°C). Solid triethylamine hydrochloride

formed was filtered out and after vacuum evaporation an oily product was obtained, which was then washed with hexane. Elemental analysis: N = 4·8%; C = 69·6%; H = 9·2%, (Calculated). N = 4·9%; C = 68·2%; H = 10·1%, (Found). FTIR-analysis, (liquid film): ester $>C=O$, 1728 cm^{-1}(s); amide $>C=O$, 1651 cm^{-1}(s); unsaturation $>C=C<$, 1619 cm^{-1}(m). NMR-analysis (in $CDCl_3$), indicated proton signals: ester and amide unsaturations ($CH_2=C<$) at 6·3 ppm (singlet) 6·1 ppm (singlet), 5·7 ppm (singlet) and 5·5 ppm (singlet), hindered piperidine ring, C_4 (—O—$CH<$) at 5·2 ppm (nine splits), methyl acrylic groups at 2·1 and 2·05 ppm (two singlets), C_3 (—CH_2—) at 1·9 ppm (doublet), CH_3-groups at 1·1 and 1·2 ppm (two singlets).

2.3 Reactive processing of polymer-antioxidant systems

Unstabilised polypropylene, freshly prepared antioxidant (concentration of 5–20%), and peroxide were tumble mixed at room temperature in dichloromethane solution. The antioxidant and peroxide concentrations were varied, keeping the total weight of the polymer sample constant (35 g) to charge the full capacity of the internal mixer. After exhaustive vacuum evaporation at room temperature, the polymer sample was processed in a Hampden-RAPRA torque rheometer, under restricted oxygen access (i.e. closed mixer, cm) for 10 minutes at 180°C and rotor speed of 60 rpm (standard condition). The polymer concentrates were then compression moulded at 180°C into sheets (200 μm thick).

2.4 Assessment of binding efficiency of antioxidants

Three polymer film samples (2×3 cm^2) having the same thickness (0.1–0.2 mm) were exhaustively Soxhlet extracted in dichloromethane for 48 h, under nitrogen atmosphere, followed by drying under vacuum at room temperature for 12 h. Carbonyl (ester or amide) absorption of the antioxidants was used to calculate the amount of the antioxidants in polymer samples by using Perkin-Elmer FTIR-Spectrophotometer model 1710. The carbonyl area index, i.e. ratio of carbonyl area (at 1811–1668 cm^{-1}) to the $>CH$— area of polymer (at 2752–2697 cm^{-1}), before and after extraction were compared, from the three pieces of the polymer films. FTIR of the solvent extract was also measured.

2.5 Testing

Melt flow index measurements were carried out on the processed polymer concentrates. Polymer samples were extruded in a Davenport melt flow indexer through a die ($\phi = 0{\cdot}2362$ cm) at 230°C and under a load of 2·16 kg. The weight average of at least five samples extruded per fixed time was recorded. The MFI was calculated in grams of the molten masterbatch passed through the die within 10 min.

To measure the gel content and the concentration of the antioxidant in the gel, a correct amount (around 5 g) of the polymer concentrate (shredded) was exhaustively Soxhlet extracted in xylene under nitrogen atmosphere. The residue (gel) as well as the soluble fraction in the xylene extract were vacuum evaporated to a constant weight. The concentration of antioxidant in the soluble fraction was measured by means of FTIR spectroscopy and calculated using a calibration curve. The antioxidant concentration in the gel was calculated by difference.

Molecular weight distribution of the polymer concentrates was determined by RAPRA Technology Ltd using Gel Permeation Chromatography. Around 0·1 g of polymer sample was dissolved in gently boiling 1,2-dichlorobenzene. The solution was then filtered and injected into GPC columns (P L gel 2× Mixed gel, 20 Micron packing, 30 cm columns) at 140°C with flow rate = 1·0 ml min^{-1}. The molecular weight distribution data of the sample was calibrated using polystyrene standards.

3 RESULTS

Figure 1 shows the effect of increasing HALS concentration in the standard binding procedure (180°C/10 min). It is clear that above 5 g to a maximum of 100 g of polymer, the concentration of the reacted antioxidant has little influence on the level of binding. It is also evident that none of the other reactive antioxidants binds to the same level as AATP at any concentration.

Figure 2 shows that although an increase in peroxide concentration above the 0·05 molar ratio relative to the HALS, has little effect on the level of binding, it does have a markedly

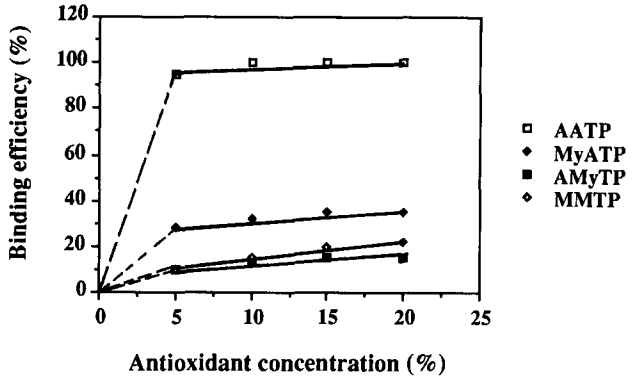


Fig. 1. Effect of concentration of antioxidants (**I–IV**), processed with PP at 180°C for 10 min in the presence of 0·010 molar ratio DCP) on their binding efficiency.

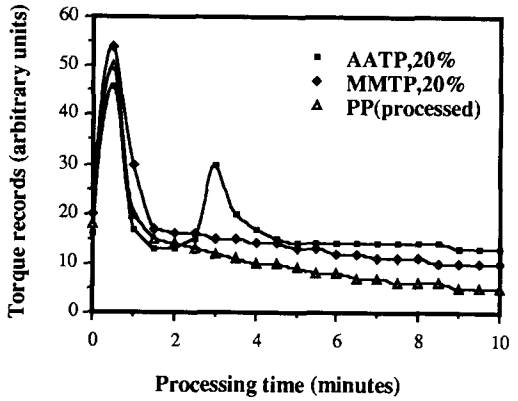


Fig. 3. Comparison of torque developed during melt processing of PP in the presence of 20% AATP and MMTP with that of processed PP in the absence of antioxidant.

deleterious effect on the melt stability of the polymer containing the monoacryloyl compounds. The bis-acryloyl and methacryloyl compounds by contrast are very effective melt stabilisers for polypropylene.

A more detailed study of the behaviour of the bis-acryloyl and methacryloyl compounds during processing showed that AATP caused a peak in the mixing torque which was completely absent with MMTP (see Fig. 3). However, further processing reduced the polymer viscosity to a similar ultimate level. This behaviour suggested the transient formation of a cross-linked structure and in order to examine this in more detail, samples processed for various times were Soxhlet extracted with xylene and the insoluble gel content measured. Table 2 shows that at 3 min processing, the gel content is high, but this decreases to a very low value after 10 min. Furthermore, at 3 min processing, almost the whole of the AATP was found in the gel fraction by IR examination, whereas after 10 min there was almost no HALS in the small amount of gel remaining; almost all of it was found to be present in the soluble fraction. Table 2 also shows molecular weight of the soluble fraction of AATP-B measured after 3 min processing when the gel content is maximal and after 10 min processing. It can be seen that the molecular weight of the main phase remains constant and is little different from normally processed PP whereas the molecular weight of the polypropylene phase processed with peroxide without AATP is very much reduced.

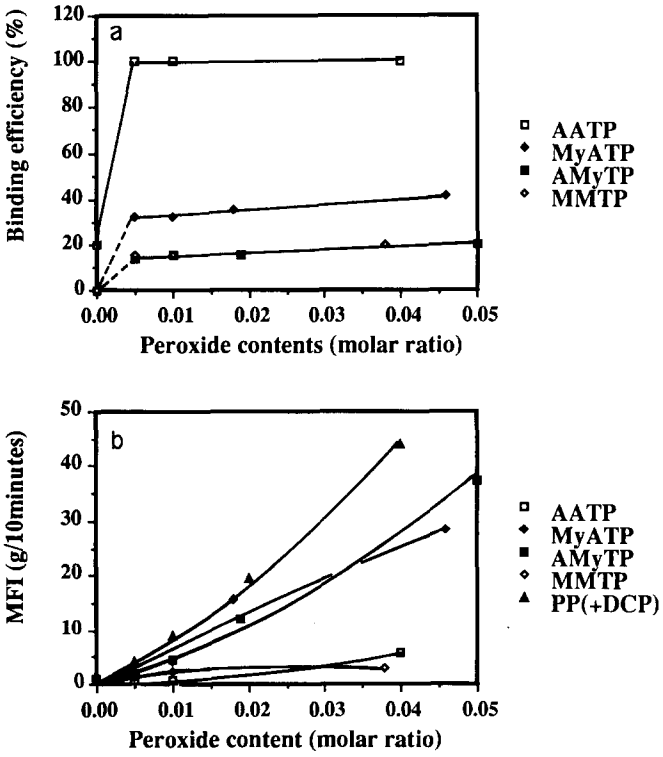


Fig. 2. Effect of concentration of peroxide (DCP) on binding efficiency (a) and melt flow index (b) of 10% antioxidant (**I–IV**) concentrates (processed in PP at 180°C for 10 min).

4 DISCUSSION

A number of deductions can be drawn from the present work.

1 Bis-acryloyl or methacryloyl HALS present in polypropylene in substantial concentration during processing appears to inhibit the normal degradation reactions that lead to reduction in molecular weight in the presence of peroxides.
2 Unlike the mono acryloyl HALS (**II** and **III**) which appears to homopolymerise rather

Table 2. Insoluble gel content, MFI, molecular weight of soluble fraction, as well as antioxidant content in the gel and in the soluble fraction of AATP concentrates (MB), processed at 180°C and various processing times in the presence of 0·005 molar ratio of DCP

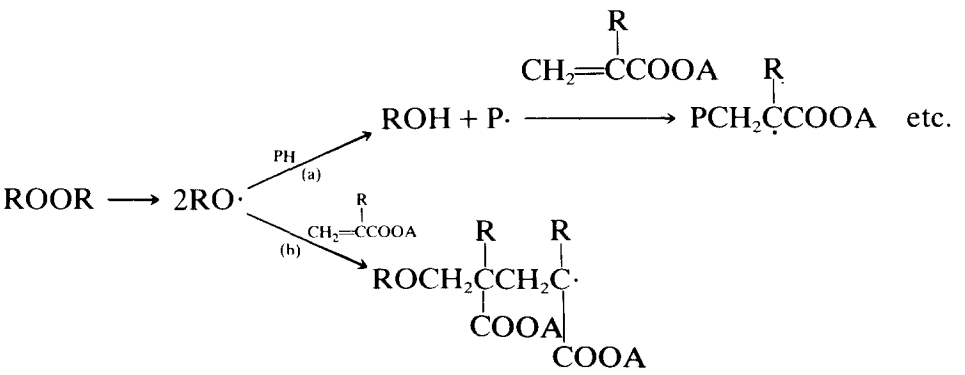
Polymer concentrate	Processing time (min)	M_n (10^4)	MFI (g/10 min)	Gel content (g/100 g MB)	AATP in soluble fraction (g/100 g MB)	AATP in the gel (g/100 g MB)
AATP, 20%	3	2·83	0·0	27	0·4	19·6
	5	2·75	0·5	22	3·1	16·9
	10	2·82	3·2	3	18·9	1·1
AATP, 10%	3	2·77	0·1	25	0·7	9·3
	5	2·67	2·8	20	1·6	8·4
	10	2·76	8·0	2	8·8	1·2
PP (unprocessed)	0	3·28				
PP (processed)	10	3·08				
PP (with DCP)	10	1·95				

than graft to PP, the bis-acryloyl HALS (**I**, AATP) initially reacts with the polymer by cross-linking and this is followed by a structural rearrangement of the graft co-polymer to give a 100% bound HALS adduct which can be blended with normal polypropylene (see Ref. 1).

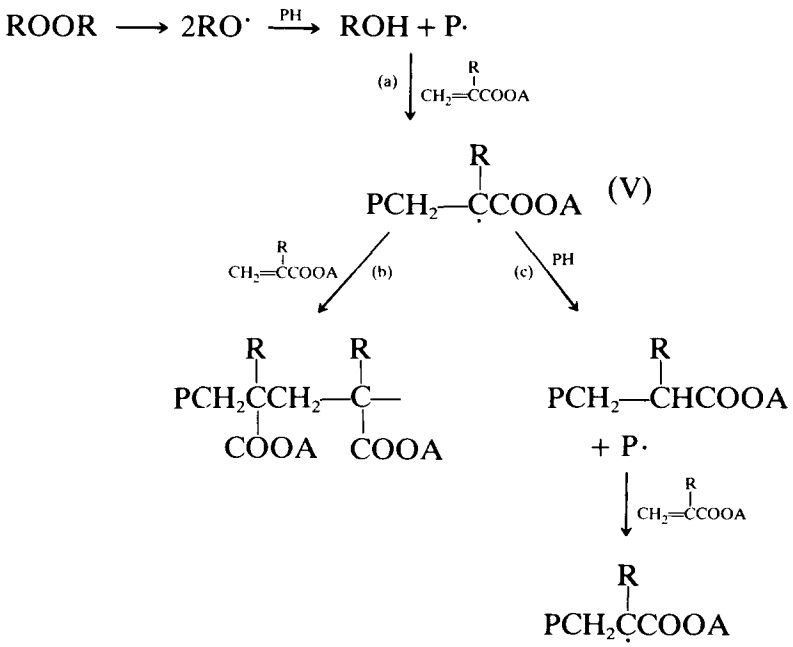
3 The bis-methacryloyl HALS (**IV**, MMTP) grafts to the polymer to a much smaller extent than AATP under the same conditions.

Munteanu[5] has pointed out that in the case of monovinyl-reactive antioxidants, homopolymerisation (Scheme 1, (b)) is in competition with grafting (Scheme 1, (a)). The much lower grafting levels of the methacryloyl HALS in the present study has to be understood in the light of the reactivity of the intermediate radicals. The propagation reaction almost certainly involves both homopolymerisation Scheme 2, reaction (b) and chain transfer from the PP chain (Scheme 2, reaction (c)) and in the latter process, the radical derived from methacylate (**V**, R = Me) will be less reactive than that from acrylate (**V**, R = H). This combined with the higher reactivity of methacrylates in homopolymerisation (Scheme 1, reaction (b)) results in the lower level of graft formation.

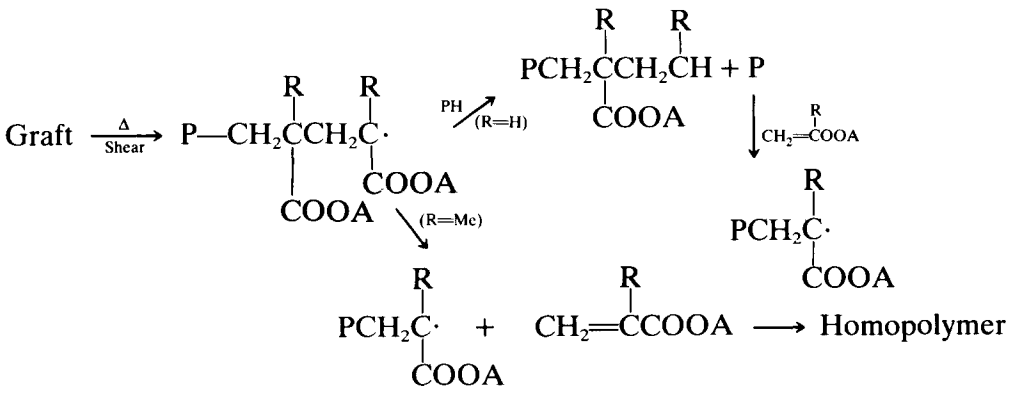
A further reason why the ultimate level of HALS binding is lower in the case of the methacryloyl compounds is that the ceiling temperature for stable graft formation is lower than in the case of the acrylates. Consequently, the restructurisation of the graft copolymer occurs more readily in the case of methacryloyl, but the products are different. The mechanism of the structural rearrangement reaction is not at present entirely clear. It almost certainly involves preferential chain scission of the graft under the influence of both high shear and high temperatures (see Scheme 3). However, whereas depolymerisation to monomer and repolymerisation to homopolymer is the more likely subsequent reaction in the case of methacryloyl, hydrogen abstraction and further grafting of



Scheme 1.



Scheme 2.



Scheme 3.

residual monomer is more likely in the case of acryloyl. In neither case does the hydrocarbon polymer backbone appear to be involved.

5 CONCLUSIONS

1 The grafting of bis-acryloyl HALS to polypropylene provides a useful method of preparing highly bound HALS concentrates with good photoantioxidant activity (see Ref. 1).
2 Monoacryloyl and bis-methacryloyl HALS are bound to a much lower extent.
3 Initial cross-linking occurs followed by structural rearrangement of the cross-linked product to give gel-free homogeneous polymer grafts that melt blend with unmodified polypropylene.

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