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SYNTHESIS AND POLYMERIZATION OF NEW METHACRYLOYL UREAS CARRYING A HINDERED PIPERIDINE AND A HYDROXYL GROUP

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ABSTRACT

New sterically hindered piperidine derivatives (**10–17)** were prepared by ring-opening reaction of various oxiranes with the commercially available 2,2,6,6-tetramethylpiperidin-4-yl-amine. By the addition of these sterically hindered piperidine derivatives (**10–17)** on 2-methylacryloyl isocyanate, eight novel multifunctional methacryloyl ureas, containing a hindered piperidine and a hydroxyl group (**M1**–**M8)** were synthesized. Five of these new multifunctional methacryloyl urea monomers (**M1**–**M5**) were homopolymerized, and copolymerized with styrene and methyl methacrylate by AIBN as initiator at 70°C. The new methacryloyl urea monomers (**M1**–**M8**) and their polymers (**P1**–**P13**) were characterized by Fourier transform infrared and nuclear magnetic resonance spectroscopy and by gel permeation chromatagraphy.

Key Words: Ring-opening reaction; Hindered piperidine derivatives; 2-Methylacryloyl isocyanate; Methacryloyl ureas; Radical polymerization.

INTRODUCTION

Sterically hindered piperidine derivatives are very effective light and thermal stabilizers for polymers and have been widely studied (1–11). For many polymer

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applications, however, the use of stabilizers with low volatility and low extractability is desired. One effective way for this purpose is the polymerization of the functional monomers containing a hindered amine moiety (1–12). Therefore, the synthesis of new polymeric Hindered Amine Stabilizer (HAS) is of great interest to design stabilizer systems for polymers with improved thermal and light stability.

There have been some polymeric HAS reported in the literatures (1–3, 5–8, 11, 13). Many of them are based on tetra- and pentamethylpiperidine derivatives of methacrylic acid (1, 2, 13–17). In the previous studies on polymeric HAS, we reported the reactions of the highly active 2-methylacryloyl isocyanate (MAI) with commercially available 2,2,6,6-tetramethyl and 1,2,2,6,6-pentamethyl piperidine derivatives (18). In this article, we chose various oxiranes to modify 2,2,6,6-tetramethylpiperidin-4-yl-amines to obtain a series of new sterically hindered piperidine derivatives (10–17). Their reaction with 2-methylacryloyl isocyanate led to the formation of novel multifunctional methacryloyl ureas carrying a hindered piperidine and a hydroxyl group, which were homopolymerized, and copolymerized with styrene and methyl methacrylate.

EXPERIMENTAL

Reagents and Analyses

MAI as a gift was kindly supplied by Nippon Paint Co. Ltd. 2,2,6,6-Tetramethylpiperidin-4-yl-amine was obtained from Huels. Oxiranes were from Fluka Chemical company. 2,2'-Azoisobutyronitrile (Fluka) was recrystallized from 96% ethanol. Styrene (Merck) and methyl methacrylate (Merck) were redistilled before use. Common organic reagents were used as received. The solvents were purified according to standard methods (19).

Infrared (IR) spectra were recorded on a Nicolet 205 Fourier transform infrared (FT-IR) spectrometer. Nuclear magnetic resonance (NMR) spectra were obtained on a Bruker AC-300 NMR spectrometer, ^{1}H at 300.1 MHz, ^{13}C at 75.5 MHz, with tetramethylsilane (TMS) as internal standard. The number (M_n) and weight average (M_w) molecular weight and the molecular weight distribution (M_w/M_n) of the polymers were determined by gel permeation chromatography (GPC) under the following conditions: for **P1–P5** and **P9–P13**, KNAUER instrument equipped with ultraviolet (UV) and refractive index (RI) detectors; column: Zorbax PSM 60 and Zorbax PSM 300; solvent: *N,N*,-dimethylacetamide with 3 g/l LiCl and 2 vol% H_2O; flow rate: 0.5 mL/min; For **P6-P8**, Hewlett Packard HP 1090 GPC system with UV and RI detectors using tetrahydrofuran as solvent. The molecular weight data are reported relative to a polystyrene calibration. Melting points were measured by light microscopy with a heating table at a heating rate of 0.5–4°C/min. Elemental analyses were performed with a Carlo Erba CHNS-O EA 1108 Elemental Analyzer.

Synthesis of Monomers

General Procedure A: Ring-Opening Reaction of Oxiranes with 2,2,6,6-Tetramethylpiperidin-4-yl-amine

Oxirane (1-8) and 2,2,6,6-tetramethylpiperidin-4-yl-amine (9) are placed in a three-neck flask equipped with condenser, stirrer and thermometer. The reaction is carried out at 30–100°C for several hours or days under stirring. The products (10–17) are purified by distillation at reduced pressure.

General Procedure B: Addition of Piperidine Derivatives on 2-Methylacryloyl Isocyanate

N-(2-Hydroxyalkyl)-2,2,6,6-tetramethylpiperidin-4-yl-amine (**10**–**17**) and dry solvent are charged under nitrogen into a three-neck flask equipped with stirrer, condenser, and thermometer. MAI in dry solvent is added dropwise to the above solution at 0–5°C and the mixture is stirred for 1–6 h at room temperature. The reaction product is concentrated on a rotary evaporator. Hexane was added to the residue to precipitate the product. The product is filtered off, washed several times with hexane, and then purified by recrystallization from acetonitrile.

1-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-propan-2-ol **(10)**

1-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-propan-2-ol (**10**) was prepared according to *General procedure A* from 2-methyl-oxirane (**1**, 29.04 g, 0.5 mol) and 2,2,6,6-tetramethyl-piperidin-4-yl-amine (**9**, 46.88 g, 0.3 mol) for 10 days at 30°C. Colorless semisolid; yield: 63.01 g (98%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 3.64-3.75 (m, 1H, CH), 2.37, 2.69 (2dd, *J* = 9.27, 11.74; 3.15, 11.74 Hz, 2H, CH_2), 1.09 (d, 3H, Me), piperidine ring: 1.05, 1.12 (2s, 12H, *cis-, trans*-2,6-Me), 0.78 (dd, *J* = 12.10, 12.10 Hz, 2H, *cis*-3,5-H), 1.79 (dd, *J* = 1.74, 12.50 Hz, 2H, *trans*-3,5-H), 2.76-2.86 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 65.55 (CH), 53.64 (CH_2), 20.75 (CH_3); piperidine ring: 28.43, 28.45, 34.83 (4Me, *cis-, trans*-2,6-Me), 46.02, 46.26 ($2CH_2$), 49.65(CH), 50.71(*tert*-C).

3-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-propane-1,2-diol **(11)**

3-(2,2,6,6-Tetramethylpiperidin-4-ylamino)-propane-1,2-diol (**11**) was prepared according to *General procedure A* from 2-hydroxymethyl-oxriane (**2**, 7.41 g, 0.10 mol) and 2,2,6,6-tetra-methylpiperidin-4-yl-amine (**9**, 15.63 g, 0.1 mol) for 2 h at 80°C. White semisolid; yield: 18.38 g (80%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 3.70-3.73 (m, 1H, CH), 2.71, 2.87-2.93 (2d, m, *J* = 6.48, 11.99 Hz, 2H, CH_2), 3.62, 3.70-3.73 (2d, m, *J* = 5.58, 12.28 Hz,

2H, CH_2OH), piperidine ring: 1.11, 1.18 (2s, 12H, *cis-, trans*-2,6-Me), 0.77-0.97 (m, 2H, CH_2), 1.82-1.88 (m, 2H, CH_2), 2.82-2.93 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 69.89 (CH), 49.32 (CH_2), 65.75 (CH_2OH); piperidine ring: 28.70, 35.05 (4Me, *cis-, trans*-2,6-Me), 46.21, 46.36 ($2CH_2$), 50.20 (CH), 50.98 (*tert*-C).

1-Phenoxy-3-(2,2,6,6-tetramethylpiperidin-4-ylamino)-propan-2-ol (**12**)

1-Phenoxy-3-(2,2,6,6-tetramethylpiperidin-4-ylamino)-propan-2-ol (12) was prepared according to *General procedure A* from 2-phenoxymethyl-oxriane (3, 7.51 g, 0.05 mol) and 2,2,6,6-tetramethylpiperidin-4-yl-amine (9, 7.81 g, 0.05 mol) for 24 h at 80°C. Colorless viscous oil; yield: 13.18 g (86%).

^1H NMR($CDCl_3$, 300.1 MHz): δ = 3.95-4.05 (m, 1H, CH), 2.67, 2.83 (2dd, *J* = 8.16, 11.75; 3.24, 11.75 Hz, 2H, CH_2), 3.82-3.91 (m, 2H, OCH_2), 6.80-6.87 (m, 3H, o-, p-PhH), 7.14-7.20 (m, 2H, m-PhH); piperidine ring: 1.02, 1.09 (2s, 12H, *cis-, trans*-2,6-Me), 0.77 (dd, *J* = 12.01, 12.01 Hz, 2H, *cis*-3,5-H), 1.76 (d, *J* = 11.80 Hz, 2H, *trans*-3,5-H), 2.73-2.78 (m, 1H, CH).

^{13}C NMR($CDCl_3$, 75.5 MHz): δ = 68.48 (CH), 48.80 (CH_2), 70.55 (OCH_2); phenyl ring: 158.62 (C-O), 129.35 (p), 121.03 (p), 120.91 (o), 114.51 (o), 114.47 (m); piperidine ring: 28.57, 34.93 (4Me, *cis-, trans*-2,6-Me), 46.11, 46.20 ($2CH_2$), 50.02 (CH), 50.93 (*tert*-C).

1-Butyloxyl-3-(2,2,6,6-tetramethylpiperidin-4-ylamino)-propan-2-ol (**13**)

1-Butyloxyl-3-(2,2,6,6-tetramethylpiperidin-4-ylamino)-propan-2-ol (**13**) was prepared according to *General procedure A* from 2-butoxymethyl-oxriane (**4**, 3.91 g, 0.03 mol) and 2,2,6,6-tetramethylpiperidin-4-yl-amine (**9**, 7.81 g, 0.05 mol) for 22 h at 100°C. Reddish-brown oil; yield: 8.2 g (95%).

^1H NMR ($CDCl_3$, 300.1 MHz): δ = 3.66-3.74 (m, 1H,CH), 2.52, 2.68 (2dd, *J* = 8.07, 11.83; 3.81, 11.83 Hz, 2H, CH_2), 3.31-3.36, 3.29-3.31, 1.39-1.49, 1.09-1.30, 0.79 (4m, t, 11H, $CH_2OC_4H_9$), piperidine ring: 1.00, 1.06 (2s, 12H, *cis-, trans*-2,6-Me), 0.68-0.79 (m, 2H, *cis*-3,5-H), 1.73 (dd, *J* = 3.48, 12.64 Hz, 2H, *trans*-3,5-H), 2.72-2.81 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 68.77 (CH), 48.96 (CH_2), 73.47, 71.10, 31.45, 19.04, 13.68 ($CH_2OC_4H_9$); piperidine ring: 28.46,34.85 (4Me, *cis-, trans*-2,6-Me), 45.98, 46.10 ($2CH_2$), 49.78 (CH), 50.75 (*tert*-C).

1-Phenyl-2-(2,2,6,6-tetramethylpiperidin-4-ylamino)-ethanol (**14**)

1-Phenyl-2-(2,2,6,6-tetramethylpiperidin-4-ylamino)-ethanol (**14**) was prepared according to *General procedure A* from 2-phenyl-oxirane (**5**, 6.01 g, 0.05

mol) and 2,2,6,6-tetra-methyl-piperidin-4-yl-amine (**9**, 7.81 g, 0.05 mol) for 21 h at 100°C. Colorless semisolid; yield: 12.59 g (91%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 4.66-4.73 (m, 1H, CH), 2.70, 2.94 (2dd, *J* = 3.54, 11.90; 9.09, 11.90 Hz, 2H, CH_2), 7.27-7.35 (m, 5H, PhH), piperidine ring: 1.06, 1.13 (2d, *J* = 5.34, 2.61 Hz, *cis-, trans*-2,6-Me), 0.78 (dd, *J* = 12.16, 12.16 Hz, 2H, *cis*-3,5-H), 1.80 (dd, *J* = 3.39, 12.58 Hz, 2H, *trans*-3,5-H), 2.81-2.90 (m, 1H, CH).

^{13}C NMR($CDCl_3$, 75.5 MHz): δ = 72.06 (CH), 54.07 (CH_2); phenyl ring: 142.95 (C=), 128.27 (p), 127.36 (p), 127.50 (o), 125.71(o), 125.86 (m); piperidine ring: 28.55, 35.06 (4Me, *cis-, trans*-2,6-Me), 46.16, 46.33 ($2CH_2$), 49.83 (CH), 50.95 (*tert*-C).

1-*tert*-Butyloxyl-3-(2,2,6,6-tetramethylpiperidin-4-ylamino)-propan-2-ol (**15**)

1-*tert*-Butyloxyl-3-(2,2,6,6-tetramethylpiperidin-4-ylamino)-propan-2-ol (**15**) was prepared according to *General procedure A* from 2-*tert*-butoxymethyl-oxirane (**6**, 6.51 g, 0.05 mol) and 2,2,6,6-tetramethylpiperidin-4-yl-amine (**9**, 7.81 g, 0.05 mol) for 22 h at 100°C. Light yellow semisolid; yield: 12.77 g (89%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 3.68-3.74 (m, 1H, CH), 2.58, 2.74 (2dd, *J* = 7.95, 11.83; 3.78, 11.83 Hz, 2H, CH_2), 3.25-3.34, 1.13 (m, s, 11H, CH_2OCMe_3), piperidine ring: 1.06, 1.12 (2s, 12H, *cis-, trans*-2,6-Me), 0.79 (dd, *J* = 12.04, 12.04 Hz, 2H, *cis*-3,5-H), 1.79 (dd, *J* = 3.57, 12.68 Hz, 2H, *trans*-3,5-H), 2.77-2.87 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 69.47 (CH), 49.20 (CH_2), 64.50 (CH_2O), 72.97, 27.39 ($OCMe_3$), piperidine ring: 28.54, 34.93 (4Me, *cis-, trans*-2,6-Me), 46.07, 46.17 ($2CH_2$), 49.89 (CH), 50.89 (*tert*-C).

1-(2,2,6,6-Tetramethylpiperidin-4-yl-amino)-butan-2-ol (**16**)

1-(2,2,6,6-Tetramethylpiperidin-4-yl-amino)-butan-2-ol (**16**) was prepared according to *General procedure A* from 2-ethyl-oxirane (**7**, 7.21 g, 0.10 mol) and 2,2,6,6-tetramethyl-piperidin-4-yl-amine (**9**, 15.62 g, 0.10 mol) for 3 days at 60°C. Colorless oil; yield: 15.10 g (66%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 3.32-3.34 (d-like m,1H, CH), 2.26, 2.38 (2d,d, *J* = 9.39, 9.39; 11.49 Hz, 2H, CH_2), 1.22-1.29, 0.77 (m, t, 5H, CH_2CH_3), piperidine ring: 0.92, 0.99 (2s, 12H, *cis-, trans*-2,6-Me), 0.66 (dd, *J* = 11.98, 11.98 Hz, 2H, *cis*-3,5-H), 1.66 (d, *J* = 12.43 Hz, 2H, *trans*-3,5-H), 2.64-2.72 (t-like m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 70.64 (CH), 51.59 (CH_2), 27.93, 9.71 (CH_2CH_3) piperidine ring: 28.43, 28.45, 34.83(4Me, *cis-, trans*-2,6-Me), 45.72, 45.88 ($2CH_2$), 49.53(CH), 50.54 (*tert*-C).

1-(2,2,6,6-Tetramethylpiperidin-4-yl-amino)-octan-2-ol (**17**)

1-(2,2,6,6-Tetramethylpiperidin-4-yl-amino)-octan-2-ol (**17**) was prepared according to *General procedure A* from 2-hexyl-oxirane (**8**, 4.41 g, 0.05 mol), 2,2,6,6-tetramethylpiperidin-4-yl-amine (**9**, 7.81 g, 0.05 mol) for 3 days at 100°C. Reddish-brown oil; yield: 13.16 g (93%).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 3.51-3.54 (t-like m, 1H, CH), 2.38, 2.57 (2dd, *J* = 9.42, 11.68; 2.91, 11.68 Hz, 2H, CH_2), 1.24-1.39, 0.84 (m, t, 13H, C_6H_{13}), piperidine ring: 1.08, 1.14 (2s, 12H, *cis-, trans*-2,6-Me), 0.76 (dd, *J* = 6.0, 12.16 Hz, 2H, *cis*-3,5-H), 1.78-1.85 (m, 2H, *trans*-3,5-H), 2.82-2.88 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 69.78 (CH), 52.06 (CH_2), 35.14, 31.62, 29.24, 25.50, 22.40, 13.87 (C_6H_{13}), piperidine ring: 28.54, 34.91 (4Me, *cis-, trans*-2,6-Me), 46.15, 46.46 ($2CH_2$), 49.77 (CH), 50.83 (*tert*-C).

1-(2-Hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M1**)

1-(2-Hydroxypropyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M1**) was synthesized from 1-(2,2,6,6-tetramethylpiperidin-4-yl-amino)-propan-2-ol (**10**, 0.50 g, 2.33 mmol) and MAI (**18**, 0.26 g, 2.33 mmol) in dry toluene (40 mL) according to *General procedure B.* White powder, mp 161–161.5°C; yield: 0.57 g (75%).

IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3437.5 (ss, br. OH), 3233.6 (s, br. NH), 1714.8 (ss, C=O), 1665.6 (s, C=O, urea), 1637.5 (m, C=C), 1518.0 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 5.51, 5.68 (2s, 2H, CH_2=), 1.86 (s, 3H, =CCH_3), 1.08 (d, CH_3), 3.06-3.19 (m, NCH_2), 4.42 (br.s-like m, C<u>H</u>OH), piperidine ring: 1.04, 1.14 (2d, *J* = 4.23, 8.01 Hz, 12H, *cis-, trans*-2,6-Me), 1.25, 1.27 (2dd, *J* = 12.25, 12.25, 11.83, 11.83 Hz, 2H, *cis*-3,5-H), 1.41, 1.51 (2dd, *J* = 9.93, 9.72 Hz, 2H, *trans*-3,5-H), 3.76 (s-like m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.21(C=O, acryloyl), 153.27(C=O, urea), 139.96 (=C), 120.51 (CH_2=), 18.14 (=CCH_3), 20.99 (CH_3), 49.81(NCH_2), 68.03(CHOH); piperidine ring: 28.17, 28.42, 34.37, 34.44 (4Me, *cis-, trans*-2,6-Me), 40.60, 41.98 ($2CH_2$), 47.83 (CH), 50.49, 50.63 (*tert*-C).

$C_{17}H_{31}O_3N_3$ (325.45)	Calcd: C 62.74	H 9.60	N 12.91
	Found: C 62.99	H 9.73	N 12.83

1-(2,3-Dihydroxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M2**)

1-(2,3-Dihydroxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M2**) was synthesized from 3-(2,2,6,6-tetramethyl-

piperidin-4-ylamino)-propane-1,2-diol (**11**, 0.46 g, 2 mmol) and MAI (**18**, 0.22 g, 2 mmol) in dry chloroform (60 mL) according to *General procedure B.* White solid, mp 97-98°C; yield: 0.59 g (87%).

IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3423.4 (ss, br. OH), 3261.7 (s, br. NH), 1721.9 (ss, C=O), 1665.6 (s, C=O, urea), 1630.5 (m, C=C), 1518.0 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 5.68, 5.50 (2s, 2H, CH_2=), 4.45 (m, 1H, C<u>H</u>OH), 3.58, 3.40-3.24 (d-like m, m, 2H, C<u>H</u>$_2$OH), 3.15, 3.24-3.40 (dd, m, *J* = 9.24, 15.68 Hz, 2H, NCH_2), 1.85 (s, 3H, =CCH_3), piperidine ring: 1.04, 1.15 (2d, *J* = 1.50, 7.83 Hz, 12H, *cis-, trans*-2,6-Me), 1.29, 1.46 (2 dd, *J* = 12.13, 26.83; 9.75, 22.85 Hz, 4H, 2CH_2, *cis*-, *trans*-3,5-H), 3.24-3.40 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.46 (C=O, acryloyl), 153.48 (C=O, urea), 140.18 (=C), 120.79 (CH_2=), 18.37 (=CCH_3), 46.17 (NCH_2), 73.19 (CHOH), 63.49 (CH_2OH), piperidine ring: 28.43, 28.64, 34.58, 34.67 (4Me, *cis-, trans*-2,6-Me), 40.94, 42.13 (2CH_2), 48.00 (CH), 50.76, 50.90 (*tert*-C).

$C_{17}H_{31}N_3O_4$ (341.45)	Calcd: C 59.80	H 9.15	N 12.31
	Found: C 59.60	H 9.22	N 12.23

1-(2-Hydroxy-3-phenoxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea **(M3)**

1-(2-Hydroxy-3-phenoxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl) urea (**M3**) was synthesized from 1-phenoxy-3-(2,2,6,6-tetramethylpiperidin-4-yl-amino) propan-2-ol (**12**, 15.84 g, 51.69 mmol) and MAI (**18**, 5.74 g, 51.69 mmol) in dry toluene (200 mL) according to *General procedure B.* White powder, mp 183.5-184.5°C; yield: 13.06 g (61%).

IR (KBr): $\tilde{\nu}$(cm^{-1}) = 3430.5 (s, br. OH), 3247.6 (m, NH), 1714.8 (ss, C=O), 1665.6 (s, C=O, urea), 1637.5 (m, C=C), 1496.9 (s, NH), phenyl ring: 3029.7-3093.0 (ww, m), 1602.3 (m), 758.6 (m), 695.3 (m).

^{1}H NMR ($CDCl_3$+DMSO-d_6, 300.1 MHz): δ = 7.29-7.24 (m, 5H, PhH), 5.74, 5.48 (2s, 2H, CH_2=), 1.88 (s, 3H, =CCH_3), 4.47 (s-like m, C<u>H</u>OH), 3.94 (s, 2H, CH_2O), 3.37 (br.s, 3H, NCH_2 and OH), piperidine ring: 1.03, 1.15 (2 d, *J* = 2.64, 11.07 Hz, 12H, *cis-, trans*-2,6-Me), 1.29 (dd, *J* = 12.16, 27.13 Hz, 2H, *cis*-3,5-H), 1.51 (dd, *J* = 2.79, 12.37 Hz, 2H, *trans*-3,5-H), 3.94 (s, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.05 (C=O, acryloyl), 153.22 (C=O, urea), 139.81 (=C), 120.43 (CH_2=), 70.30 (CH), 68.97 (CH_2O), 45.64 (NCH_2), 18.06 (=CCH_3), phenyl ring: 139.81 (C=), 129.11 (o), 120.43 (p), 114.07 (m), piperidine ring: 28.08, 28.26, 34.34, 34.43 (4Me, *cis-, trans*-2,6-Me), 41.89, 45.64 (2CH_2), 47.87 (CH), 50.40, 50.51 (*tert*-C).

$C_{23}H_{35}N_3O_4$ (417.54)	Calcd: C 66.16	H 8.45	N 10.07
	Found: C 66.53	H 8.49	N 10.15

1-(2-Hydroxy-3-butoxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea (**M4**)

1-(2-Hydroxy-3-butoxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea (**M4**) was synthesized from 1-butyloxyl-3-(2,2,6,6-tetramethylpiperidin-4-yl-amino)-propan-2-ol (**13**, 0.57 g, 2 mmol) and MAI (**18**, 0.22 g, 2 mmol) in dry toluene (40 mL) according to *General procedure B.* White powder, mp 155–156°C; yield: 0.46 g (52%).

IR (KBr): $\tilde{\nu}(cm^{-1})$ = 3430.5 (ss, br. m, OH), 3243.6 (m, NH), 1714.8 (ss, C=O), 1665.6 (s, C=O, urea), 1637.5 (m, C=C), 1518.0 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 5.43, 5.75 (s,s, 2H, CH_2=), 1.95 (s, 3H, =CCH_3), 3.38, 3.18-3.28, 1.51-1.60, 1.30-1.42, 0.91 (s-like m, 3m, t, 11H, $CH_2OC_4H_9$), 3.45-3.49 (m, CH_2), 4.61 (s-like m, 1H, CH); piperidine ring: 1.11, 1.24 (s, d, *J* = 11.22 Hz, 12H, *cis-, trans*-2,6-Me), 1.11-1.22 (m, 2H, *cis*-3,5-H), 1.68 (dd, *J* = 11.92, 11.92 Hz, 2H, *trans*-3,5-H), 3.91-3.93 (d-like m, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 167.39 (C=O, acryloyl), 154.53 (C=O, urea), 140.15 (=C), 121.23 (CH_2=), 18.44 (=CCH_3), 72.47, 71.21, 31.62, 19.19, 13.77 ($CH_2OC_4H_9$), 71.92 (CH_2), 48.36 (CH), piperidine ring: 28.14, 34.84, 34.94 (4Me, *cis-, trans*-2,6-Me), 41.32, 42.80 (2CH_2), 48.36 (CH), 51.17, 51.25 (*tert*-C).

$C_{21}H_{39}N_3O_4$ (397.55)	Calcd:	C 63.44	H 9.89	N 10.57
	Found:	C 63.54	H 10.05	N 10.50

1-(2-Hydroxy-2-phenyl-ethyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea (**M5**)

1-(2-Hydroxy-2-phenyl-ethyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M5**) was synthesized from 1-phenyl-2-(2,2,6,6-tetramethylpiperidin-4-yl-amino)-ethanol (**14**, 3.85 g, 0.014 mol) and MAI (**18**, 1.55 g, 0.014 mol) in dry toluene (80 mL) according to *General procedure B.* White powder, mp 165.5–166.5°C; yield: 3.65 g (70%).

IR (KBr): $\tilde{\nu}(cm^{-1})$ = 3416.4 (s, br. OH), 3254.4 (m, NH), 1721.9 (ss, C=O), 1665.6 (s, C=O, urea), 1630.5 (m, C=C), 1510.9 (s, NH), phenyl ring: 3029.7-3093.0 (ww, m), 1602.3 (ww), 751.6 (m), 702.3 (m).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 5.49, 5.84 (2s, 2H, CH_2=), 2.01 (s, 3H, =CCH_3), 3.21, 3.50 (d, 2d, *J* = 15.75; 9.60, 16.60 Hz, 2H, CH_2), 4.86-4.89 (d-like m, C<u>H</u>OH), 7.33-7.39 (m, 5H, PhH), piperidine ring: 1.16, 1.23 (2s, 12H, *cis-, trans*-2,6-Me), 1.06-1.13, 1.33 (m, 2d, *J* = 12.19, 12.19 Hz, 2H, *cis*-3,5-H), 1.66, 1.80 (2d, *J* = 11.89, 11.34 Hz, 2H, *trans*-3,5-H), 4.58 (t-like m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.25 (C=O, acryloyl), 153.45 (C=O, urea), 139.79 (=C), 119.91 (CH_2=), 17.80 (=CCH_3), 50.49 (CH_2), 74.51 (CH), phenyl ring: 141.39 (C=), 127.77 (p), 127.17 (o), 124.86 (m); piperidine ring:

27.65, 27.74, 34.09, 34.37 (4Me, *cis-, trans*-2,6-Me), 40.39, 42.54 ($2CH_2$), 47.85 (CH), 50.34, 50.60 (*tert*-C).

$C_{22}H_{33}N_3O_3$ (387.514)	Calcd: C 68.18	H 8.58	N 10.85
	Found: C 68.37	H 8.69	N 10.88

1-(2-Hydroxy-3-*tert*-butoxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M6**)

1-(2-Hydroxy-3-*tert*-butoxy-propyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M6**) was synthesized from 1-*tert*-butyloxyl-3-(2,2,6,6-tetramethylpiperidin-4-yl-amino)-propan-2-ol (**15**, 9.90 g, 34.56 mmol) and MAI (**18**, 3.84 g, 34.56 mmol) in dry toluene (200 ml) according to *General procedure B.* White powder, mp 175-176°C; yield: 10.67 g (78%).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (ss, br. OH), 3247.6 (m, NH), 1721.9 (ss, C=O), 1665.6 (s, C=O, urea), 1630.5 (m, C=C), 1518.0 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 5.74, 5.42 (2s, 2H, CH_2=), 4.61 (m, 1H, C<u>H</u>OH), 3.16-3.35 (m, 4H, CH_2O and NCH_2), 1.95 (s, 3H, =CCH_3), 1.20 (s, 9H, 3Me, Bu^t); piperidine ring: 1.11, 1.24 (2d, *J* = 3.18, 11.43 Hz, 12H, *cis-, trans*-2,6-Me), 1.14-1.26 (m, 2H, *cis*-3,5-H), 1.68 (dd, *J* = 11.31, 11.31 Hz, 2H, *trans*-3,5-H), 3.82 (m, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 167.54 (C=O, acryloyl), 154.22 (C=O, urea), 140.64 (=C), 120.75 (CH_2=), 73.79 (*t*-C, Bu^t), 72.91 (C<u>H</u>OH), 63.34 (CH_2O), 46.29 (NCH_2), 27.44 (3Me, Bu^t), 18.59 (=CCH_3); piperidine ring: 28.37, 28.45, 35.04, 35.19 (4Me, *cis-, trans*-2,6-Me), 41.39, 43.15 ($2CH_2$), 47.50 (CH), 51.27, 51.36 (*tert*-C).

$C_{21}H_{39}N_3O_4$ (397.55)	Calcd: C 63.44	H 9.89	N 10.57
	Found: C 63.61	H 9.97	N 10.42

1-(2-Hydroxybutyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M7**)

1-(2-Hydroxybutyl)-3-(2-methylacyloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M7**) was synthesized from 1-(2,2,6,6-tetramethylpiperidin-4-yl-amino)-butan-2-ol (**16**, 2.28 g, 0.01 mol) and MAI (**18**, 1.11 g, 0.01 mol) in dry toluene (60 mL) according to *General procedure B.* White powder, mp 168.5–170°C; yield: 2.64 g (78%).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3427.8 (ss, br. OH), 3230.7 (s, br. NH), 1721.9 (ss, C=O), 1665.6 (s, C=O, urea), 1630.5 (m, C=C), 1518.0 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 10.69 (br.s, 1H, OH), 6.28, 8.12 (2br.s, 2H, NH), 5.48, 5.76 (2s, 2H, CH_2=), 1.92 (s, 3H, =CCH_3), 3.07-3.21, 0.95 (q-like

m, t, 5H, CH_2CH_3) 3.26-3.34 (d, CH_2), 4.55 (br.s-like m, CH), piperidine ring: 1.10, 1.21 (2d, J = 6.27, 6.87 Hz, 12H, *cis-, trans*-2,6-Me), 1.44 (dd, J = 7.08, 7.08 Hz, 2H, *cis*-3,5-H), 1.60 (dd, J = 12.79, 12.79 Hz, 2H, *trans*-3,5-H), 3.56 (s-like m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 167.48 (C=O, acryloyl), 154.66 (C=O, urea), 140.27 (=C), 121.27 (CH_2=), 18.55 (=CCH_3), 28.38, 9.61 (CH_2CH_3), 48.69 (NCH_2), 74.51(CHOH); piperidine ring: 28.31, 28.38, 34.93, 35.10 (4Me, *cis-, trans*-2,6-Me), 41.40, 43.22 (2CH_2), 48.33 (CH), 51.27, 51.34 (*tert*-C).

$C_{18}H_{33}O_3N_3$ (339.47)	Calcd: C 63.68	H 9.80	N 12.38
	Found: C 63.45	H 9.71	N 12.44

1-(2-Hydroxyoctyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M8**)

1-(2-Hydroxyoctyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M8**) was synthesized from 1-(2,2,6,6-tetramethylpiperidin-4-yl-amino)-octan-2-ol (**17**, 12.81g, 45.03 mmol) and MAI (**18**, 5.00 g, 45.03 mmol) in dry toluene (200 mL) according to *General procedure B.* White powder, mp 162-163°C; yield: 10.43 g (59%).

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (ss, br. OH), 3226.6 (s, br. NH), 1714.8 (ss, C=O), 1665.6 (s, C=O, urea), 1630.5 (m, C=C), 1510.9 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 5.76, 5.42 (2s, 2H, CH_2=), 4.59 (m, 1H, C<u>H</u>OH), CH_2CH_3) 3.25, 3.06 (2dd, J = 9.69, 15.80; 0, 15.80 Hz, 2H, CH_2), 1.94 (s, 3H, =CCH_3), 1.10-1.45 (m, 10H, 5CH_2), 0.87 (t, J = 6.12 Hz, 3H, CH_3), piperidine ring: 1.11, 1.24 (2d, J = 3.90, 11.13 Hz, 12H, *cis-, trans*-2,6-Me), 1.10-1.28 (m, 2H, *cis*-3,5-H),1.69 (dd, J = 12.91, 12.91 Hz, 2H, *trans*-3,5-H), 3.76 (m, 1H, CH).

^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 167.47 (C=O, acryloyl), 154.52(C=O, urea), 140.44 (=C), 121.08 (CH_2=), 73.58 (CHOH), 49.14 (NCH_2), 18.61 (=CCH_3), 35.51, 31.68, 29.25, 25.21, 22.56 (C_6H_{13}), piperidine ring: 28.37, 28.46, 34.99, 35.17 (4Me, *cis-, trans*-2,6-Me), 41.42, 43.37 (2CH_2), 48.56 (CH), 51.29, 51.36 (*tert*-C).

$C_{22}H_{41}O_3N_3$ (395.58)	Calcd: C 66.79	H 10.45	N 10.62
	Found: C 67.01	H 10.40	N 10.71

Synthesis of Polymers

General Procedure

In a polymerization bottle, the monomers (M1-M5, 0.3 g) were dissolved in 2 to 3 mL of dry *N,N*-dimethylformamide (DMF), degassed, and sealed. AIBN in

DMF was injected, and the solution was stirred for 24 h at 70°C under argon. The polymer product was precipitated with diethyl ether, purified by reprecipitation from methanol into diethyl ether 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 h, 2 mol.-% AIBN was added and the solution was further polymerized for 24 h under the same condition.

Copolymerization was carried out according to the general procedure. For copolymerization of monomers **M1**, **M2**, and **M5** with methyl methacrylate (the molar ratio of these monomers to methyl methacrylate is 1:2) 2.5 mol.-% AIBN of monomer was used. For copolymerization of monomers **M1**–**M5** with styrene (the molar ratio of these monomers to styrene is 1:3) 1.5 mol.-% AIBN of monomer was used**.**

Poly[1-(2-hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea] (**P1**)

1-(2-Hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M1**) was polymerized in dry DMF according to *General procedure.* White powder, mp 194-200°C; yield: 66%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5, 3290.3 (ss, s, OH, NH), 1721.9 (ss, C=O), 1665.6 (ss, C=O, urea), 1468.7 (s, NH).

^{1}H NMR (DMSO-d_6, 300.1 MHz): δ = 0.50-2.30 (br.m, $2CH_3$, CH_2-C), 2.70-4.0 (br.m, NCH_2), 4.23 (br.s, C<u>H</u>OH); piperidine ring: 0.87, 0.95 (2d, 4Me), 0.50-2.30 (br.m, $2CH_2$), 2.70-4.0 (br.m, CH).

$(C_{17}H_{31}O_3N_3)_n$ (325.45)$_n$	Calcd: C 62.74	H 9.60	N 12.91
	Found: C 61.74	H 9.20	N 11.86
GPC	$\bar{M}_n$ ($\bar{P}_n$)	$\bar{M}_w$ ($\bar{P}_w$)	$\bar{M}_w/\bar{M}_n$
	11,400 (35)	25,300 (78)	2.22

Poly[1-(2,3-dihydroxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetra-methylpiperidin-4-yl)-urea] (**P2**)

1-(2,3-Dihydroxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea **(M2)** was polymerized in dry DMF according to *General procedure.* White powder, m.p. 178–185°C; yield: 73%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3416.4, 3320.1 (ss, s, OH, NH), 1721.9 (ss, C=O), 1665.6 (m, C=O, urea), 1560.2 (m, NH).

^{1}H NMR ($CDCl_3$+DMSO-d_6, 300.1 MHz): δ = 0.35-2.50 (br.m, CH_3, CH_2-C), 3.0-4.20 (br.m, NCH_2, C<u>H</u>$_2$OH), 4.80 (br.s, C<u>H</u>OH); piperidine ring: 1.16, 1.22 (2s, 4Me), 0.35-2.50 (br.m, $2CH_2$), 3.0-4.20 (br.m, CH).

$(C_{17}H_{31}N_3O_4)_n$ (341.45)$_n$	Calcd: C 59.80	H 9.15	N 12.31
	Found: C 58.02	H 9.59	N 12.63
GPC	$\bar{M}_n$ ($\bar{P}_n$)	$\bar{M}_w$ ($\bar{P}_w$)	$\bar{M}_w/\bar{M}_n$
	10200 (30)	31800 (93)	3.12

Poly[1-(2-hydroxy-3-phenoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea] (**P3**)

1-(2-Hydroxy-3-phenoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M3**) was polymerized in dry DMF according to *General procedure.* White powder, mp 166–171°C; yield: 51%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (br. ss, OH, NH), 1721.9 (s, C=O), 1665.6 (s, C=O, urea), 1503.9 (s, NH), benzene ring: 3029.7-3093.0 (ww), 702.3 (m), 758.6 (m).

^{1}H NMR ($CDCl_3$+DMSO-d_6, 300.1 MHz): δ = 0.50-2.50 (br.m, CH_3 CH_2-C), 3.0-4.10 (br.s, NCH_2, OCH_2), 4.25 (br.s, C<u>H</u>OH), 7.20-7.50 (br.m, PhH); piperidine ring: 1.10, 1.18 (2s, 4Me), 0.50-2.50 (br.m, 2CH_2), 3.0-4.10 (br.s, CH).

$(C_{23}H_{35}N_3O_4)_n$ (417.54)$_n$	Calcd: C 66.16	H 8.45	N 10.07
	Found: C 67.13	H 8.86	N 9.65
GPC	$\bar{M}_n$ ($\bar{P}_n$)	$\bar{M}_w$ ($\bar{P}_w$)	$\bar{M}_w/\bar{M}_n$
	3900 (9)	6800 (16)	1.74

Poly[1-(2-hydroxy-3-butoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea] (**P4**)

1-(2-Hydroxy-3-butoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl) urea (**M4**) was polymerized in dry DMF according to *General procedure.* White powder, mp 169-174°C; yield: 54%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (br. ss, OH, NH), 1728.9 (ss, C=O), 1665.6 (s, C=O, urea), 1503.9 (s, NH).

^{1}H NMR (DMSO-d_6+$CDCl_3$, 300.1 MHz): δ = 0.60-2.50 (br.m, $CH_2CH_2CH_3$, CH_3, CH_2-C), 3.0-3.9 (br.s, NCH_2, OCH_2), 4.49 (br.s, C<u>H</u>OH); piperidine ring: 1.05, 1.17 (2s, 4Me), 0.60-2.50 (br.m, 2CH_2), 3.69 (br.s, CH).

$(C_{21}H_{39}N_3O_4)_n$ (397.55)$_n$	Calcd: C 63.44	H 9.8	N 10.57
	Found: C 64.56	H 10.3	N 10.23
GPC	$\bar{M}_n$ ($\bar{P}_n$)	$\bar{M}_w$ ($\bar{P}_w$)	$\bar{M}_w/\bar{M}_n$
	8000 (20)	21000 (53)	2.63

Poly[1-(2-hydroxy-2-phenyl-ethyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea] (**P5**)

1-(2-Hydroxy-2-phenyl-ethyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M5**) was polymerized in dry DMF according to *General procedure.* White powder, mp 172–177°C; yield: 52%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5, 3300.5 (ss, s, OH, NH), 1721.9 (ss, C=O), 1672.6 (ss, C=O, urea), 1496.9 (s, NH), benzene ring : 3029.7-3093.0 (ww), 702.3 (m), 758.6 (m).

^{1}H NMR ($CDCl_3$+DMSO-d_6, 300.1 MHz): δ = 0.60-2.50 (br.m, CH_3, CH_2-C), 3.33 (br.s, NCH_2), 4.74 (br.s, C<u>H</u>OH), 7.20-7.50 (br.m, PhH); piperidine ring: 1.14, 1.20 (2s, 4Me), 0.60–2.50 (br.m, $2CH_2$), 4.52 (br.s, CH).

$(C_{22}H_{33}N_3O_3)_n$ (387.51)$_n$	Calcd: C 68.18	H 8.58	N 10.85
	Found: C 67.29	H 8.90	N 11.17
GPC	$\bar{M}_n$ ($\bar{P}_n$)	$\bar{M}_w$ ($\bar{P}_w$)	$\bar{M}_w/\bar{M}_n$
	7700 (20)	12500 (32)	1.62

Poly{[1-(2-hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea]-co-methyl methacrylate} (**P6**)

1-(2-Hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M1**) was copolymerized with methyl methacrylate in dry DMF according to *General procedure.* White powder, mp 160-168°C; yield: 68%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3444.5, 3315.5 (ss, s, OH, NH), 1728.9 (ss, C=O, MMA), 1672.6 (m, C=O), 1665.6 (m, C=O, urea), 1482.8 (s, NH).

^{1}H NMR (DMSO-d_6+$CDCl_3$, 300.1MHz): δ = 0.60-2.50 (br.m, $3CH_3$, $2CH_2$-C), 3.36 (br.s, NCH_2), 3.60 (s, OCH_3), piperidine ring: 1.14, 1.23 (2s, 4Me), (br.m, $2CH_2$), 0.60-2.50 (br.m, $2CH_2$).

$(C_5H_8O_2)_x(C_{17}H_{31}O_3N_3)_y$ Found C 59.48 H 8.69 N 6.17 ; x = 78.04, y = 21.96.

GPC (THF)	$\bar{M}_n$ ($\bar{P}_n$)	$\bar{M}_w$ ($\bar{P}_w$)	$\bar{M}_w/\bar{M}_n$
	3170	5484	1.73

Poly{[1-(2,3-dihydroxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea]-co-methyl methacrylate} (**P7**)

1-(2,3-Dihydroxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M2**) was copolymerized with methyl methacrylate in dry DMF according to *General procedure.* White powder, mp 96-106°C; yield: 78%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (ss, OH, NH), 1728.9 (ss, 2C=O), 1665.6 (m, C=O, urea), 1482.8 (s, NH).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 0.60-2.20 (br.m, $2CH_3$, $2CH_2$-C), 3.1-4.0 (br.m, NCH_2, $C\underline{H}_2OH$), 3.59 (s, OCH_3), 4.21 (br.s, $C\underline{H}OH$); piperidine ring: 1.12, 1.18 (2s, 4Me), 0.60-2.20 (br.m, $2CH_2$). 3.1-4.0 (br.m, CH).

$(C_5H_8O_2)_x(C_{17}H_{31}N_3O_4)_y$ Found: C 60.32 H 9.19 N 5.32; x = 81.75, y = 18.25.

GPC (THF)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	1898	4940	2.60

Poly{[1-(2-hydroxy-2-phenyl-ethyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea]-*co*-methyl methacrylate} (**P8**)

1-(2-Hydroxy-2-phenyl-ethyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M5**) was copolymerized with methyl methacrylate in dry DMF according to *General procedure.* White powder, mp 162–170°C; yield: 66%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3444.5, 3310.0 (ss, s, OH, NH), 1728.9 (ss, C=O, MMA), 1672.6 (m, C=O), 1665.6 (m, C=O, urea), 1482.8 (s, NH), benzene ring : 3029.7-3093.0 (ww), 702.3 (m), 758.6 (m).

^{1}H NMR ($CDCl_3$+DMSO-d_6, 300.1 MHz): δ = 0.50-2.50 (br.m, $2CH_3$, $2CH_2$-C), 3.21 (br.m, NCH_2), 3.59 (s, OCH_3), 4.74 (br.s, $C\underline{H}OH$), 7.20-7.55 (br.m, PhH); piperidine ring: 1.07, 1.25 (2s, 4Me), (br.m, $2CH_2$), 0.50-2.50 (br.m, $2CH_2$), 4.63 (br.s, CH).

$(C_5H_8O_2)_x(C_{22}H_{33}N_3O_3)_y$ Found: C 63.96 H 8.67 N 5.46 ; x = 79.22, y = 20.78.

GPC (THF)	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	2590	4688	1.81

Poly{[1-(2-hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethyl-piperidin-4-yl)-urea]-*co*-styrene} (**P9**)

1-(2-Hydroxypropyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M1**) was copolymerized with styrene in dry DMF according to *General procedure.* White powder, mp 163–167°C; yield: 69%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3416.4, 3282.8 (ss, s, OH, NH), 1728.9 (ss, C=O), 1672.6 (s, C=O, urea), 1503.9 (s, NH); styrene unit: 3029.7-3093.0 (mw), 1602.3 (m), 709.4 (ss), 758.6 (s).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 0.35–2.80 (br.m, $2CH_3$, CH_2-C, CH_2-CH), 3.50–4.15 (br.m, NCH_2), 4.66 (br.s, $C\underline{H}OH$), 6.30–7.50 (br.m, PhH); piperi-

dine ring: 1.20, 1.23 (2s, 4Me), (br.m, $2CH_2$), 0.35–2.80 (br.m, $2CH_2$), 3.50-4.15 (br.m, CH).

$(C_8H_8)_x$ $(C_{17}H_{31}O_3N_3)_y$ Found: C 80.09 H 8.60 N 5.19; x = 82.30, y = 17.70.

GPC	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	21,600	30,800	1.43

Poly{[1-(2,3-dihydroxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea]-*co*-styrene} (**P10**)

1-(2,3-Dihydroxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M2**) was copolymerized with styrene in dry DMF according to *General procedure.* White powder, mp 155–160°C; yield: 78%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3416.9, 3350.0 (ss, s, OH, NH), 1721.9 (ss, C=O), 1665.6 (w, C=O, urea), 1496.9 (s, NH); styrene unit: 3029.7–3093.0 (w), 1602.3 (w), 702.4 (ss), 758.6 (s).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 0.30–2.80 (br.m, CH_3, CH_2-C, CH_2-CH), 3.20–4.25 (br.m, NCH_2, C<u>H</u>$_2$OH), 4.75 (br.s, C<u>H</u>OH), 6.30–7.60 (br.m, PhH); piperidine ring: 1.12, 1.19 (2s, 4Me), (br.m, $2CH_2$), 0.30–2.80 (br.m, $2CH_2$), 3.20–4.25 (br.m, CH).

$(C_8H_8)_x(C_{17}H_{31}N_3O_4)_y$ Found: C 78.02 H 8.44 N 9.65; x = 82.54, y = 17.46.

GPC	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	22,100	35,300	1.60

Poly{[1-(2-hydroxy-3-phenoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea]-*co*-styrene} (**P11***)*

1-(2-Hydroxy-3-phenoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M3**) was copolymerized with styrene in dry DMF according to *General procedure.* White powder, mp 158–162°C; yield: 58%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (br. ss, OH, NH), 1728.9 (s, C=O), 1665.6 (s, C=O, urea), 1503.9 (s, NH), styrene unit : 3029.7-3093.0 (w), 1602.3 (m), 702.3 (s), 758.6 (s).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 0.50–2.50 (br.m, CH_3, CH_2-C, CH_2-CH), 3.0–4.15 (br.s, NCH_2, OCH_2), 4.20 (br.s, C<u>H</u>OH), 6.0–7.50 (br.m, PhH); piperidine ring: 1.11, 1.20 (2s, 4Me), 0.50-2.50 (br.m, $2CH_2$), 3.0–4.15 (br.s, CH).

$(C_8H_8)_x(C_{23}H_{35}N_3O_4)_y$. Found: C 79.89 H 8.70 N 4.51 ; x = 83.18, y = 16.82.

GPC	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	16,200	22,300	1.38

Poly{[1-(2-hydroxy-3-butoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea]-*co*-styrene} (**P12**)

1-(2-Hydroxy-3-butoxy-propyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M4**) was copolymerized with styrene in dry DMF according to *General procedure.* White powder, mp 155–158°C; yield: 55%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3437.5 (br. ss, OH, NH), 1728.9 (s, C=O), 1665.6 (s, C=O, urea), 1503.9 (s, NH), styrene unit : 3029.7-3093.0 (w), 1602.3 (m), 702.4 (s), 758.6 (s).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 0.50–2.50 (br.m, $CH_2CH_2CH_3$, CH_3, CH_2-C, CH_2-CH), 2.90–4.0 (br.s, NCH_2, OCH_2), 4.50 (br.s, CHOH), 6.30–7.50 (br.m, PhH); piperidine ring: 1.07, 1.19 (2s, 4Me), 0.50–2.50 (br.m, $2CH_2$), 3.72 (br.s, CH).

$(C_8H_8)_x(C_{21}H_{39}N_3O_4)_y$ Found: C 79.52 H 8.64 N 4.66; x = 82.89, y = 17.11.

GPC	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	27,200	38,200	1.40

Poly{[1-(2-hydroxy-2-phenyl-ethyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea]-*co*-styrene} (**P13**)

1-(2-Hydroxy-2-phenyl-ethyl)-3-(2-methylacryloyl)-1-(2,2,6,6-tetramethylpiperidin-4-yl)-urea (**M5**) was copolymerized with styrene in dry DMF according to *General procedure.* White powder, mp 150–157°C; yield: 69%.

IR (KBr): $\tilde{\nu}$ (cm^{-1}) = 3430.5, 3280.3 (ss, s, OH, NH), 1728.9 (ss, C=O), 1665.6 (s, C=O, urea), 1496.9 (s, NH); styrene unit : 3029.7–3093.0 (w), 1602.3 (w), 702.4 (ss), 758.6 (s).

^{1}H NMR ($CDCl_3$, 300.1 MHz): δ = 0.50–2.50 (br.m, CH_3, CH_2-C, CH_2-CH), 3.50 (br.s, NCH_2), 4.87 (br.s, CHOH), 6.0–7.50 (br.m, PhH); piperidine ring: 1.17, 1.24 (2s, 4Me), 0.50–2.50 (br.m, $2CH_2$), 4.62 (br.s, CH).

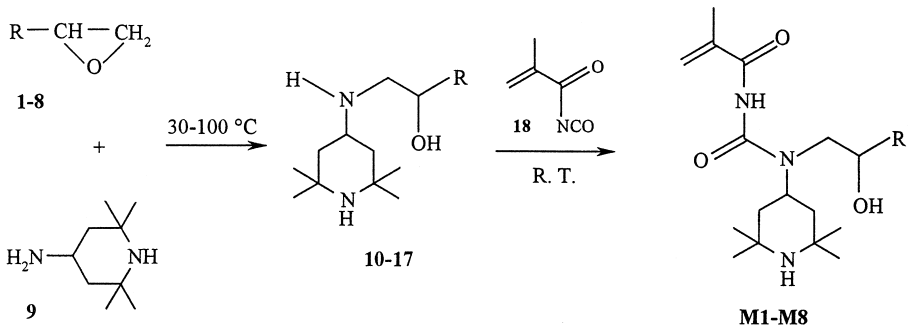
$(C_8H_8)_x(C_{22}H_{33}N_3O_3)_y$ Found: C 77.26 H 8.27 N 6.50 ; x = 71.33, y = 28.67.

GPC	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
	15100	28300	1.87

RESULTS AND DISCUSSION

Synthesis of Multifunctional Methacryloyl Ureas Carrying a Hindered Piperidine and a Hydroxyl Group

It has been reported that oxiranes can readily react with amines in stoichiometric quantities to form amino alcohols (20, 21). This reaction was used to synthesize several new derivatives of 2,2,6,6-tetramethylpiperidin-4-yl-amine by ring-opening reaction of various oxiranes (**1**–**8**) with 2,2,6,6-tetramethylpiperidin-4-yl-amine (**9**) (Sch. 1). Our experiments showed that 2-oxiranyl-methanol (**11**) displayed a high reactivity compared with other oxiranes selected in the experiments. For lower boiling point oxiranes, such as 2-methyloxirane (**10**, b.p. 34–35°C) and 2-ethyloxriane (**16**, b.p. 61–65°C), although a reflux condenser was used to avoid oxiranes loss through evaporation on heating, it is necessary to control the reaction temperature below their boiling point and to take a relatively long time to guarantee a high yield. Thus, the use of a sealed reaction device such as an autoclave is recommended. The reaction products, *N*-(2-hydroxyalkyl)-2,2,6,6-tetramethylpiperidin-4-yl-amine (**10–17**), were purified by distillation at reduced pressure and confirmed by ^{1}H- and ^{13}C NMR spectroscopy. These sterically hindered piperidine derivatives synthesized have two reactive groups and may be thus used for further modification. MAI was selected for this purpose. It has a polymerizable double bond and a highly reactive acyl isocyanate group (22–24). Either end group of the molecule may be reacted independently, leaving the other func-



	1, 10	2, 11	3, 12	4, 13	5, 14	6, 15	7, 16	8, 17
	M1	**M2**	**M3**	**M4**	**M5**	**M6**	**M7**	**M8**
R	CH_3	CH_2OH	CH_2OPh	CH_2OBu^n	Ph	CH_2OBu^t	C_2H_5	$C_6H_{13}^n$

Scheme 1. Synthesis of methacryloyl ureas with a hindered piperidine and a hydroxyl group (**M1**–**M8**).

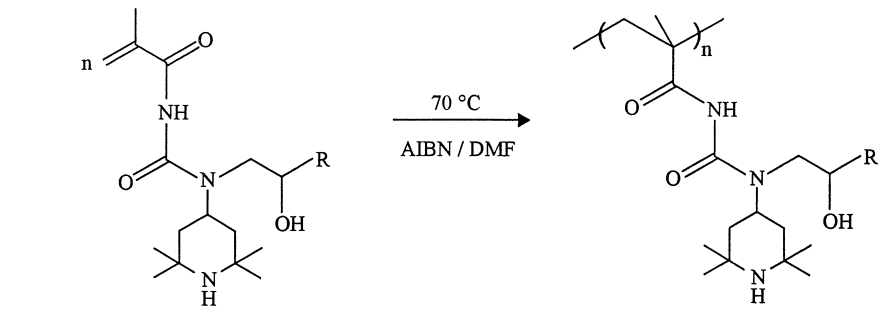
tion available for subsequent reactions. 2-Methylacryloyl isocyanate reacts cleanly with amine or hydroxy compounds to form vinyl-substituted acyl ureas or carbamates (18, 24, 25). Its high reactivity allows the easy introduction of vinyl functionality into various compounds, which have hitherto resisted such treatment. Therefore, multifunctional methacryloyl ureas (**M1–M8**) containing not only a hindered piperidine moiety but also a free hydroxyl group were obtained by subsequent addition of *N*-(2-hydroxyalkyl)-2,2,6,6-tetramethylpiperidin-4-yl-amine (**10**–**17**) to 2-methacryloyl isocyanate (Scheme 1). The addition was fast and exothermic at room temperature. The formation of urethanes was not observed under the applied conditions. The structures of methacryloyl ureas with a hindered piperidine and a hydroxyl moiety were characterized by FI-IR and ^{1}H- and ^{13}C NMR spectroscopy.

Polymerization of Multifunctional Methacryloyl Ureas Carrying a Hindered Piperidine and a Hydroxyl Group

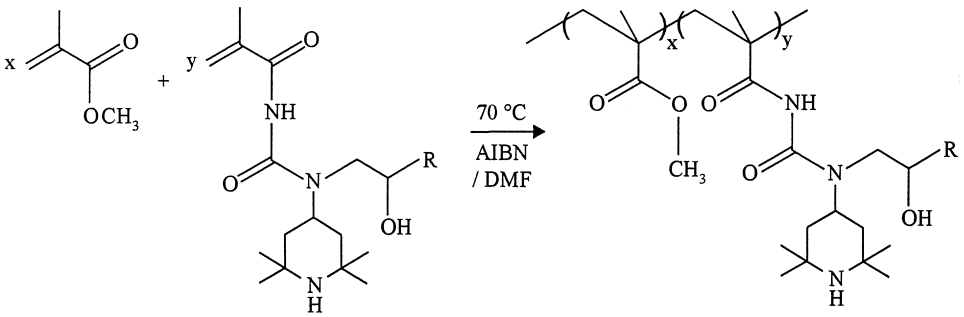
The new monomers synthesized (**M1–M5**) were homopolymerized, and copolymerized with methyl methacrylate and styrene at 70°C using AIBN as initiator, and dry *N,N*-dimethylformamide as solvent (Sch. 2). The polymers were purified by reprecipitation from methanol into diethyl ether, and characterized by FI-IR and ^{1}H- and ^{13}C NMR spectroscopy, elemental analysis and GPC.

The disappearance of the double bond peaks at 1630.5–1637.5 cm^{-1} in IR and the signals of the vinyl protons at 5.43–5.84 ppm in ^{1}H NMR is clearly documented in all cases. The other characteristic bands in IR and characteristic peaks in NMR were identical in terms of the absorption presence. This revealed that the monomers have been incorporated into the corresponding homopolymers or copolymers.

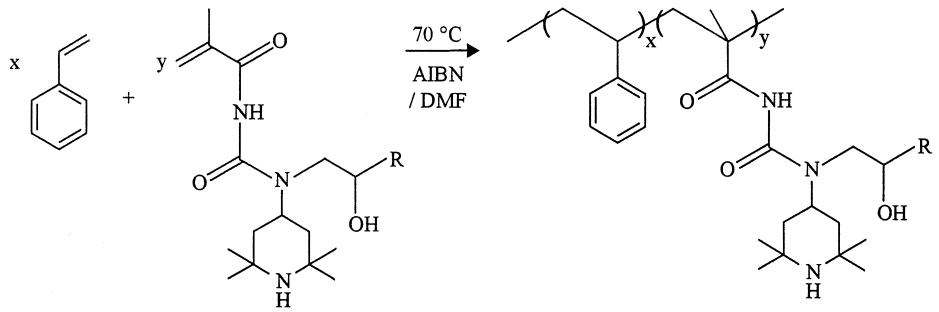
The monomers **M1, M2,** and **M5** were copolymerized with methyl methacrylate (MMA) in a molar ratio of 1:2, and the monomers **M1–M5** were copolymerized with styrene (St) in a molar ratio of 1:3. The composition of the resulting copolymers were determined with elemental analysis based on the nitrogen content (% N) and are summarized in Table 2. For the monomers **M1**–**M5,** the content of each kind of monomer in the copolymer is lower than that in the feed. This suggests that these new monomers are less reactive than both styrene and methyl methacrylate. The number-average ($\bar{M}_n$), weight-average ($\bar{M}_w$) molecular weights and the molecular weight distribution ($\bar{M}_w$ /$\bar{M}_n$) of all polymers, presented in Table 2, were determined by GPC with polystyrene as standard. The lower molecular weights of the copolymers **P6–P8** may be due to bad solubility of these copolymers in THF. Some other parameters are also given in Table 1 and 2. Due to the pronounced polar structure of the urea moieties, the synthesized polymers show to a certain degree a crystalline behavior, which is reflected in the relative high melting temperatures of these polymers.



M1-M5 **P1-P5**



MMA **M1, M2, M5** **P6-P8**



ST **M1-M5** **P9-P13**

	M1, P1, P6, P9	M2, P2, P7, P10	M3, P3, P11	M4, P4, P12	M5, P5, P8, P13
R	CH_3	CH_2OH	CH_2OPh	CH_2OBu^n	Ph

Scheme 2. Polymerization of methacryloyl ureas with a hindered piperidine and a hydroxyl group (**M1–M5**).

Table 1. Some Parameters of Homopolymers with a Hindered Piperidine and a Hydroxyl Group

Polymer	Monomer	mp (°C)	Yield (%)	$\overline{M}_n$ ($\overline{P}_n$)	$\overline{M}_w$ ($\overline{P}_w$)	$\overline{M}_w / \overline{M}_n$
P1	**M1**	194–200	66	11400 (35)	25300 (78)	2.22
P2	**M2**	178–185	73	10200 (30)	31800 (93)	3.12
P3	**M3**	166–171	51	3900 (9)	6800 (16)	1.74
P4	**M4**	169-174	54	8000 (20)	21000 (53)	2.63
P5	**M5**	172–177	52	7700 (20)	12500 (32)	1.62

CONCLUSION

Eight new sterically hindered piperidine derivatives were prepared by chemical modification of the commercially available 2,2,6,6-tetramethyl piperidin-4-yl-amine. Thus novel multifunctional methacryloyl ureas containing a hindered piperidine and a hydroxyl group were synthesized by addition of these sterically

Table 2. Some Parameters of Copolymers with a Hindered Piperidine and a Hydroxyl Group was Allowed to Proceed for 2.75 Hours

Polymer	M_1	M_2	f_1	F_1	mp (°C)	Yield	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w / \overline{M}_n$
P6	**M1**	**MMA**	33.33	21.96	160–168	68	3170 [a]	5484	1.73
P7	**M2**	**MMA**	33.33	18.25	96–106	78	1898 [a]	4940	2.60
P8	**M5**	**MMA**	33.33	20.78	162–170	66	2590 [a]	4688	1.81
P9	**M1**	**St**	25.00	17.70	163–167	69	21600	30800	1.43
P10	**M2**	**St**	25.00	17.46	155–160	78	22100	35300	1.60
M11	**M3**	**St**	25.00	16.82	158–162	58	16200	22300	1.38
M12	**M4**	**St**	25.00	17.11	155–158	55	27200	38200	1.40
M13	**M5**	**St**	33.00	28.67	150–157	69	15100	28300	1.87

f_1: molar fraction of monomer M_1 in the feed, F_1: molar fraction of monomer M_1 in the copolymer.

[a]Hewlett Packard HP 1090 GPC system with THF as solvent.

hindered piperidine derivatives on 2-methylacryloyl isocyanate. These novel multifunctional methacryloyl urea monomers were polymerized and copolymerized with other vinyl monomers into new polymeric sterically hindered amines, which can be used as polymeric additives against oxidative degradation reaction of polymers.

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