Buckybowl polymers: Synthesis of corannulene-containing polymers through post-polymerization modification strategy

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Abstract

In this study, we explore the synthesis of methacrylate polymers carrying buckybowl corannulene as the polymer side-chain. For this, a general reactive scaffold, poly(glycidyl methacrylate) (PGMA), was prepared through an atom transfer radical polymerization process. The glycidyl units of this polymer could be subjected to a nucleophilic ring-opening reaction with mercaptocorannulene. The ring-opening reaction produced a reactive secondary hydroxyl group. These sites could be used to anchor alkyl chains through an esterification reaction. Alternatively, the post-polymerization functionalization could be carried out in one step albeit in a random fashion using two different thiol molecules. Here, the incorporation of an electron-rich thienothiophene moiety is demonstrated along with electron-deficient corannulenes in the polymer chain. The PGMA homopolymer could also be replaced with a random copolymer of methyl methacrylate. In some cases, the ring-opening reaction is carried out only partially to retain the reactive epoxide groups in the molecular structure, which enables further functionalization to alter polymer solubility or allow for intermolecular crosslinking of the structure to obtain thick

polymer films. In essence, various simple synthetic strategies to corannulene-encoded and reactive/functionalizable polymers are established in this work.

Introduction

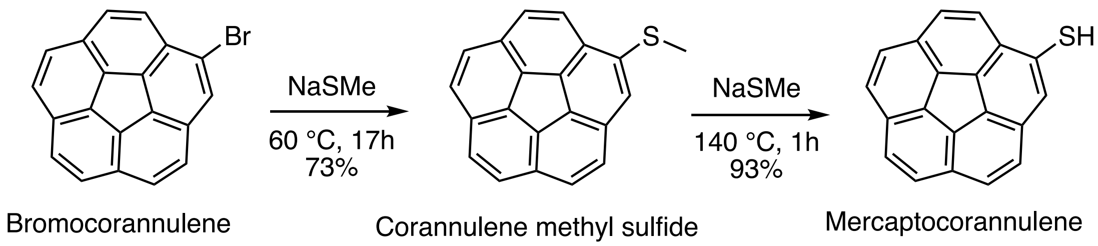
Corannulene ($C_{20}H_{10}$) is a bowl-shaped polycyclic aromatic hydrocarbon.[1-6] It can be conveniently visualized as a fragment of fullerene C_{60}. Interestingly, however, Barth and Lawton envisaged and synthesized this molecule nearly two decades earlier than the discovery of fullerene C_{60}.[7] Their 17-steps synthesis was pioneering and elegant yet a formidable synthetic challenge. A quarter of a century later, in 1991, Scott revived this area of research by developing an efficient gas-phase synthesis.[8] In 1997, Siegel re-introduced the concept of solution-phase synthesis.[9] In 2000, Sygula and Rabideau enhanced its practicality.[10] Nearly half a century after the first synthesis, Siegel developed a kilogram-scale synthesis of corannulene.[11] These synthetic developments have allowed a properties study of this unique molecule. As a result, it is now established that corannulene can invert,[12] accept electrons,[13] and form host-guest complexes.[14-17] This molecular motif, therefore, has considerable potential in materials chemistry.[18]

One particular avenue is the design of hosts for fullerene C_{60}.[14] Corannulene is comparatively less curved than fullerene C_{60} due to the presence of fewer five-membered rings. This relatively relaxed geometry allows corannulene to wrap around the curved surface of fullerene C_{60}. The stabilization to such an ordered structure comes from the π-π stacking interactions between the concave and convex aromatic surfaces. However, to overcome the entropic penalty, multiple interactions are necessary and a 1:1 corannulene:C_{60} complex is not known to exist in solution. The first breakthrough in this direction came from Sygula's buckycatcher in which two corannulenes are joined together to give a rigid molecular clip that can form high-affinity complexes with fullerenes C_{60} and C_{70}.[19] Alvarez and coworkers have utilized flexible porphyrin scaffolds to further increase the number of corannulenes to 4 and 8 and found the latter to be a high-affinity host for fullerenes.[20-21] These small molecule-based corannulene hosts are elegant in their design and efficient at encapsulating fullerenes. However, multistep organic synthesis and a lack of structural modularity are their two major drawbacks.

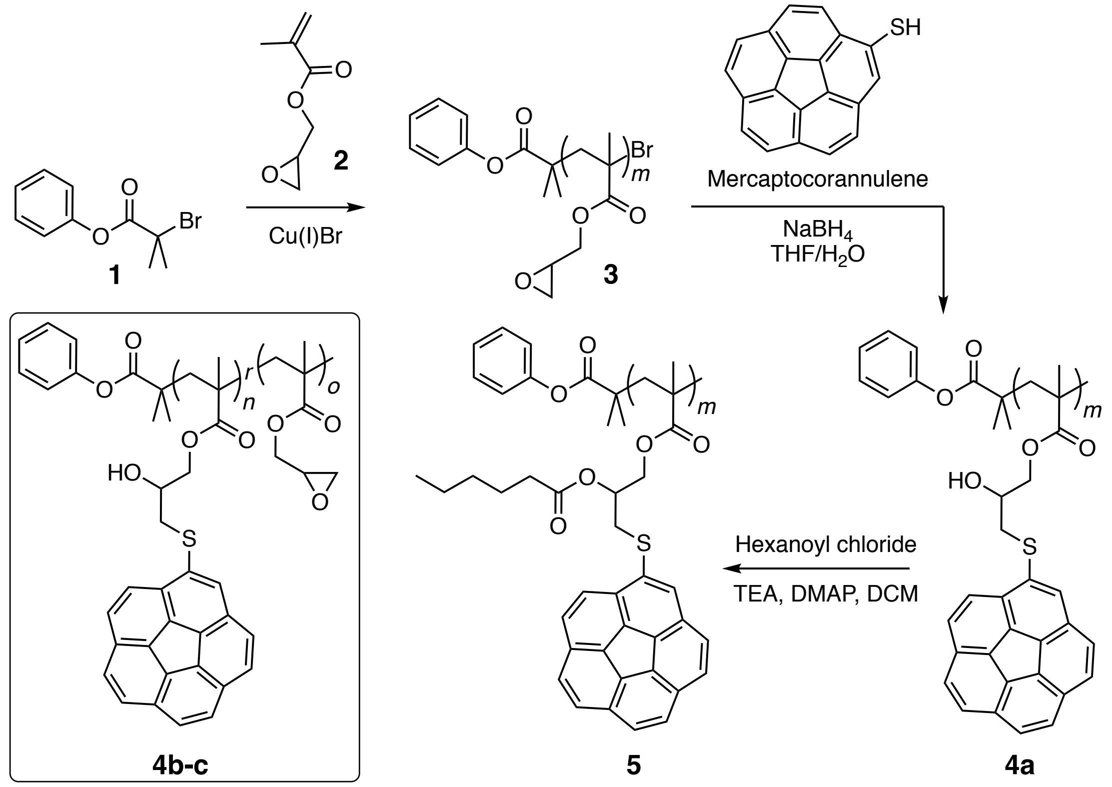
To address these issues, corannulene-based polymeric scaffolds are designed which offer multivalency, structural flexibility, and tunable chemical composition.[22-23] The multivalency is key to hosting a large number of fullerenes (up to 8 wt%) while structural flexibility can allow for accommodation of different fullerene sizes (C_{60} and C_{70}).[23] Finally, complexed fullerenes can be transported into any given medium (organic or aqueous) depending upon polymer composition. The original corannulene polymer synthesis in this context relied upon a macromonomer approach.[22] However, the monomer synthesis is arduous. Furthermore, each monomer poses a different kinetic behavior during polymerization. Therefore, alternative and general synthetic approaches are required to access corannulene-containing polymers.[23] An efficient access to such structures would allow for further study of their hosting capabilities especially in context with higher fullerenes (C_{76} and C_{84}) that are expected to have superior properties but so far studies in this regard are limited due to challenges associated with their processability. For instance, an evaluation of their bio-relevant properties would require solubility in an aqueous media. In the arena of organic electronics, the ability to disperse fullerenes in crosslinkable films may be beneficial for utility in devices. Corannulene itself is also an interesting motif for the preparation of electrochemical devices,[24] and its complexation with lithium ions[25] makes it a potential candidate for use in lithium-ion batteries. It is anticipated, therefore, that the demand for corannulene polymers will continue to grow. Towards this end, in this work, we explore the generality of a recently developed post-polymerization modification strategy[23] to prepare corannulene-containing methacrylate polymers and avenues for further functionalization of these scaffolds.

Results and Discussion

Post-polymerization modification is a practical strategy to prepare functionalized polymer chains.[26-29] In this regard, poly(glycidyl methacrylate) (PGMA) presents a suitable reactive scaffold.[30] The epoxide side-chains of this polymer can be subjected to a nucleophilic ring-opening reaction under basic conditions.[31] Sulfur-based nucleophiles are particularly successful in this context as a few hours of reaction time is sufficient to quantitatively convert high molecular weight PGMA into side-chain polythio-ethers.[32-34] Therefore, bromocorannulene was subjected to a nucleophilic substitution (isolated yield = 73%) followed by a demethylation reaction (isolated yield = 93%) to obtain mercaptocorannulene (Scheme 1).[23] On the other hand, glycidyl methacrylate monomer **2** was polymerized through an atom transfer radical polymerization (ATRP) using aromatic initiator **1** to yield the reactive poly(glycidyl methacrylate) scaffold **3** (Table 1, Scheme 2). In the ^{1}H-NMR spectrum, polymer **3** featured three proton resonances located at 2.6, 2.8, and 3.2 ppm belonging to the reactive epoxide unit of the polymer repeat unit (Figure 1). The aromatic proton resonances arising from the initiating species could be observed at 7.05, 7.25, and 7.39 ppm. These signals allowed for the determination of the average number of repeating units in the polymer chains to be 72-73 in polymer **3**.



Scheme 1. Synthesis of mercaptocorannulene.



Scheme 2. Synthesis of polymers **3**, **4**, and **5**.

Table 1. Gel permeation chromatography-based characterization details of polymers **3-11**.

Entry	Polymer	M_n	M_w	M_w/M_n
1[a]	**3**	7,500	9,600	1.2
2[a]	**4a**	10,300	13,600	1.3
3[a]	**4b**	9,800	13,000	1.3
4[a]	**4c**	8,800	12,000	1.3
5[a]	**5**	12,700	16,000	1.2
6[a]	**6**	5,600	7,200	1.2
7[a]	**7**	7,800	10,200	1.3
8[a]	**8**	10,600	13,700	1.2
9[a]	**9a**	10,500	14,200	1.3
10[a]	**9b**	10,600	14,300	1.3
11[a]	**10**	10,400	13,500	1.2
12[b]	**11**	11,200	14,500	1.2

[a]Measured in tetrahydrofuran. [b]Measured in dimethylformamide.

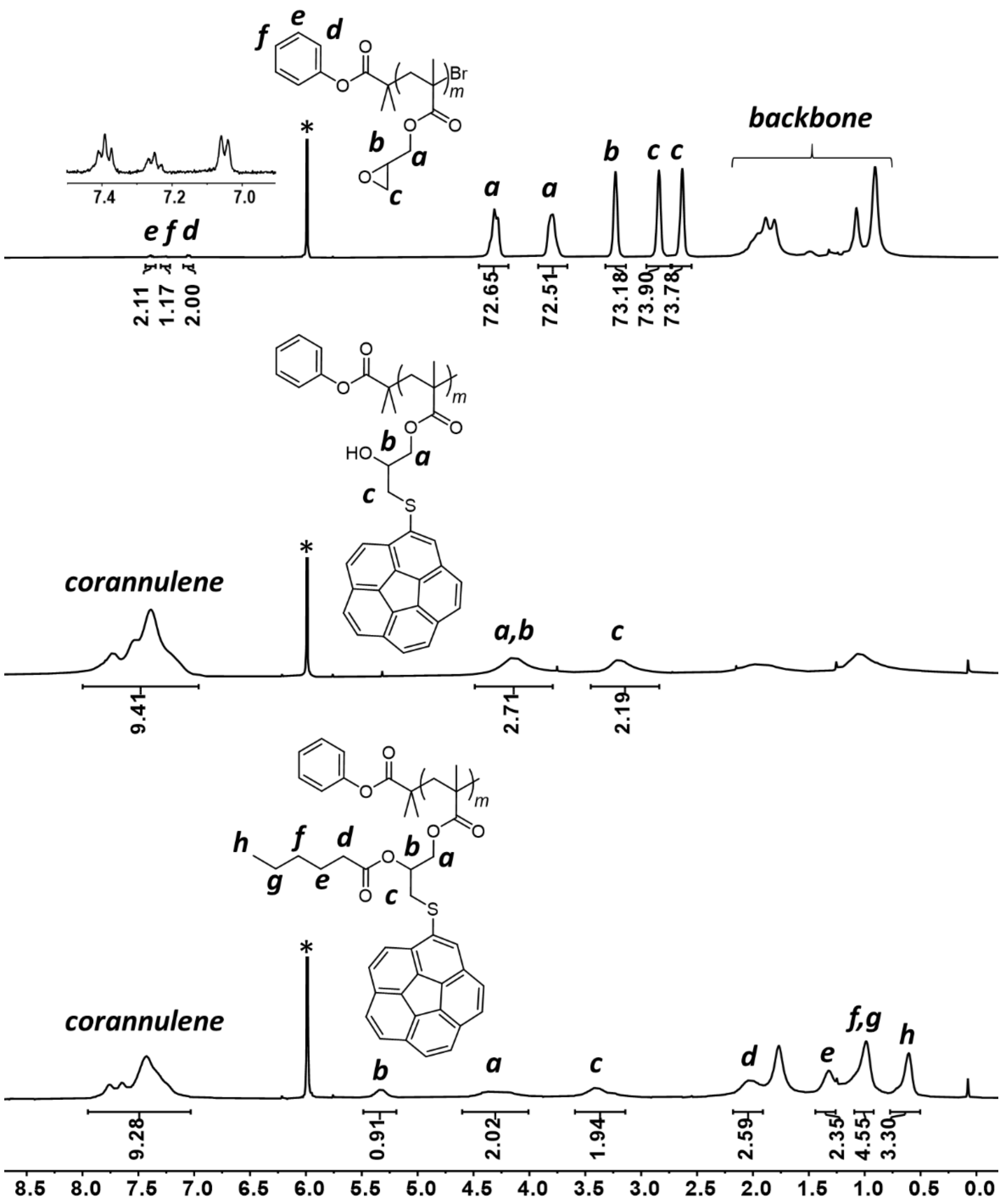


Figure 1. ^{1}H-NMR of polymers **3**, **4**, and **5** in deuterated dichloroethane. The chemical shifts are given in δ/ppm scale.

Having access to the necessary thiol and epoxide precursors, the ring-opening reaction was carried out using sodium borohydride in an aqueous tetrahydrofuran solution. Sharpless and Lauer have shown that sodium borohydride is effective in this regard through their pioneering work on epoxide ring-opening reaction by the selenium nucleophiles.[35] The use of sodium borohydride generates the sodium thiolate necessary for the ring-opening reaction. Sodium borohydride also reduces any disulfide of mercaptocorannulene that might form upon oxidative dimerization during the course of the reaction to the active thiolate form.[36-37] The reactions proceeded smoothly and in 2 hours the corannulene functionalized polymers **4a-c** could be obtained with varying degrees of side-chain functionalization (Figure 1 and Figures S1-S2). A comparison of the area underneath the proton resonances of the unreacted epoxide unit (2.5 and 2.8 ppm) and the corannulene (7-8 ppm) allows for determining the corannulene functionalization to be 100, 50, and 25% in polymers **4a**, **4b**, and **4c**, respectively.

Next, the hydroxyl groups generated as a result of the first polymer modification were used as anchor points for the attachment of a second functional group to the polymer chain (Scheme 2). For this, the hydroxyl groups of polymer **4a** were involved in an esterification reaction with hexanoyl chloride. The signals from the alkyl chain can be located in the aliphatic region (0.5-2 ppm) of the ^{1}H-NMR spectrum (Figure 1). The newly formed ester bond also results in a downfield shift of the proton located at the adjacent carbon atom to 5.4 ppm. An area integration ratio of approximately 3:1 between the terminal methylene group of the alkyl chain (0.6 ppm) and the proton located at the neighboring carbon atom to the ester bond indicates a near quantitative conversion of the free hydroxyl groups in polymer **4** to the ester bonds in polymer **5**. This result suggests the availability of the secondary hydroxyl groups for further polymer modification. Gel permeation chromatography (GPC) analysis suggested that the introduction of bulky side-chains resulted in an increase in the hydrodynamic diameter of the polymer chains and a shift to lower retention time is observed for the functionalized polymers (Figure 2).

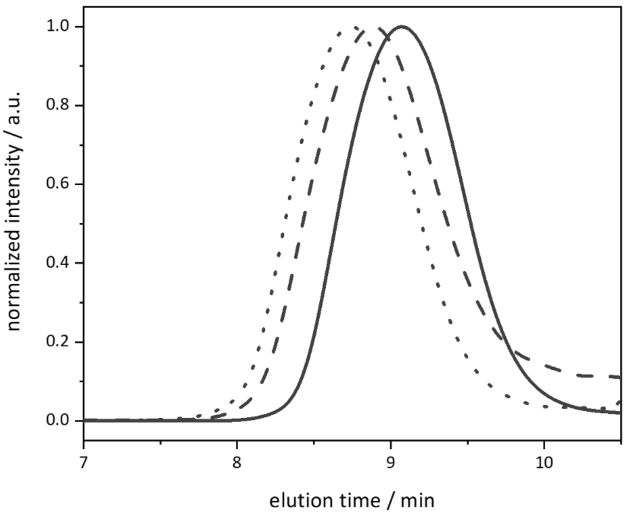
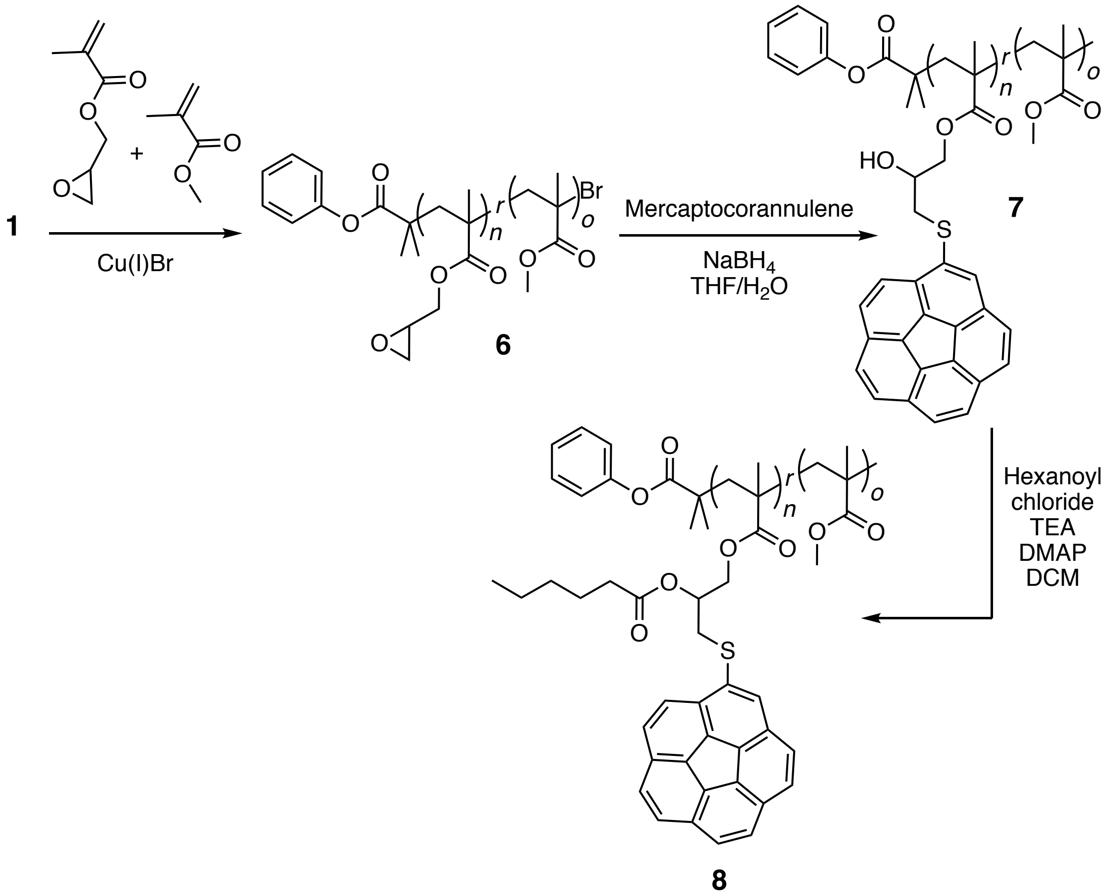


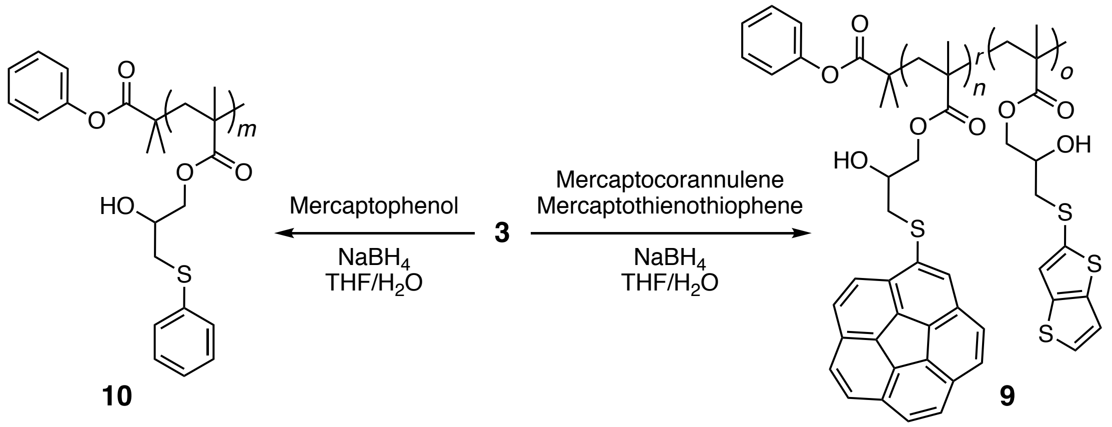
Figure 2. Gel permeation chromatograms for **3** (solid line), **4a** (dash line), and **5** (dot line) in tetrahydrofuran (THF).

The PGMA scaffold could be replaced with a copolymer of methyl methacrylate (MMA) monomer to yield polymer **6** containing 25% MMA repeating units (Scheme 3). A similar sequence of modifications as described earlier led to the synthesis of singly and doubly functionalized polymers **7** and **8** (Figure S3 and S4).

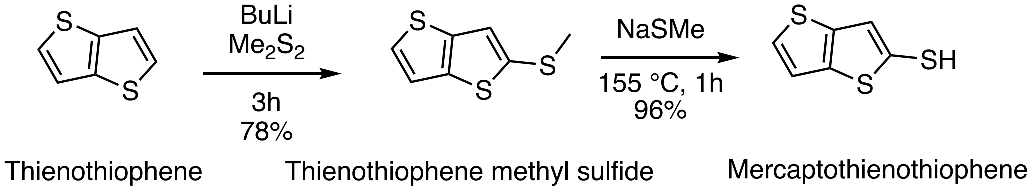


Scheme 3. Synthesis of polymers **6**, **7**, and **8**.

Alternatively, the use of two different thiols allows for random incorporation of the corannulene and a functional group such as an electron-rich thienothiophene moiety (**9**) (Scheme 4 and Figures S5-S6). The thiophene-based donor fragment could be functionalized with a free thiol group by first installing a methylthioether group and then removing the methyl group (Scheme 5). Although thienothiophene is a very simple molecule, one can envisage other electron-rich fragments to potentially prepare corannulene-based donor-acceptor polymers through employing the developed synthetic scheme.



Scheme 4. Synthesis of polymers **9** and **10**.



Scheme 5. Synthesis of mercaptothienothiophene.

To investigate the interaction of corannulene polymers with fullerenes, the best approach is to utilize C_{60}. C_{60} shows only a singlet in its ^{13}C-NMR spectrum that shifts up-field due to the aromatic shielding effect upon complexation with corannulene. In contrast, higher fullerenes, for example, C_{84} show 30 signals in their ^{13}C-NMR spectrum thus making it difficult to unambiguously study the signal shifts upon supramolecular complexation event. Furthermore, ^{13}C-enriched C_{60} can be obtained from commercial suppliers to enhance the signal-to-noise ratio (Figure 3). To rule out any unspecific interactions as the cause for the signal shift, an external-standard tube containing a pure solution of C_{60} in deuterated tetrachloroethane is used. These samples show signals from the uncomplexed fullerene (present as an external standard) and the signal from the polymer complexes. In the case of polymers **4a-c**, an up-field shift of 0.4, 0.8, and 0.8 ppm was observed in the ^{13}C-resonance of C_{60}. A broadening of the C_{60} signal was also observed most likely due to the restricted rotational freedom of the complexed C_{60} molecules. The chemical shift was relatively lower (0.2-0.6 ppm) for polymers **7** containing (Figure S7) PMMA or **9** containing thienothiophene repeating units (Figure S8). Overall, these results indicated that to achieve a maximum interaction, a higher content (≥50%) of corannulenes is necessary in the polymer chain. A control experiment confirmed that the side-chain corannulene units were essential for association with fullerenes as no signal shift was observed when a thiophenol-carrying polymer **10** was dissolved with fullerene C_{60} (Figures S9-11).

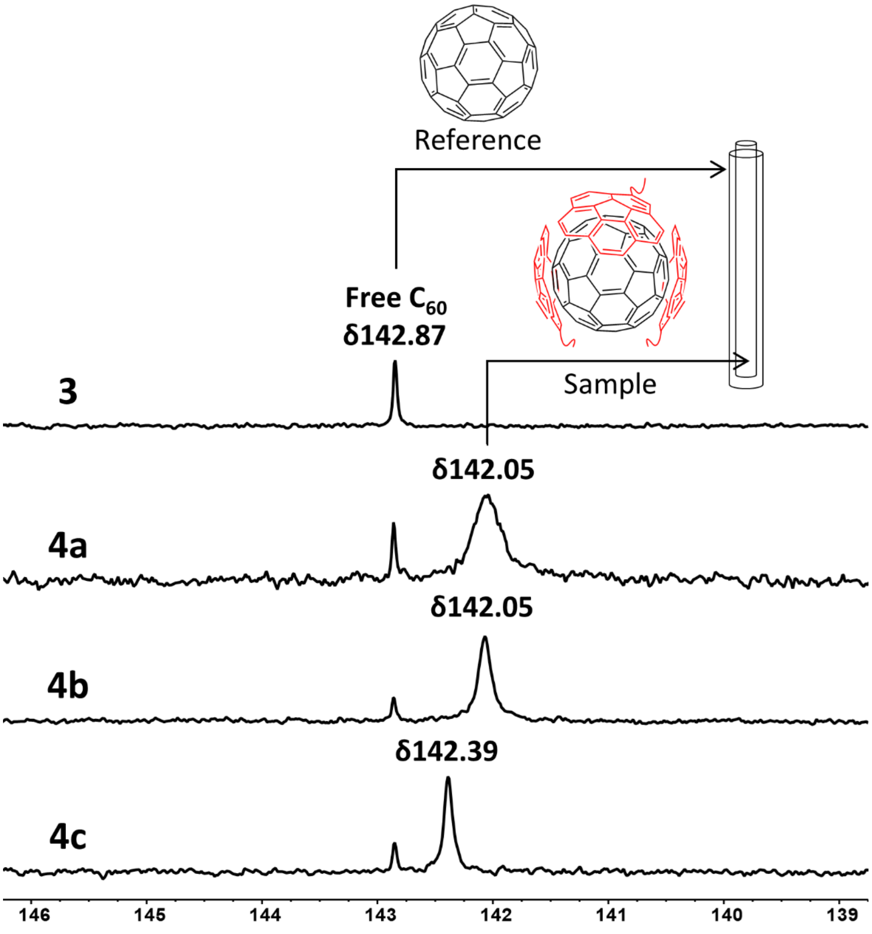
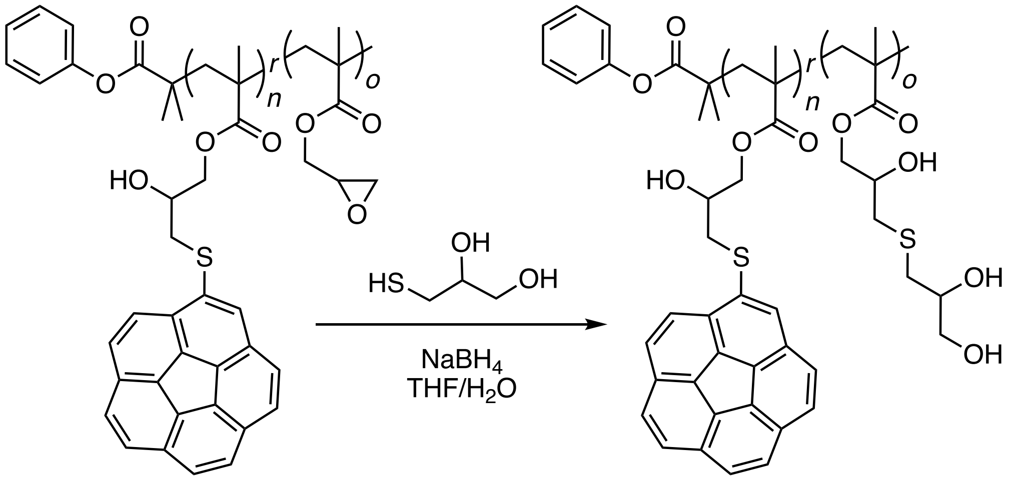


Figure 3. ^{13}C-NMR of fullerene C_{60} in the presence of polymers **3** and **4a-c** in deuterated tetrachloroethane. The chemical shifts are given in δ/ppm scale.

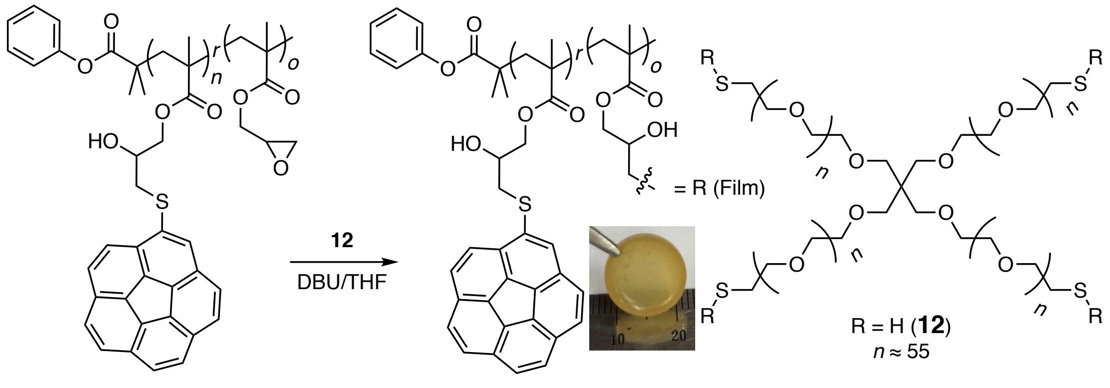
The utility of the residual epoxide units in polymer **4c** is examined next through reaction with thioglycerol to alter polymer solubility (Scheme 6 and Figures S12-13).

Indeed, the glycerol functionalized polymer **11** was observed to be soluble in water due to the hydrophilic nature of the side-chain. Interestingly, while the signal from the aromatic protons is apparent in deuterated DMSO, in deuterated water only the aliphatic resonances could be observed from polymer **11**. This indicates that the hydrophobic corannulene moieties are shielded in water by the glycerol-bearing hydrophilic repeating units (Figures S12). Aqueous solution of polymer **11** allowed for solubilizing fullerene C_{60} in water. The molar absorption coefficient of fullerene C_{60} is 49,000 M^{-1} cm^{-1} at 340 nm. Therefore, by employing UV-Vis spectroscopy, the C_{60} loading% could be calculated to be 3 wt% in the aqueous solution (Figure S14). Such water-soluble corannulene-containing polymers will be useful in evaluating bio-relevant properties of higher fullerenes as discussed in the introduction.



Scheme 6. Synthesis of water-soluble polymer **11**.

Finally, the residual epoxides in **4c** could be used in the intermolecular crosslinking reaction with a commercially available branched polyethylene glycol (**12**) containing 4 terminal thiol functionalities.[38-40] The crosslinking reaction was carried out using diazabicycloundecene (DBU) (1 wt%) as a base and afforded thick polymer films simply upon mixing the reactants under ambient conditions in a minimal amount of THF at room temperature (Figure 4).



4c (n:o = 1:3)

Figure 4. Chemical structures of precursor polymer **4c**, crosslinker **12**, and the crosslinked polymer film. A digital picture showing 1 mm thick free-standing film made from polymers **4c** and **12**.

Conclusions

To summarize, a post-polymerization modification strategy is established for the synthesis of methacrylate polymers carrying corannulenes in their side-chains. To achieve this, poly(glycidyl methacrylate)-based reactive scaffolds are prepared by a free radical polymerization process. The side-chain epoxide units could be subjected to a ring-opening reaction by mercaptocorannulene. The hydroxyl group generated as a result of the ring-opening reaction could be involved in an esterification reaction for further functionalization. Alternatively, the identity of the thiol nucleophiles could be mixed to allow for two functional groups to be incorporated in a random fashion in the polymer chain. These polymers can interact with fullerene C_{60} through aromatic interactions. Higher cornannulene content is observed to enhance the supramolecular interaction. In some cases, the extent of the ring-opening reaction is kept non-quantitative to allow for further functionalization of the residual epoxides to obtain water-soluble polymers or to involve them in a crosslinking process to obtain thick polymer films. The synthetic strategies developed in this work will be useful in the preparation of corannulene polymers and their composites with fullerenes to allow for the study of their potential in organic electronics and biomedical applications.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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