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Synthesis and characterization of two new monomers containing hindered amine

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Two new monomers, 2,2,6,6-tetramethyl-4-piperidinyl allyl carbamate and 2,2,6,6-tetramethyl-4-piperidinyl m-isopropenyl-α,α'-dimethyl benzyl carbamate, were synthesized by direct addition of 2,2,6,6-tetramethyl-4-piperidinol (TMP) to allyl isocyanate (AI) or to m-isopropenyl-α,α'-dimethylbenzyl isocyanate (m-TMI) in the presence of dibutyltin dilaurate catalyst at 80°C. The structures of these two new monomers were characterized by FT-IR. ^{1}H-NMR, XPS, MS and elemental analysis. The properties of these monomers are also described.

INTRODUCTION

It is well known that hindered-amine light stabilizers (HALS) are the most effective light stabilizers, on which extensive research and reviews have been published.[1,2] However, HALS with low MW are relatively volatile and are easily extracted by liquids.[3–12] The effectiveness of low MW HALS therefore is limited.

A new trend for HALS development is to prepare HALS with higher MW.[1–5] Copolymerization or homopolymerization of functional monomers containing hindered amines are the usual methods for preparation of higher MW HALS. Therefore the preparation of a monomer containing hindered amine is a very important step for the preparation of HALS with higher MW. Several polymeric HALS are described in the literature;[1–7] many of them are based on 2,2,6,6-tetramethyl-4-piperidinyl methacrylate.[12–17] Recently, a new monomer has been made by reacting m-isopropenyl-α,α'-dimethyl-benzyl isocyanate (m-TMI) with 1,2,2,6,6-pentamethyl-4-piperidinol, and its copolymers with styrene and methyl methacrylate have also been reported.[18,19] In this paper, two new monomers containing HA are reported.

EXPERIMENTAL

Materials

Allyl isocyanate (AI) was supplied by Aldrich Chemical Company Inc. m-Isopropenyl-α,α'-dimethyl-benzyl isocyanate (m-TMI), supplied by American Cyanamid Company, was distilled before use. 2,2,6,6-Tetramethyl-4-piperidinol (TMP) and dibutyltin dilaurate (DBTDL) were supplied by Fluka, AG. DBTDL was in the form of a solution of 80% in benzene.

Syntheses

2,2,6,6-Tetramethyl-4-piperidinyl allyl carbamate
Into a three-neck flask equipped with a condenser, a nitrogen inlet, an addition funnel and magnetic stirrer was placed 5·6755 g

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(0·03615 mol) of TMP and 20 ml of dry benzene with stirring under nitrogen. The solution in the flask was heated in an oil bath to 70°C, and 3·00 g (0·03615 mol) of AI was added dropwise, then 0·1 ml of 80% DBTDL in benzene was added under stirring. After about 20 min, the oil-bath temperature was raised to and maintained at 80°C for 6 h. The reaction product was a solution at 80°C. A white crystalline solid was formed when this hot solution was cooled to room temperature. After filtering and washing with benzene (2 × 20 ml) and pentane (5 × 50 ml), a crude product was separated. A white needle-like crystal solid with 91% yield was obtained by recrystallization of the crude product from benzene after drying.

2,2,6,6-tetramethyl-4-piperidinyl m*-isopropenyl-α,α-dimethyl-benzyl carbamate*

Into a three-neck flask equipped with a condenser, a nitrogen inlet, an addition funnel and a magnetic stirrer was added 1·9523 g (0·01244 mol) of TMP and 20 ml of dry benzene with stirring under nitrogen. The solution was heated with an oil bath to 70°C, and then 2·5000 g (0·01244 mol) of *m*-TMI was added dropwise under stirring. Then, 0·1 ml of 80% DBTDL in benzene was then added dropwise under stirring. After about 20 min, the oil-bath temperature was raised to and maintained at 80°C for 6 h. The reaction product was a solution at 80°C. After cooling to room temperature, pentane was added and a white precipitate was formed. After filtration, washing with pentane (5 × 50 ml) and drying, a white powder was obtained with 80% yield.

Characterization of products

IR Spectra were recorded by a Shimadzu FT-IR 8101 Fourier transform Infra-red Spectrophotometer. ^{1}H-NMR spectra were obtained by a Jeol FX-900 FTNMR, with $DCCl_3$ as solvent and TMS as an internal standard. MS spectra were recorded using a MICROMASS 7035E. C, H, N analytical values were obtained using a Perkin-Elmer 2400 CHN Elemental Analyzer. X-ray photoelectron spectroscopy (XPS) was carried out on a VG ESCALAB MKII Spectrometer, using Mg Kα X-ray source, (1253·6 eV, 120 W) at a constant analyzer pass energy of 20 eV.

RESULTS AND DISCUSSION

Synthesis

It has been reported in the literature[20–23] that isocyanates can easily react with simple primary alcohols in stoichiometric quantities. Our experimental results show that the reaction of isocyanate with 2,2,6,6-tetramethyl-4-piperidinol is stoichiometric. It is a slow reaction without catalyst at 80°C but it is a faster, exothermic reaction in the presence of DBTDL catalyst. The use of a reflux condenser was necessary to keep it below the reaction temperature of 80°C. After addition of DBTDL, it was necessary to raise the temperature to, and keep it at 80°C for 6 h for higher yield and less side reaction. DBTDL is a wax-like substance at room temperature, it is therefore more convenient to add DBTDL catalyst as a solution of 80% DBTDL in benzene.

Results from IR, ^{1}H-NMR and elemental analysis show that pure product from reacting AI and TMP can be obtained by recrystallization from a benzene solution and pure product from reacting *m*-TMI with TMP can be obtained by precipitation from a benzene solution with pentane.

Structural characterization of products

The IR spectra of reaction products are shown in Figs 1 and 2. From Fig. 1, it can be seen that after

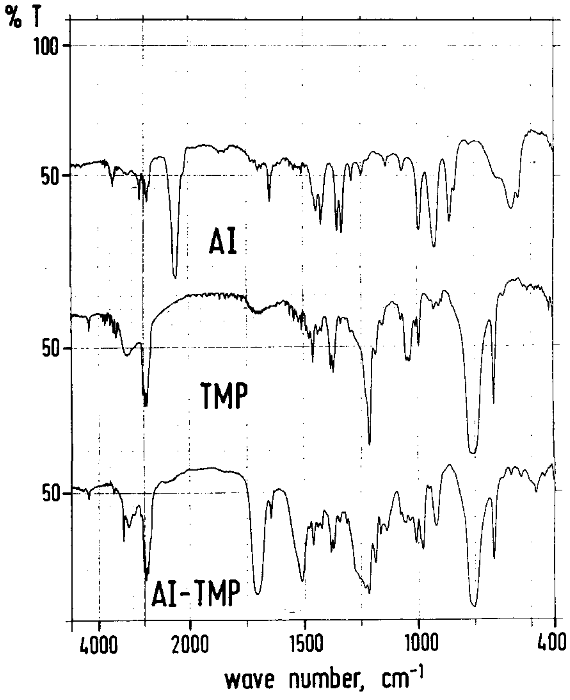


Fig. 1. IR spectrum of reaction product from AI + TMP.

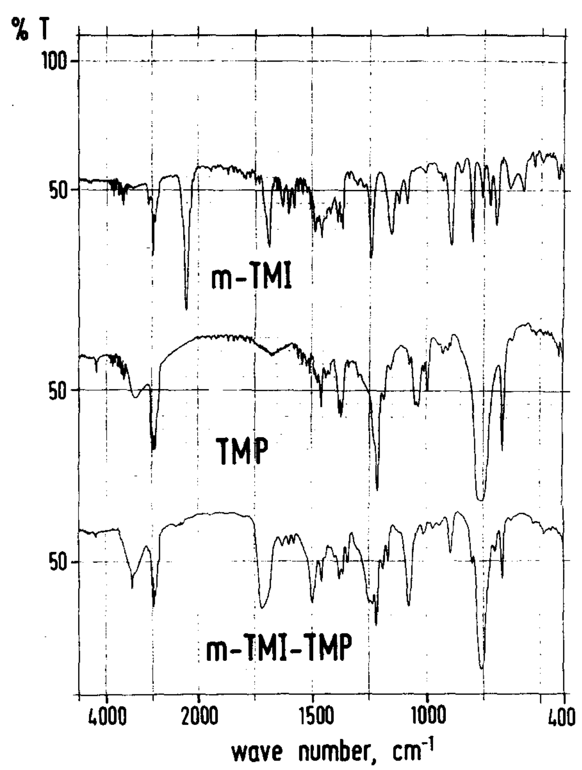
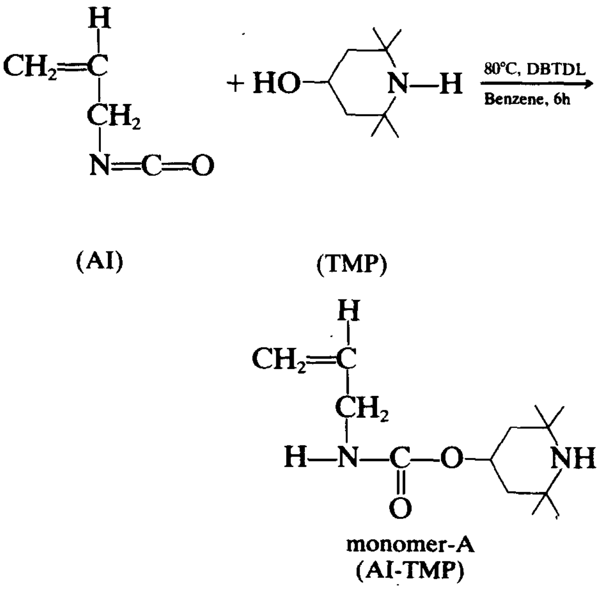
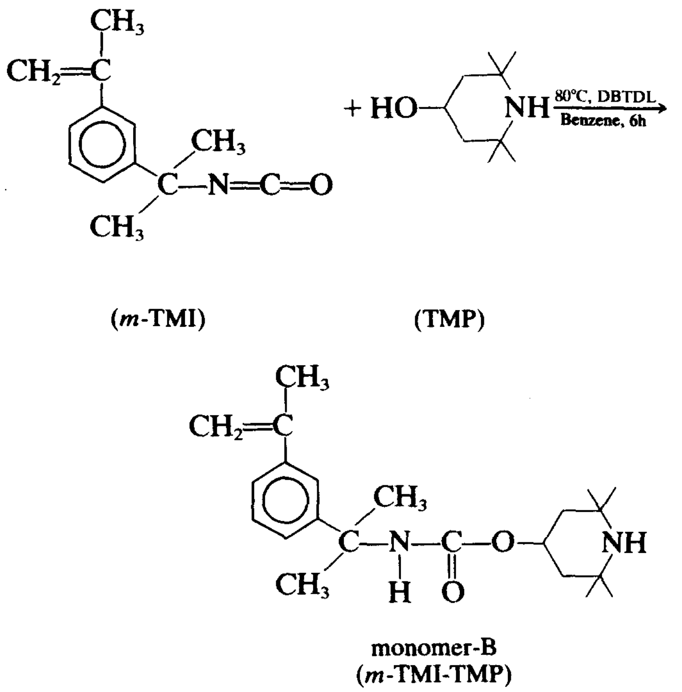


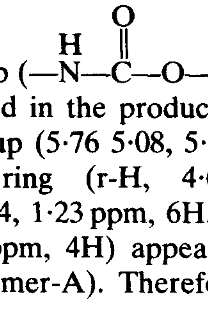
Fig. 2. IR spectrum of reaction product from *m*-TMI + TMP.

reacting for 6 h at 80°C the isocyanate group in AI (2260 cm^{-1}) had disappeared; the double bond (1650 cm^{-1}) in the allyl group remained in the product and a new carbamate group (1710 cm^{-1}, 3400 cm^{-1}) was formed in the product. These IR results indicate that the following reaction had taken place:



From Fig. 2, it can be seen that the isocyanate group in *m*-TMI (2260 cm^{-1}) had disappeared after the reaction, and a new carbamate group (1720 cm^{-1}, 3400 cm^{-1}) was formed in the product (monomer-B) which contains a benzene ring (3040 cm^{-1}). Therefore, one can conclude that the following reaction had occurred:



The ^{1}H-NMR spectra of the products are shown in Figs 3 and 4. From Fig. 3 it can be seen that a carbamate group  $(\text{—}\overset{\text{H}}{\text{N}}\text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—})$ (5·18 ppm, 1H) had been formed in the product, a double bond in the allyl group (5·76 5·08, 5·28 ppm, 3H) and a piperidine ring (r-H, 4·68 ppm, 2,2,6,6-tetramethyl, 1·14, 1·23 ppm, 6H, 3.5-two methylenes, 1·87–2·0 ppm, 4H) appear in the product AI-TMP (monomer-A). Therefore the structure

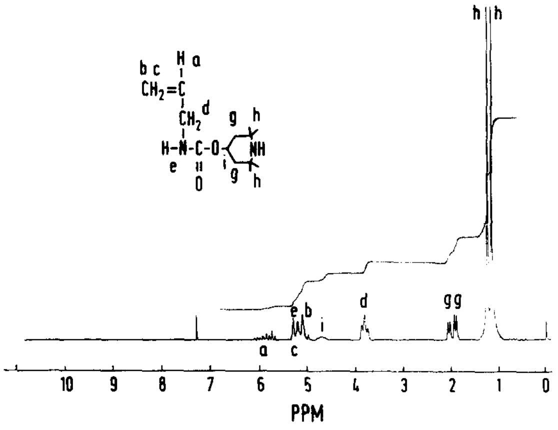


Fig. 3. ^{1}H-NMR spectrum of reaction product from AI + TMP.

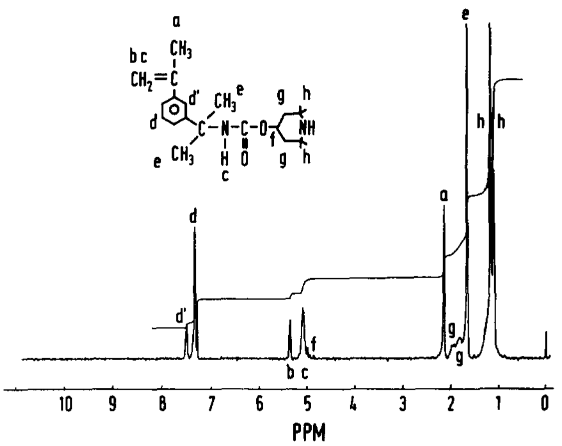


Fig. 4. ^{1}H-NMR spectrum of reaction product from *m*-TMI + TMP.

of monomer-A is the structure of an addition product of AI and TMP.

From Fig. 4 it can be seen that product B (monomer-B) contains carbamate group ($\overset{H}{—N}—\overset{\overset{O}{\|}}{C}—O—$, 5·08 ppm, 1H), benzene ring (7·32, 7·48 ppm), isopropenyl (double bond 5·08, 5·34 ppm, $—CH_3—$2·15), α,α-dimethyl (1·67 ppm, 6H) and piperidine ring (r-H, 4·7–4·9 ppm, 2,2,6,6-tetramethyl, 1·11, 1·18 ppm, 3·5-two methylenes 1·8–2·0 ppm). Therefore, the structure of monomer-B is the structure of an addition product of *m*-TMI and TMP. These NMR results support the conclusions drawn from IR spectral analysis.

Results of XPS analysis on the products are shown in Figs 5 and 6. Monomer-A (Fig. 5) contains the carbamate group[24] ($\underset{H}{—N}—\underset{\underset{O}{\|}}{C}—O—$, C_{1s} 288·6 O_{1s} 531·6, 532·8 N_{1s} 399·45 eV), monomer-B (Fig. 6) also contains this carbamate group[24] ($\overset{H}{—N}—\overset{\overset{O}{\|}}{C}—O—$, C_{1s} 289·2 O_{1s} 531·75, 532·65 N_{1s} 399·35 eV). Note that this carbamate group in the products does not exist in the reactant chemicals. Therefore, results from XPS analysis on the reaction products support the conclusions drawn from IR and NMR spectra. A more detailed study of these products by XPS will be reported later.

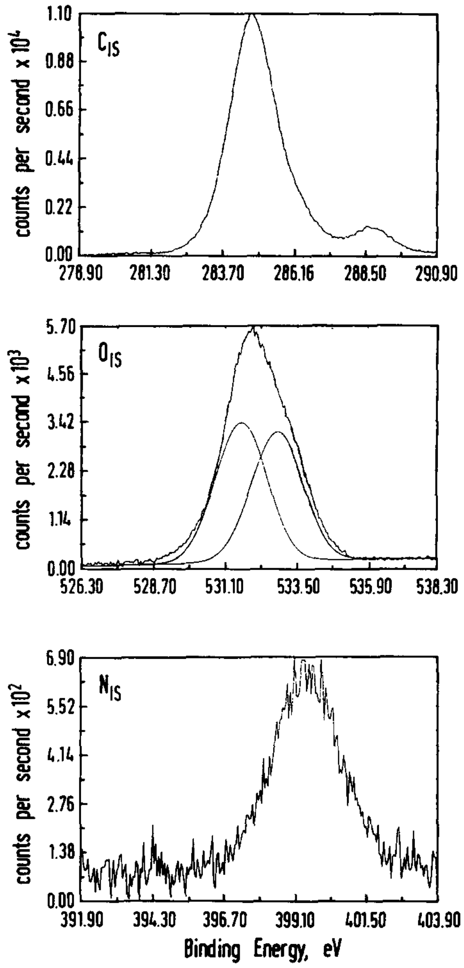


Fig. 5. XPS of reaction product from AI + TMP.

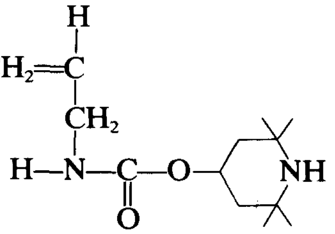
Results from MS show that molecular weight of monomer-A is 240, and that for monomer-B is 358. They are the same as those calculated from the chemical structures of monomer-A and monomer-B. The following main segments of the products can be found in the MS spectra:

Monomer-A (*m*/*e*)
240 (MW)
225 (10%), (monomer-A, $—CH_3$)
140 (12%) (piperidinol, —OH)
124 (100%) (piperidinol, $—H_2O$, $—CH_3$)
58 (77%)(C_3H_7 NH^+)
41 (37%) ($C_3H_5^+$ from allyl)

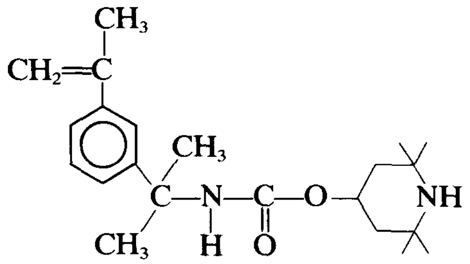
Monomer-B (*m*/*e*)
358 (MW)
343 (3%) (monomer-B, $—CH_3$)
343 (3%) (monomer-B, $—CH_3$)
186 (52%) (isocyanate, $—CH_3$)
142 (30%) (piperidinol, $—CH_3$)
124 (100%) (piperidinol, $—H_2O$, $—CH_3$)
58 (77%) (C_3H_7 NH^+)
41 (25%) ($C_3H_5^+$, from isopropenyl)

Results of elemental analysis are shown in Table 1, which agree well with these calculated from the chemical structures of monomer-A and monomer-B.

Based on the results of IR, NMR, XPS, MS and elemental analysis, it can be concluded that the two new monomers synthesized by us must be of the chemical structure of monomer-A and monomer-B shown below:



monomer-A



monomer-B

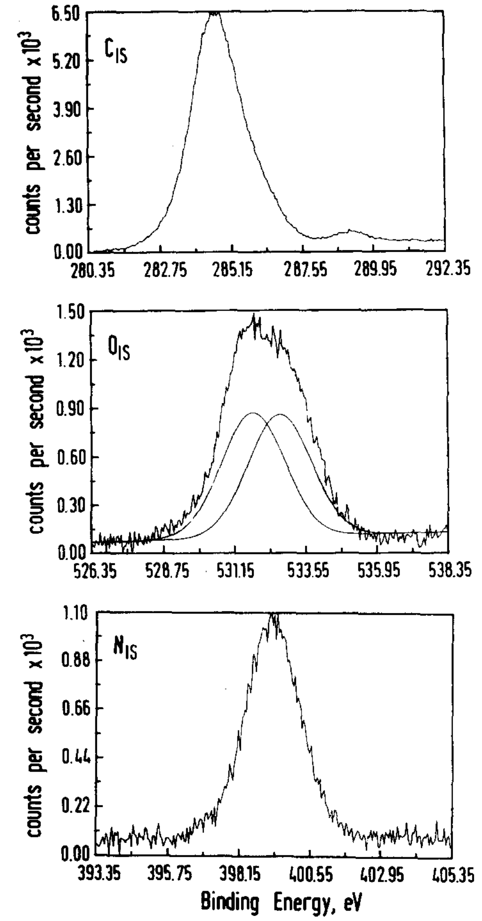


Fig. 6. XPS of reaction product from *m*-TMI + TMP.

Properties of products

Monomer-A is a white needle-like crystalline solid with a m.p. of 93–94°C. It can be dissolved in chloroform, acetone, methanol and slowly in water but not in pentane or hexane. Monomer-B is a white powder with a m.p. of 118·5°C. It can be dissolved in chloroform, acetone, methanol but not in pentane, hexane or water. Their UV spectra show that both monomers do not absorb UV light beyond 300 nm. Preliminary experiments showed that these monomers can be copolymerized with another vinyl monomer like styrene by free radical initiation. Therefore they can be used as monomers for preparing polymeric HALS. Study of their polymerization behaviours and evaluation of these monomers and their derivatives as effective light stabilizers are in progress.

CONCLUSION

Two new functional monomers containing hindered amines were prepared by reacting isocyanate and 2,2,6,6-tetramethyl-4-piperidinol. The chemical structures of these monomers are

Table 1. Elemental content of the reaction products

Product	Found (%)			Calc. (%)		
	C	H	N	C	H	N
Monomer-A	64·78	11·32	11·57	65·00	10·00	11·67
Monomer-B	72·86	9·93	7·77	73·74	9·50	7·82

confirmed by IR, ^{1}H-NMR, XPS, MS and elemental analysis. These new monomers are potential functional blocks for the preparation of new polymeric HALS.

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