[60]Fullerene-Containing Poly(dimethylsiloxane)s: Easy Access to Soluble Polymers with High Fullerene Content

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ABSTRACT: The attachment of [60]fullerene to poly(dimethylsiloxane)s leads to soluble and structurally defined fullerene-containing polymers, exhibiting excellent film-forming properties. Different strategies for the synthesis of polymers, either containing [60]fullerene in the polymer backbone or bearing [60]fullerene as part of the side chains, are described. In the latter case, [60]fullerene contents up to 30 wt % were obtained.

Introduction

Many applications of [60]fullerenes, e.g., as catalysts[1−3] or as stationary phases for the separation of PAH's,[4] require immobilization of the [60]fullerene unit.[5−13] Moreover, it is often desirable to combine the properties of polymer materials such as elasticity and film formation with the characteristic properties of [60]fullerene, among which are electron deficiency[14] and optical limiting behavior.[15] Thus, the synthesis of [60]fullerene-containing polymers represents one of the most important challenges of fullerene chemistry.[16−30] Despite many different approaches toward functionalizing [60]fullerenes,[32−42] the synthesis of structurally defined fullerene-containing polymers still remains a challenge. One problem is the electron-withdrawing character of [60]fullerene, which causes reactions with both nucleophiles and radicals. Thus, radical or anionic polymerization in the presence of C_{60} often leads either to star-shaped polymers[26] with a relative low fullerene content or, in the worst case, to nonprocessible cross-linked polymers. Another difficulty lies in the multifunctional character of [60]fullerene, which contains 30 reactive double bonds. This feature complicates the preparation of pure mono- or bifunctional fullerene adducts.

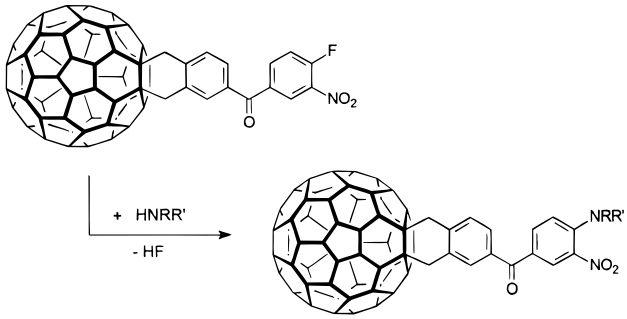
The controlled incorporation of fullerenes into well-defined linear polymers can, in principle, proceed in two synthetic ways: (i) the polycondensation of bifunctional fullerene adducts with suitable bifunctional reagents or end-functionalized polymers and (ii) the polymer analogous reaction of side-chain functionalized polymers with monofunctional fullerene adducts.

Herein, we describe a new approach toward well-defined fullerene-containing poly(dimethylsiloxane)s, using the *o*-xylylene derivatization method[35−37,43,44,46] for [60]fullerene. The polymers obtained exhibit outstanding solubility in common solvents (such as chloroform, THF, and benzene), a high thermal stability, and excellent film-forming properties.

Results and Discussion

The solubility and hence the processibility of fullerene-containing polymers is drastically decreased by $\pi-\pi$ interactions between the fullerene and aromatic units of the polymer chain.[37] To avoid such problems, we decided to use only nonaromatic monomers or polymer chains as building blocks for polymer synthesis. Among several possibilities, poly(dimethylsiloxane) (PDMS) seemed to be the most feasable polymer backbone, since it possesses an extraordinary high chain mobility,[47] leading to a very good solubility, and it shows a high thermal stability.

Scheme 1



To attach the C_{60} units, we applied the well-established *o*-xylylene method,[35−37,43−46,48,49] because *o*-xylylene−C_{60} adducts reveal advantages similar to those of PDMS: They are highly soluble, even if not substituted, and thermally stable up to temperatures of 400 °C. One method for generating *o*-xylylenes is the thermal ring opening of benzocyclobutenes. Substituted benzocyclobutenes can easily be prepared, and the required temperature for ring opening is relatively low compared to other methods.[36,43]

Recent results from our group showed that activation of fluoro substituents by nitro groups enables C_{60} adducts to undergo nucleophilic substitutions[36] (Scheme 1).

The introduction of a second nitro group results in a dramatically increased reactivity.[43,50] Thus, the fluorodinitro substituted C_{60} adducts $\mathbf{2}_n$, whereby *n* describes the number of addends attached to one fullerene unit, appear to be well-suited for polycondensation or analogous polymer reactions. To favor the bisadduct formation, an excess of ±-1-(4-fluoro-3,5-dinitrobenzoyl)benzocyclobutenylester (**1**) was allowed to react with [60]-fullerene. Upon being heated to 180 °C, compound **1** was converted in situ into the highly reactive *o*-xylylene derivative (**1a**) which enters into a Diels−Alder reaction with the [60]fullerene. Bisadduct ($\mathbf{2}_2$) was separated from the monoadduct ($\mathbf{2}_1$) and higher adducts $\mathbf{2}_{n>2}$ by

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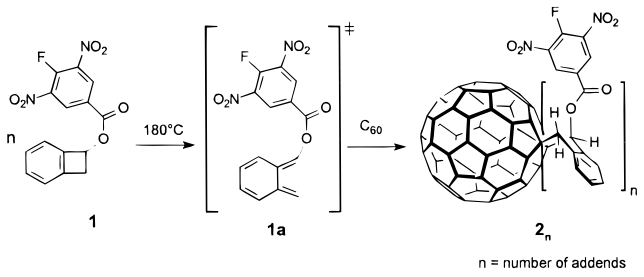
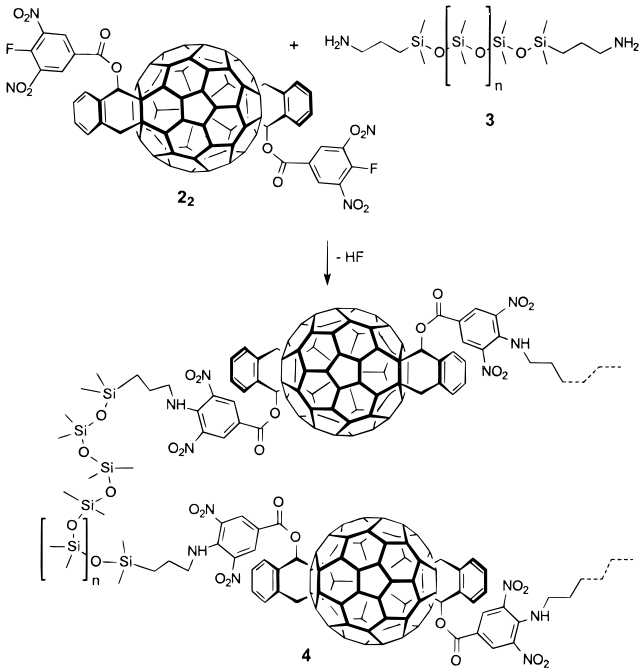
Scheme 2



Scheme 3



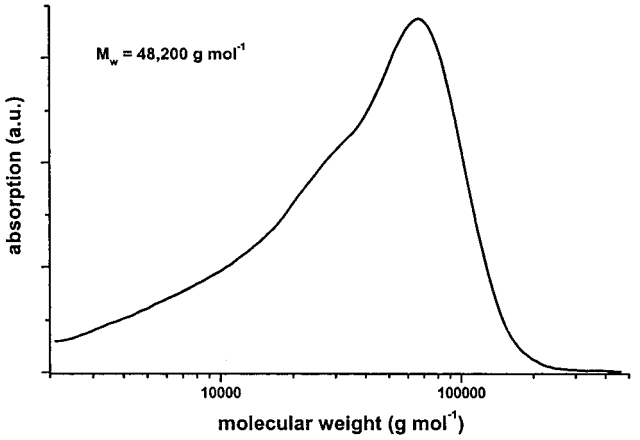


Figure 1. Molecular weight distribution of the unfractionated polymer **4** (detected at $\lambda = 320$ nm).

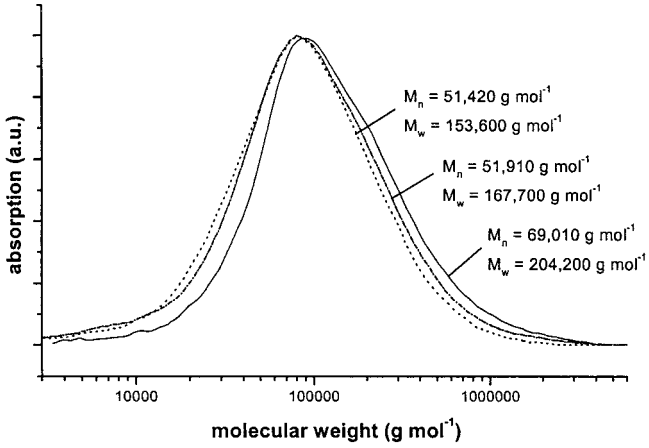


Figure 2. Molecular weight distribution after SEC fractionation of **4** (detected at $\lambda = 320$ nm).

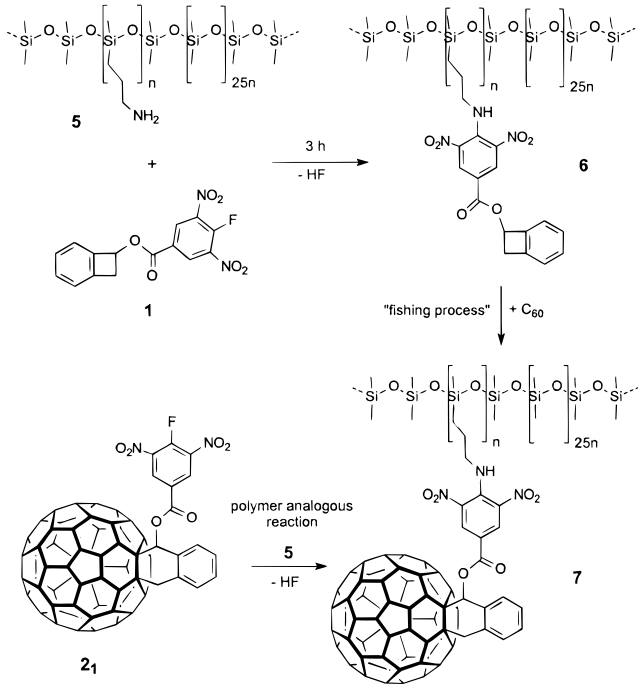
preparative SEC using chloroform as the mobile phase.[51,52]

2_2 as an AA type building block was then allowed to react with a suitable bifunctionalized BB component to yield a polymer containing fullerene units in the main chain. We chose an aminopropyl end-capped poly(dimethylsiloxane) (**3**), which is commercially available and has an average molecular weight of approximately 35 000. The reaction of **2_2** with **3** was performed in dry dichloromethane at room temperature for 3 days (Scheme 3). After workup the fullerene-containing poly(dimethylsiloxane) **4** was isolated as a rubbery solid, soluble in common solvents such as THF, toluene, and chloroform. Analytical SEC of the unfractionated polymer showed an average molecular weight of only $M_n = 19\,800$ and $M_w = 48\,200$, respectively (calibrated vs polystyrene, Figure 1). The molecular weight distribution shows a long tailing toward lower molecular weights. The relatively high content of low molecular weight material in the polymer probably reflects problems of meeting the exact 1:1 stoichiometry, due to the small amounts of the starting materials **2_2** and **3**. However, the lower molecular parts of polymer **4** could be readily separated by preparative SEC. The remaining polymer fraction of high molecular weight (56 wt % of the raw material) was further fractionated by SEC yielding three fractions of average molecular weights $M_n > 50\,000$ and $M_w > 150\,000$, respectively, as can be seen in Figure 2.

Previous results of our group[43] showed that SEC analysis of fullerene-containing materials tends to reveal lower than expected molecular weights. This phenomenon is most probably caused by $\pi-\pi$ interactions between the fullerene units and the phenyl units of the polystyrene stationary phase, leading to an increase of the elution volume with a corresponding decrease in the apparent molecular weight. Comparison of the molecular weights determined by SEC and those determined by absolute methods such as vapor pressure osmometry leads to a correction factor of approximately 2. Considering this correction factor, an average polymer chain of **4** consists of nine PDMS and fullerene units. The average fullerene content is 4%. The incorporation of C_{60} units into the polymer was also confirmed by the UV/vis absorption of **4**. The absorption spectrum shows an unstructured band shape with shoulders at 289, 326, and 415 nm, which is characteristic for [60]fullerene bisadducts. The high molecular weight of **4** resulted in excellent film-building properties and allowed the production of free-standing films.

An alternative route toward fullerene-containing polymers is to bind fullerene monoadducts to a suitably functionalized polymer backbone. This can be achieved in a direct coupling reaction or by first attaching an *o*-xylylene precursor to the polymer, followed by reaction of the modified polymer with unfunctionalized C_{60} ("fishing process").[45] The latter has the advantage that the troublesome chromatographic separation of monoadducts can be avoided and that *o*-xylylene-modified polymers are easy accessible. However, to suppress the formation of higher adducts and thus branching or

Scheme 4



cross-linking processes, one has to apply an excess of [60]fullerene.

We prepared the same polymer by using both the polymer analogous reaction and the fishing process. Among commercially available functionalized poly(dimethylsiloxane)s, a copolymer (**5**) of diethoxydimethylsilane with 4−6% (3-aminopropyldiethoxy)methylsilane seemed to be most appropriate. This polymer has an average molecular weight of about 10 000. Thus, each chain bears six to seven aminopropyl groups. These may be further allowed to react either in one step, by nucleophilic substitution of monoadduct (**2₁**), or in a two-step procedure with ±-1-(4-fluoro-3,5-dinitrobenzoyl)-benzocyclobutenylester (**1**) followed by addition to [60]fullerene (Scheme 4).

The reaction of the polymer **5** with **1**, performed at room temperature in dry dichloromethane, was complete after 3 h (Scheme 4). The successful nucleophilic substitution of **1** was indicated by a color change from yellow-green to yellow-orange. The modified polymer (**6**) was then allowed to react with 2 equiv of [60]fullerene in boiling 1,2-dichlorobenzene for 12 h. The fullerene-containing polymer (**7**) was isolated as a dark brown rubbery solid that was completely soluble in dichloromethane, THF, and toluene. The dark color of the polymer is caused by the high fullerene content. ^{1}H NMR measurements confirmed the attachment of one [60]fullerene unit to each aminopropyl group. Since the molecular weight of **5** (10 000) and the average number of amino groups (6.5 per chain) is known, the average fullerene content can be calculated to be approximately 30 wt %. The absence of insoluble material provides evidence that cross-linking by multiadduct formation has been suppressed by using an excess of C_{60}.

When, in the direct route, **2₁** was allowed to react with **5** in dry dichloromethane for 3 h, the isolated polymer (**7**), again a soluble dark brown solid, turned out to be very similar to the material synthesized by the fishing process. SEC analysis revealed identical values M_n = 8300 and M_w = 19 000 for both samples (Figure 3). Comparison with the average molecular weight of the

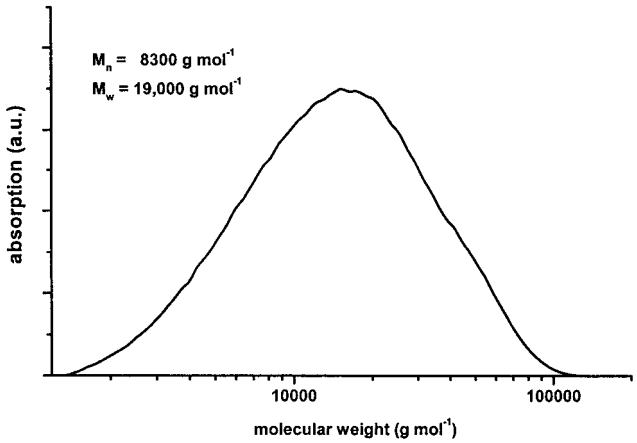


Figure 3. Molecular weight distribution of **7** (detected at λ = 320 nm).

starting material **5** (M_n = 10 000) shows that the above values are significantly too low. Again, ^{1}H NMR measurements showed no evidence for the existence of unreacted aminopropyl groups. Thus, based on a fullerene content of 30 wt %, the average molecular weight is calculated to be approximately M_n = 17 000 (=6.5 × 1052 + 10 000), corresponding to an average fullerene content of 30 wt %. The difference between the SEC result and the calculated value once again confirms the correction factor of 2.

The UV/vis spectrum of **7** is typical for [60]fullerene monoadducts showing the characteristic absorption maximum at λ = 433 nm. Furthermore, **7** possesses a high thermal stability. Thermal decomposition occurs only at temperatures above 300 °C. In contrast to the starting material, which does not show any glass transition above −150 °C, both samples of **7** show a glass transition at −107 °C.

Thus, both methods, the fishing process and the polymer analogous reaction with functionalized monoadducts, prove to be suitable for the synthesis of structurally defined polymers with a high fullerene content. A second example for the successful use of the fishing process was achieved by attaching benzocyclobutene-1-carboxylic acid (**8**) to the aminopropyl-modified poly(dimethylsiloxane) (**5**). Due to the instability of benzocyclobutenes in acids, it is difficult to convert **8** into the acid chloride. Instead we used diisopropylcarbodiimide and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)[53] to produce the corresponding benzocyclobuten-1-acid amide modified polymer (**9**) (Scheme 5). The reaction was performed in dry dichloromethane at room temperature for 24 h. The reaction mixture was then precipitated in methanol to separate **9** from the catalyst and the diisopropylurea that was formed during the reaction. In the subsequent step, **9** and 2 equiv of C_{60} were refluxed in 1,2-dichlorobenzene, yielding a dark brown (due to the high fullerene content) polymer (**10**) (Scheme 5). Since the backbone of this polymer is identical to that of **7** and no unreacted aminopropyl side chains were detected by ^{1}H NMR spectroscopy, the average molecular weight and the fullerene content must be similar to the case of **7**.

While the shape of the SEC chromatogram of **10** was similar to that of **7** (Figure 4), the analysis results in slightly larger average molecular weights M_n = 9500 and M_w = 20 000. One explanation might be the absence of the extremely electron-deficient dinitroarene in **10**. The dinitroarene unit could cause additional $\pi-\pi$

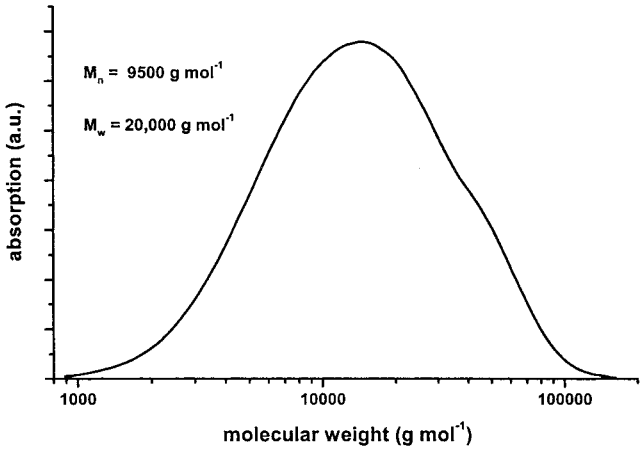
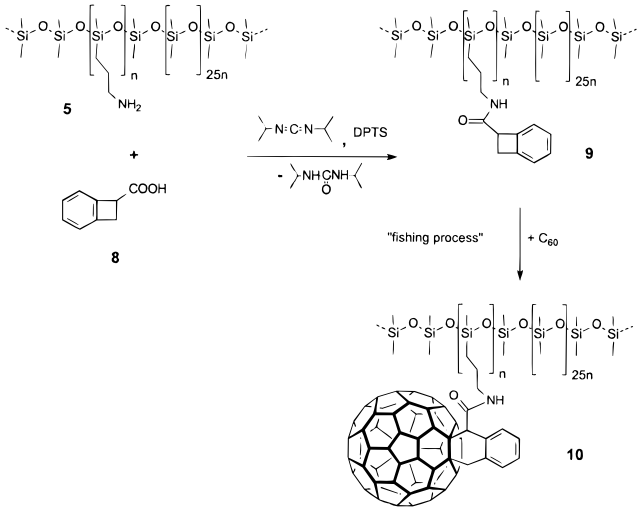


Figure 4. Molecular weight distribution of **10** (detected at λ = 320 nm).

Scheme 5



interactions with the stationary phase in the case of **7**, leading to slightly lower molecular weights.

The molecular weights were also confirmed by solution viscometry. The determined intrinsic viscosities (in toluene at 20 °C) were $[\eta] = 0.109$ for both **7** and **10**. Since **7** and **10** have similar structures and since both measurements were performed under the same conditions, the $[\eta]$ values are truly comparable.

As expected, DSC reveals nearly the same glass transition temperature for **10**: $T_g = -107.2$ °C. However, the thermogravimetric analysis of **10** shows an improved thermal stability as compared to **7**. Thermal decomposition occurred above 435 °C and thus proved **10** to be more stable than the starting compound **5** (T_d = 390 °C).

Conclusion

We have shown that the use of reactive fullerene bisadducts allows the incorporation of fullerene units into the polymer backbone of polysiloxanes, whereas reactive monoadducts may be attached to side chain functionalized polysiloxanes. The latter can be achieved either by the direct polymer analogous reaction of fullerene monoadducts with functionalized polymers or by attaching an *o*-xylylene precursor (e.g., benzocyclobutene) to the polymer, followed by the addition of [60]fullerene. Furthermore, we have demonstrated that the fishing process leads to similar results as compared to the attachment of reactive monoadducts.

Consequently, the covalent coupling of [60]fullerene to poly(dimethylsiloxane)s appears to be a versatile method for the synthesis of polymers with high contents of fullerene. All of these polymers show excellent solubility in common solvents and a high thermal stability up to 435 °C. Moreover, the polymers are characterized by good film-forming properties on nonpolar surfaces, which is an important property for many applications. For example, it is well-known that doping of conjugated polymers in photovoltaic cells with fullerenes or fullerene adducts results in dramatically increased quantum yields.[54−57] Thus, it is likely that both the charge separation and the percolation of the charge carriers to the electrodes can be further improved by using alternating thin layers of fullerene-containing and conjugated polymers.

Experimental Part

The poly(dimethylsiloxane)s were purchased from ABCR GmbH&Co. KG, Karlsruhe, Germany, and were used without further purification.

4. Aminopropyl-terminated poly(dimethylsiloxane) (**3**) (M_n = 33 000 , 1.44 g) and $\mathbf{2_2}$ (110 mg, 0.08 mmol) were dissolved in 20 mL of dry dichloromethane. When the polymer **3** and $\mathbf{2_2}$ were mixed, a color change from a greenish glimmer of $\mathbf{2_2}$ to red was observed. After 30 min the solvent was evaporated, and the modified polymer (**4**) was isolated as a brown rubbery solid.

NMR: Since $\mathbf{2_2}$ consists of several regioisomers, it is not possible to assign the NMR signals of the benzylic and aromatic protons of **4**. UV: λ_{max} = 242, 289, 326, and 415 nm. IR: ν (cm^{-1}) = 2962, 2915, 2905, 2359, 2342, 1682, 1412, 1260, 1093, 1020, 865, 800, 700. Analytical SEC: M_n = 18 200; M_w = 48 200. After SEC fractionation: fraction No. 1, M_n = 51 420, M_w = 153 600, 23 wt % of the raw polymer; fraction No. 2, M_n = 51 910, M_w = 167 700, 22 wt % of the raw polymer; fraction No. 3, M_n = 69 010, M_w = 204 200, 11 wt % of the raw polymer.

Polymer 6. 4-Fluoro-3,5-dinitrobenzoic acid benzocyclobutene-1-yl ester (**1**) (500 mg, 1.5 mmol), **5** (2.8 g), and dry triethylamine (200 mg) were dissolved in 50 mL of dry dichloromethane. Within seconds, the color of the reaction mixture changed from green-yellow to yellow-orange. After 3 h, the solvent was evaporated and the residue was purified by precipitating from methanol. The polymer (**6**) was isolated as a yellow highly viscous oil. Yield: 3.2 g (98%).

anal.	% C	% H	% O	% N	% Si
calcd	36.66	7.58	19.54	1.91	34.31
found	35.8	7.1	20.1	1.9	35.1

^{1}H NMR of **6** (300 MHz, $CDCl_3$, 28 °C): δ 0.03 (br s, 2H, CH_2), 0.55 (m, 2H, CH_2), 1.74 (m, 2H, CH_2), 3.03 (m, 2H, CH_2), 3.40 (dd, 1 H, CH_2, J = 14.3 and 6 Hz), 3.78 (dd, 1 H, CH_2, J = 14.3 and 6 Hz), 6.15 (dd, 1 H, CH_2, J = 6 and 2.4 Hz), 7.21 (m, 2 H, CH), 7.52 (m, 2 H, CH), 8.78 (s, 2 H, CH). ^{13}C NMR of **6** (125 MHz, $CDCl_3$, 28 °C): δ 1.56, 14.75, 24.18, 39.41, 49.75, 116.00, 123.84, 124.22, 128.15, 130.84, 133.41, 137.23, 142.33, 143.04, 143.91, 163.74, 174.52.

7. (a) Via a "Fishing Process". The modified PDMS (**6**) (1.5 g) and [60]fullerene (1.1 g, 1.53 mmol, 1.5 equiv of C_{60} per benzocyclobutene unit) were dissolved in 100 mL of 1,2-dichlorobenzene and heated at reflux for 12 h. The solvent was removed by distillation. The residue was extracted with THF until the extracts were colorless, and then the solvent was removed by distillation. **7** was isolated as a black rubbery solid (yield: 2.05 g (79%)).

7. (b) Via a Polymer Analogous Reaction of 5 and $\mathbf{2_1}$. $\mathbf{2_1}$ (pure mono adduct) (300 mg, 0.22 mmol) and **5** (320 mg) were dissolved in 50 mL of dry dichloromethane and stirred for 3 h at room temperature. After the dichloromethane was

evaporated off, 610 mg of the fullerene-containing PDMS (**7**) was isolated as a black rubbery solid (almost quantitative yield).

UV/vis of **7**: λ_{max} = 254, 327, 420 nm. T_g = −107,0 °C. Analytical SEC: M_n = 8300; M_w = 19 000. ^{1}H NMR of **7** (300 MHz, $C_2D_2Cl_4$, 28 °C): δ 0.06 (br s, 2H, CH_3), 0.48 (m, 2 H, CH_2), 1.65 (m, 2 H, CH_2), 2.96 (m, 2 H, CH_2), 4.47 (d, 1 H, CH_2, J = 12 Hz), 4.51 (d, 1 H, CH_2, J = 12 Hz), 4.90 (d, 1 H, CH_2, J = 12 Hz), 5.31 (d, 1 H, CH_2, J = 12 Hz), 7.14−7.93 (m, 4 H, CH), 8.75 (br s, 1 H, CH), 8.83 (s, 1 H, CH), 8.99 (s, 1 H, CH).

9. Poly(dimethylsiloxane) (**5**) (1.29 g), benzocyclobutene-1-carboxylic acid (**8**) (1 g, 6.76 mmol), and diisopropylcarbodiimide (1.81 g, 8.8 mmol) were dissolved in 50 mL of dry dichloromethane and mixed with 4-diethylaminopyridine-4-toluenesulfonic acid salt (400 mg, 1.35 mmol). The reaction mixture was stirred for 12 h at room temperature. During the reaction, the urea precipitated as a white solid. After the reaction was terminated, the urea was removed by filtration and the filtrate was washed three times with water. After the solvent was evaporated off, the modified PDMS (**9**) was isolated as a highly viscous colorless liquid in nearly quantitative yield. Traces of the starting materials were separated by precipitation of **9** from methanol.

anal.	% C	% H	% O	% N	% Si
calcd	36.40	8.16	19.87	0.70	34.86
found	35.18	8.25	20.3	0.66	35.6

^{1}H NMR of **9** (300 MHz, $CDCl_3$, 28 °C): δ 0.01 (br s, 2H, CH_2), 0.38 (m, 2H, CH_2), 1.44 (m, 2H, CH_2), 3.12 (m, 2H, CH_2), 3.22 (dd, 1 H, CH_2, J = 14.5 and 6 Hz), 3.50 (dd, 1 H, CH_2, J = 14.5 and 6 Hz), 4.12 (dd, 1 H, CH_2, J = 6 and 2.6 Hz), 5.63 (br s, 1 H, NH), 7.06 (m, 2 H, CH), 7.18 (m, 2 H, CH). ^{13}C NMR of **9** (125 MHz, $CDCl_3$, 28 °C): δ 0.09, 14.84, 23.48, 35.88, 42.67, 54.12, 122.59, 123.92, 128.08, 128.94, 142.94, 145.13, 172.52.

10. The modified PDMS (**9**) (1 g) and [60]fullerene (570 mg, 0.8 mmol) were dissolved in 100 mL of 1,2-dichlorobenzene. The reaction mixture was heated to reflux for 12 h. During this time, the color changed from violet to brown. The solvent was removed by distillation. The residue was extracted with THF until the extracts were colorless, and the solvent was removed. **10** was isolated as a black rubbery solid (yield: 1 g (72%)).

UV/vis of **10**: λ_{max} = 255, 328, and 433 nm. T_g = −107,2 °C. Analytical SEC: M_n = 9500; M_w = 20 000. ^{1}H NMR of **10** (300 MHz, $C_2D_2Cl_4$, 28 °C): δ 0.05 (br s, 3H, CH_3), 0.47 (m, 2 H, CH_2), 1.61 (m, 2 H, CH_2), 2.94 (m, 2 H, CH_2), 4.43 (d, 1 H, CH_2, J = 12 Hz), 4.48 (d, 1 H, CH_2, J = 12 Hz), 4.88 (d, 1 H, CH_2, J = 12 Hz), 5.28 (d, 1 H, CH_2, J = 12 Hz), 7.18−7.63 (m, 4 H, CH). ^{13}C NMR of **10** (125 MHz, $CDCl_3$, 28 °C, J-modulated spin−echo): δ 1.74 (primary, aliphatic C-atoms), 14.66, 23.49, 43.16, 45.22 (secondary, aliphatic C-atoms), 128.12, 128.93, 129.30, 129.71, 129.89 (ternary, aromatic C-atoms, several signals overlapping), 135.11, 138.65, 139.98, 140.07, 140.30, 141.70, 141.89, 142.27, 142.58, 142.67, 142.88, 144.90, 144.98, 145.09, 145.46, 145.62, 145.79, 145.93, 146.19, 146.38, 146.48, 146.74, 146.81, 148.01, 149.53, 155.86, 156.80, 157.83 (quaternary, aromatic C atoms and C_{60} atoms, several signals overlapping), 170.75 (C=O).

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