



Fullerene containing norbornenes: synthesis and ring-opening metathesis polymerization



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ABSTRACT

New norbornenes with the covalently bonded fullerene C₆₀ have been prepared as monomers for ring-opening metathesis polymerization. Under the Grubbs catalyst these monomers smoothly enter homopolymerization as well as co-polymerization reactions with the parent 'non-fullerene' monomers. Homopolymers are insoluble in organic solvents whereas co-polymers obtained by 1:1 co-polymerization of the norbornenes with their 'non-fullerene' analogues are well soluble.

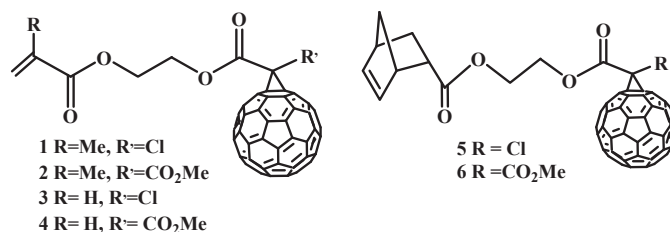
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1. Introduction

Fullerene derivatives and fullerene containing thin polymer films are used as acceptor components of bulk heterojunction (BHJ) photovoltaic devices.^{1–3} Although organic materials in solar cells are inferior to inorganic ones as far as turnaround efficiency of light (power conversion efficiency, PCE) is concerned, a number of their obvious advantages enable us to consider them as a possible alternative to traditional silicon batteries in future.^{4,5} These advantages can be outlined as follows: wide-range conductivity, diversity of forms (films, lines, composites), environmental safety, execution simplicity, flexibility, levity and constant PCE increase. As stated in the literature,⁶ further film development is directed to optimizing the donor–acceptor relation and improving electric properties and morphology of the bulk heterojunction. A chain of fullerene monomers was suggested after searching new film forming polymer materials with n-type conductivity.⁷ In earlier works⁸ monomers **1–4** suitable for obtaining the corresponding acrylate and methacrylate homo- and co-polymers by a radical mechanism were also described.

2. Results and discussion

It is known that the metathesis of olefins, acetylenes, polyenes, etc. in intermolecular and intramolecular variants is widely applied in organic synthesis⁹ as well as polymer chemistry.¹⁰ In the paper given the synthesis of new monomers **5, 6** and macromolecular compounds obtained by the ring-opening metathesis polymerization (ROMP) has been shown.

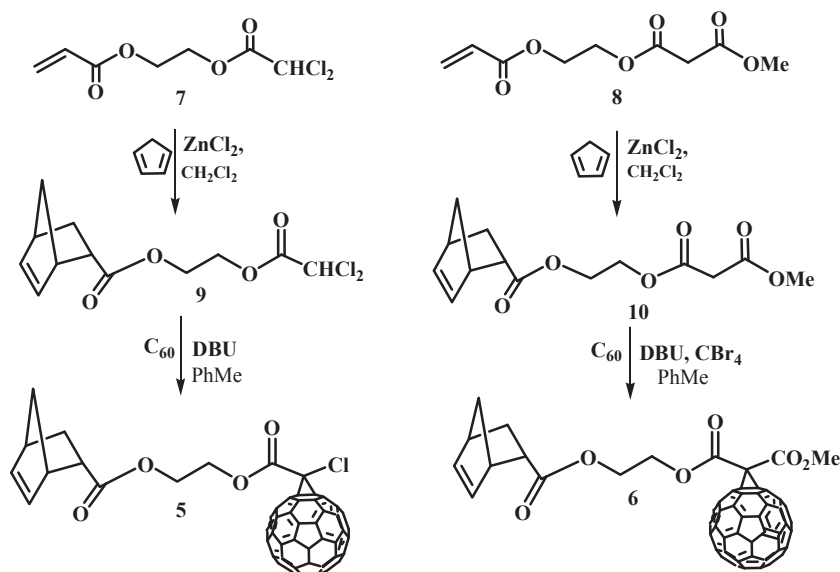


As seen from the structures presented, monomers **5** and **6** contain the highly active norbornene fragment in ROMP. The choice of the metathesis method of macromolecular compounds is explained primarily by the irreversible polymerization of the norbornene monomers on the living catalyst system, the possibility of obtaining 'block co-polymers' and simplicity of the experiment and ease of its control.¹¹

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In synthesizing **5** and **6** the blocks **7** and **8** have been used.⁸ The experiment revealed that **7** and **8** catalyzed by ZnCl₂ and cyclopentadiene under the Diels–Alder reaction react smoothly at room temperature. They provide a high yield of *endo*-adducts **9** and **10**

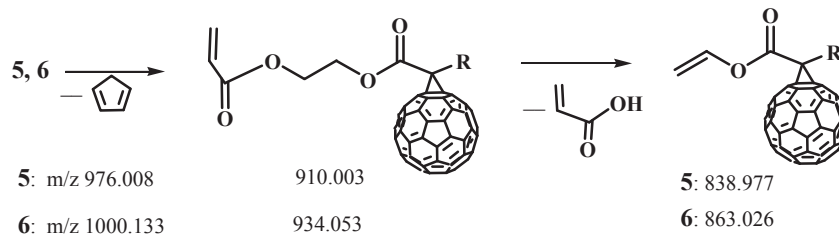
does not contain the concomitant *exo*-isomer. In **5** and **6** ¹³C NMR spectra, the signals of the fullerene nucleus in the range of 138–145 ppm, cyclopropane (71 and 75 ppm) and C_{sp3} fullerene at ~52 ppm are found (Scheme 1).



Scheme 1. The synthesis of monomers **5** and **6**.

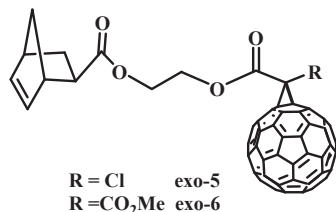
with minor *exo*-adducts contained in the ratio *endo/exo* ~6:1. It was estimated by the integral intensity of the ¹H NMR spectra differing in the singlet signals H-1; for *exo*-**9** δ_{H-1} =3.0 ppm, *endo*-**9**

MALDI-TOF spectra of **5** and **6** are similar in [M]⁺ molecular ions as well as ions relevant to the retrodiene decay products with elimination of cyclopentadiene and acrylic acid have been revealed.



δ_{H-1} =3.2 ppm, for *exo*-**10** δ_{H-1} =3.03 ppm, *endo*-**10** δ_{H-1} =3.2 ppm. The bridge C-7 signals in their ¹³C NMR spectra are characteristic for *exo*- and *endo*-isomers. Due to steric factors in *exo*-adducts they are of a stronger field, e.g., for *endo*-**10** δ_{C-7} =49.6 ppm and for *exo*-**10** δ_{C-7} =46.6 ppm.

The obtained esters **9** and **10** are activated CH-acids reacting smoothly with C₆₀ under the Bingel–Hirsch conditions¹² and the target monomers **5** and **6** have been obtained after purification in the chromatography column on SiO₂.



The fullerene monomers **5** and **6** are dark brown powders well dissolved in typical organic solvents (CHCl₃, C₆H₆). In monomer **6** the ¹H NMR spectrum allows detecting the minor *exo*-isomer in the ratio *6-endo*/*6-exo* ~7:1. According to the ¹H NMR data, monomer **5**

Polymerization of monomer **5** was carried out under inert atmosphere at the presence of the Grubbs I catalyst at room temperature in CH₂Cl₂ solution. During the first 3 h consumption of the initial monomer **5** (TLC control) and precipitation were observed. After the reaction completed, the precipitate was filtered and washed with ethyl vinyl ether (removal of catalyst residues) and toluene (separation of unreacted fullerene component) (Scheme 2).

The IR-spectrum of polymer **11** comprises signals ranging 528, 574, 1167 cm⁻¹, which are appropriate to the fullerene nucleus, and 1741 cm⁻¹ to the carbonyl group and 966 cm⁻¹ to trans-double bonds accordingly. The polymer is insoluble in CHCl₃, C₆H₆, C₆H₅CH₃, THF and EtOAc and is partially plumped at keeping in DMSO, so the molecular weight of **11** was impossible to estimate.

Under similar conditions, monomer **6** would be likely to turn into an insoluble homopolymer. Thus, co-polymers of fullerene monomers **5** and **6** with related fullerene-free norbornenes have been synthesized for improving their solubility. First the polymerization of fullerene-free monomers **9** and **10** were tested in similar conditions to **11**. The polymerization of **9** proceeded quickly enough and the forming product **12** was well dissolved in CHCl₃ enabling us to take its NMR spectra and determine its molecular weight. The identical results were obtained in the polymerization of **10** (Scheme 3).

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