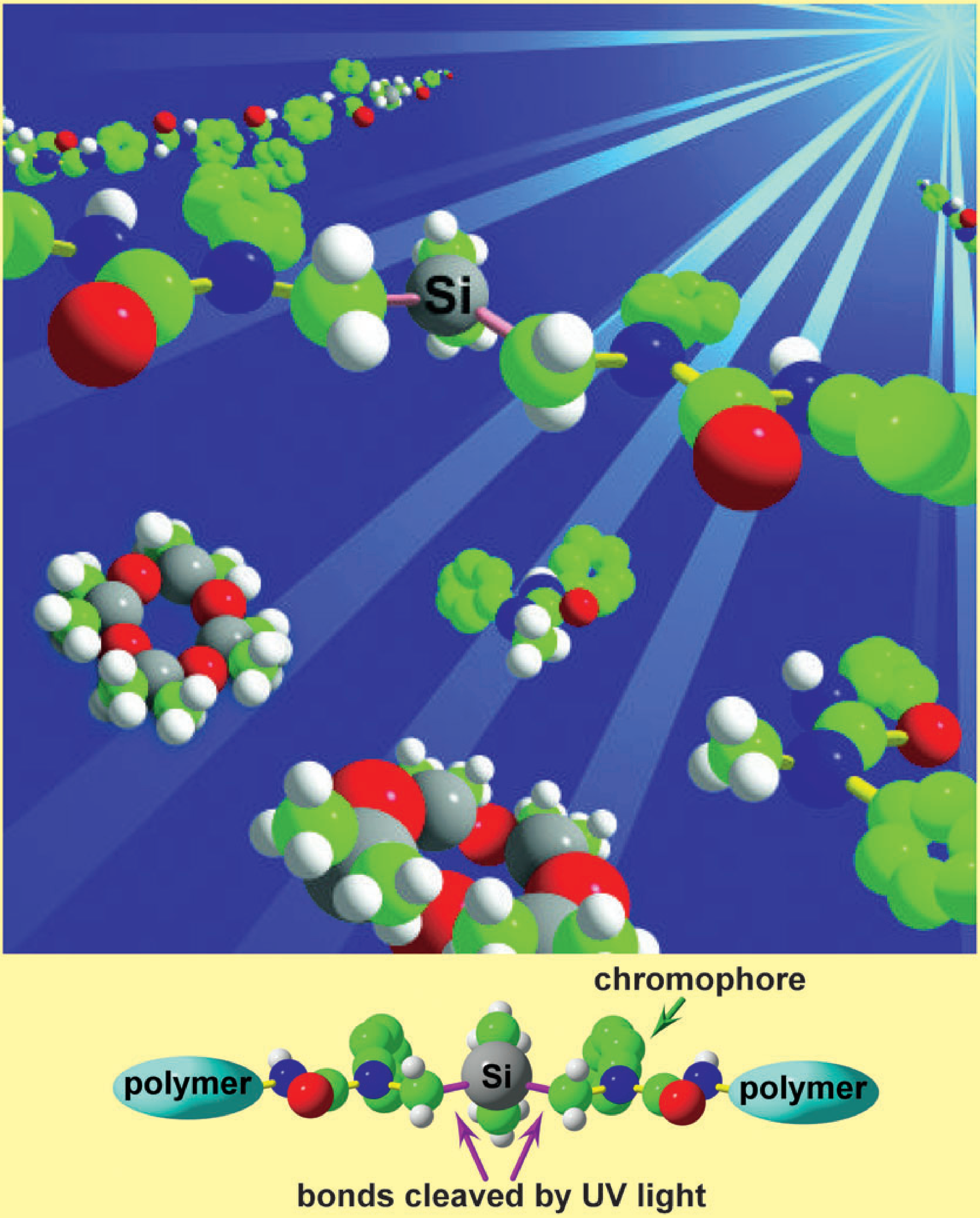
Photodegradable Silicon-Containing Polyureas



See the following pages for more details...

DOI: 10.1002/chem.200401321

Design, Synthesis, and Photodegradation of Silicon-Containing Polyureas

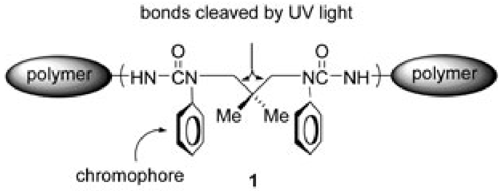
Jih Ru Hwu*[a, b] and Ke Yung King[a]

Abstract: Novel *N*-phenyl aromatic polyureas containing bis[(*N*,*N*′-diphenylureylene)methyl]silane units in the skeleton were designed as a new type of photodegradable polymer. These materials were successfully prepared in 88–93 % yields by copolymerization of bis(anilinomethyl)dimethylsilane and dianilino-*p*-xylene with 4,4′-methylene-bis(phenylisocyanate). Their photodegradability was found to be 10.1 times higher than that of polymers of similar structure, but lacking the silyl unit. Furthermore, the photodegradation mechanism of polyureas was elucidated, and involves single-electron transfer between silyl and carbonyl groups, silyl group migration, and solvolysis. These novel polymers are potential materials of high economic value for use in photolithography and microelectronics.

Keywords: photolysis · polymerization · polymers · silicon · solvolysis

Introduction

Polyureas have been widely used during the past three decades as industrial cast elastomers.[1–5] These materials are essentially nondegradable and, consequently, their use in large quantities can cause serious waste disposal problems. Protection of the global environment poses a major challenge to chemists in the development of novel, degradable polymers. Moreover, photodegradable polymers play a vital role in the photolithography and microelectronics industries.[6–17] These materials can be prepared by the addition of suitable light-sensitive chromophores onto "normal" polymers. The product can be used as a photoresistor in the fabrication of integrated circuits. Recently, polyureas have been used as negative resistance materials, and in an all-dry lithographic process.[18–20] In response to environmental concerns, and the demands of the modern electronics industry, we investigated the synthesis of a novel type of silicon-containing, photodegradable polyurea (**1**).



Incorporation of a bis[(*N*,*N*′-diphenylureylene)methyl]silane unit into polyureas allowed their photodegradability to be improved dramatically, relative to traditional polyureas. The degradation mechanism could involve an SET process; the photofragmentation was attributed to the cleavage of σ_{C-Si} bonds.

Results

Model study on the cleavage of an Si−C bond in β-silyl ureas: We performed model studies on monomeric ureas **4a–d** to test the possibility of cleaving an Si−C bond in the skeleton of polyureas **1**. Preparation began with silicon-containing halides **2a–d**, as shown in Scheme 1. In the first step, a series of (anilinomethyl)silanes **3a–d** were synthesized in 68–76 % yields by reaction of silylmethyl halides **2a–d** with aniline in toluene at 130 °C. Next, we treated these (anilinomethyl)silanes with phenylisocyanate in CH_2Cl_2 at 25 °C. The corresponding *N*,*N*′-diphenylurea adducts **4a–d** were produced in 87–95 % yields.

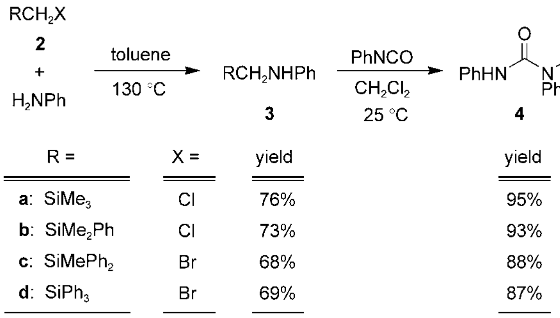
In the second step, we irradiated silicon-containing urea **4a** in a mixture of $CHCl_3/CH_3OH$ (9:1) with UV light ($\lambda >$ 300 nm) for 12 h (Scheme 2). Photodesilylation took place

---

[a] Prof. J. R. Hwu, Dr. K. Y. King
Department of Chemistry, National Tsing Hua University
Hsinchu, Taiwan 30013 (Republic of China)
Fax: (+886) 3-572-1594
E-mail: jrhwu@mx.nthu.edu.tw

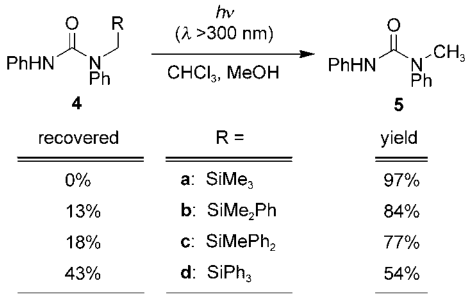
[b] Prof. J. R. Hwu
Center for Nano-Science and Technology
University System of Taiwan (Republic of China)

DOI: 10.1002/chem.200401321



R =	X =	yield (3)	yield (4)
a: $SiMe_3$	Cl	76%	95%
b: $SiMe_2Ph$	Cl	73%	93%
c: $SiMePh_2$	Br	68%	88%
d: $SiPh_3$	Br	69%	87%

Scheme 1. Synthesis of silyl-containing *N,N'*-diphenylureas **4a–d**.

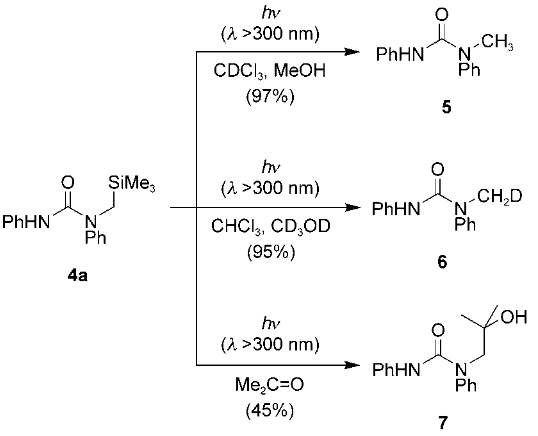


recovered	R =	yield
0%	**a**: $SiMe_3$	97%
13%	**b**: $SiMe_2Ph$	84%
18%	**c**: $SiMePh_2$	77%
43%	**d**: $SiPh_3$	54%

Scheme 2. Photolysis of silyl-containing *N,N'*-diphenylureas **4a–d**, during which photodesilylation occurred to give *N,N'*-diphenyl-*N*-methylurea (**5**).

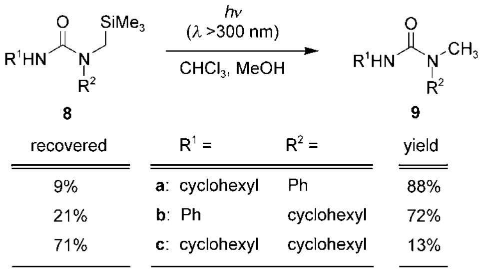
to give *N,N'*-diphenyl-*N*-methylurea (**5**) in 97 % yield. We applied the identical conditions to substrates **4b–d** to investigate the effect of the substituents attached to the silicon atom. The silicon atoms in these substrates contained one, two, or three phenyl groups. Photolysis of **4b–d** for 12 h afforded the same product **5** in 54–84 % yields; a longer irradiation time enabled a greater conversion to **5** (>85 %).

Performance of the same reaction from **4a** by replacement of methanol with CD_3OD gave *N,N'*-diphenyl-*N*-[D_1]-methylurea (**6**) in 95 % yield (Scheme 3). Furthermore, photolysis of **4a** in acetone afforded the solvent-incorporated product **7** in 45 % yield.



Scheme 3. Photolysis of silyl-containing *N,N'*-diphenylurea **4a** to produce the solvent-incorporated products **5–7**.

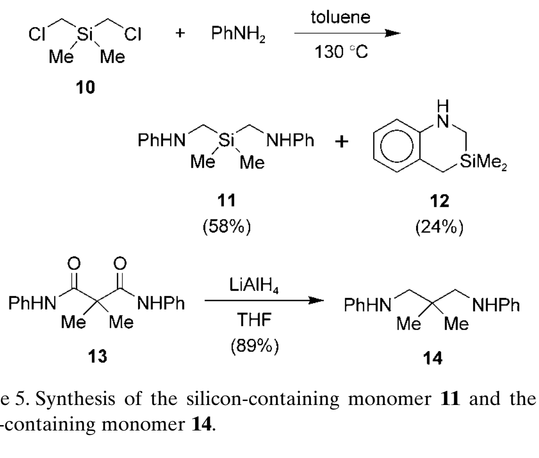
To corroborate the importance of the chromophore, we replaced the phenyl group with a cyclohexyl ring in the substrate (**8a–c**). These compounds were prepared by using the same synthetic strategies as depicted in Scheme 1; *N*-(trimethylsilylmethyl)cyclohexylamine and cyclohexylisocyanate were used as the starting materials. Their photolytic results are shown in Scheme 4, in which desilylation products **9a–c** were isolated in 13–88 % yields. The yields were highly dependent upon whether a chromophore exists in the substrate.



recovered	R^1 =	R^2 =	yield
9%	**a**: cyclohexyl	Ph	88%
21%	**b**: Ph	cyclohexyl	72%
71%	**c**: cyclohexyl	cyclohexyl	13%

Scheme 4. Photolysis of silyl-containing ureas **8a–c**, demonstrating the importance of the chromophore.

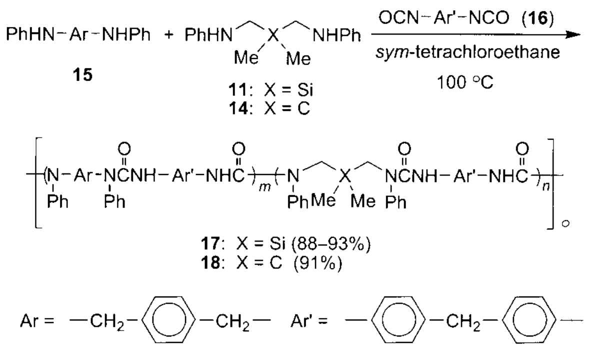
Synthesis of silicon-containing polyureas: We designed a means of synthesizing novel silicon-containing polyureas by attaching the bis[(*N,N'*-diphenylureylene)methyl]silane units to the main chain (**1**). Consequently, a novel dianilino compound bis(anilinomethyl)dimethylsilane (**11**) was required, and this was prepared (58 % yield) by the coupling of bis(chloromethyl)dimethylsilane (**10**) with excess aniline in toluene at 130 °C (Scheme 5). This reaction also led to a byproduct **12** in 24 % yield through intramolecular cyclization.



Scheme 5. Synthesis of the silicon-containing monomer **11** and the non-silicon-containing monomer **14**.

Furthermore, we planned to compare the photodegradability of the silicon-containing and the non-silicon-containing polymers. Thus, 2,2-dimethyl-*N,N'*-diphenyl-1,3-propanediamine (**14**) was required, which did not contain a silyl unit. This compound was obtained in 89 % yield by reduction of the corresponding bisamide **13** with lithium aluminum hydride in THF (Scheme 5).

For the syntheses of polyureas, we added 4,4′-methylenebis(phenylisocyanate) (**16**) to a mixture of non-silicon diamine **15** and silyldiamine monomer **11** in *sym*-tetrachloroethane at 100 °C (Scheme 6). The former was in a fixed equivalent and the latter was present in various amounts. Accordingly, polyureas **17a–f** with different percentages of silicon-containing units were produced in 88–93 % yields. By the same procedure, polymers **18** were synthesized in 91 % yield by using the carbon analog **14** to replace silyldiamine **11**. The molecular weights, polydispersity index, and glass transition points (T_g) of these novel polymers (i.e., **17a–f** and **18**) are listed in Table 1.



Scheme 6. Copolymerization of monomers with 4,4′-methylenebis(phenylisocyanate) in *sym*-tetrachloroethane at 100 °C.

Table 1. Physical properties of *N*-phenylated aromatic polyureas.

Polyureas	% of Si-monomer[a]	M_w [g mol^{-1}][b]	M_n [g mol^{-1}][b]	I_p[c]	T_g [°C][d]
17a	0.00	49.200	25.900	1.9	125
17b	6.30	54.900	23.900	2.3	121
17c	11.7	52.100	21.700	2.4	118
17d	15.1	50.500	16.750	3.0	113
17e	16.3	40.610	13.100	3.1	108
17f	20.5	28.600	8.150	3.5	104
18	8.40[e]	46.100	24.200	1.9	123

[a] Percentage of monomer **11** in polymers **17**, determined by conducting ^{1}H NMR spectroscopy. [b] Determined by performing gel permeation chromatography. [c] Polydispersity index. [d] Determined by performing differential scanning calorimetry at a heating rate of 10 °C min^{-1}. [e] 2,2-Dimethylpropane unit.

The IR spectra of the polyureas exhibited absorption bands at 3425 cm^{-1} for the non-hydrogen-bonded N−H, 3345 cm^{-1} for the hydrogen-bonded N−H, 1677 cm^{-1} for the C=O stretching vibration, and 1248 cm^{-1} for the Si−C stretching vibration. These polyureas were found to be soluble in organic solvents, such as chloroform, THF, DMF, and DMSO.

Studies on photodegradability of silicon-containing polyureas: We conducted photolysis of the novel polymers **17a–c** and **18** in $CHCl_3/CH_3OH$ (0.26 % w/v) at room temperature to investigate their degradability. A 450 W medium-pressure mercury UV lamp and a Pyrex filter ($\lambda \geq 300$ nm) were used to generate light with intensity of 26.5 ± 0.8 mW cm^{-2}. Polymers **17a**, **17b**, and **17c** possessed 0, 6.3, and 11.7 % of the silicon-containing unit, respectively; polymers **18** possessed 8.4 % of the 2,2-dimethylpropane unit.

The results shown in Figure 1 indicate the average numbers of bonds broken ($[(M_n)_o/M_n]-1$) in polymers **17a–c** and **18**. The term $(M_n)_o$ represents the molecular weights of these polyureas before their exposure to UV light; M_n represents their molecular weights after irradiation for a certain period of time. The quantities of M_n were determined by performing gel permeation chromatography (GPC) at various time intervals. Polyureas **17a** and **18** were found to be primarily resistant to photolysis. In contrast, silicon-containing polyureas **17b** and **17c** manifested great photodegradability.

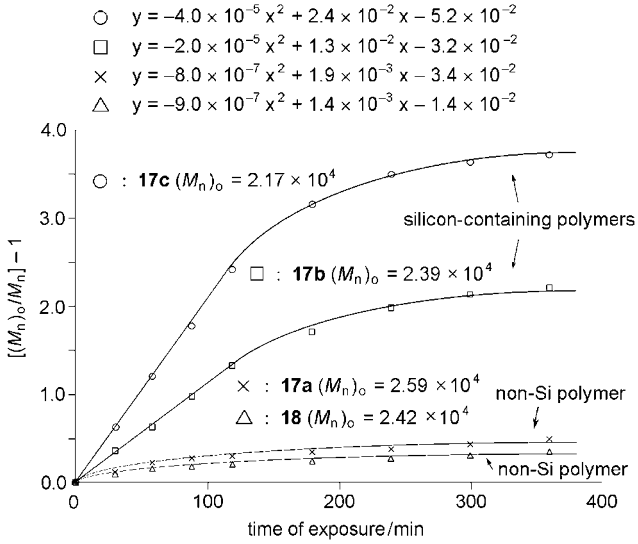
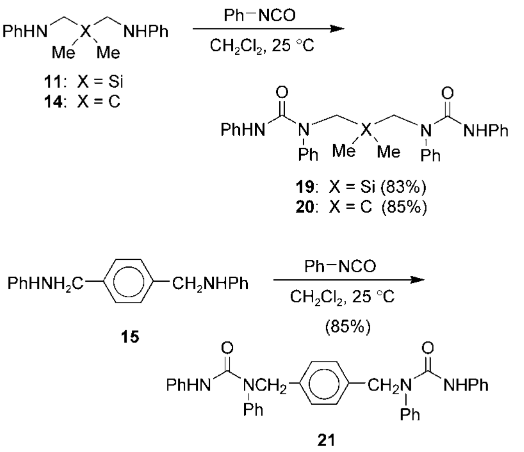


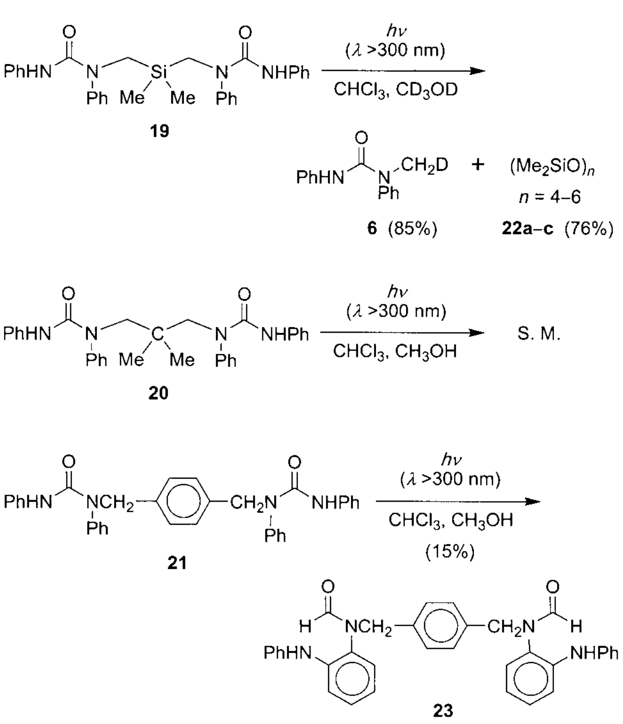
Figure 1. Average numbers of bonds broken ($[(M_n)_o/M_n]-1$) as a function of irradiation time using UV light of $\lambda \geq 300$ nm and intensity 26.5 ± 0.8 mW cm^{-2} at room temperature.

Mechanistic studies on photodegradability of silicon-containing ureas: To explore the mechanism of photodegradation of the novel silicon-containing polyureas, we investigated the photolytic behavior of monomers **19–21**. The structural features of these model molecules with low molecular weights are similar to a segment in polyureas **17b–f** and **18**. Thus, we synthesized the monomers **19–21** (83–85 % yields) by reacting the corresponding dianilino compounds (1 equivalent) with phenylisocyanate (2 equivalents) in CH_2Cl_2 at 25 °C (Scheme 7).

Photolysis of **19** in a mixture of $CHCl_3/CD_3OD$ for 6.0 h gave *N*,*N*′-diphenyl-*N*-[D$_1$]-methylurea (**6**) in 85 % yield, and the cyclic siloxanes **22a–c** as the byproducts in 76 % yield (Scheme 8). In contrast, photolysis of the non-silicon-



Scheme 7. Synthesis of the model molecules **19**–**21** with low molecular weights, which are similar to a segment in polyureas.



Scheme 8. Mechanistic studies on the photodegradability of silicon-containing ureas **19**–**21**. S.M. = starting material.

containing compound 1,3-bis(*N*,*N'*-diphenylureylene)-2,2-dimethylpropane (**20**) under the same conditions led to the recovery of almost all of the starting material ($\geq$95% yield). Furthermore, the monomer **21** was irradiated in $CHCl_3$/MeOH for 24 h to afford bis[*N*-(2-anilinophenyl)formamide]-*p*-xylene (**23**) in 15% yield only. Its ^1H NMR spectrum exhibited a peak at $\delta = 9.96$ ppm for the CHO proton; its IR spectrum displayed absorption bands at 2836 and 2743 cm^{-1} for the aldehydic C–H stretching vibration, and at 1692 cm^{-1} for the C=O stretching vibration.

Discussion

Factors influencing the photodegradability of the novel silicon-containing bisurea unit: The polymers **1** contain a novel photodegradable unit, in which a silyl group joins two urea functioinalities. The presence of a silicon atom was essential for their photodegradability, as reflected by the results from the photolysis of the model compound **19**, a silicon-containing bisurea. As shown in Scheme 8, the outcomes were found to be contrary to those from its carbon analog **20**, in which a carbon atom replaces the silicon atom in **19**. Irradiation of **19** in a mixture of $CHCl_3$ and CD_3OD produced 1.7 equivalents of duteriated urea **6**. Upon solvolysis, both of the Si–CH_2N single bonds in the substrate **19** were cleaved efficiently. The dimethylsilyl residues were then cyclized in situ to give cyclosiloxanes **22a**–**c**. On the other hand, we found that the closely related bisurea **20** remained inert to UV light.

To investigate which bonds were cleaved by UV light, we performed control experiments, as shown in Scheme 3. Results from the conversions of **4a**→**5** and **4a**→**6** indicate that the σ_{Si-CH_2N} bond was broken in silicon-containing urea **4a**. The trimethylsilyl group can be replaced by either the acidic proton in methanol or the deuterium atom in CD_3OD. This proton or deuterium atom, however, did not come from the C–H of chloroform or the C–D of CD_3OD.

The $-C(=O)NR(CH_2SiMe_3)$ moiety exists in both photodecomposable urea **4a** and *N*-[(trimethylsilyl)methyl]phthalimide; the former was developed by us and the latter was reported by Mariano and co-workers,[21] who irradiated *N*-[(trimethylsilyl)methyl]phthalimide to give novel azomethine ylides by single-electron transfer (SET) from σ_{C-Si} to $\pi_{C=O}$, which was followed by a silyl group migration. Thus, cleavage of a σ_{C-Si} bond occurs in [(trimethylsilyl)methyl]-phthalimide. Our results from the reaction of **4a**+acetone→**7** indicate that the entire process included photodesilylation and a 1,2-addition, which is consistent with the case of silicon-containing phthalimides. Thus, an azomethine ylide is probably generated as the intermediate.

We found that variation in the substituents on the silicon atom affected photodegradability of silicon-containing ureas (Scheme 2). Irradiation of ureas **4a**–**d** in $CHCl_3$/MeOH for 12 h gave *N*,*N'*-diphenyl-*N*-methylurea (**5**) as the exclusive product, along with recovered starting materials. Among **4a**–**d**, the trimethyl analog **4a** gave the highest yield (97%) of the desilylated product. The yields decreased gradually as the methyl groups on the silicon atom were replaced by phenyl groups. The lowest yield was 54% for **4d**, which bears an $SiPh_3$ group. This could be due to the steric effect that obstructed the desilylation process.

Photolysis of silicon-containing urea **8c** gave the corresponding desilylated urea **9c** in only 13% yield (Scheme 4). The poor photodegradability of **8c** may be due to its lack of a chromophore. For a substrate bearing only one phenyl ring at the nitrogen atom on either side of the carbonyl groups (e.g., **8a** and **8b**), the photodegradability was improved significantly to 72–88% yields. By having two phenyl groups, substrate **4a** gave the photodesilylation product (**5**) in an almost quantitative yield (97 %). Thus, the presence of a chromophore in the photodegradation unit of polyureas **1** is essential.

Comparison of photodegradability of various polyureas: We were able to incorporate the photodegradable unit $-[HNC(=O)NPhCH_2SiMe_2CH_2NPhC(=O)NH]-$ into polyureas **17b–f** in different amounts (6.3–20.5 %). These polyureas originated from dianilino-*p*-xylene (**15**) and 4,4′-methylenebis(phenylisocyanate) (**16**, Scheme 6). The photodegradability of the novel silicon-containing polymers (e.g., **17b** and **17c**) was compared with that of the parent polyureas **17a**, as well as the analogous carbon-containing polyureas **18**. The degradability is reflected by the average number of bonds broken ($[(M_n)_o/M_n]-1$) in different time intervals.

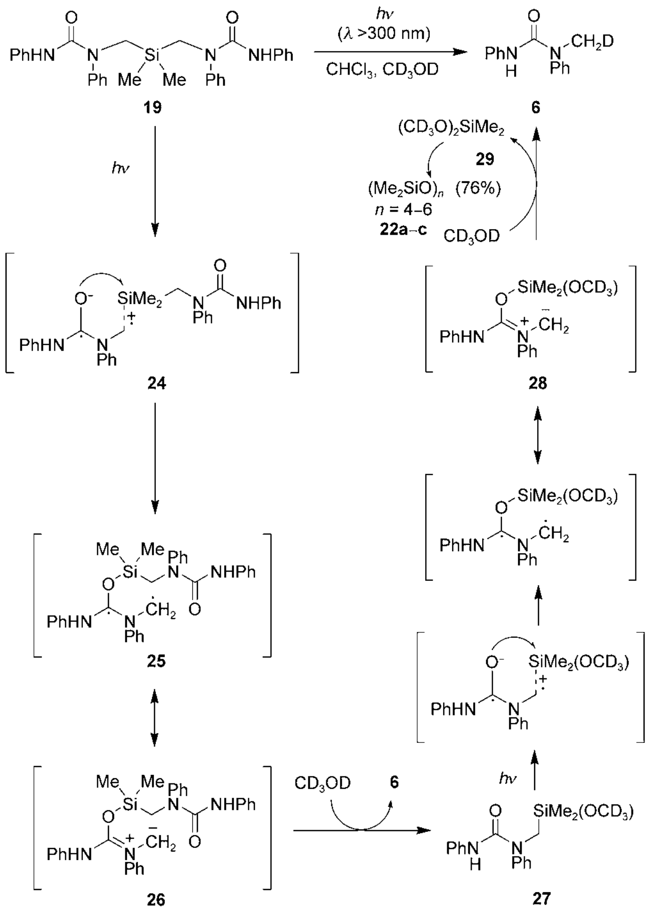
The results shown in Figure 1 indicate that the non-silicon-containing polymers **17a** and **18** exhibited very low photodegradability. These polymers possessed the skeleton of the parent polyurea either alone or with the partial 1,3-bis(*N*,*N*′-diphenylureylene)-2,2-dimethylpropane unit. We calculated the degradability to be 7.3 % for **18**, based on the ratio of the average numbers of bonds broken to the number of their degradable units (Table 2). In sharp contrast, the degradability reached up to 70.7 and 73.6 % for silicon-containing polyureas **17b** and **17c**, respectively. These results confirm our rationale that the photodegradability is attributable to the bis[(*N*,*N*′-diphenylureylene)methyl]silane unit. It can increase the degradability to as much as 10.1 times higher than that of the polymers lacking this silyl unit (73.6 % compared to 7.3 %).

Table 2. Results of photodegradation of polyureas **17a–c** and **18** upon irradiation for 4 h.[a]

Polyureas	Average number of bonds broken[b]	Number of degradable units[c]	Efficiency [%][d]
17a	0.38	0	–
17b	1.98	2.80	70.7
17c	3.49	4.74	73.6
18	0.28	3.82	7.3

[a] Polyureas in $CHCl_3$/MeOH were irradiated at room temperature under nitrogen by using UV light of $\lambda \geq 300$ nm, 450 W, and intensity 26.5 ± 0.8 mW cm^{-2}. [b] $[(M_n)_o/M_n]-1$. [c] Calculated from $(M_n/M_m) \times$ (% of Si-containing monomer), in which the term M_m represents the average molecular weight of monomers. [d] Reflected by the (average number of bonds broken)/(number of degradable units).

Photodegradation pathway of silicon-containing polyureas: In view of the results of photolysis shown in Schemes 2, 3, and 8, we envisioned a plausible pathway for the degradation of the silicon-containing polyureas **1**. As shown in Scheme 9, the monomer bis(ureylenemethyl)dimethylsilane **19** is used to represent the segment $-[HNC(=O)NPhCH_2Si-Me_2CH_2NPhC(=O)NH]-$ in polyureas **1**. Upon irradiation with UV light, (bisureylene)silane **19** gives diradical **25** through a single-electron transfer from σ_{C-Si} to $\pi_{C=O}$. A silyl group then transfers from a carbon atom to an oxide center in intermediate **24**.[21] A canonical form of diradical **25** is azomethine ylide **26**, which can trap a deuterium atom from the solvent CD_3OD. Upon solvolysis, deuteriated urea **6** is generated along with siloxide **27**. At this stage, the first $Si-CH_2N$ bond in **19** is cleaved.



Scheme 9. A plausible mechanism of the photodegradation of silicon-containing polyureas.

Under photolytic conditions, silicon-containing urea **27** can be converted to azomethine ylide **28** by the same mechanism as for the process of **19**→**24**→**25** and **26** (Scheme 9). Trapping of a deuterium atom from CD_3OD by **28** would occur again to give the second equivalent of deuteriated urea **6**, along with $[D_6]$(dimethoxy)dimethylsilane **29**. Consequently, the second $Si-CH_2N$ bond in **19** is also cleaved. Meanwhile, cyclization to **29** gives a mixture of cyclosiloxanes **22a–c**.[22]

We found that the parent, non-silicon-containing polyureas **17a** possessed limited photodegradability (Figure 1). The results of the third reaction in Scheme 8 suggest a reason for this. Upon irradiation with UV light for 24 h, bisurea **21** underwent photochemical rearrangement to give bisamide **23** in a modest yield (15 %). The ureido $N-C(=O)$ single bond therein was found to be broken, which probably also occurred in polyureas **17a** during their photodegradation.

Conclusion

The silicon-containing moiety $-[HNC(=O)NPhCH_2SiMe_2CH_2\,NPhC(=O)NH]-$ was developed as a novel and efficient photodegradable unit in polyureas. Copolymerization of 4,4′-methylenebis(phenylisocyanate) (**16**) with dianilino-*p*-xylene (**15**) in the presence of various amounts of bis(anilinomethyl)dimethylsilane (**11**) gave silicon-containing polyureas (**17b–f**). All of these novel polymers were found to have high degradability upon UV irradiation. In contrast, the parent non-silicon-containing polyureas **17a** and the analogous carbon-containing polyureas **18** exhibited very low photodegradability.

The results of our mechanistic studies indicate that both of the σ_{Si-CH_2N} bonds in the $-[HNC(=O)Ph\mathbf{NCH_2{-}SiMe_2{-}CH_2N}PhC(=O)NH]-$ unit were cleaved by a sequential process that includes single-electron transfer, silyl group migration, and solvolysis.

Experimental Section

General: All reactions were carried out using oven-dried glassware (120 °C) under an atmosphere of nitrogen, unless indicated otherwise. Photolytic experiments were performed at room temperature by using a medium-pressure mercury lamp (450 W) from Hanovia. The light intensity was measured by using a PowerMax® 5200 laser power meter.

(Bromomethyl)diphenylmethylsilane (**2c**), (bromomethyl)triphenylsilane (**2d**), dianilino-*p*-xylene (**15**), 2,2-dimethyl-*N*,*N*′-diphenyl malonamide (**13**), and *N*-(trimethylsilylmethyl) cyclohexylamine were prepared according to literature methods.[23–27] The experimental details for compounds **6**, **11**, and **19** will be reported elsewhere. The spectroscopic data and melting points of silicon-containing products **3a–d**,[28,29] **4a–d**, and **8a–c** are listed in Table 3.

Analytical thin layer chromatography (TLC) was performed by using precoated plates (silica gel 60 F-254), purchased from Merck. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed by using a Hewlett–Packard 5890 Series II instrument, equipped with a 25 m cross-linked methyl silicone gum capillary column (0.32 mm internal diameter). Nitrogen gas was used as a carrier gas and the flow rate was kept constant at 14.0 mL min^{-1}. The retention time t_R was measured under the following conditions: injector temperature 260 °C, initial temperature for the column 70 °C, duration 2 min, increment rate 15 °C min^{-1}, and final temperature for the column 280 °C. Gas chromatography and low resolution mass spectral analyses were performed by using a Hewlett–Packard 5890 Series II instrument, equipped with a Hewlett–Packard 5971A Mass Selective Detector and a capillary HP-1 column. Purification by gravity column chromatography was performed using Merck Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM).

Molecular weights of all synthesized polymers were determined by performing GPC on the basis of polystyrene standards. Three columns packed with 10^3, 10^4, and 10^5 Å-styragel, respectively, were arranged in sequence onto a Hewlett–Packard 1050 series HPLC instrument, equipped with ultraviolet and refractive index detectors. The flow rate was kept at 1.0 mL min^{-1} for a sample containing the synthesized polymers (0.26 mg mL^{-1}) in THF at 45 °C. The thermal properties of all synthesized polymers were analyzed by using Seiko SSC 5000, DSC 200, and TGA 300 instruments, with increments of 10 °C min^{-1}.

Preparation of (anilinomethyl)silanes 3a–d: Aniline (5 equiv) was added to a solution containing a haloalkylsilane (**2a–d**, 764 mg–1.49 g, 1 equiv) in toluene (10 mL) After the reaction mixture was stirred at 130 °C for 12 h, it was quenched with water (2.0 mL) at 25 °C, neutralized with aqueous HCl (1.0 N), and extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (5.0 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure. The residue was purified by performing column chromatography with silica gel to give the desired (anilinomethyl)silanes **3a–d** in 68–76 % yields, as a yellow oil or white solids with purity > 99.5 %, as determined by conducting GC.

Preparation of *N*,*N*′-diphenyl-*N*-(silylmethyl)ureas 4a–d: Phenylisocyanate (1 equiv) was added to a solution containing an (anilinomethyl)silane (**3a–d**, 103.2–523.6 mg, 1 equiv) in CH_2Cl_2 (10 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched with water (2.0 mL) at 25 °C, and extracted with Et_2O (3 × 10 mL). The combined organic layers were washed with saturated aqueous NaCl (5.0 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure. The residue was purified by performing column chromatography with silica gel to provide the desired *N*,*N*′-diphenylureas **4a–d** in 87–95 % yields, as white solids with purity > 99.5 %.

Standard procedure 1 for the photolysis of *N*,*N*′-diphenyl-*N*-[(trimethylsilyl)methyl]ureas 4a–d: A solution containing **4a–d** in $CDCl_3$/MeOH, $CHCl_3/CD_3OD$, or acetone was irradiated with UV light by using a medium-pressure mercury lamp (450 W) equipped with a Pyrex glass filter, at room temperature under nitrogen for 12 h. After the solution was concentrated under reduced pressure, the residue was purified by performing column chromatography with silica gel to provide the desired products.

***N*,*N*′-Diphenyl-*N*-methylurea (5)**:[30] The standard procedure 1 was followed by using urea **4a** (31.2 mg, 0.105 mmol) in $CDCl_3$/MeOH (9:1, 1.0 mL). After the reaction mixture was formed, the residue was purified by performing column chromatography (20 % EtOAc in hexanes as eluant). *N*-Methylurea **5** (23.1 mg, 0.102 mmol) was obtained in 97 % yield as white solids. M.p. 103–104 °C (published m.p. 102–103 °C[30]); TLC R_f: 0.60 (20 % EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 3.32$ (s, 3H; NCH_3), 6.22 (s, 1H; NH), 6.96 (t, $J = 7.3$ Hz, 1H; 1 × ArH), 7.20–7.38 (m, 7H; 7 × ArH), 7.46 ppm (t, $J = 7.4$ Hz, 2H; 2 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 37.01$ (NCH_3), 119.15, 122.81, 127.40, 127.83, 128.71, 130.30, 138.78, 142.85, 154.35 ppm (C=O); IR (neat) 3282 (m, N-H), 3042 (w), 1649 (s, C=O), 1594 (m), 1493 (s, Ph), 1363 (m), 1242 (m), 1135 (w), 908 (w), 754 (m), 697 cm^{-1} (m); MS *m*/*z* (relative intensity): 226 (56) [M^+], 134 (30), 107 (100), 91 (6), 77 (45), 65 (9), 51 (10).

Identical reaction conditions were applied to the substrates **4b–d**. The same photolytic product **5** was obtained in 84, 77, and 54 % yields, respectively.

***N*,*N*′-Diphenyl-*N*-(2-hydroxy-2-methylpropyl)urea (7)**: The standard procedure 1 was followed by using urea **4a** (51.6 mg, 0.173 mmol) and acetone (2.0 mL). After the reaction mixture was formed, the residue was purified by performing column chromatography (10 % EtOAc in hexanes as eluant). *N*-(2-Hydroxy-2-methylpropyl)urea **7** (22.1 mg, 0.0778 mmol) was obtained in 45 % yield as yellow solids. M.p. (recrystallized from ethanol) 145–146 °C; TLC R_f: 0.42 (20 % EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.23$ (s, 6H; 2 × CH_3), 3.78 (s, 2H; CH_2N), 4.95 (s, 1H; OH), 6.46 (s, 1H; NH), 6.98–7.01 (m, 1H; 1 × ArH), 7.19–7.45 (m, 7H; 7 × ArH), 7.48 ppm (m, 2H; 2 × ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 27.80$, 62.37, 71.86, 119.69, 123.38, 127.91, 128.74, 129.21, 130.37, 138.18, 143.22, 156.81 ppm (C=O); IR (neat) 3253 (br, OH), 3060 (w), 2974 (m), 1642 (s, C=O), 1594 (s), 1496 (s, Ph), 1371 (m), 1235 (s), 1167 (s), 978 (m), 748 (m), 697 cm^{-1} (s); MS *m*/*z* (relative intensity): 284 (1) [M^+], 226 (63), 183 (13), 150 (5), 134 (6), 119 (5), 106 (100), 93 (17), 77 (27), 59 (9); HRMS *m*/*z*: calcd for $C_{17}H_{20}O_2N_2$: 284.1525; found: 284.1521; elemental analysis calcd (%) for $C_{17}H_{20}O_2N_2$: C 71.79, H 7.09, N 9.86; found: C 71.76, H 7.08, N 9.82.

Preparation of *N*-[(trimethylsilyl)methyl]ureas 8a–c: Cyclohexylisocyanate or phenylisocyanate (11 equiv) was added to a solution containing **3a** or *N*-(trimethylsilylmethyl)cyclohexylamine (108.6–203.6 mg, 1 equiv) in CH_2Cl_2 (10 mL). The reaction mixture was stirred under nitrogen at 25 °C for 4.0 h, then quenched with water (2.0 mL) at 25 °C, and extracted with Et_2O (3 × 20 mL). The combined organic layers were washed with saturated aqueous NaCl (5.0 mL), dried over $MgSO_4$ (s), filtered, and

Table 3. Spectroscopic data of silicon-containing compounds **3a–d**, **4a–d**, and **8a–c**.

	M.p. [°C] (hexanes)	^{1}H NMR (CDCl$_3$, 400 MHz) δ [ppm]	^{13}C NMR (CDCl$_3$, 75 MHz) δ [ppm]	UV (CHCl$_3$) λ_{max} [nm] (ε)	IR [cm^{-1}]	HRMS [calcd/ found]
3a	–	0.15 (s, 9H; Si(CH$_3$)$_3$), 2.50 (s, 2H; CH$_2$N), 3.38 (br, 1H; NH), 6.64–6.67 (m, 3H; 3 × ArH), 7.19 (dd, J = 8.0, 7.2 Hz, 2H; 2 × ArH)	−2.83 (Si(CH$_3$)$_3$), 33.37 (CH$_2$N), 112.26, 116.84, 128.97, 150.36	–	3418 (m, N-H), 1250 (s, Si-CH$_3$)	–
3b	–	0.48 (s, 6H; Si(CH$_3$)$_2$), 2.81 (s, 2H; CH$_2$N), 3.43 (br, 1H; NH), 6.70 (d, J = 8.4 Hz, 2H; 2 × ArH), 6.76 (t, J = 7.2 Hz, 1H; 1 × ArH), 7.24 (t, J = 7.2 Hz, 2H; 2 × ArH), 7.46–7.48 (m, 3H; 3 × ArH), 7.65 (m, 2H; 2 × ArH)	−3.98 (Si(CH$_3$)$_2$), 32.48 (CH$_2$N), 112.45, 117.05, 128.05, 129.02, 129.54, 133.74, 136.50, 150.26	–	3412 (m, N-H), 1250 (s, Si-CH$_3$), 1113 (m, Si-Ph)	–
3c	–	0.78 (s, 3H; SiCH$_3$), 3.13 (s, 2H; CH$_2$N), 3.61 (br, 1H; NH), 6.74 (d, J = 8.8 Hz, 2H; 2 × ArH), 6.80 (t, J = 8.4 Hz, 1H; 1 × ArH), 7.27 (t, J = 8.4 Hz, 2H; 2 × ArH), 7.46–7.69 (m, 6H; 6 × ArH), 7.71 (m, 4H; 4 × ArH)	−5.04 (SiCH$_3$), 31.27 (CH$_2$N), 112.55, 117.22, 128.15, 129.07, 129.83, 134.62, 137.38, 150.13	–	3409 (m, N-H), 1254 (s, Si-CH$_3$), 1114 (s, Si-Ph)	303.1443/ 303.1448
3d	151–152	3.30 (s, 2H; CH$_2$N), 3.63 (br, 1H; NH), 6.64–6.76 (m, 3H; 3 × ArH), 7.18 (dd, J = 8.2, 7.4 Hz, 2H; 2 × ArH), 7.37–7.47 (m, 9H; 9 × ArH), 7.62 (d, J = 7.5 Hz, 6H; 6 × ArH)	37.23 (CH$_2$N), 119.18, 122.87, 127.43, 127.86, 128.78, 130.32, 138.78, 142.85	–	3392 (m, N-H), 1111 (s, Si-Ph)	365.1599/ 365.1597
4a	110–111	0.038 (s, 9H; Si(CH$_3$)$_3$), 3.34 (s, 2H; CH$_2$N), 6.18 (s, 1H; NH), 6.97 (t, J = 7.2 Hz, 1H; 1 × ArH), 7.18–7.26 (m, 4H; 4 × ArH), 7.31–7.36 (m, 3H; 3 × ArH), 7.43–7.47 (m, 2H; 2 × ArH)	−1.70 (Si(CH$_3$)$_3$), 41.39 (CH$_2$N), 119.01, 122.56, 127.72, 127.98, 128.73, 130.15, 139.04, 143.15, 154.15 (C=O)	247 (6388)	3266 (m, N-H), 1644 (s, C=O), 1248 (s, Si-CH$_3$)	298.1501/ 298.1508
4b	79–80	0.26 (s, 6H; Si(CH$_3$)$_2$), 3.55 (s, 2H; CH$_2$N), 6.11 (s, 1H; NH), 6.85 (t, J = 7.4 Hz, 1H; 1 × ArH), 7.12–7.36 (m, 12H; 12 × ArH), 7.45 (d, J = 8.0 Hz, 2H; 2 × ArH)	−3.04 (Si(CH$_3$)$_2$), 40.77 (CH$_2$N), 111.09, 119.10, 122.62, 127.70, 128.01, 128.74, 129.02, 130.03, 133.71, 137.82, 138.99, 142.85, 154.19 (C=O)	248 (11598)	3305 (m, N-H), 1645 (s, C=O), 1255 (m, Si-CH$_3$), 1113 (s, Si-Ph)	360.1657/ 360.1646
4c	87–88	0.42 (s, 3H; SiCH$_3$), 3.83 (s, 2H; CH$_2$N), 5.99 (s, 1H; NH), 6.88–6.91 (m, 3H; 3 × ArH), 7.11–7.25 (m, 13H; 13 × ArH), 7.39 (d, J = 5.6 Hz, 4H; 4 × ArH)	−4.33 (SiCH$_3$), 39.08 (CH$_2$N), 119.27, 122.71, 127.78, 128.20, 128.72, 129.30, 129.93, 129.98, 134.56, 135.64, 138.90, 142.33, 154.25 (C=O)	248 (12164)	3333 (m, N-H), 1674 (s, C=O), 1246 (m, Si-CH$_3$), 1112 (s, Si-Ph)	422.1814/ 422.1810
4d	93–94	4.26 (s, 2H; CH$_2$N), 6.03 (s, 1H; NH), 6.89–6.91 (m, 3H; 3 × ArH), 7.11–7.35 (m, 16H; 16 × ArH), 7.45 (d, J = 7.5 Hz, 6H; 6 × ArH)	38.25 (CH$_2$N), 119.39, 122.73, 127.79, 128.26, 128.70, 129.47, 129.51, 129.95, 133.88, 135.77, 138.90, 142.24, 154.18 (C=O)	249 (14550)	3275 (m, N-H), 1667 (s, C=O), 1108 (s, Si-Ph)	484.1970/ 484.1964
8a	67–68	0.090 (s, 9H; Si(CH$_3$)$_3$), 0.85–1.83 (m, 10H; 5 × CH$_2$), 3.21 (s, 2H; CH$_2$N), 3.53–3.61 (m, 1H; CHN), 4.12 (d, J = 8.2 Hz, 1H; NH), 7.17–7.25 (m, 3H; 3 × ArH), 7.35 (t, J = 8.0 Hz, 2H; 2 × ArH)	−1.64 (Si(CH$_3$)$_3$), 24.78, 25.49, 33.59, 41.25, 49.22, 126.84, 127.74, 129.71, 143.99, 156.50 (C=O)	262 (3913)	3308 (s, N-H), 1631 (s, C=O), 1258 (s, Si-CH$_3$)	304.1971/ 304.1967
8b	83–84	0.12 (s, 9H; Si(CH$_3$)$_3$), 1.05–1.81 (m, 10H; 5 × CH$_2$), 2.64 (s, 2H; CH$_2$N), 3.97–4.09 (m, 1H; CHN), 6.12 (s, 1H; NH), 6.97 (t, J = 7.6 Hz, 1H; 1 × ArH), 7.25 (dd, J = 8.4, 7.6 Hz, 2H; 2 × ArH), 7.34 (d, J = 8.4 Hz, 2H; 2 × ArH)	−1.27 (Si(CH$_3$)$_3$), 25.31, 25.67, 30.85, 33.24, 55.13, 119.28, 122.25, 128.67, 139.35, 154.95 (C=O)	259 (3887)	3350 (s, N-H), 1651 (s, C=O), 1248 (s, Si-CH$_3$)	304.1971/ 304.1977
8c	122–123	0.057 (s, 9H; Si(CH$_3$)$_3$), 0.98–1.36 (m, 10H; 5 × CH$_2$), 1.57–1.98 (m, 10H; 5 × CH$_2$), 2.46 (s, 2H; CH$_2$N), 3.52–3.65 (m, 1H; CHN), 3.78–3.89 (m, 1H; CHN), 3.96 (d, J = 8.0 Hz, 1H; NH)	0.96 (Si(CH$_3$)$_3$), 25.17, 25.54, 25.71, 25.90, 30.96, 32.82, 34.20, 49.48, 54.94, 157.12 (C=O)	–	3303 (m, N-H), 1612 (s, C=O), 1245 (s, Si-CH$_3$)	310.2440/ 310.2436

concentrated under reduced pressure. The residue was purified by performing column chromatography (20% EtOAc in hexanes as eluant) to give the desired pure **8a–c** in 89–91% yields as white solids with purity >99.5%.

***N′*-Cyclohexyl-*N*-methyl-*N*-phenylurea (9a)**: A solution of urea **8a** (78.6 mg, 0.259 mmol) in CHCl$_3$/MeOH (9:1, 5.0 mL) was irradiated with UV light by using a medium-pressure mercury lamp (450 W) equipped with a Pyrex glass filter, at room temperature under nitrogen for 12 h. The resultant solution was concentrated under reduced pressure to give a residue that was purified by performing column chromatography (10% EtOAc in hexanes as eluant). *N*-Methylurea **9a** (52.9 mg, 0.228 mmol) was obtained in 88% yield as white solids. M.p. (recrystallized from hexanes) 112–113 °C; TLC R_f: 0.58 (30% EtOAc in hexanes as eluant); ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.87–1.82 (m, 10H; 5 × CH$_2$), 3.18 (s, 3H; CH$_3$), 3.54–3.60 (m, 1H; CHN), 4.14 (d, J = 7.2 Hz, 1H; NH), 7.12–7.24 (m, 3H; 3 × ArH), 7.34 ppm (t, J = 8.0 Hz, 2H; 2 × ArH); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 24.64, 25.36, 33.40, 36.79, 49.08, 126.81, 126.96, 129.71, 143.47, 156.36 ppm (C=O); IR (neat) 3343 (s, N-H), 2931 (s), 1650 (s, C=O), 1596 (s), 1443 (s), 1343 (s), 1117 (m), 1072 (m), 891 (w), 758 (m), 700 cm^{-1} (s); MS *m*/*z* (relative intensity): 232 (10) [M^+], 149 (8), 107 (100), 91 (8), 77 (36), 55 (10); HRMS calcd for $C_{14}H_{20}ON_2$: 232.1576; found: 232.1571; elemental analysis calcd (%) for $C_{14}H_{20}ON_2$: C 72.38, H 8.68, N 12.06; found: C 72.33, H 8.64, N 12.09.

***N*-Cyclohexyl-*N*-methyl-*N′*-phenylurea (9b)**:[31] A solution of urea **8b** (68.3 mg, 0.225 mmol) in CHCl$_3$/MeOH (9:1, 5.0 mL) was irradiated with UV light by using a medium-pressure mercury lamp (450 W) equipped with a Pyrex glass filter, at room temperature under nitrogen for 12 h. The resultant solution was concentrated under reduced pressure to give a residue that was purified by performing column chromatography (10% EtOAc in hexanes as eluant). *N*-Methylurea **9b** (37.6 mg, 0.162 mmol) was obtained in 72% yield as white solids. M.p. 195–196 °C (published m.p. 195–197 °C[31]); TLC R_f: 0.68 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.04–1.82$ (m, 10H; 5×CH_2), 2.84 (s, 3H; CH_3), 4.02–4.14 (m, 1H; CHN), 6.38–6.42 (br, 1H; NH), 6.99 (t, $J = 7.6$ Hz, 1H; ArH), 7.26 (t, $J = 7.6$ Hz, 2H; 2×ArH), 7.38 ppm (d, $J = 8.4$ Hz, 2H; 2×ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 25.49$, 25.72, 28.48, 30.48, 54.04, 119.79, 122.71, 128.71, 139.33, 155.17 ppm (C=O); IR (neat) 3302 (s, N-H), 2929 (s), 2853 (s), 1638 (s, C=O), 1594 (s), 1527 (s), 1441 (s), 1322 (m), 1168 (m), 879 (m), 753 (m), 697 cm^{-1} (m); MS *m/z* (relative intensity): 232 (16) [M^+], 140 (12), 120 (8), 112 (100), 97 (9), 77 (15), 55 (25).

***N,N′*-Dicyclohexyl-*N*-methylurea (9c)**:[32] A solution of urea **8c** (88.5 mg, 0.285 mmol) in $CHCl_3$/MeOH (9:1, 5.0 mL) was irradiated with UV light by using a medium-pressure mercury lamp (450 W) equipped with a Pyrex glass filter, at room temperature under nitrogen for 12 h. The resultant solution was concentrated under reduced pressure to give a residue that was purified by performing column chromatography (10% EtOAc in hexanes as eluant). *N*-Methylurea **9c** (8.8 mg, 0.037 mmol) was obtained in 13% yield as white solids. M.p. 106–107 °C (published m.p. 106–109 °C[32]); TLC R_f: 0.70 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.99–1.41$ (m, 10H; 5×CH_2), 1.51–1.96 (m, 10H; 5×CH_2), 2.63 (s, 3H; CH_3), 3.47–3.62 (m, 1H; CHN), 3.86–3.97 (m, 1H; CHN), 4.08–4.21 ppm (br, 1H; NH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 25.02$, 25.54, 25.64, 25.75, 28.02, 30.45, 34.02, 49.29, 53.61, 157.20 ppm (C=O); IR (neat) 3303 (m, N-H), 2925 (m), 2851 (m), 1619 (s, C=O), 1537 (s), 1453 (s), 1391 (s), 1223 (s), 1038 (s), 893 (s), 744 (m), 629 cm^{-1} (w); MS *m/z* (relative intensity): 238 (23) [M^+], 155 (8), 112 (100), 97(13), 83 (9).

2,2-Dimethyl-*N,N′*-diphenyl-1,3-propanediamine (14): Lithium aluminum hydride (53.4 mg, 1.41 mmol) was added to a solution of diamide **13** (158.7 mg, 0.5628 mmol, 1 equiv) in THF (20 mL). The reaction mixture was heated at reflux under nitrogen for 16 h, then quenched with saturated aqueous Na_2SO_4 (5.0 mL) at 0 °C, and extracted with Et_2O (3× 20 mL). The combined organic layers were washed with saturated aqueous NaCl (5.0 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure. The residue was purified by performing column chromatography (10% EtOAc in hexanes as eluant). Diamine **14** (127.2 mg, 0.5008 mmol) was obtained in 89% yield as yellow solids. M.p. (recrystallized from ethanol) 80–81 °C; GC t_R: 11.47 min; TLC R_f: 0.71 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 1.09$ (s, 6H; 2×CH_3), 3.07 (s, 4H; 2×CH_2N), 3.79 (br, 2H; 2×NH), 6.63 (d, $J = 8.2$ Hz, 4H; 4×ArH), 6.70 (t, $J = 7.4$ Hz, 2H; 2×ArH), 7.17 ppm (dd, $J = 8.2$, 7.4 Hz, 4H; 4×ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 24.15$, 35.54, 52.92 (CH_2N), 112.89, 117.29, 129.14, 148.71 ppm; IR (neat) 3295 (m, N-H), 3057 (w), 2956 (m), 1603 (s), 1495 (s, Ph), 1303 (m), 1187 (m), 1068 (m), 877 (m), 754 (s), 693 cm^{-1} (s); MS *m/z* (relative intensity): 254 (60) [M^+], 146 (36), 132 (10), 119 (8), 106 (100), 93 (95), 77 (43); HRMS calcd for $C_{17}H_{22}N_2$: 254.1783; found: 254.1780; elemental analysis calcd (%) for $C_{17}H_{22}N_2$: C 80.26, H 8.72, N 11.02; found: C 80.22, H 8.68, N 10.97.

Standard procedure 2 for the synthesis of polyureas 17 by addition of dianilino compounds to diisocyanate: 4,4′-Methylenebis(phenylisocyanate) (**16**) (0.10–0.40 equiv)) was added to a solution of anilinomethylsilane **11** and dianilino-*p*-xylene (**15**) (0.60–0.90 equiv) in *sym*-tetrachloroethane (1.8 mL) and the reaction mixture was stirred under nitrogen at 100 °C for 12 h. The resultant viscous solution of polymers was diluted with *sym*-tetrachloroethane (5.0 mL) and poured into MeOH (80 mL) to give a precipitate, which was redissolved in chloroform (5.0 mL). This precipitation procedure was repeated twice. The precipitate was dried over phosphorous pentoxide under reduced pressure at room temperature for 24 h to provide the desired polyureas **17**.

Poly[bis(anilinomethyl)dimethylsilane-*co*-dianilino-*p*-xylene-*co*-4,4′-methylenebis(phenylisocyanate)] (17b) from bis(anilinomethyl)dimethylsilane (11, 0.1 equiv): The standard procedure 2 was followed by using anilinomethylsilane **11** (50.5 mg, 0.187 mmol, 0.1 equiv), dianilino-*p*-xylene (**15**, 483.8 mg, 1.680 mmol, 0.9 equiv), *sym*-tetrachloroethane (1.8 mL), and isocyanate **16** (467.2 mg, 1.867 mmol, 1 equiv). After purification, **17b** (911.4 mg, 1.698 mmol) was obtained in 91% yield as white elastomers, which were soluble in THF and chloroform. Data for **17b**: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.017$ (s, 6H; Si$(CH_3)_2$, 6%), 3.27 (s, 4H; 2× $SiCH_2N$, 6%), 3.77 (s, 4H; 2×$ArCH_2Ar$), 4.84 (s, 4H; 2×NCH_2Ar), 6.07 (s, 4H; 4×NH), 6.95–7.38 ppm (brm, 40H; 40×ArH); IR (neat) 3425 (m, NH), 3345 (m, NH), 3008 (m), 2921 (w), 1677 (s, C=O), 1593 (s), 1514 (s), 1411 (s), 1309 (s), 1248 (m, Si-CH_3), 1019 (m), 811 (m), 756 (s), 701 cm^{-1} (s); UV/Vis ($CHCl_3$): $\lambda_{max,}$ (ε) = 249 nm (241); M_w 5.49×10^4; M_n 2.39×10^4; T_g 121 °C.

Poly[bis(anilinomethyl)dimethylsilane-*co*-dianilino-*p*-xylene-*co*-4,4′-methylenebis(phenylisocyanate)] (17c) from bis(anilinomethyl)dimethylsilane (11, 0.2 equiv): The standard procedure 2 was followed by using anilinomethylsilane **11** (121.8 mg, 0.451 mmol, 0.2 equiv), dianilino-*p*-xylene (**15**, 519.0 mg, 1.802 mmol, 0.8 equiv), *sym*-tetrachloroethane (2.1 mL), and isocyanate **16** (563.8 mg, 2.253 mmol, 1 equiv). After purification, **17c** (1.08 g, 2.02 mmol) was obtained in 90% yield as white elastomers: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.017$ (s, 6H; Si$(CH_3)_2$, 12%), 3.28 (s, 4H; 2×$SiCH_2N$, 12%), 3.77 (s, 4H; 2×$ArCH_2Ar$), 4.85 (s, 4H; 2× NCH_2Ar), 6.08 (s, 4H; 4×NH), 6.96–7.40 ppm (brm, 40H; 40×ArH); IR (neat) 3426 (m, NH), 3345 (m, NH), 3007 (m), 2922 (w), 1679 (s, C=O), 1593 (s), 1518 (s), 1411 (s), 1308 (s), 1251 (m, Si-CH_3), 1023 (m), 814 (m), 758 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max}, (ε) = 251 nm (243); M_w 5.21×10^4; M_n 2.17×10^4; T_g 118 °C.

Poly[bis(anilinomethyl)dimethylsilane-*co*-dianilino-*p*-xylene-*co*-4,4′-methylenebis(phenylisocyanate)] (17d) from bis(anilinomethyl)dimethylsilane (11, 0.3 equiv): The standard procedure 2 was followed by using anilinomethylsilane **11** (101.4 mg, 0.376 mmol, 0.3 equiv), dianilino-*p*-xylene (**15**, 252.6 mg, 0.877 mmol, 0.7 equiv), *sym*-tetrachloroethane (1.8 mL), and isocyanate **16** (313.6 mg, 1.253 mmol, 1 equiv). After purification, **17d** (607.5 mg, 1.135 mmol) was obtained in 91% yield as white elastomers: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.019$ (s, 6H; Si$(CH_3)_2$, 15%), 3.29 (s, 4H; 2×$SiCH_2N$, 15%), 3.77 (s, 4H; 2×$ArCH_2Ar$), 4.86 (s, 4H; 2× NCH_2Ar), 6.07 (s, 4H; 4×NH), 6.95–7.42 ppm (brm, 40H; 40×ArH); IR (neat) 3428 (m, NH), 3348 (m, NH), 3009 (m), 2921 (w), 1677 (s, C=O), 1594 (s), 1518 (s), 1413 (s), 1310 (s), 1255 (m, Si-CH_3), 1026 (m), 818 (m), 762 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max}, (ε) = 250 nm (244); M_w 5.05×10^4; M_n 1.68×10^4; T_g 113 °C.

Poly[bis(anilinomethyl)dimethylsilane-*co*-dianilino-*p*-xylene-*co*-4,4′-methylenebis(phenylisocyanate)] (17e) from bis(anilinomethyl)dimethylsilane (11, 0.35 equiv): The standard procedure 2 was followed by using anilinomethylsilane **11** (101.0 mg, 0.374 mmol, 0.35 equiv), dianilino-*p*-xylene (**15**, 200.2 mg, 0.695 mmol, 0.65 equiv), *sym*-tetrachloroethane (1.8 mL), and isocyanate **16** (267.5 mg, 1.069 mmol, 1 equiv). After purification, **17e** (511.8 mg, 0.9565 mmol) was obtained in 90% yield as white elastomers: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.017$ (s, 6H; Si$(CH_3)_2$, 16%), 3.28 (s, 4H; 2×$SiCH_2N$, 16%), 3.77 (s, 4H; 2×$ArCH_2Ar$), 4.84 (s, 4H; 2×NCH_2Ar), 6.09 (s, 4H; 4×NH), 6.96–7.41 ppm (brm, 40H; 40×ArH); IR (neat) 3425 (m, NH), 3348 (m, NH), 3006 (m), 2922 (w), 1678 (s, C=O), 1591 (s), 1519 (s), 1411 (s), 1309 (s), 1253 (m, Si-CH_3), 1020 (m), 816 (m), 758 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max}, (ε) = 249 nm (245); M_w 4.06× 10^4; M_n 1.31×10^4; T_g 108 °C.

Poly[bis(anilinomethyl)dimethylsilane-*co*-dianilino-*p*-xylene-*co*-4,4′-methylenebis(phenylisocyanate)] (17f) from bis(anilinomethyl)dimethylsilane (11, 0.4 equiv): The standard procedure 2 was followed by using anilinomethylsilane **11** (137.6 mg, 0.510 mmol, 0.4 equiv), dianilino-*p*-xylene (**15**, 220.3 mg, 0.765 mmol, 0.6 equiv), *sym*-tetrachloroethane (1.8 mL), and isocyanate **16** (319.1 mg, 1.275 mmol, 1 equiv). After purification, **17f** (595.8 mg, 1.115 mmol) was obtained in 88% yield as white elastomers: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.018$ (s, 6H; Si$(CH_3)_2$, 21%), 3.28 (s, 4H; 2×$SiCH_2N$, 21%), 3.78 (s, 4H; 2×$ArCH_2Ar$), 4.85 (s, 4H; 2× NCH_2Ar), 6.07 (s, 4H; 4×NH), 6.98–7.42 ppm (brm, 40H; 40×ArH); IR (neat) 3422 (m, NH), 3341 (m, NH), 3010 (m), 2924 (w), 1677 (s, C=O), 1590 (s), 1516 (s), 1412 (s), 1307 (s), 1254 (m, Si-CH_3), 1025 (m), 820 (m), 756 cm^{-1} (s); UV/Vis ($CHCl_3$): λ_{max}, (ε) = 249 nm (246); M_w 2.86×10^4; M_n 8.15×10^3; T_g 104 °C.

Poly[2,2-dimethyl-*N*,*N'*-diphenyl-1,3-propanediamine-*co*-dianilino-*p*-xylene-*co*-4,4'-methylenebis(phenylisocyanate)] (18) from 2,2-dimethyl-*N*,*N'*-diphenyl-1,3-propanediamine (14, 0.1 equiv): The standard procedure 2 was followed by using diamine **14** (30.5 mg, 0.120 mmol, 0.1 equiv), dianilino-*p*-xylene (**15**, 311.6 mg, 1.082 mmol, 0.9 equiv), *sym*-tetrachloroethane (1.2 mL), and isocyanate **16** (300.9 mg, 1.202 mmol, 1 equiv). After purification, **18** (585.1 mg, 1.093 mmol) was obtained in 91 % yield as white elastomers: ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.81$ (s, 6H; 2×CH_3, 8 %), 3.79 (s, 8H; 2×NCH_2C + 2×$ArCH_2Ar$), 4.86 (s, 4H; 2×NCH_2Ar), 6.09 (s, 4H; 4×NH), 6.97–7.40 ppm (brm, 40H; 40×ArH); IR (neat) 3422 (m, NH), 3347 (m, NH), 3010 (m), 2922 (w), 1676 (s, C=O), 1594 (s), 1520 (s), 1415 (s), 1308 (s), 1028 (m), 821 (m), 756 cm^{-1} (s); M_w 4.61×10^4; M_n 2.42×10^4; T_g 123 °C.

Photolysis of polyureas: A solution containing a single type of polymer (i.e., **17a–c** and **18**; 26.0 mg) in $CHCl_3$/MeOH (9:1, 10 mL) was irradiated with UV light by using a medium-pressure mercury lamp (450 W) equipped with a Pyrex glass filter, at room temperature under nitrogen. After photolysis, the molecular weights of degraded polyureas were determined by performing GPC at different time intervals. The results are summarized in Figure 1.

Standard procedure 3 for the preparation of bis(*N*,*N'*-diphenylureylene) compounds 20 and 21: Phenylisocyanate (2 equiv) was added to a solution containing a diamine (1 equiv) in CH_2Cl_2 (20 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched with water (5.0 mL) at 25 °C, and extracted with Et_2O (3×20 mL). The combined organic layers were washed with saturated aqueous NaCl (5.0 mL), dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure. The residue was purified by performing column chromatography with silica gel to provide the desired bis(*N*,*N'*-diphenylureylene) compounds.

1,3-Bis(*N*,*N'*-diphenylureylene)-2,2-dimethylpropane (20): The standard procedure 3 was followed by using diamine **14** (58.6 mg, 0.231 mmol, 1 equiv) and phenylisocyanate (55.0 mg, 0.462 mmol, 2 equiv). After the reaction mixture was formed, the residue was purified by performing column chromatography (20 % EtOAc in hexanes as eluant). Bisurea **20** (96.4 mg, 0.196 mmol) was obtained in 85 % yield as white solids. M.p. (recrystallized from hexanes) 196–197 °C; TLC R_f: 0.62 (30 % EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 0.81$ (s, 6H; 2×CH_3), 3.79 (s, 4H; 2×CH_2N), 6.25 (s, 2H; 2×NH), 6.95–6.97 (m, 2H; 2×ArH), 7.17–7.48 ppm (m, 18H; 18×ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 24.71$ (CH_3), 40.11 (CH_2N), 57.99, 119.40, 122.85, 127.71, 128.53, 128.71, 130.19, 138.75, 143.33, 154.90 ppm (C=O); IR (neat) 3312 (s, N-H), 2963 (w), 1661 (s, C=O), 1592 (s), 1513 (s), 1313 (m), 1164 (s), 1077 (w), 890 (m), 759 (s), 695 cm^{-1} (s); UV/Vis ($CHCl_3$) λ_{max}, nm (ε): 250 (23116), 228 (21553); MS *m*/*z* (relative intensity): 492 (5) [M^+], 477 (8), 267 (100), 164 (18), 148 (25), 135 (25), 106 (31), 93 (12), 77 (29); HRMS calcd for $C_{31}H_{32}O_2N_4$: 492.2525; found: 492.2521; elemental analysis calcd (%) for $C_{31}H_{32}O_2N_4$: C 75.57, H 6.55, N 11.38; found: C 75.52, H 6.53, N 11.35.

Bis(*N*,*N'*-diphenylureylene)-*p*-xylene (21): The standard procedure 3 was followed by using dianilino-*p*-xylene (**15**, 124.2 mg, 0.4313 mmol, 1 equiv) and phenylisocyanate (102.8 mg, 0.8630 mmol, 2 equiv). After the reaction mixture was formed, the residue was purified by performing column chromatography (30 % EtOAc in hexanes as eluant). Bisurea **21** (192.8 mg, 0.3665 mmol) was obtained in 85 % yield as white solids. M.p. (recrystallized from hexanes) 198–199 °C; TLC R_f: 0.28 (30 % EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.97$ (s, 4H; 2×CH_2N), 6.22 (s, 2H; 2×NH), 7.08–7.48 ppm (m, 24H; 24×ArH); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 52.77$ (CH_2N), 119.29, 122.95, 128.23, 128.57, 128.73, 128.86, 130.15, 137.22, 138.75, 141.03, 154.29 ppm (C=O); IR (neat) 3327 (s, N-H), 2930 (w), 1681 (s, C=O), 1595 (s), 1495 (s, Ph), 1443 (m), 1313 (s), 1215 (s), 1021 (m), 752 (s), 693 cm^{-1} (s); UV/Vis ($CHCl_3$) λ_{max}, nm (ε): 250 (26835), 226 (26330); MS *m*/*z* (relative intensity): 526 (2) [M^+], 407 (62), 315 (21), 288 (49), 196 (100), 181 (10), 119 (53), 104 (70), 91 (76), 77 (48); HRMS calcd for $C_{34}H_{30}O_2N_4$: 526.2369; found: 526.2363; elemental analysis calcd (%) for $C_{34}H_{30}O_2N_4$: C 77.53, H 5.75, N 10.64; found: C 77.50, H 5.72, N 10.61.

Bis[*N*-(2-anilinophenyl)formamide]-*p*-xylene (23): A solution of bisurea **21** (32.4 mg, 0.0616 mmol) in $CHCl_3$/CH_3OH (9:1, 2.0 mL) was irradiated with UV light by using a medium-pressure mercury lamp (450 W) equipped with a Pyrex glass filter, at room temperature under nitrogen for 24 h. The resultant solution was concentrated under reduced pressure to give a residue that was purified by performing column chromatography (10 % EtOAc in hexanes as eluant). Bisamide **23** (4.86 mg, 9.24 μmol) was obtained in 15 % yield as yellow solids. M.p. (recrystallized from hexanes) 135–136 °C; TLC R_f: 0.31 (20 % EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 4.99$ (s, 4H; 2×CH_2N), 6.21 (s, 2H; 2×NH), 6.99 (t, $J = 7.4$ Hz, 1H; 1×ArH), 7.18–7.46 (m, 19H; 19×ArH), 7.79 (d, $J = 8.0$ Hz, 2H; 2×ArH), 9.96 ppm (s, 2H; 2×CHO); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 53.06$, 119.43, 120.78, 123.27, 123.94, 128.45, 128.91, 129.20, 129.96, 130.44, 138.46, 140.89, 145.24, 191.94 ppm (C=O); IR (neat) 3327 (m, NH), 3062 (w), 2924 (m), 2836 (m), 2743 (m), 1692 (s, C=O), 1595 (s), 1495 (s, Ph), 1441 (m), 1238 (m), 1110 (w), 753 (m), 698 cm^{-1} (s); MS *m*/*z* (relative intensity): 526 (2) [M^+], 407 (2), 301 (4), 225 (5), 211 (100), 182 (16), 119 (25), 106 (48), 91 (94), 77(42), 65 (36); HRMS calcd for $C_{34}H_{30}O_2N_4$: 526.2369; found: 526.2364; elemental analysis calcd (%) for $C_{34}H_{30}O_2N_4$: C 77.53, H 5.75, N 10.64, found: C 77.49, H 5.72, N 10.61.

Acknowledgements

For financial support, we thank the National Science Council of the Republic of China.

---

[1] G. A. Howarth, *Surf. Coat. Int. Part B* **2003**, *86*, 111–118.
[2] J. Hajas, A. Woocker, *Macromol. Symp.* **2002**, *187*, 215–224.
[3] B. R. Baxter in *Coating Technology Handbook*, 2nd ed. (Eds.: D. Satas, A. A. Tracton), Marcel Dekker, New York, **2001**, pp. 447–451.
[4] M. P. Stevens in *Polymer Chemistry*, Oxford University Press, New York, **1999**, Chapter 13.
[5] K. Buecking, *Eur. Coat. J.* **1998**, *10*, 730–731.
[6] "Polymers in Microlithography, Materials and Processes": *ACS Symp. Ser.* **1989**, *412*, entire volume.
[7] "Polymers for Microelectronics: Resists and Dielectrics": *ACS Symp. Ser.* **1994**, *537*, entire volume.
[8] D. R. Tyler, *Coord. Chem. Rev.* **2003**, *246*, 291–303.
[9] T. Czvikovszky, *Radiat. Phys. Chem.* **2003**, *67*, 437–440.
[10] S. O. Kim, H. H. Solak, M. P. Stoykovich, N. J. Ferrier, J. J. de Pablo, P. F. Nealey, *Nature* **2003**, *424*, 411–414.
[11] Y. Lee, K. Hashimoto, H. Fujishima, R. Hanawa, Y. Uetani, *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5039*, 682–688.
[12] K. G. Pruden, K. Sinclair, S. Beaudoin, *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 1486–1496.
[13] T. S. Li, J. F. Chen, M. Mitsuishi, T. Miyashita, *J. Mater. Chem.* **2003**, *13*, 1565–1569.
[14] E. Reichmanis, O. Nalamasu, *J. Appl. Polym. Sci.* **2000**, 635–657.
[15] K. Sugita, *Prog. Org. Coat.* **1997**, *31*, 87–95.
[16] E. Reichmanis, L. F. Thompson, *Chem. Rev.* **1989**, *89*, 1273–1289.
[17] D. A. Holden, *Encycl. Polym. Sci. Eng.* **1988**, *11*, 126–154.
[18] M. Sato, M. Lijima, Y. Takahashi, *Thin Solid Films* **1997**, *308*, 90–93.
[19] M. Lijima, M. Sato, Y. Takahashi, *Appl. Surf. Sci*, **1996**, *101*, 120–123.
[20] M. Sato, M. Lijima, Y. Takahashi, *Jpn. J. Appl. Phys. Part 2.* **1994**, *33*, L1721–L1724.
[21] U. C. Yoon, D. U. Kim, C. W. Lee, Y. S. Choi, Y.-J. Lee, H. L. Ammon, P. S. Mariano, *J. Am. Chem. Soc.* **1995**, *117*, 2698–2710.
[22] L. Birkofer, O. Stuhl in *The Chemistry of Organic Silicon Compounds* (Eds.: S. Patai, Z. Rappoport), Wiley, New York, **1989**, Part 1, Chapter 10.
[23] Y. Oishi, M.-A. Kakimoto, Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.* **1987**, *25*, 2185–2193.
[24] E. A. Andreeshchev, V. S. Viktorova, S. F. Kilin, K. A. Kovyrzina, L. N. Kosyakina, Yu. P. Kushakevich, I. M. Rozman, Yu. P. Chkhik-

vadze, I. M. Rozman, Yu. G. Chkhikvadze, *Chem. Heterocycl. Compd.* **1986**, *22*, 1262–1266.

[25] A. G. Brook, J. M. Duff, D. G. Anderson, *Can. J. Chem.* **1970**, *48*, 561–569.

[26] S. Yanagida, T. Fujita, M. Ohoka, R. Kumagai, S. Komori, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 299–302.

[27] A. R. Katritzky, J. Koditz, H. Lang, *Tetrahedron* **1994**, *50*, 12571–12578.

[28] H. K. Oh, C. H. Shin, I. Lee, *J. Chem. Soc. Perkin Trans. 2* **1993**, *12*, 2411–2414.

[29] B. E. Copper, W. J. Owen, *J. Organomet. Chem.* **1971**, *29*, 33–40.

[30] Y. Wakita, T. Kobayashi, M. Maeda, M. Kojima, *Chem. Pharm. Bull.* **1982**, *30*, 3395–3398.

[31] Y. Mido, H. Okada, T. Itoh, *J. Mol. Struct.* **1980**, *65*, 35–42.

[32] E. Vowinkel, P. Gleichenhagen, *Tetrahedron Lett.* **1974**, *15*, 143–146.

Received: December 23, 2004