

# Synthesis and Properties of New Copolymers Containing Hindered Amine

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## SYNOPSIS

Eight new copolymers containing hindered amine (HA) were synthesized by copolymerization of vinyl monomers [styrene (St), methyl methacrylate (MMA)] with new functional monomers produced by reaction of 4-amino-2,2,6,6-tetramethylpiperidine (ATMP) and epoxy compounds containing double bond, and mixture copolymerization of vinyl monomers (St and MMA) with a mixture of ATMP and above epoxy compounds. The structure of these new copolymers were characterized by IR, NMR, and elemental analysis. The properties of these new copolymers were described and their photoprotecting effectiveness examined. Experimental results indicate that they possess high photoprotecting effectiveness comparable to or higher than that of a commercial polymeric HALS "PDS." © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

It is well known that hindered amine light stabilizers (HALS) are the most effective light stabilizers. Extensive research work and reviews of HALS have been published.<sup>1-7</sup> However, HALS with low molecular weight (MW) are relatively volatile and are easy to be extracted by liquid;<sup>8-13</sup> therefore, the effectiveness of low MW HALS is limited. A new trend for HALS development is to prepare HALS with higher MW.<sup>1-5</sup> Copolymerization or homopolymerization of functional monomers containing hindered amine is the usual method for preparation of higher MW HALS. There are several polymeric HALS reported in the literature;<sup>1-7,13</sup> many of them are based on 2,2,6,6-tetramethyl-4-piperidinyl methacrylate.<sup>12-18</sup> Recently, a new monomer made from isopropenyl- $\alpha,\alpha$ -dimethylbenzyl isocyanate (m-TMI) reacting with 1,2,2,6,6-pentamethyl-4-piperidinol and its copolymers with St and MMA have been reported.<sup>19,20</sup> New monomeric HALS based on isocyanate and hindered piperidine have also been reported.<sup>21,22</sup> In

this article, eight new copolymers containing HA are described.

## EXPERIMENTAL

### Materials

Allyl glycidyl ether (AG) and 1,2-epoxy-5-hexene (HEPO) were supplied by Aldrich Chemical Company Inc.; 4-amino-2,2,6,6-tetramethylpiperidine (ATMP) was from Fluka. These chemicals were used without further purification. Styrene (St) and methyl methacrylate (MMA) were also supplied by Aldrich Chemical Company; they were distilled before use. The initiator,  $\alpha,\alpha$ -azobis(isobutyronitrile) (AIBN) was supplied by Tokyo Chem. Ind. Comp., Japan.

### Synthesis

#### Monomers

*N*-3-Alloxy-2-hydroxypropyl-4-amino-2,2,6,6-tetramethylpiperidine (monomer **I**). In a three-neck flask equipped with a condenser, a nitrogen inlet, a magnetic stirrer, and an oil bath were placed 13.6842 g (0.0872 mol) ATMP and 10.0000 g (0.0872 mol) AG.

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**Table I** Preparation of Copolymers A, B, C, and D

Copolymer	Comonomer				AIBN (g)	<i>T</i> (°C)	Time (h)	Yield (%)
	1	2	Mol <sub>1</sub>	Mol <sub>2</sub>				
<b>A</b>	<b>I</b>	MMA	0.008	0.028	0.0480	80	8	43.52
<b>B</b>	<b>I</b>	St	0.083	0.026	0.0480	80	13.45	41.07
<b>C</b>	<b>II</b>	MMA	0.0025	0.018	0.0200	80	10.20	25.00
<b>D</b>	<b>II</b>	St	0.0022	0.020	0.0200	80	11.20	50.48

The reaction was carried out at 80°C for 6 h under nitrogen and stirring. The reaction product was a yellow viscous-oil-like substance. Distillation at 125°C/82 mmHg removed unreacted AG and ATMP. A yellowish paste product remained. Yield was 90.10%.

*N*-2-Hydroxyhexenyl-5-4-amino-2,2,6,6-tetramethylpiperidine (monomer **II**). Using same reaction apparatus as above, 7.9188 g (0.0507 mol) ATMP and 5.0000 g (0.0507 mol) HEPO were placed in the flask, the oil bath temperature was then raised and maintained at 80°C with stirring under nitrogen for 6 h. The reaction product was a viscous-oil-like substance. Distillation at 110°C/100 mmHg removed unreacted HEPO and ATMP. A yellowish paste product was obtained with 25.60% yield.

### Copolymerization

A typical copolymerization to produce new copolymer in this work is described as follows: in a three-neck flask equipped with a condenser, a nitrogen inlet, a magnetic stirrer, and an oil bath were placed 2.8080 g (0.0280 mol) MMA, 2.1635 g (0.0080 mol) monomer **I** and 0.048 g AIBN. The oil bath temperature was raised and maintained at 80°C with stirring under nitrogen for 8 h. A rubberlike substance was obtained. Extraction with pentane (3

× 50 mL) yielded a white solid product (**A**) with 43.52% yield.

The other copolymers were obtained through the same procedure described above, and are summarized in Table I.

### Mixture Copolymerization

A typical mixture copolymerization to produce copolymers in this work is described as follows: in a three-neck flask equipped with a condenser, a nitrogen inlet, a magnetic stirrer, and an oil bath were placed 10.1795 g (0.0980 mol) St, 5.1456 g (0.052 mol) HEPO, 8.0475 g (0.052 mol) ATMP, and 0.0318 g AIBN. The oil bath temperature was raised and maintained at 80°C for 10 h with stirring under nitrogen. An oil-like substance was obtained. Extraction with pentane (3 × 50 mL), and after drying, a yellowish product (**E**) was obtained with 44.20% yield.

The other copolymers were obtained by the same mixture copolymerization procedure and are summarized in Table II.

### Characterization

IR spectra were recorded using a Shimadzu FT-IR 1801 Fourier Transform Infra Red Spectrophotometer. Proton-NMR spectra were obtained using a

**Table II** Preparation of Copolymers E, F, G, and H

Copolymer	Vinyl <sup>a</sup>	Mixture <sup>a</sup>		AIBN (g)	<i>T</i> (°C)	Time (h)	Yield (%)
<b>E</b>	St 0.098	HEPO 0.052	ATMP 0.052	0.0318	80	10	44.20
<b>F</b>	MMA 0.107	HEPO 0.052	ATMP 0.052	0.0818	80	10	51.64
<b>G</b>	St 0.097	AG 0.044	ATMP 0.044	0.1138	80	10	52.15
<b>H</b>	MMA 0.157	AG 0.044	ATMP 0.044	0.0890	80	10	65.64

<sup>a</sup> In moles.

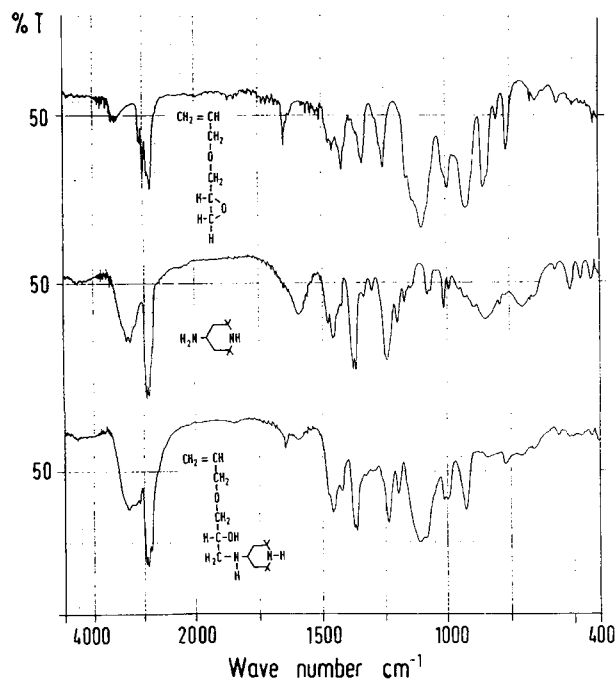


Figure 1 IR spectrum of product from AG + ATMP.

JOEL FX-900 FTNMR,  $DCCl_3$  as solvent and TMS as internal standard; MS spectra were recorded using a MICROMASS 7305E. CHN analytical values were obtained using a Perkin-Elmer 2400CHN Elemental analyzer.

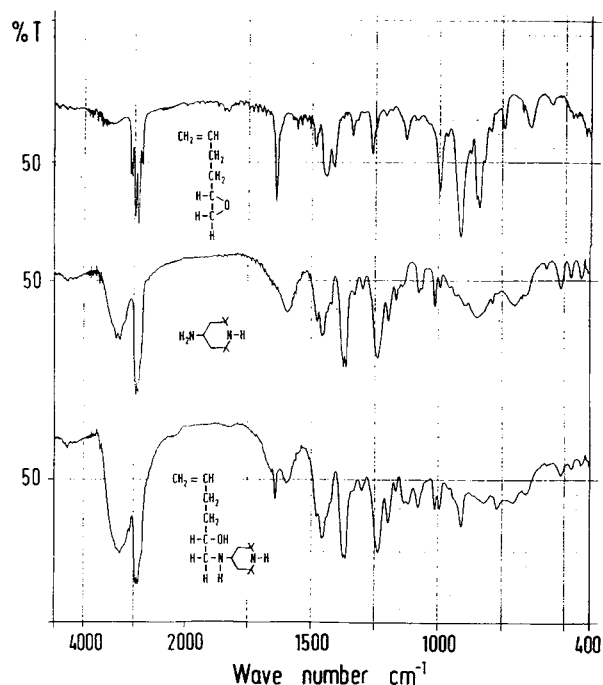


Figure 2 IR spectrum of product from HEPO + ATMP.

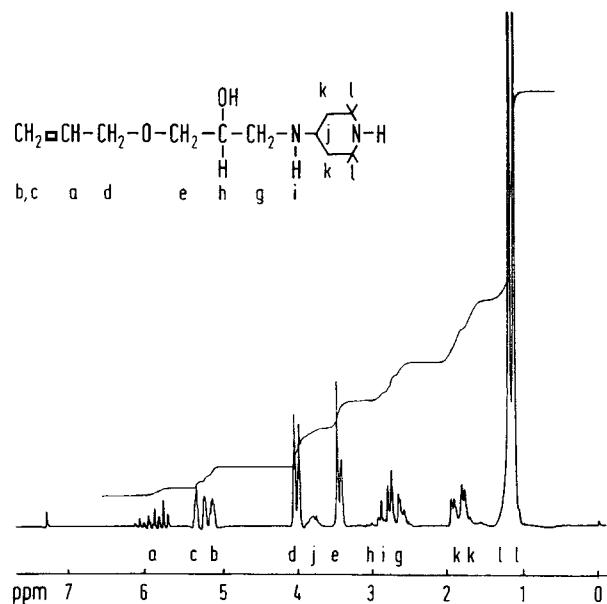


Figure 3 Proton-NMR of product from AG + ATMP.

### Photooxidation

The preparation and photooxidation of polypropylene samples containing these new copolymers followed the usual procedure reported elsewhere.<sup>23</sup> Photooxidation of the samples was monitored using a Perkin-Elmer 782 IR spectrophotometer at a wave number of  $1710\text{ cm}^{-1}$ . Induction period was determined from plot of carbonyl absorption versus irradiation time.

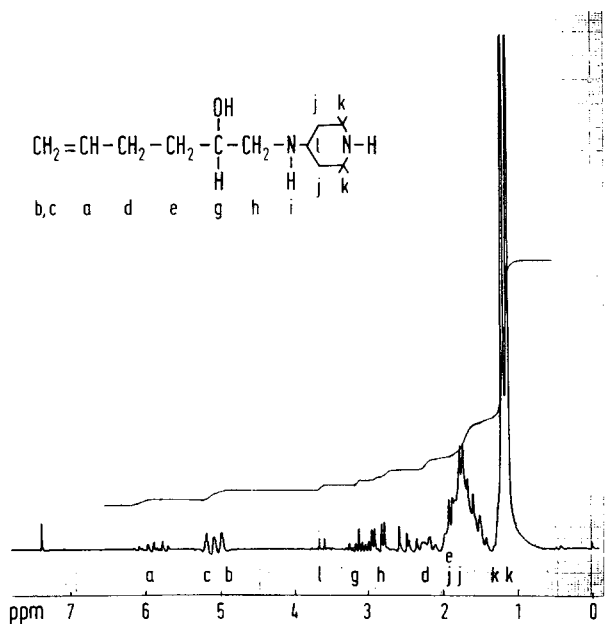


Figure 4 Proton-NMR of product from HEPO + ATMP.

**Table III C-H-N Content of Monomeric Products**

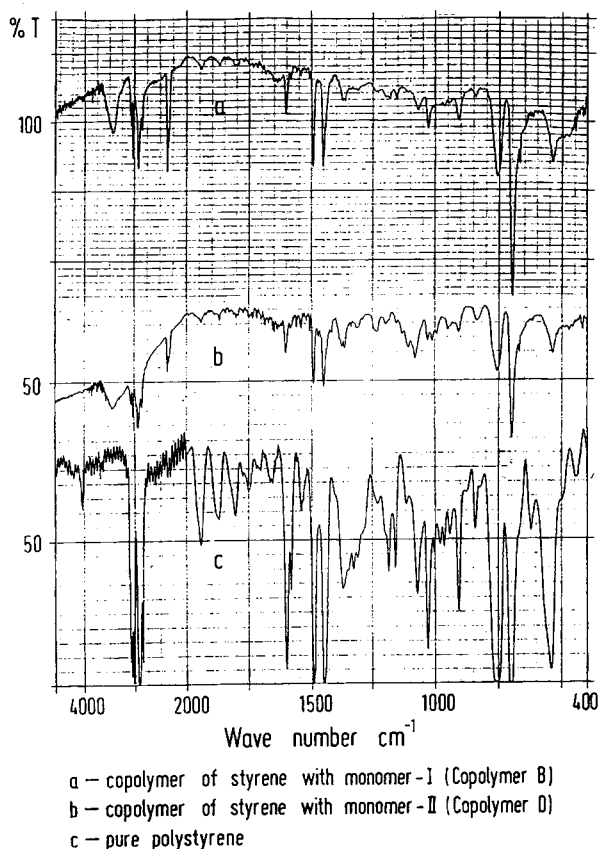
Product	Found (%)			Calcd (%)		
	C	H	N	C	H	N
Monomer I	66.13	12.93	10.50	66.67	11.11	10.37
Monomer II	69.06	12.90	12.10	70.87	11.81	11.02

## RESULTS AND DISCUSSION

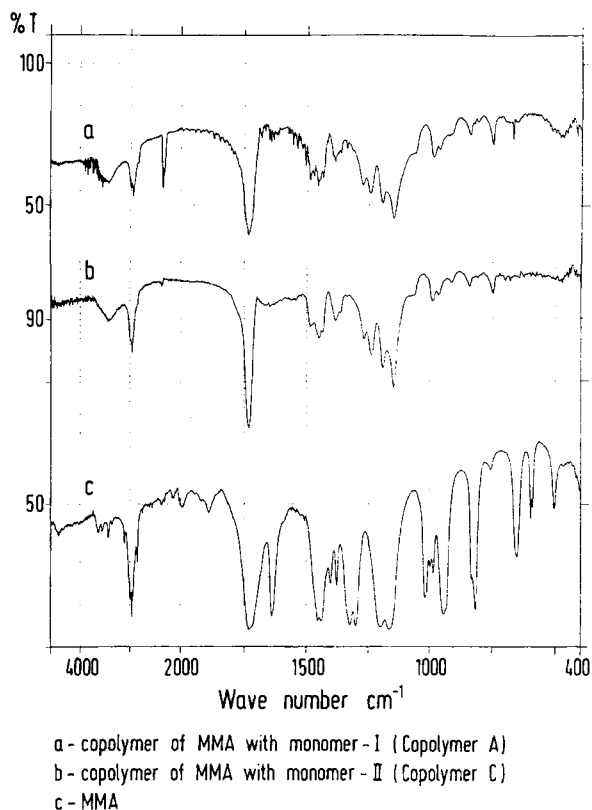
### Synthesis

It has been reported<sup>24</sup> that epoxide readily reacts with amine in a stoichiometric reaction. Our experimental results show that the reaction of epoxides (HEPO and AG) with ATMP was stoichiometric. The reaction of AG with ATMP was faster than HEPO with ATMP. The yield in the former reaction was, thus, higher than in the latter (90.10 vs. 25.60%). It has been observed that the reaction of AG with ATMP occurred even at room temperature, but not so for the HEPO-ATMP system. AG,

HEPO, and ATMP with boiling points of 154, 119, and 198°C, respectively, will evaporate on heating; therefore, use of a reflux condenser was necessary to avoid loss through evaporation. AG, HEPO, ATMP, and their reaction products are liquids that are soluble in most organic solvents and water; therefore, common purification methods such as liquid extraction and precipitation cannot be used. Monomers I and II were purified by removal of unreacted starting materials by reduced pressure distillation. Experimental results show that monomer I and monomer II are reluctant to homopolymerize by free radical initiation. This may be associated with the "degradative chain transfer of the allylic" (autoinhibition).<sup>25</sup> However, these monomers can be



**Figure 5** IR spectra of copolymers made from styrene with monomer I and monomer II.



**Figure 6** IR spectra of copolymers made from MMA with monomer I and monomer II.

**Table IV Characterization of Copolymers A, B, C, and D**

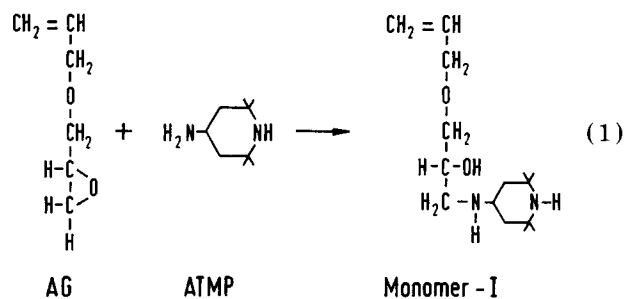
Copolymer	A			B			C			D		
Copolymerization	MMA + I			St + I			MMA + II			St + II		
NMR (ppm)	3.60, 3.40, 4.00,			7.07-7.25, 3.4,			3.60, 1.20, 1.24			6.8-7.0, 6.4-6.6		
Major peaks	1.13, 1.19			6.4-6.5, 4.0						1.14, 1.19		
				1.12, 1.18								
Element	C	H	N	C	H	N	C	H	N	C	H	N
Content (%)	59.87	9.13	2.74	86.86	9.37	3.05	60.52	9.30	3.80	88.38	8.57	1.74

copolymerized with vinyl monomers such as styrene and MMA by free radical initiation.

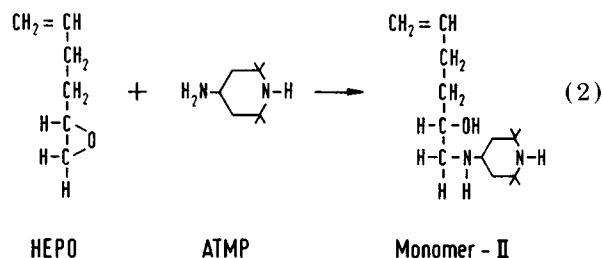
Experimental results also showed that new copolymers containing hindered amine can also be obtained by free radical copolymerization of vinyl monomers (St and MMA) with a mixture of ATMP and epoxy compounds with double bond.

#### Structure Characterization of Monomers I and II

IR spectra of the reaction products are shown in Figures 1 and 2. From Figure 1 it can be seen that after reacting at 80°C for 6 h the epoxy group (3040 and 840  $\text{cm}^{-1}$ ) in AG had disappeared,<sup>26</sup> the double bond (1650  $\text{cm}^{-1}$ ) in allyl remained in the product and new peaks at 3080, 3200, and 3300  $\text{cm}^{-1}$  were formed, indicating that the following reaction had taken place.



From Figure 2, it can be seen that after reacting at 80°C for 6 h, the epoxy group (3040 and 840  $\text{cm}^{-1}$ ) in HEPO had disappeared, and new peaks at 3080 and 3260  $\text{cm}^{-1}$  in the product appeared, which contained double bond (1640  $\text{cm}^{-1}$ ).<sup>26</sup> Therefore, the following reaction had occurred:

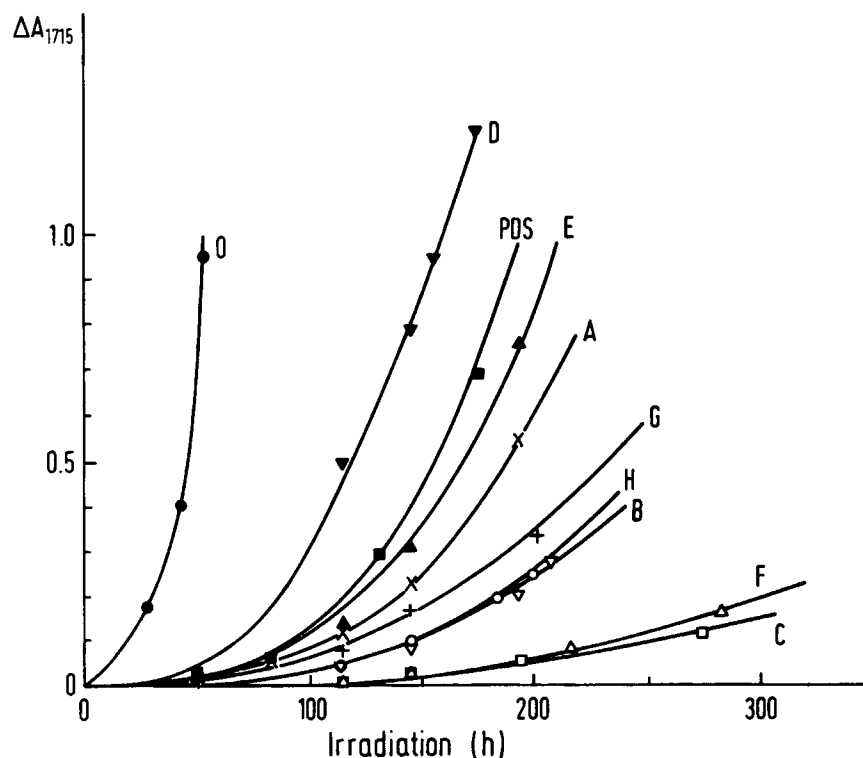


Proton-NMR spectra of the products are shown in Figures 3 and 4. From Figure 3 it can be seen that product (monomer I) contains allyl group (double bond: 5.89 and 5.15, 5.35,  $\alpha$ -methylene connecting ether group: 4.05 ppm)<sup>27,28</sup> and 4-amino,2,2,6,6-tetramethylpiperidine (2,2,6,6-tetramethyl: 1.12, 1.18; 3,5-two methylenes: 1.80, 1.90; and  $r$ -proton: 3.80 ppm), consistent with IR results.

From Figure 4 it can be seen that monomer II contains hexenyl (double bond—5.80, and 5.00, 5.20,  $\alpha$ -methylene—2.15 ppm) and 4-amino-2,2,6,6-tetramethyl piperidine (2,2,6,6-tetramethyl-1.12, 1.18,

**Table V Characterization of Copolymers E, F, G, and H**

Copolymer	E			F			G			H		
Copolymerization	St-HEPO-ATMP			MMA-HEPO-ATMP			St-AG-ATMP			MMA-AG-ATMP		
IR ( $\text{cm}^{-1}$ )	1600, 3400			1735, 3400			1600, 3400			1735, 3400, 1240		
	3080, 1240			1240			3080, 1240					
NMR (ppm)	7.0-7.25, 1.18			3.60, 1.19			7.0-7.24, 3.49			3.60, 3.49, 4.05		
Major peaks	6.4-6.6, 1.20			1.13			6.4-6.60, 4.05			1.15, 1.20		
							1.18-1.20					
Element	C	H	N	C	H	N	C	H	N	C	H	N
Content (%)	87.34	8.84	2.20	57.86	9.61	3.84	84.82	9.46	2.89	59.19	9.49	2.91

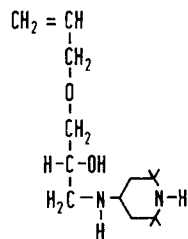


**Figure 7** Change in carbonyl absorption in PP film containing polymeric HALS (0.3%) during irradiation. (0) blank, (A) copolymer A, (B) copolymer B, (C) copolymer C, (D) copolymer D, (E) copolymer E, (F) copolymer F, (G) copolymer G, (H) copolymer H.

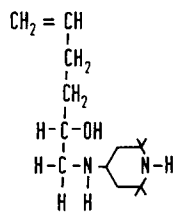
3,5-two methylene—1.74, 1.78, r-proton—3.50 ppm),<sup>21,22,25,26</sup> consistent with IR results.

The results from MS show that the molecular weight is 270 for monomer I and 254 for monomer II. The results of elemental analysis shown in Table III agree with that calculated from the structure.

Based on the results of IR, NMR, MS, and elemental analysis, one can conclude that the two monomers synthesized in this work conform to the following structure:



Monomer - I



Monomer - II

### Structure Characterization of Copolymers A, B, C, and D

The IR spectra of copolymers made from styrene with monomer I and monomer II are shown in Fig-

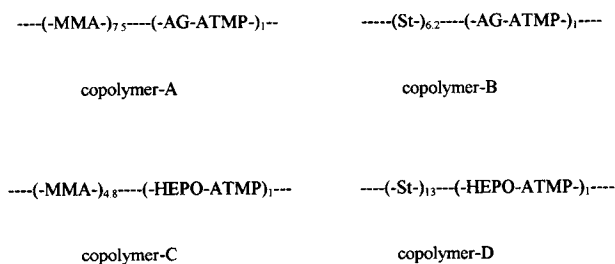
ure 5. From Figure 5 it can be seen that in these products, besides the polystyrene unit (1600, 3080, and 700  $\text{cm}^{-1}$ ), there are new peaks at 3400  $\text{cm}^{-1}$  (—OH and —NH) and inbetween 1230  $\text{cm}^{-1}$  and 1240  $\text{cm}^{-1}$  (which is weak but still discernible) derived from monomer I and monomer II. The double bonds in monomer I, monomer II, and styrene (1650, 1640, and 1630  $\text{cm}^{-1}$ ), respectively, had disappeared after copolymerization. Therefore, the above results indicate that these two new monomers can be copolymerized with styrene by free radical initiation.

The IR spectra of copolymer made from MMA with monomer I and monomer II are shown in Figure 6. From Figure 6 it can be seen that in these copolymers, besides the polymethyl methacrylate unit (1735  $\text{cm}^{-1}$ ), there are new peaks at 3400  $\text{cm}^{-1}$  (—OH and —NH) and 1240  $\text{cm}^{-1}$  derived from monomer I and monomer II, the double bond in monomer I, monomer II, and MMA (1650, 1640, and 1640  $\text{cm}^{-1}$ ), respectively, had disappeared after copolymerization. Therefore, the above results indicate that these two new monomers can be copolymerized with MMA by free radical initiation.

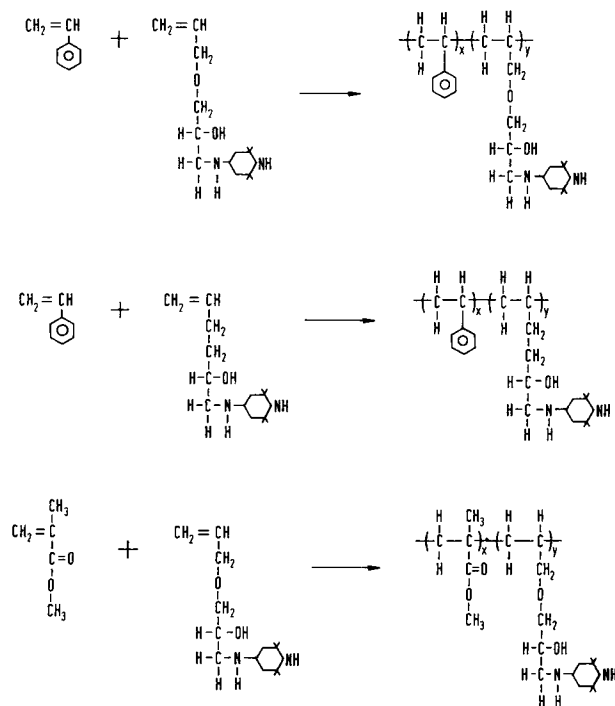
The results of NMR spectra and elemental analysis of copolymers A, B, C, and D are shown in Table IV. From Table IV it can be seen that the

structure unit of monomer **I** (3.40, 4.00, 1.13, and 1.19 ppm), monomer **II** (1.14 and 1.23 ppm), styrene (7.07–7.25 and 6.40–6.70 ppm), and MMA (3.60 ppm), respectively, existed in the copolymer. These NMR results are consistent with IR results.

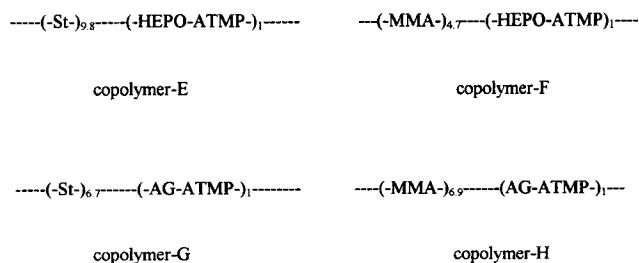
Based on the results of elemental analysis, IR, and NMR, the four new copolymers (**A**, **B**, **C**, and **D**) formed from monomer **I**, monomer **II** and vinyl monomers (St and MMA) possess the following structure:



From Table V it can be seen that after mixture copolymerization, the double bond in the vinyl monomer St, MMA, and AG, HEPO (1630, 1640, 1650, and 1640  $\text{cm}^{-1}$ ), respectively, had disappeared, and the structure unit of monomer **I** (AG-ATMP) and monomer **II** (HEPO-ATMP), styrene, and MMA, respectively, existed in these copolymers produced by the mixture copolymerization. Therefore, the following reactions had occurred: reactions (1) and (2) for formation of the new monomers containing HA, and the copolymerization of above new monomers with vinyl monomer:



Based on results from IR, NMR, and elemental analyses, the structures of new copolymers **E**, **F**, **G**, and **H** are as follows:



## PRODUCT PROPERTIES

Monomer **I** and monomer **II** are yellowish paste substances. They can be dissolved in water and most organic solvents such as pentane, hexane, benzene, chloroform, acetone, ethanol, and methanol.

Copolymers **A** and **F** are white solids and copolymers **B**, **C**, **D**, **E**, **G**, and **H** are yellowish solids. They can be dissolved in benzene, toluene, acetone, chloroform, but cannot be dissolved in pentane, hexane, alcohol, and water. The temperature ranges in which these new copolymers start to melt are: 105–115°C [**A**], 78–85°C [**B**], 108–118°C [**C**], 78–90°C [**D**], 85–95°C [**E**], 110–118°C [**F**], 75–85°C [**G**], and 110–120°C [**H**].

## PHOTOPROTECTING EFFECTIVENESS

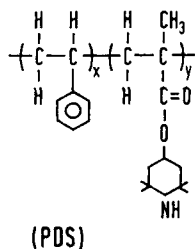
The photoprotecting effectiveness of these new copolymer HALS for polypropylene is shown in Figure 7. Photooxidation induction periods of these new copolymer HALS with different effective nitrogen content (nitrogen content in the piperidine ring) are shown in Table VI.

From Figure 7 and Table VI it can be seen that with increasing content of effective nitrogen (nitrogen in the piperidine ring) in the copolymer, their photoprotecting effectiveness for PP film was increased. Their photoprotecting effectiveness is higher than that of a commercial polymeric HALS PDS produced in China.<sup>7,13,16</sup> The photoprotecting effectiveness of PDS had been reported to lie in-between polymeric HALS Tinuvin-622 and Chimmassor-944.<sup>29</sup> PDS has been successfully applied to polypropylene fiber against photooxidation.<sup>16</sup>

**Table VI Photooxidation Induction Periods of PP Film Containing the New Copolymer HALS**

Copolymer	Blank	A	B	C	D	E	F	G	H	PDS
N% <sup>a</sup>	—	1.37	1.53	1.90	0.87	1.10	1.94	1.45	1.46	2.20
IP (h) <sup>a</sup>	20	108	145	260	68	94	240	120	145	92

<sup>a</sup> N in piperidine ring; IP, induction period.



## CONCLUSION

Eight new copolymers containing HA were prepared by copolymerization of vinyl monomers St and MMA, with new functional monomers produced from reacting ATMP with epoxy compounds containing double bond and mixture copolymerization of vinyl monomers St and MMA with a mixture of ATMP and the epoxy compounds. These new copolymers are potential photostabilizers with high photoprotecting effectiveness.

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