# Attempt toward 1D Cross-Linked Thermoplastic Elastomers: Structure and Mechanical Properties of a New System

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ABSTRACT: "1D cross-linked" thermoplastic elastomers could be an interesting class of materials, where the elastomer would be physically cross-linked by the self-association of functional groups forming long supramolecular chains. These materials could present both a high strength (due to the very large functionality of the cross-linking domains) and reversibility at room temperature (due to the intrinsic reversibility of the supramolecular chains). To obtain such materials, poly(dimethylsiloxane)s (PDMS) grafted with hydrogen bonding bis-ureas have been synthesized by modification of amino-functional PDMS. The materials obtained are physically cross-linked at room temperature by aggregation of strongly but reversibly self-associated bis-ureas. PDMS combining high bis-urea content and long polymer chains can undergo high strains and stresses at room temperature, but they can be processed at higher temperature. A wide control of the mechanical properties of the materials has been achieved by adjusting the structure of the polymer (molecular weight, grafting density, nature of the bis-urea). Although 3D cross-linking has been obtained instead of the aimed 1D cross-linking, new thermoplastic elastomers with easily tunable processing temperature and mechanical properties are presented.

## Introduction

Elastomers, which are soft and resilient polymeric materials able to undergo reversible deformations, find a lot of applications in everyday life (tires, cable sheathing, plastic gloves). Such materials are usually obtained by the chemical cross-linking of a flexible polymer. The softness of the material is granted by the low $T_g$ of the polymer, and a good elasticity is achieved through the formation of covalent bonds, which hold the chains together. Unfortunately, such materials can hardly be reprocessed because of the covalent links between the polymer chains. Consequently, most of these materials end their life as energy supplies.

To cope with these recycling problems, thermoplastic elastomers have been developed. The most common way to obtain thermoplastic elastomers consists of forming a noncovalent network by creating physical interactions between the chains.[1,2] These polymers exhibit elastomer properties as long as the physical interactions are strong enough. Then, the physical network can be destroyed by external action, such as heating, which leads to a processable polymer.

The formation of a noncovalent network can result from weak interactions such as ionic interactions[1,3] or hydrogen bonds[1,4−13] and/or from polymer/polymer segregation.[1] Hydrogen bonds are particularly useful to form and control the toughness of noncovalent networks thanks to their directionality and relative strength. Thus, thermoplastic elastomers relying on well-organized hydrogen bonds have already been obtained, the most widely used being polyurethanes.[1] In these multiblock copolymers, soft blocks are physically cross-linked by hard three-dimensional (3D) crystalline domains strengthened by hydrogen bonds. In a similar way, Stadler et al. presented polybutadienes grafted by 4-carboxyphenylurazoles which self-assemble by hydrogen bonds and self-organize in the polymer. Here, the "crystalline" zones are bidimensional (2D)[14] and act as strong and multiple cross-linking points that lead to impressive rheological and tensile properties.[6] Moreover, when the melting point of the ordered domains is reached, the material can easily be processed.

Other systems bear functional groups which dimerize by hydrogen-bonding, but do not crystallize. For example, Stadler et al.[5,15] presented polybutadienes cross-linked through the pairwise hydrogen bonding of phenyl urazoles grafted on the polymer. These systems have a higher elastic modulus than nonmodified polybutadienes, but their viscoelastic properties are limited because of the relative weakness of the association constant of phenyl urazoles ($10^2$ L/mol in chloroform[16]). Other authors showed that it is possible to dramatically improve the rheological and tensile properties of non polar polymers when the reversible cross-linking is realized with ureido-pyrimidones.[7,11,17] Indeed the dimerization constant of these molecules is much higher ($10^7$ L/mol in chloroform[18]), which leads to the formation of very strong physical networks. Unlike previously cited thermoplastic elastomers with 3D or 2D ordered domains, these elastomers are reversibly cross-linked through dimerization only (0D). The advantages of this

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"zero-dimensional cross-linking" is that these systems are expected to be in a thermodynamic equilibrium[7] and that reversibility is possible even at room temperature. On the other hand, the tensile properties of "0D cross-linked" elastomers are much weaker than those of "2D or 3D cross-linked" elastomers.

In this respect, "1D cross-linked" elastomers would be an interesting intermediate class of materials, where the elastomer would be physically cross-linked by the self-association of functional groups forming long supramolecular chains. These materials could present both a high strength (due to the very large functionality of the cross-linking domains), and reversibility at room temperature (due to the intrinsic reversibility of the supramolecular chains).

This paper presents our first attempt toward the synthesis of such materials. Bis-ureas, which have been reported to self-assemble in apolar solvents into long and rigid one-dimensional cylinders[19,20] by four strong cooperative hydrogen bonds ($10^5$ L/mol in chloroform[21]), were chosen as the cross-linking element. Poly(dimethylsiloxane) (PDMS) was chosen as the polymer backbone, because of its flexibility, low polarity, and availability. Moreover, Yilgor et al.[4] have already shown that PDMS bearing bis-urea linkages in the main chain exhibit very good tensile properties. Finally, it was checked by an FTIR study in chloroform that bis-ureas grafted onto poly(dimethylsiloxane) chains self-assemble efficiently.[22] In this paper, we report the functionalization of poly(dimethylsiloxane)s with urea or bis-ureas. The microstructure of the polymers as well as their tensile and rheological properties are described. Although 3D cross-linking has been obtained instead of the aimed 1D cross-linking, new thermoplastic elastomers with easily tunable processing temperature and mechanical properties are presented.

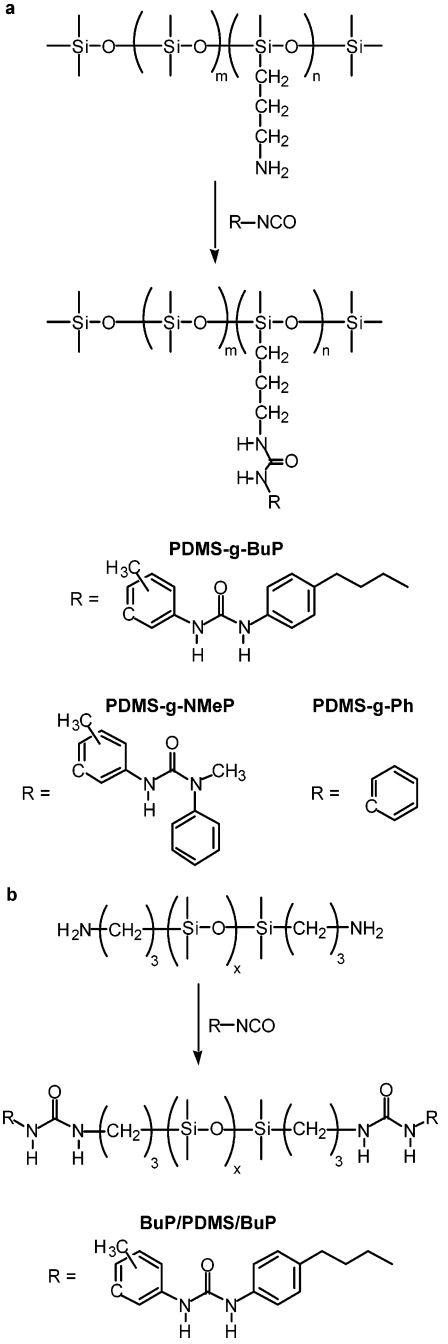
## Results

**1. Synthesis.** Seven urea functional PDMS were obtained by reacting commercial amino-functional PDMS with mono-isocyanates (Scheme 1, Tables 1 and 2). The synthesis was performed at room temperature and in solution, which ensured a quantitative modification of amines into urea functions according to $^1$H NMR spectroscopy. Moreover, size exclusion chromatography (SEC) showed that neither scission of the backbone nor chain coupling occurred during the modification.[23] Finally, OC106-4, OC120-1, and OC128-1, corresponding to three different batches of PDMS(30)-*g*-BuP synthesized under almost the same conditions,[24] are very similar in terms of molar masses and functionality (Table 1). As a conclusion, this synthesis is an easy, quantitative, and reproducible way to obtain various urea-functional PDMS.

**2. Structural Characterization. 2.1. FTIR.** The infrared spectra of all the present polymers show a broad band at 3310−3340 cm$^{-1}$ characteristic of hydrogen bonded NH groups.[25] Moreover, PDMS(37)-*g*-NMeP is the only polymer with detectable free NH groups (3430 cm$^{-1}$).

**2.2. DSC.** All the present polymers have a low-temperature $T_g$ (below −115 °C) characteristic of the poly(dimethylsiloxane) backbone. Moreover, the DSC thermogram of BuP/PDMS(4)/BuP (respectively PDMS-(37)-*g*-NMeP) presents a sharp endothermic peak (Figure 1), which is close to the melting point of its model bis-urea BuP/EH (mp = 190 °C) (respectively NMeP/EH (mp = 88 °C)). These two compounds are low molecular weight bis-ureas (Scheme 2) similar to the moieties grafted on the polymer backbone. On the contrary, a very broad endothermic transition is observed for PDMS(10)-*g*-BuP and PDMS(13)-*g*-BuP, and no peak is observed for PDMS(30)-*g*-Ph and PDMS(30)-*g*-BuP.

**Scheme 1. Synthesis of Urea or Bis-Urea Grafted PDMS (a) and of Bis-Urea Telechelic PDMS (b)**




**2.3. Small-Angle X-ray Scattering (SAXS).** BuP/PDMS(4)/BuP, PDMS(13)-*g*-BuP and PDMS(30)-*g*-BuP were compared to BuP/EH (Figure 2). Each of these compounds presents a diffraction peak broader than for the low molecular weight reference compound (BuP/EH). The distances in the 4−6 nm zone are characteristic of long range order, suggesting a pseudo-ordered structure.

Similarly to EH/EH,[20] BuP/EH has been shown by small-angle neutron scattering (SANS) to form long

**Table 1. Synthesis Conditions and Characteristics of Urea or Bis-urea Grafted PDMS (Scheme 1)**

| | reactants | | products | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| sample | *m*/n | (NCO/$NH_2$) ratio | *m*/n[a] | $M_n$[b] (g/mol) | $M_w$[b] (g/mol) | $I_p$[b] | n[c] | $M_{1f}$[d] (g/mol) | yield (%) |
| PDMS(10)-*g*-BuP (OC121-1) | 81 | 1.2 | 71 | 10500 | 14500 | 1.4 | 1.8 | 5700 | 74 |
| PDMS(13)-*g*-BuP (OC123-1) | 26 | 1.2 | 26 | 13000 | 20000 | 1.5 | 6 | 2400 | 69 |
| PDMS(30)-*g*-BuP (OC106-4) | 22 | 2.2 | 23 | 31000 | 73000 | 2.4 | 15 | 2100 | 64 |
| PDMS(30)-*g*-BuP (OC120-1) | 23 | 1.2 | 22 | 28000 | 78000 | 2.8 | 14 | 2100 | 76 |
| PDMS(30)-*g*-BuP (OC128-1) | 21 | 1.2 | 22 | 27000 | 84000 | 3.1 | 13 | 2100 | 69 |
| PDMS(37)-*g*-NMeP (OC125-4) | 23 | 1.2 | 21 | 37000 | 130000 | 3.5 | 19 | 2000 | 69 |
| PDMS(30)-*g*-Ph (OC132-4) | 21 | 1.3 | 24 | 28000 | 63000 | 2.3 | 14 | 2000 | 54 |

[a] Determined by $^1$H NMR. [b] Determined by SEC. [c] Average number of functional groups per chain, determined using *m*/*n* and $M_n$. [d] $M_{1f}$ corresponds to the average molecular weight between two functional groups and was determined using m/n value.

**Table 2. Synthesis Conditions and Characteristics of Bis-urea Telechelic PDMS (Scheme 1)**

| | reactants | | | products | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| sample | $M_n$[a] (g/mol) | *x*[a] | (NCO/$NH_2$) ratio | *x*[a] | $M_n$[a] (g/mol) | $M_n$[b] (g/mol) | $M_w$[b] (g/mol) | $I_p$[b] | yield (%) |
| BuP/PDMS(3)/BuP (OC086-1) | 2800 | 35 | 2.2 | 48 | 4500 | 4500 | 7000 | 1.6 | 54 |
| BuP/PDMS(29)/BuP (OC098-3) | 27500 | 370 | 3.3 | 386 | 29500 | 25000 | 46000 | 1.8 | 86 |

[a] Determined by $^1$H NMR. [b] Determined by SEC.

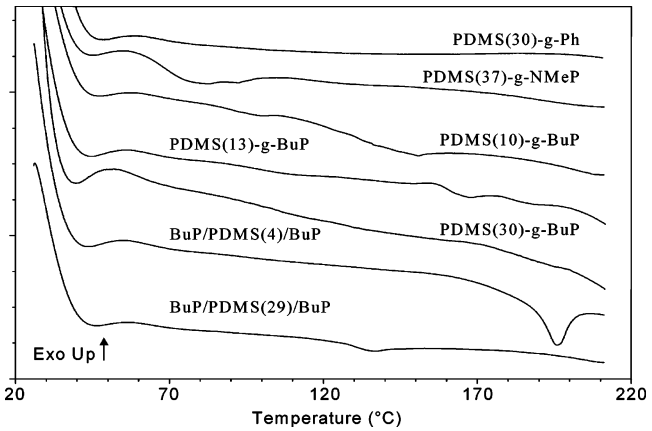
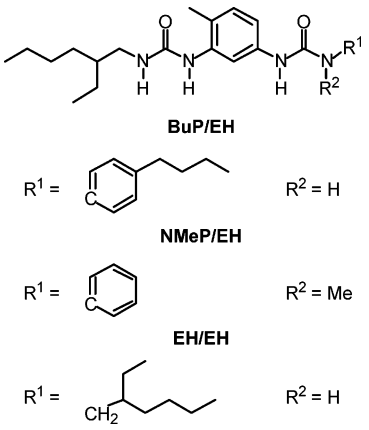



**Figure 1.** DSC scans of the urea and bis-urea functional PDMS (20 °C/min, first heating ramp, under nitrogen).

**Scheme 2. Chemical Structure of Low Molecular Weight Bis-Ureas**




supramolecular cylinders of diameter 3.0 nm in dilute toluene solution. If we assume that the SAXS diffraction peak at 2.3 nm for BuP/EH in the bulk results from long range order among such supramolecular cylinders, then by analogy, the SAXS diffraction peak at 4−6 nm for the polymers could result from similar supramolecular cylinders, which would be farther apart because of the presence of the macromolecular backbone.

**3. Tensile Properties at 22 °C.** PDMS(30)-*g*-BuP and PDMS(37)-*g*-NMeP can undergo high strain and stress before breaking (Figure 3). PDMS(13)-*g*-BuP, and BuP/PDMS(29)/BuP are tough enough to be tested but cannot withstand high strains (Table 3). Finally, BuP/PDMS(4)/BuP and PDMS(10)-*g*-BuP are too brittle to be tested, and PDMS(30)-*g*-Ph is a liquid.

**4. Rheological Properties at 30 °C.** The amino-functional PDMS are liquids even for the highest molar masses, but the present bis-urea functional PDMS are elastic solids. This qualitative observation is confirmed by rheology (Figure 4): PDMS(30)-*g*-BuP is characterized by a rubbery plateau over 2 decades at 30 °C, whereas its amino-functional precursor is a viscous liquid on the same frequency range. Moreover, *G*′ is more than 7 orders of magnitude higher for PDMS(30)-*g*-BuP than for its precursor.

Figures 5 and 6 show that PDMS(13 or 30)-*g*-BuP, BuP/PDMS(29)/BuP, and PDMS(37)-*g*-NMeP are also elastic solids at 30 °C. Additionally, the height of their

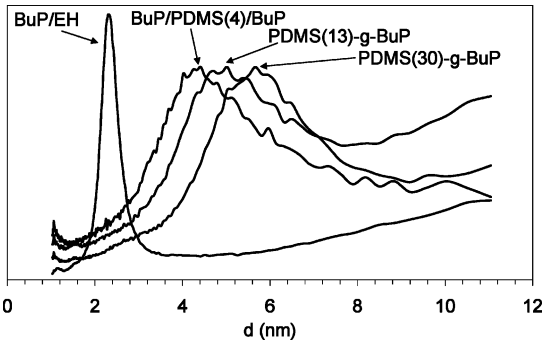



**Figure 2.** Small-angle X-ray scattering curves obtained for three bis-urea functional PDMS (Scheme 1 and Tables 1 and 2) and a model bis-urea (Scheme 2) at 25 °C.

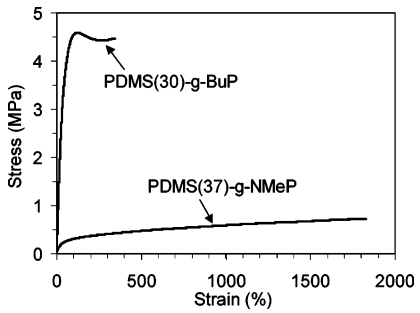



**Figure 3.** Tensile tests of PDMS(30)-*g*-BuP and PDMS(37)-*g*-NMeP (22 °C, 200 mm/min).

**Table 3. Tensile Properties of the Bis-Urea Functional PDMS (22 °C, Speed = 200 mm/min)**

| name | % N[a] | $M_n$[b] (g/mol) | stress at break (MPa) | strain at break (%) | Young modulus (MPa) |
|---|---|---|---|---|---|
| BuP/PDMS(4)/BuP (OC086-1) | 2.73 | 4500 | | too brittle to be tested | |
| BuP/PDMS(29)/BuP (OC098-3) | 0.43 | 25000 | 0.15 ± 0.05 | 25 ± 7 | 0.55 |
| PDMS(10)-*g*-BuP (OC121-1) | 0.98 | 10500 | | too brittle to be tested | |
| PDMS(13)-*g*-BuP (OC123-1) | 2.26 | 13000 | 0.35 ± 0.1 | 5 ± 2 | 5.5 |
| PDMS(30)-*g*-BuP (OC106-4) | 2.76 | 31000 | 4.0 ± 0.1 | 280 ± 30 | 10.1 |
| PDMS(30)-*g*-BuP (OC120-1) | 2.82 | 28000 | 4.0 ± 0.1 | 390 ± 75 | 9.7 |
| PDMS(30)-*g*-BuP (OC128-1) | 2.72 | 27000 | 4.3 ± 0.3 | 350 ± 50 | 10.6 |
| PDMS(37)-*g*-NMeP (OC125-4) | 2.67 | 37000 | 0.7 ± 0.1 | 1800 ± 230 | 1.0 |

[a] Nitrogen content determined by elemental analysis, and proportional to the bis-urea content. [b] Determined by SEC.

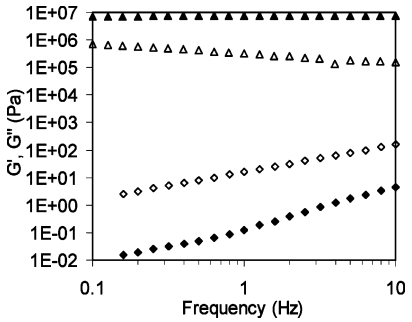



**Figure 4.** Rheological properties of bis-urea grafted PDMS-(30)-*g*-BuP (▲, △) and its amino functional precursor (◆, ◇) at 30 °C. Elastic modulus $G'$ (full symbols); loss modulus $G''$ (hollow symbols).

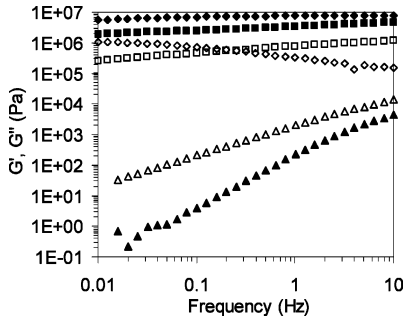



**Figure 5.** Rheological properties of PDMS(30)-*g*-BuP (◆, ◇), PDMS(37)-*g*-NMeP (■, □), and PDMS(30)-*g*-Ph (▲, △) at 30 °C. Elastic modulus $G'$ (full symbols), loss modulus $G''$ (hollow symbols).

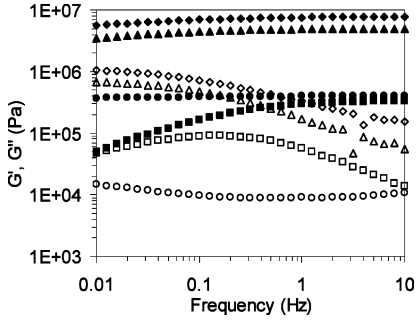



**Figure 6.** Rheological properties of PDMS(30)-*g*-BuP (◆, ◇), PDMS(13)-*g*-BuP (▲, △), BuP/PDMS(29)/BuP (●, ○), and PDMS(10)-*g*-BuP (■, □) at 30 °C. Elastic modulus $G'$ (full symbols), loss modulus $G''$ (hollow symbols).

elastic plateau increases in the order BuP/PDMS(29)/BuP ≪ PDMS(13)-*g*-BuP < PDMS(37)-*g*-NMeP < PDMS-(30)-*g*-BuP. On the contrary, PDMS(10)-*g*-BuP has an elastic behavior only for the highest frequencies (Figure 6), and PDMS(30)-*g*-Ph is a viscous liquid, even for high frequencies (Figure 5). The viscosity of mono-urea grafted PDMS(30)-*g*-Ph is Newtonian over a wide shear

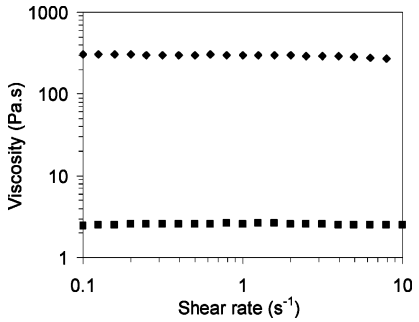



**Figure 7.** Viscosity of PDMS(30)-*g*-Ph (◆) and its amino-functional precursor (■) at 30 °C.

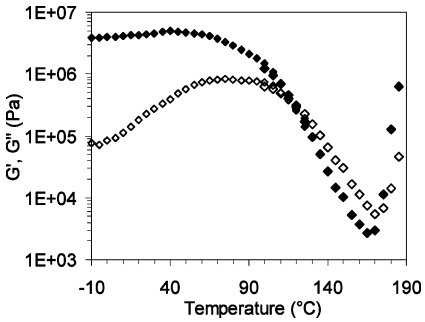



**Figure 8.** Evolution of the elastic modulus $G'$ (◆) and of the loss modulus $G''$ (◇) for PDMS(13)-*g*-BuP at 1 Hz.

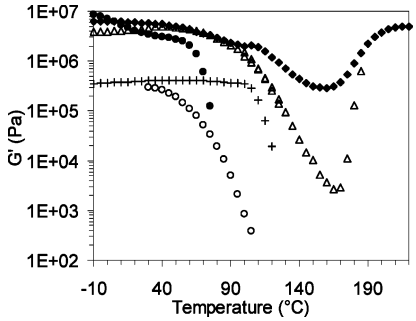



**Figure 9.** Temperature dependence of the elastic modulus $G'$ for PDMS(30)-*g*-BuP (◆), PDMS(13)-*g*-BuP (△), PDMS(10)-*g*-BuP (○), PDMS(37)-*g*-NMeP (●), and BuP/PDMS(29)/BuP (+) at 1 Hz.

rate range, but it is $10^2$ times as high as the viscosity of its amino-functional precursor (Figure 7). Finally, BuP/PDMS(4)/BuP could not be tested because it did not stick to the rheometer plates and was very brittle below 190 °C.

**5. Rheological Properties at High Temperatures.** Figures 8 and 9 show the thermomechanical behavior of the modified PDMS. PDMS(13)-*g*-BuP is a rubber up to 80 °C. Then, $G'$ decreases and the polymer becomes viscous above 100 °C, which makes it easy to process from 100 to 140 °C. Above 160 °C, a rapid increase of

the elastic and loss moduli is observed, and the polymer can then hardly be processed.

The evolution of the elastic moduli of the different bis-urea modified PDMS are compared in Figure 9. Although the rheological properties of PDMS(30)-*g*-BuP and PDMS(37)-*g*-NMeP are very similar at 30 °C, a huge difference is observed at higher temperatures. Indeed, the end of the rubbery plateau occurs at 60 °C for PDMS(37)-*g*-NMeP, but at 110 °C for PDMS(30)-*g*-BuP. Finally, PDMS(10)-*g*-BuP flows at about 40−50 °C, BuP/PDMS(29)/BuP flows at 110 °C, and BuP/PDMS(4)/BuP could not be analyzed by rheology but softens at 190 °C.[26]

## Discussion

The fact that all the materials described here are fully soluble in THF proves that no covalent cross-linking occurred during synthesis or processing. Nevertheless, the PDMS modified by bis-ureas present much better rheological and tensile properties than their amino-functional precursors. The origin of this improvement, as well as the differences between the seven samples, are now discussed.

**1. Telechelic Polymers. BuP/PDMS(4 or 29)/BuP.** The observation of an endothermic peak close to the melting temperature of low molecular weight reference bis-ureas (Figure 1) suggests that the chain-ends of the telechelic polymers are organized in a crystallike structure. The ordered phase of hydrogen bonded bis-ureas must be responsible for the physical cross-linking of the polymers and the improvement of their mechanical properties (Figure 6, Table 3), compared to their amino-functional precursors. Moreover, the melting of the ordered domains of bis-ureas at high temperatures leads to a weakening of the physical network, which enables the processing of these materials. The rapid decrease of the elastic modulus $G'$ of BuP/PDMS(29)/BuP (at 110 °C) is indeed very close to the melting point (135 °C) observed for this polymer (Figures 1 and 9).

Despite these interesting observations, neither BuP/PDMS(4)/BuP nor BuP/PDMS(29)/BuP are strong elastomers, probably because the chains of BuP/PDMS(4)/BuP are too short to entangle and the bis-urea content of BuP/PDMS(29)/BuP is too low for an efficient cross-linking.

In fact, these polymers behave similarly to 4-carboxyphenylurazole telechelic polyisobutylenes described by Stadler et al.[27,28] The latter are physically cross-linked by 4-carboxyphenylurazoles which self-assemble by hydrogen bonds and form ordered structures in the polymer. However, bis-ureas melt at higher temperatures than 4-carboxyphenylurazoles, which enhances the thermomechanical properties.

In an effort to reduce the crystallization tendency of bis-urea functions, randomly grafted polymers were then considered.

**2. Grafted Polymers. PDMS(10, 13 or 30)-*g*-BuP.**
**2.1. Mechanical Properties at Room Temperature.** These materials are also physically cross-linked by an ordered phase of hydrogen bonded bis-ureas according to SAXS experiments (Figure 2). However, the ordered domains are not as regular as in the telechelic polymers: no sharp endothermic peak is observed by DSC for PDMS(30)-*g*-BuP.

Since, PDMS(10, 13, or 30)-*g*-BuP are grafted polymers, it is possible to vary their molecular weight and their bis-urea content independently. In particular, PDMS(30)-*g*-BuP combines a high bis-urea content with long polymer chains. As a consequence, this material is a strong elastomer at room temperature (Figures 3 and 6 and Table 3). On the contrary, PDMS(13)-*g*-BuP, whose bis-urea content is close to that of PDMS(30)-*g*-BuP, has a high rubbery plateau (Figure 6), but its shorter chains are probably responsible for its poor tensile properties (Table 3). Finally, PDMS(10)-*g*-BuP possesses neither long chains nor high bis-urea content, which explains its poor tensile and rheological properties (Figure 6 and Table 3).

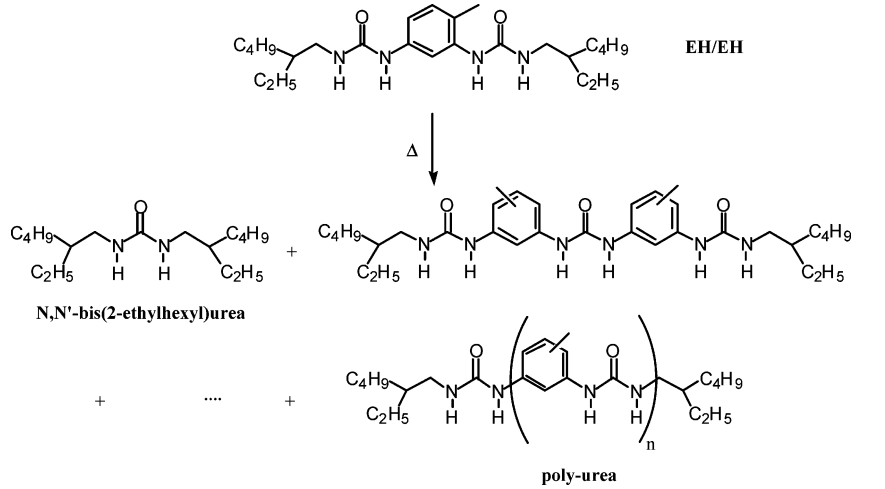
**2.2. Degradation of Bis-Ureas.** According to Figure 8, PDMS(13)-*g*-BuP can be processed above 100 °C. However, a rapid increase of the elastic modulus at 160 °C forbids the processing at higher temperatures. The increase of the elastic and loss moduli above 160 °C is actually caused by chemical cross-linking of the material. Indeed, the sample used for this analysis swelled, but was not soluble in THF at the end of the experiment. Similarly, after one night at 150 °C, a sample of PDMS(30)-*g*-BuP is insoluble in THF, although one night at 100 °C does not affect the solubility.

To understand the nature of this cross-linking reaction, a thermogravimetric analysis was performed. TGA experiment on PDMS(30)-*g*-BuP (under air atmosphere) reveals that no significant weight loss is observed up to 200 °C, whereas the chemical cross-linking happens as soon as 150 °C. On the basis of literature, it is possible to attribute this cross-linking without weight loss to degradation of urea functions.[29] Indeed, at high temperatures, urea functions can generate isocyanate and amine functions which recombine randomly, thus eventually leading to the formation of urea linkages between macromolecules.[30] This interpretation was checked with a model bis-urea: EH/EH (Scheme 2). When this model compound is heated at 200 °C during 1 h, it is degraded, and *N*,*N*′-bis(2-ethylhexyl)urea is identified by $^1$H NMR spectroscopy among the degradation products (Scheme 3).[26] This is in agreement with the random rearrangement of urea functions at high temperatures, which leads to cross-linking in the case of PDMS-*g*-BuP.

**2.3. Processing at High Temperatures.** PDMS(10)-*g*-BuP and PDMS(13)-*g*-BuP were easily processed at 100 °C under pressure. Homogeneous plates were obtained, because the polymers flow but do not degrade at this temperature. The case of PDMS(30)-*g*-BuP is more tricky, since this polymer does not flow at 100 °C. The optimum processing temperature was found to be 140 °C (see Supporting Information). At this temperature, homogeneous plates can be obtained, but degradation occurs to a limited extent, which makes it impossible to recycle the polymer a large number of times. To obtain undegraded plates of PDMS(30)-*g*-BuP for this study, the polymer was pressed at 100 °C and put into contact of THF vapors (see Experimental Section). This procedure reproducibly yielded perfectly homogeneous and undegraded samples.

**3. PDMS(37)-*g*-NMeP and PDMS(30)-*g*-Ph.** PDMS(30)-*g*-BuP, PDMS(37)-*g*-NMeP, and PDMS(30)-*g*-Ph were obtained from the same amino-functional PDMS and have thus similar functionalities and molar masses (Table 1). However, they are grafted with very different associative groups, which results in huge differences of thermomechanical properties (Figures 3, 5, and 9 and Table 3).

**Scheme 3. Degradation Reactions of Bis-Urea EH/EH at High Temperatures**




These properties can be related to the strength of the physical network formed in each case. Indeed, DSC and SAXS experiments (Figures 1 and 2) show that the bis-ureas grafted on PDMS(30)-*g*-BuP and PDMS(37)-*g*-NMeP are ordered, whereas the mono-ureas grafted on PDMS(30)-*g*-Ph are not. Consequently, at room temperature, the crystallization of bis-ureas is responsible for the very good tensile properties of PDMS(30)-*g*-BuP and PDMS(37)-*g*-NMeP. However, when temperature is increased, the strength of the network depends on the precise nature of the bis-urea moiety grafted on the polymer. A previous study in solution has shown that the strength of the self-assembly of bis-ureas increases in the order: NMeP/EH ≪ BuP/EH.[22] This explains the better thermomechanical properties of PDMS(30)-*g*-BuP compared to that of PDMS(37)-*g*-NMeP.

Finally, in PDMS(30)-*g*-Ph, the formation of hydrogen bonds without crystallization is not sufficient to obtain an elastomer at room temperature, because of the low association constant of mono-ureas. Nevertheless, the formation of hydrogen bonds in PDMS(30)-*g*-Ph leads to a polymer much more viscous than its amino-functional precursor (Figure 7): the effect of hydrogen bonds cannot be neglected.

## Conclusion

A quantitative and reproducible synthesis was used to functionalize poly(dimethylsiloxane)s (PDMS) by mono-ureas or bis-ureas without degrading the polymer backbone.

Although the aimed "one-dimensional" physical cross-linking of these polymers was not reached because bis-ureas self-organize at least partially in crystallike domains, the modified materials exhibit impressive viscoelastic and tensile properties compared to their amino-functional precursors.

In particular, all PDMS modified by bis-ureas are elastic solids whereas the amino-functional polymers are Newtonian liquids. Moreover, in the case of PDMS(30)-*g*-BuP and PDMS(37)-*g*-NMeP, the physical cross-linking due to the ordered hydrogen bonded bis-ureas leads to strong elastomers at room temperature. Indeed, these polymers contain enough bis-ureas and have long enough polymeric chains to undergo high strains and stresses during tensile tests. Furthermore, PDMS(37)-*g*-NMeP can be easily processed at 80 °C where its bis-urea domains melt. On the contrary, PDMS(30)-*g*-BuP has very good rheological properties up to 120 °C, but its processing is limited by the degradation of bis-ureas above 150 °C. This material can however be processed at 140 °C and 110 bar without becoming chemically cross-linked.

Finally, tuning the thermomechanical properties of these materials is possible through engineering of the bis-urea functions.

## Experimental Section

**Synthesis.** Amino-functional PDMS (ABCR), and phenylisocyanate (99%, Aldrich), were used as received. THF (analytical grade) was distilled over sodium wire. The synthesis and characterization of the two mono-isocyanate/mono-ureas and of PDMS(30)-*g*-BuP (runs OC106-4, OC120-1, OC128-1), BuP/PDMS(4)/BuP (run OC086-1), BuP/PDMS(29)/BuP (run OC098-3), and PDMS(37)-*g*-NMeP (run OC125-4) was previously reported.[22]

**PDMS(13)-*g*-BuP (Run OC123-1).** A solution of the amino-functional PDMS (AMS-152, 35.0 g, $16.8 \times 10^{-3}$ molar equivalent of $NH_2$ functions) in dry THF (300 mL) was slowly added, at room temperature and under nitrogen, to a stirred solution of mono-isocyanate/mono-urea (OC084,[22] 6.50 g, $20.1 \times 10^{-3}$ mol) in dry THF (260 mL). After 1 week, the reaction mixture was concentrated down to about 200 mL by evaporation of the solvent and precipitated in 2 L of methanol. The precipitate was then filtered on a no. 2 fritted funnel, washed thoroughly with methanol and dried under vacuum. Thus 27.9 g (69% yield) of an off-white rubbery solid was obtained. The full conversion of $-NH_2$ functions was confirmed by $^1$H NMR (the $-CH_2NH_2$ group ($\delta = 2.58$ ppm) was not detected on the final product). $^1$H NMR (200 MHz, $CDCl_3$/[D$_6$]DMSO (85/15 v/v), 22 °C): $\delta$ (ppm) = 8.12/8.00 (s, 2H, Ar−N*H*), $\delta = 7.64$ (d, 1H, Ar−*H*), $\delta = 7.26$ (s, 1H, Ar−N*H*), $\delta = 7.22/6.94$ (m, 6H, Ar−*H*), $\delta = 6.06$ (t, 1H, $CH_2$−N*H*), $\delta = 3.07$ (m, 2H, N−C*H*$_2$), $\delta = 2.46$ (t, 2H, Ar−C*H*$_2$), $\delta = 2.08$ (s, 3H, Ar−C*H*$_3$), $\delta = 1.45$ (m, 4H, $CH_2$−C*H*$_2$−$CH_2$/Ar−$CH_2$−C*H*$_2$), $\delta = 1.26$ (m, 2H, Ar−$CH_2$−$CH_2$−C*H*$_2$), $\delta = 0.82$ (t, 3H, C*H*$_3$), $\delta = 0.47$ (m, 2H, Si−C*H*$_2$), $\delta = -0.01$ (s, 162H, Si−C*H*$_3$). $^{29}$Si NMR (40 MHz, $CDCl_3$/[D$_6$]DMSO (85/15 v/v), 22 °C): $\delta$(ppm) = 7.1 (s, 2Si, O−*Si*(CH$_3$)$_3$), $\delta = -22.0$ (m, 152Si, O−*Si*(CH$_3$)$_2$−O/O−*Si*(CH$_3$)(CH$_2$−)−O). $M_n$ = 13000 g/mol according to $^{29}$Si NMR. IR (film): $\nu$ = 3316 cm$^{-1}$(N−H), $\nu$ = 1640 cm$^{-1}$(C=O). Anal. Calcd: C, 38.1; H, 8.0; N, 2.37. Found: C, 37.91; H, 8.10; N, 2.26. DSC (20 °C/min, $N_2$): $T_g = -118$ °C (inflection point). SEC (THF): $M_n$ = 13000, $M_w$ = 20000, $I_p$ = 1.5.

**PDMS(10)-*g*-BuP (Run OC121-1).** The synthesis of PDMS(10)-*g*-BuP is derived from that of PDMS(13)-*g*-BuP and only the purification method and the mono-isocyanate/mono-urea used (OC116[22]) are slightly different. After 1 week, the reaction mixture was concentrated down to about 70 mL by evaporation of the solvent and precipitated in 2L of methanol. The viscous oil obtained was decanted and washed three times with

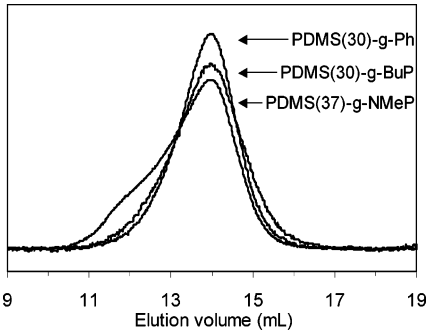



**Figure 10.** SEC chromatograms of PDMS(30)-*g*-Ph, PDMS-(30)-*g*-BuP, and PDMS(37)-*g*-NMeP (UV detection).

methanol and dried under vacuum to afford a transparent brittle rubbery solid (74% yield). $^1$H NMR (200 MHz, $CDCl_3$/[$D_6$]DMSO (85/15 v/v), 22 °C): $\delta$ (ppm) = 8.15/8.01 (s, 2H, Ar−N*H*), $\delta$ = 7.65 (d, 1H, Ar−*H*), $\delta$ = 7.26 (s, 1H, Ar−N*H*), $\delta$ = 7.22/7.16/6.96/6.90 (d, 6H, Ar−*H*), $\delta$ = 6.06 (t, 1H, $CH_2$−N*H*), $\delta$ = 3.06 (m, 2H, N−C$H_2$), $\delta$ = 2.45 (t, 2H, Ar−C$H_2$), $\delta$ = 2.08 (s, 3H, Ar−C$H_3$), $\delta$ = 1.47 (m, 4H, $CH_2$−C$H_2$−$CH_2$/Ar−$CH_2$−C$H_2$), $\delta$ = 1.24 (m, 2H, Ar−$CH_2$−$CH_2$−C$H_2$), $\delta$ = 0.82 (t, 3H, C$H_3$), $\delta$ = 0.49 (m, 2H, Si−C$H_2$), $\delta$ = −0.02 (s, 435H, Si−C$H_3$). $^{29}$Si NMR (40 MHz, $CDCl_3$/[$D_6$]DMSO (85/15 v/v), 22 °C): $\delta$-(ppm) = 7.2 (s, 2Si, O−*Si*($CH_3$)$_3$), $\delta$ = −22.0 (m, 82Si, O−*Si*($CH_3$)$_2$−O/O−*Si*($CH_3$)($CH_2$−)−O), $M_n$ = 6500 g/mol according to $^{29}$Si NMR. IR (film): $\nu$ = 3319 cm$^{-1}$(N−H), $\nu$ = 1638 cm$^{-1}$(C=O). Anal. Calcd: C, 34.8; H, 8.0; N, 0.98. Found: C, 35.36; H, 8.03; N, 0.98. DSC (20 °C/min, $N_2$): $T_g$ = −123 °C (inflection point). SEC (THF): $M_n$ = 10500, $M_w$ = 14500, $I_p$ = 1.4.

**PDMS(30)-*g*-Ph (Run OC132-4).** The synthesis of PDMS-(30)-*g*-Ph is derived from that of PDMS(13)-*g*-BuP except that phenylisocyanate is used to modify the amino functions. After 1 week, 25 mL of methanol were added into the reaction mixture, which was then concentrated down to about 70 mL by evaporation of the solvent. The polymer was precipitated in 2 L of methanol and formed a viscous oil. The oil was decanted, washed three times with methanol, and dried under vacuum to afford a viscous liquid. As the yield was low, a second fraction of PDMS(30)-*g*-Ph was obtained after elimination of the methanol from the soluble part, redissolution in a minimum of THF, and precipitation in methanol. SEC and $^1$H NMR revealed that both fractions were similar and they were combined by dissolution in THF and evaporation of the solvent (54% yield). $^1$H NMR (200 MHz, $CDCl_3$/[$D_6$]DMSO (85/15 v/v), 22 °C): $\delta$ (ppm) = 7.91 (s, 1H, Ar−N*H*), $\delta$ = 7.28/7.12/6.81 (m, 5H, Ar−*H*), $\delta$ = 5.70 (t, 1H, $CH_2$−N*H*), $\delta$ = 3.07(q, 2H, N−C$H_2$), $\delta$ = 1.46 (m, 2H, N−$CH_2$−C$H_2$−$CH_2$), $\delta$ = 0.45 (m, 2H, Si−C$H_2$), $\delta$ = −0.01 (s, 148H, Si−C$H_3$). IR (film): $\nu$ = 3335 cm$^{-1}$(N−H), $\nu$ = 1650 cm$^{-1}$(C=O). Anal. Calcd: C, 35.2; H, 8.0; N, 1.39. Found: C, 35.14; H, 8.11; N, 1.35. DSC (20 °C/min, $N_2$): $T_g$ = −117 °C (inflection point). SEC (THF): $M_n$ = 28000, $M_w$ = 63000, $I_p$ = 2.3.

$^1$H and $^{29}$Si NMR spectra were recorded on a Brüker AC200 200 MHz spectrometer at 20 °C. FTIR spectra were obtained, from THF or chloroform solutions evaporated on KBr disks, with a Nicolet Avatar 320 spectrometer at 20 °C. SEC was performed in THF with PL-gel columns and with ultraviolet (UV) and refractive index (RI) detectors. The samples were injected at 5 g/L. The number and mass average molecular weights of the modified polymers were determined with the RI detection, using a polystyrene calibration. The absence of low molecular weight residual compounds such as hydrolyzed mono-isocyanate was checked by UV detection.

The amino-functional precursors could not be analyzed by SEC because of the adsorption of amines on the columns. Thus, PDMS(30)-*g*-Ph, which was obtained from a commercial mono-isocyanate containing no diisocyanate, was used as a reference. Indeed, if the fractionation during precipitation is neglected, PDMS(30)-*g*-Ph is expected to be almost identical to its amino-functional precursor. Figure 10 shows that the chromatograms of PDMS(30)-*g*-BuP and PDMS(30)-*g*-Ph (UV detection) are almost identical. This confirms that BuP/NCO + NCO/BuP does not contain any residual diisocyanates.[22] On the contrary, a small increase of molecular weight can be observed for PDMS(37)-*g*-NMeP, which confirms that the mono-isocyanate/mono-urea used for the synthesis of this polymer contained a small amount of residual diisocyanate.[22,26] Nevertheless, PDMS-(37)-*g*-NMeP is not chemically cross-linked.

**Mechanical Analysis. Processing of the Testing Plates.** Homogeneous plates of the modified PDMS were obtained by pressing the polymer powder between two steel plates spaced by a 1 mm mold at 100 °C and 110 bar during 10 min and then cooling to room temperature under 110 bar for 10 min more. Teflon-coated paper sheets were used to help unmolding.

PDMS(30)-*g*-BuP did not yield homogeneous plates with this method. Then, after a first pressing at 100 °C and 110 bar, the unhomogeneous plates of PDMS(30)-*g*-BuP were placed in a container saturated with THF vapors. When the polymer seemed homogeneous, it was taken out of the container and left overnight under a hood. When only small amounts of THF were present in the polymer, the latter was pressed again at 100 °C and 110 bar. Finally, it was dried under vacuum to eliminate the remaining THF.

**Tensile Tests.** Tensile tests were performed according to European norm CEI 60811 with dumbbell tensile plates cut from the plates. The section of the testing plates, measured before each run, was about 1 by 4 mm. The strain percentage was determined by measuring the deformation of 20 mm of the dumbbell. The tests were performed on a computer-controlled Zwick tensile tester at 22 °C and with an elongation speed of 200 mm/min. Five testing plates were used for each sample and the results were treated with Test Xpert Software.

**Rheology.** The solid samples were analyzed on a plate-to-plate RDA II rheometer (Rheometrics). Polymer disks of 8 mm diameter and 0.5 to 2 mm thickness were chosen for this analysis. These samples were analyzed by strain-fixed dynamic rheology with a temperature or a frequency sweep. A strain scanning at the highest frequency was realized to select a strain leading to accurate measures of $G'$ and $G''$ in the linear regime. The variable temperature experiments were performed by steps of 5 °C, with an equilibration time of 5 min.

The urea modified PDMS (PDMS(30)-*g*-Ph) and the amino-functional PDMS (AMS-162) were analyzed at 30 °C with a cone to plate RFSII rheometer (Rheometrics). The cone (diameter = 5 cm, angle = $4 \times 10^{-4}$ rad) was spaced from the plate by 45 $\mu$m. The strain was also chosen in the linear regime.

**Other Analyses.** Differential scanning calorimetry was performed on a modulated DSC-2920 (TA-Instruments) under nitrogen and at 20 °C/min. Results were analyzed with the Thermal Advantage software (TA-Instruments). Because of the degradation of bis-ureas above 150 °C, only one ramp from 30 to 220 °C was performed for the modified PDMS.

PDMS(30)-*g*-BuP was analyzed by thermogravimetric analysis (TGA) in a platinum cup, under air atmosphere, and at 20 °C/min, on a TGA-Q50 device (TA-Instruments).

**SAXS.** The generator was a rotating Rigaku copper anode powered by a 12 kW current. The sample was placed 38 cm away from the detector, which measured the scattered intensity ($I$) vs the incidence angle ($2\theta$). The reported distance ($d$) is related to $\theta$ by the Bragg law: $d = \lambda/(2 \sin \theta)$.

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**Supporting Information Available:** Text discussing the processing tests of PDMS(30)-*g*-BuP between 100 and 160 °C, including figures of tensile properties vs processing temperature, tensile curves, and elastic and loss moduli vs heating time. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) OC106-4 was precipitated twice since a higher excess of isocyanate was used for modification.
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