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### Synthesis and Characterization of new Monomers and Polymers Containing Hindered Piperidine Groups

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## SYNTHESIS AND CHARACTERIZATION OF NEW MONOMERS AND POLYMERS CONTAINING HINDERED PIPERIDINE GROUPS

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### ABSTRACT

Two new methacryloyl ureas, 1-(2-methylacryloyl)-3-(2,2,6,6-tetra-methylpiperidin-4-yl)-urea and 1-butyl-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (monomer I and monomer II), were prepared by the addition reaction of 2-methylacryloyl iso-cyanate with 2,2,6,6-tetramethylpiperidin-4-yl-amine or butyl-(2,2,6,6-tetramethylpiperidin-4-yl)-amine in a molar ratio of 1:1 at low or room temperature. In a similar way, the syntheses of two new methacryloyl carbamates, 1-(2,2,6,6-tetra-methylpiperidin-4-yl)-3-(2-methylacryloyl)-carbamate and 1-(1,2,2,6,6-pentamethylpiperidin-4-yl)-3-(2-methylacryloyl)-carbamate (monomer III and monomer IV), were completed by the reaction of 2,2,6,6-tetramethylpiperidin-4-ol or 1,2,2,6,6-pentamethylpiperidin-4-ol with 2-methylacryloyl isocyanate in the presence of dibutyltin dilaurate as catalyst at 60°C. The four new monomers were homopolymerized, and copolymerized with styrene by AIBN as initiator at 70°C. The structures of the new monomers and their polymers were characterized by FT-IR and NMR spectroscopy and by GPC.

### INTRODUCTION

2,2,6,6-Tetramethyl and 1,2,2,6,6-pentamethyl piperidine derivatives (HALS) are very effective light and thermal stabilizers for polymers and have been widely studied [1-9]. For many polymer applications, however, the use of stabil-

izers with low volatility and low extractability is desired. This can be achieved by increasing the molecular weight of the stabilizer, or by the introduction of the stabilizing group into the polymer structure [1-3, 7-11]. Therefore, the synthesis of new polymeric HALS is of high interest. The present paper describes the syntheses of new functional monomers containing hindered piperidine groups, their homopolymers and copolymers with styrene.

## EXPERIMENTAL

### Reagents and Measurements

2-methylacryloyl isocyanate (MAI) was supplied by Merck Chemical Company and distilled before use. 2,2,6,6-Tetramethylpiperidin-4-yl-amine, butyl-(2,2,6,6-tetramethylpiperidin-4-yl)-amine, 2,2,6,6-tetramethylpiperidin-4-ol and 1,2,2,6,6-pentamethylpiperidin-4-ol were obtained from Huels Chemical Company and dibutyltin dilaurate (DBTDL) from Fluka Chemical Company. The solvents were purified according to standard methods.

IR spectra were recorded with a Nicolet 205 FT-IR spectrometer. NMR spectra were obtained with a Bruker AC-200P NMR spectrometer,  $^1\text{H}$  at 300 MHz,  $^{13}\text{C}$  at 75 MHz,  $\text{CDCl}_3$  as solvent and TMS as internal standard. Elemental analysis was carried out on a Carlo Erba CHNS-O EA 1108 Elemental Analyzer. GPC was carried out on a Hewlett Packard HP 1090 GPC system, Two connected  $5\ \mu\text{m}$  GPC/SEC columns ( $300 \times 7\ \mu\text{m}$ ) were used with tetrahydrofuran as solvent. Molecular weight data are reported relative to a polystyrene calibration.

### Synthesis of Monomers

#### *General Procedure*

4-Amino- and 4-hydroxypiperidine derivatives and dry toluene were charged under argon into a three-neck flask equipped with stirrer, condenser and thermometer. MAI in toluene was added dropwise to the above solution at  $0\text{-}5^\circ\text{C}$  and the mixture was stirred for 1-6 hours at room temperature. The reaction product was concentrated on a rotary evaporator. Hexane was added to the residue to precipitate the product. The product was filtered off, washed several times with hexane and then purified by recrystallization from acetonitrile.

*1-(2-Methylacryloyl)-3-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (I):* **I** was prepared from 2,2,6,6-tetramethylpiperidin-4-yl-amine (4.78 g, 30.60 mmol) and MAI (3.40 g, 30.60 mmol) according to the general procedure. Yield: 7.15 g, 87.41%, white crystalline solid, mp.  $160\text{-}161^\circ\text{C}$ .

$C_{14}H_{25}N_3O_2$ (267.37)	Calcd.	C 62.89	H 9.43	N 15.72
	Found	C 63.01	H 9.86	N 15.86

*1-Butyl-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (II):* **II** was obtained from butyl-(2,2,6,6-tetramethylpiperidin-4-yl)-amine (10.62 g, 0.05 mol) and MAI (5.56 g, 0.05 mol) according to the general procedure. Yield: 15.2 g, 94.01%, white powder, mp. 119-120°C.

$C_{18}H_{33}N_3O_2$ (323.47)	Calcd.	C 66.83	H 10.28	N 12.99
	Found	C 67.09	H 10.51	N 13.01

*1-(2,2,6,6-Tetramethylpiperidin-4-yl)-3-(2-methylacryloyl)-carbamate (III):* **III** was prepared according to the general procedure from 2,2,6,6-tetramethylpiperidin-4-ol (0.31 g, 2.00 mmol) and MAI (0.22 g, 2.00 mmol) in the presence of DBTDL (4-5 drops) at 60°C. Yield: 0.44 g, 82.17 %, white crystalline solid, mp. 123.5-125 °C.

$C_{14}H_{24}N_2O_3$ (268.36)	Calcd.	C 62.65	H 9.01	N 10.44
	Found	C 62.92	H 9.32	N 10.55

*1-(1,2,2,6,6-Pentamethyl-piperidin-4-yl)-3-(2-methyl-acryloyl)-carbamate (IV):* **IV** was synthesized according to the general procedure from 1,2,2,6,6-pentamethyl-piperidin-4-ol (0.51 g, 3.00 mmol) and MAI ( 0.33 g, 3.00 mmol) in the presence of DBTDL (5-6 drops) at 60°C. Yield: 0.65g, 76.74 %), white crystalline solid, mp.128-129.5°C.

$C_{15}H_{26}N_2O_3$ (282.38)	Calcd.	C 63.80	H 9.28	N 9.92
	Found	C 63.97	H 9.40	N 9.83

## Synthesis of Polymers

### General Procedure

In a polymerization bottle, the monomers were dissolved in drydioxane (2-3 ml) degassed and sealed, AIBN in dioxane was injected. The solution was stirred for 24 hours at 70°C under argon. The reaction mixture was poured into hexane, the precipitate was washed several times with hexane and dried *in vacuo* to a constant weight.

Homopolymerization was carried out according to the general procedure in the presence of AIBN (3.5 mol% of monomer). After 24 hours, 2 mol% AIBN was added and the solution was polymerized for 24 hours under the same conditions.

Copolymerization was carried out according to the general procedure. AIBN (2.5 mol% of monomers) and a monomer **I-VI**/styrene molar ratio of 1:2 were used.

### Homopolymers

HP-1: Yield: 72.85%, white powder, mp. 218-223°C.

$(C_{14}H_{25}N_3O_2)_n$ (267.37) <sub>n</sub>	Calcd.	C 62.89	H 9.43	N 15.72
	Found	C 61.37	H 9.48	N 14.56

HP-2: Yield: 42.16%, white powder, mp. 165-175°C.

$(C_{18}H_{33}N_3O_2)_n$ (323.47) <sub>n</sub>	Calcd.	C 66.83	H 10.28	N 12.99
	Found	C 64.26	H 9.33	N 11.34

HP-3: Yield: 56.34%, white powder, mp. 184-195°C.

$(C_{14}H_{24}N_2O_3)_n$ (268.36) <sub>n</sub>	Calcd.	C 62.65	H 9.01	N 10.44
	Found	C 60.63	H 8.46	N 10.57

HP-4: Yield: 76.08%, white powder, mp. 213-220°C.

$(C_{15}H_{26}N_2O_3)_n$ (282.38) <sub>n</sub>	Calcd.	C 63.80	H 9.28	N 9.92
	Found	C 61.31	H 8.92	N 10.10

### Copolymers

CP-1: Yield: 84.32%, white powder, mp. 191-197°C

$(C_{14}H_{25}N_3O_2)_x(C_8H_8)_y$  Found: C 73.53, H 8.68, N 9.09.  $x = 34.81$ ,  $y = 65.19$ .

CP-2: Yield: 46.63%, white powder, mp. 132-138°C

$(C_{18}H_{33}N_3O_2)_x(C_8H_8)_y$  Found: C 77.66, H 8.77, N 6.68.  $x = 25.41$ ,  $y = 74.59$ .

Cp-3: Yield: 64.98%, white powder, mp. 131-138°C

$(C_{14}H_{24}N_2O_3)_x(C_8H_8)_y$  Found: C 76.50, H 8.30, N 5.40.  $x = 29.36$ ,  $y = 70.64$ .

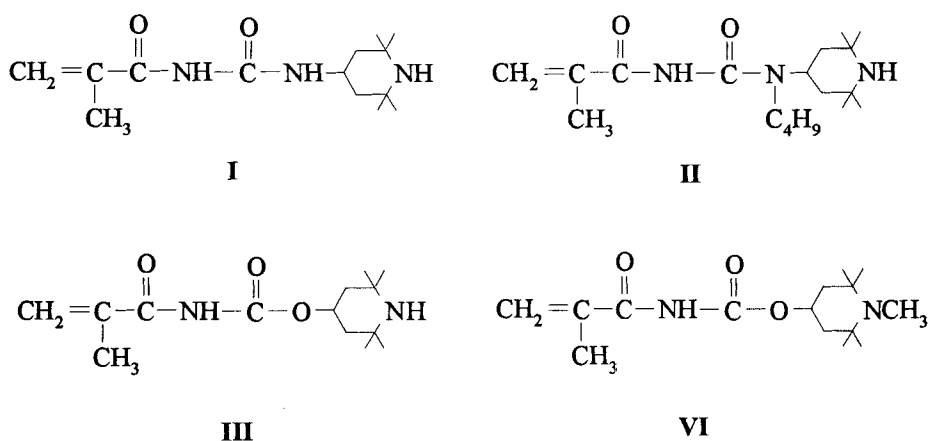
CP-4: Yield: 68.18%, white powder, mp. 142-148°C

$(C_{15}H_{26}N_2O_3)_n(C_8H_8)_y$  Found: C 76.09, H 8.49, N 5.58.  $x = 32.15$ ,  $y = 67.85$ .

## RESULTS AND DISCUSSION

### Synthesis of Methacryloyl Ureas and Methacryloyl Carbamates with Hindered Piperidine Groups

2-Methylacryloyl isocyanate (MAI) is a highly reactive multifunctional monomer with a polymerizable double bond and an isocyanate group in the same



SCHEME 1

TABLE 1. IR Absorption of Methacryloyl Ureas and Methacryloyl Carbamates (cm<sup>-1</sup>)

Monomer	NCO	C=O	C=O	C=C	N-H	C-O
		(acryloyl)	(carbamate)			
MAI	2251.0 (ss)	1698.0 (s)	—	1634.8 (m)	—	—
I	—	1700.8 (s)	1663.3 (m)	1627.1 (m)	1542.4 (ss)	—
II	—	1693.7 (s)	1651.6 (ss)	1595.3 (m)	1560.2 (s)	—
III	—	1689.0 (m)	1770.1 (ss)	1637.5 (m)	1502.6 (ss)	1156.7 (ss)
VI	—	1687.4 (m)	1770.2 (ss)	1637.5 (m)	1528.0 (ss)	1220.0 (ss)

molecule [12-14]. It can react with amines or alcohols, leaving the vinyl bond for radical polymerization. Our experimental results show that 2-methylacryloyl isocyanate reacted fast and exothermally with 2,2,6,6-tetramethyl piperidin-4-yl-amine or butyl-(2,2,6,6-tetramethylpiperidin-4-yl)-amine at low or room temperature. However, the reactions of MAI with 2,2,6,6-tetramethylpiperidin-4-ol or 1,2,2,6,6-pentamethylpiperidin-4-ol are slow without catalyst at 60°C, and the fast and exo-

TABLE 2. <sup>1</sup>H- and <sup>13</sup>C-NMR Data of Methacryloyl Ureas and Methacryloyl Carbamates (PPM)

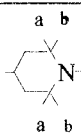
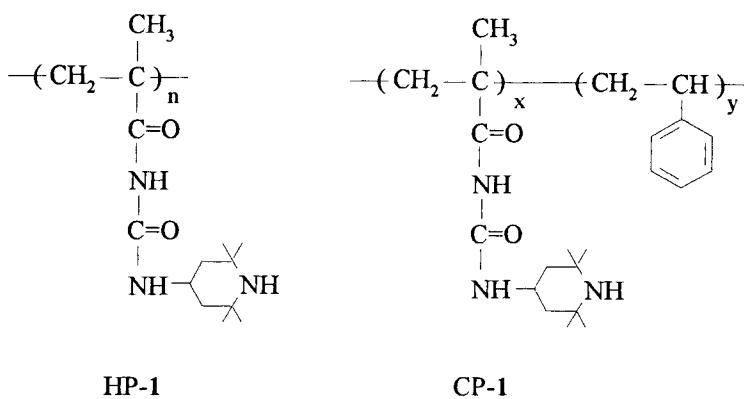
	I	II	III	VI
$\underline{\text{CH}}_2=\text{C}$	5.559, 5.564 (d)	5.480, 5.482 (d)	5.541, 5.546 (d)	5.536, 5.542 (d)
	5.941, 5.944 (d)	5.750 (s)	5.723, 5.725 (d)	5.722 (s)
$\underline{\text{C}}\text{H}_2=\text{C}$	122.5	121.42	121.56	121.50
$\text{CH}_2=\underline{\text{C}}$	138.8	139.60	139.95	139.99
$\text{CH}_3$	1.98 (s), 18.20	1.96 (s), 18.36	1.99 (s), 18.38	1.99 (s), 18.38
N-H	8.67 (s), 8.38-	7.80 (br., s)	7.69 (br., s)	7.65 (s)
	8.40 (d)			
				
2 Me <sub>a</sub> , 2 Me <sub>b</sub>	1.12 (s), 1.24 (s)	1.13 (s), 1.18 (s)	1.16 (s), 1.23 (s)	1.07 (s), 1.16 (s)
	28.49, 34.92	28.23, 34.89	28.85, 34.75	28.01, 33.22
2CH <sub>2</sub>	0.97-1.05 (t)	0.89-0.94 (t)	1.16-1.23 (t)	1.47-1.54 (t)
	1.92-1.97 (q)	1.69-1.74 (q)	1.98-2.03 (q)	1.90-1.95 (q)
	45.24	42.74	43.80	45.80
CH	4.09-4.22 (m)	4.27 (br.m)	5.15-5.26 (m)	5.01-5.12 (m)
	43.31	50.99	71.40	70.29
2C	51.00	51.25	51.62	55.30

TABLE 2. Continued

	I	II	III	VI
C=O (acryloyl)	168.79	168.00	165.61	165.63
C=O (carbamate)	152.96	154.32	150.35	150.28
CH <sub>3</sub> (N-Me)				2.23 (s), 20.58
<u>CH<sub>3</sub>CH<sub>2</sub>C<sub>2</sub>H<sub>4</sub>N</u>		1.25-1.37 (m); 13.71, 20.26		
C <sub>2</sub> H <sub>5</sub> <u>CH<sub>2</sub>CH<sub>2</sub>N</u>		1.51-1.61 (m); 31.79		
C <sub>3</sub> H <sub>7</sub> <u>CH<sub>2</sub>N</u>		3.15-3.20 (t); 43.19		



SCHEME 2

thermic reactions were observed only in the presence of dibutyltin dilaurate as catalyst at 60°C. The chemical structures of the monomers (Scheme 1) synthesized in high yield were confirmed by IR, <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. The results are summarized in Tables 1 and 2.



TABLE 3. Characterization of Polymers

Polymer	IR (cm <sup>-1</sup> )	<sup>1</sup> H-NMR (ppm)	GPC		
			M <sub>n</sub> (P <sub>n</sub> )	M <sub>w</sub> (P <sub>w</sub> )	M <sub>w</sub> /M <sub>n</sub>
HP-1	1707.8 (ss), 1686.7 (ss), 1546.1 (s)	1.98; 1.13, 1.25, 0.87, 1.58, 4.15	1397(5)	2227(8)	1.593
HP-2	1700.8 (s), 1686.7 (s)	1.97; 3.05; 1.14, 1.27, 0.93, 1.58, 4.35	1816(6)	2867(9)	1.578
HP-3	1778.1 (s), 1693.7 (s)	1.99; 1.15, 1.23, 1.57	1631(6)	2347(9)	1.438
HP-4	1778.1 (s), 1707.89 (s)	1.99; 2.24; 1.07, 1.17, 1.62	2243(8)	3615(13)	1.611
CP-1/(I) <sub>x</sub> (St) <sub>y</sub>			1874	2911	1.553
I	1707.8 (ss), 1686.7 (ss)	1.98; 1.13, 1.25, 1.55;			
St	3029.7-3093.0 (w), 1602.3 (w), 702.3 (s), 758.6 (m)	6.5-7.40			
CP-2/(II) <sub>x</sub> (St) <sub>y</sub>			2239	3398	1.517
II	1679.7 (ss)	1.13, 1.20, 0.92, 1.57			
St	3029.7-3093.0 (w), 1602.3 (w), 702.3 (s), 758.6 (m)	6.40-7.30			

TABLE 3. Continued

CP-3/(III) <sub>x</sub> (St) <sub>y</sub>		1864	2688	1.442
III	1785.2 (s), 1714.8 (s)	1.99; 1.16, 1.24, 0.87, 1.57		
St	3029.7-3093.0 (w), 1602.3 (w), 702.3 (s), 758.6 (m)	6.40-7.30		
CP-4/(VI) <sub>x</sub> (St) <sub>y</sub>		5130	7482	1.458
VI	1785.2 (s), 1714.8 (s)	1.99; 2.24; 1.07, 1.17, 0.87, 1.62		
St	3029.7-3093.0 (w), 1602.3 (w), 702.3 (s), 758.6 (m)	6.40-7.30		

### Homopolymers and Copolymers with Styrene

The monomers (I-IV) were homopolymerized, and copolymerized with styrene using AIBN as initiator (HP-1 and CP-1 are shown in Scheme 2 as examples). As expected, the double bond (1595.3-1637.5 cm<sup>-1</sup> in IR, 5.48-5.94 ppm and 121.42-139.99 ppm in NMR) in the monomer had disappeared after polymerization (see Table 3), indicating that the vinyl monomers had been incorporated into the homopolymers or copolymers. The composition of the copolymers (when the molar ratio of monomer I-VI to styrene was 1:2) were determined with elemental analysis (% N). The molecular weight and distribution were determined by Gel Permeation Chromatography (GPC) with polystyrene as standard.

## CONCLUSION

Four new functional monomers containing hindered piperidine groups were successfully synthesized by the addition reaction of 4-amino- and 4-hydroxy-piperidine derivatives to 2-methylacryloyl isocyanate. These monomers can be homopolymerized, and copolymerized with styrene by free radical initiation to new polymeric HALS derivatives with the molecular weight suitable for application as light or thermal stabilizers.

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