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Synthesis and ring-opening metathesis polymerization of fullerene-containing α,ω-bis-norbornenes

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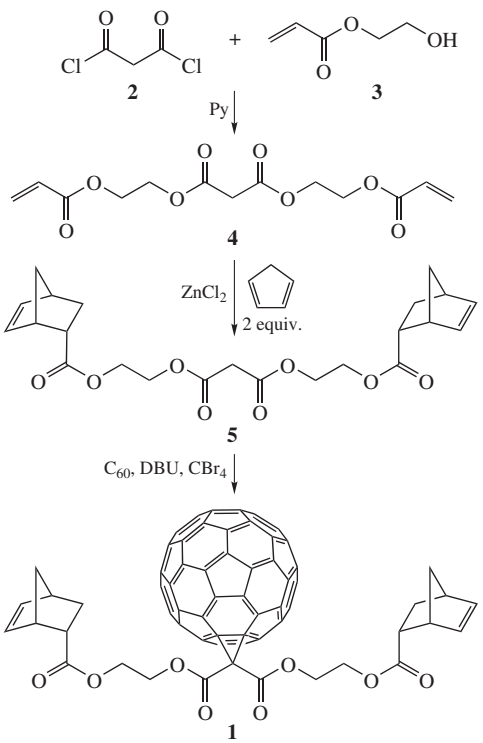
Metathesis polymerization of bis[4-(bicyclo[2.2.1]hept-5-en-2-yl)-4-oxo-3-oxabutyl]cyclopropa[1,9]-C_{60}-fullerene-3′,3′-dicarboxylate affords insoluble polymer, while a copolymer with the parent malonate is soluble in typical organic solvents.

Ring-opening metathesis polymerization of norbornenes is an effective method for synthesis of polymers with cyclopentane core in the main chain.[1–3] Ring-opening metathesis of α,ω-bis-norbornene systems by analogy with similar di- or polyenes in the construction of fused and spiro-fused ring systems,[4,5] 'bird cage' type structures,[6] molecular gyrotops and gyroscopes,[7] catenanes,[8] and other types[9] gives interesting possibilities in terms of finding new topology of polymers. In this study, we describe the synthesis of fullerene-containing bis-norbornene monomer **1** and its subsequent polymerization under metathesis ring-opening conditions. Synthesis of **1** was executed in three steps from malonyl dichloride **2** and ethylene glycol mono-acrylate **3**[10] (Scheme 1).† The product, bis-acrylate **4**, smoothly reacted with cyclopentadiene under catalysis with $ZnCl_2$ giving a bis-norbornene derivative **5** mostly as *endo*-isomer. The fraction of *exo*-moieties was at the ~11% level, which was estimated by integral signal intensities of C^1H in the ^1H NMR spectra of final product (for *endo*-**1** 3.20 ppm and for *exo*-**1** 3.05 ppm). As norbornene moieties are too distant in structures **1** and **5**, NMR data can provide only *exo*/*endo* ratio in general lacking the *exo*,*exo*, *exo*,*endo* and *endo*,*endo*-detalization. Step, combining **5** with C_{60}, was executed under Bingel–Hirsh[11] conditions, yield of product **1** in our case was 62%. The isomeric composition of **5** laid in the previous step persisted in monomer **1** (*endo*:*exo* ~ 8:1).



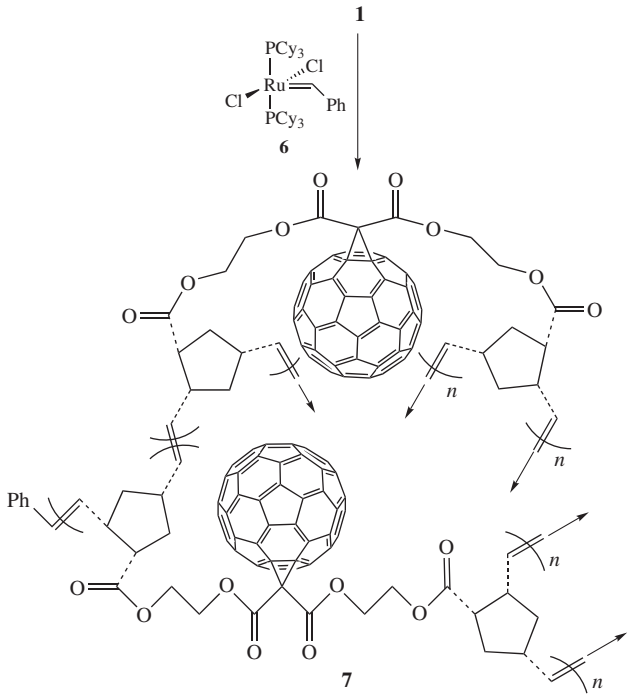
Scheme 1

During experimental testing, the polymerization of **1** proceeded smoothly at 200 °C for 2–3 h on using Grubbs I catalyst **6** (Scheme 2).‡ In the course of polymerization the precipitation of polymer **7** was observed. After monomer **1** was consumed, the polymer product was separated, washed with MeOH and dried *in vacuo*. Apparently, due to the presence of bulky fullerene sub-

† For synthesis and characteristics of bis(2-acryloyloxyethyl) malonate **4**, see Online Supplementary Materials.

Bis[4-(bicyclo[2.2.1]hept-5-en-2-yl)-4-oxo-3-oxabutyl] malonate **5**. A mixture of 1.0 g (3.33 mmol) of compound **4**, 0.45 g (6.81 mmol) of cyclopentadiene and 10 mg of calcined $ZnCl_2$ was stirred at room temperature until complete consumption of reactant **4** (~24 h, TLC control). After removal of volatiles, the residue was purified by column chromatography on silica gel (light petroleum–ethyl acetate, 5:1) giving 1.2 g (83%) of oily compound **5**. IR (ν/cm^{-1}): 810, 975, 984, 1044, 1151, 1190, 1291, 1298, 1334, 1371, 1410, 1445, 1729, 1736, 1755, 2961. ^1H NMR ($CDCl_3$), δ: 1.20 (m, 4H), 1.40 (m, 4H), 1.90 (m, 2H), 2.80–3.00 (m, 4H), 3.40 (s, 2H, CH_2-malonate), 4.20–4.40 (m, 8H, 4CH_2O), 5.20 (m, 2H) and 6.20 (m, 2H, CH=CH). ^{13}C NMR, δ: 29.24 ($C^{3'}$), 41.14 ($C^{4'}$), 42.53 (CH_2-malonate), 42.18 ($C^{2'}$), 45.71 ($C^{1'}$), 49.63 (C^7), 61.55 (CH_2O), 63.33 (CH_2O), 132.25 ($C^{6'}$), 137.90 (C^7), 166.04 (CO_2), 174.45 (CO_2). Found (%): C, 63.23; H, 6.46. Calc. for $C_{23}H_{28}O_8$ (%): C, 63.39; H, 6.53.

*Bis[4-(bicyclo[2.2.1]hept-5-en-2-yl)-4-oxo-3-oxabutyl] 3′*H*-cyclopropa-[1,9](*C_{60}*-I$_h$)[5,6]fullerene-3′,3′-dicarboxylate* **1**. Compound **5** (0.06 g, 0.138 mmol), DBU (0.021 g, 0.138 mmol) and CBr_4 (0.0458 g, 0.138 mmol) were added to solution of C_{60} (0.1 g, 0.138 mmol) in 35 ml of toluene. The mixture was stirred at room temperature for 30 min and filtered, the filtrate was washed with 5% HCl solution, dried with $MgSO_4$, the solvent was distilled off. The residue was separated using column chromatography on silica gel (eluent, toluene). Yield of product **1** was 0.1 g (62%) along with 0.04 g of unreacted fullerene. Solubility in $CHCl_3$ was 87.5 mg cm^{-3}, in *o*-$C_6H_4Cl_2$ – 110 mg cm^{-3}. IR (ν/cm^{-1}): 3432, 2927, 1743, 1723, 1666, 1506, 1427, 1405, 1302, 1264, 1174, 1114, 985, 826, 807, 658, 523. ^1H NMR ($CDCl_3$), δ: 1.20 (br. s, 4H), 1.40 (br. s, 4H), 1.80 (m, 2H), 2.80 (m, 4H), 3.20 (s, 2H), 4.40 (m, 4H, 2CH_2O), 4.70 (m, 4H, 2CH_2O), 5.85 and 6.20 (2m, 2×2H, 2CH=CH). ^{13}C NMR, δ: 29.37, 42.59, 43.29, 45.87, 49.68, 51.78, 61.49, 65.07, 71.34, 132.26, 137.98, 139.06, 140.95, 141.87, 142.17, 142.98 (2C), 143.04 (2C), 143.10, 144.57, 144.69 (2C), 144.93, 145.02 (2C), 145.08 (2C), 163.23 (CO_2), 174.38 (CO_2). MS (MALDI-TOF), *m*/*z*: 1151.039 (M^+) (calc., *m*/*z*: 1151.088). Found (%): C, 86.31; H, 2.19. Calc. for $C_{83}H_{26}O_8$ (%): C, 86.60; H, 2.28.



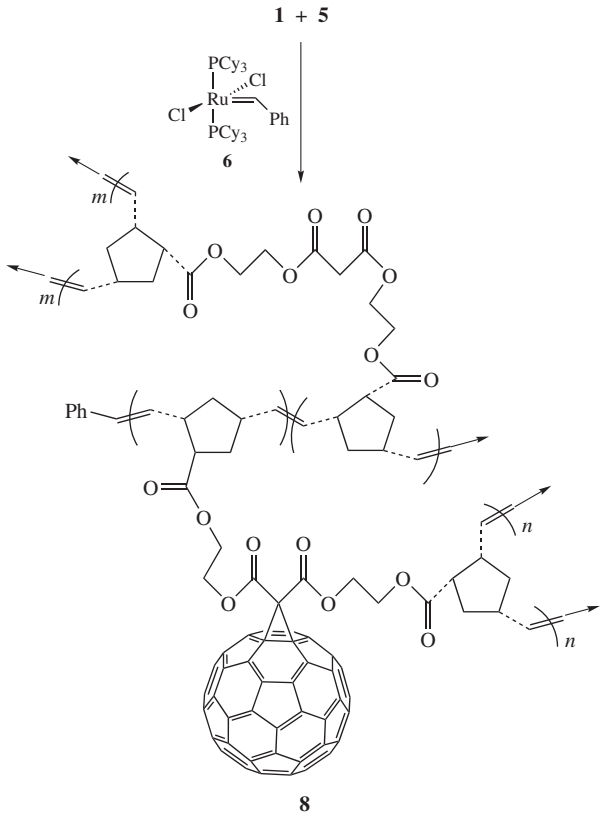
Scheme 2 The arrows indicate the direction of polymerization and the growth of chains.

stituent in the structure of compound **1**, intramolecular cyclization, dimerization and cross-linkage should less likely to occur.

The main expected product of metathesis polymerization of monomer **1** is a kind of dendrimer topology macromolecule of formula **7** not excluding chaotic 'joining' with the formation of cross-linked fragments. In a first approximation, **7** is taken as a resulting polymer structure. The polymer is insoluble in organic solvents. Its IR spectrum contained absorption bands of *trans*-double bonds (970 cm^{-1}), carbonyl ester groups (1732 cm^{-1}) and fullerene core (520 cm^{-1}); the absorption of norbornene bonds was not detected.

To obtain soluble oligomeric materials, polymerization was attempted in a CH_2Cl_2 solution under over-dilution conditions.[8] However, rapid precipitation of the insoluble polymer took place from the beginning of the reaction even under these conditions.

Copolymerization of equimolar quantities of **1** with non-fullerene monomer **5** (Scheme 3)‡ gave copolymer **8** which was



Scheme 3 The arrows indicate the direction of polymerization and the growth of chains.

soluble in typical solvents (CH_2Cl_2, $CHCl_3$, benzene, toluene, PhCl). The composition of copolymer **8** was determined on the basis of elemental analysis, content of fullerene units was 45.42 mol%.

In conclusion, we have developed the synthesis of a new soluble highly oxygenated fullerene-containing polymer with cyclopentane subunits in the main chain. The product can be suitable for fabrication of thin films for photovoltaic devices.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2015.05.014.

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‡ *Polymer* **7**. Grubbs catalyst **6** (0.002 g, 0.0025 mmol) was added to a solution of compound **1** (0.1 g, 0.087 mmol) in 30 ml of dichloromethane in argon atmosphere. Within 6 h a gradual consumption of monomer **1** (TLC) and precipitation of the polymer were observed. Upon completion of the polymerization, 1 ml of ethyl vinyl ether was added to remove residual catalyst, the precipitate was filtered, washed with 30 ml of dichloromethane and dried *in vacuo* for 24 h to give 0.07 g (70%) of dark brown powder **7**. IR (ν/cm^{-1}): 2930, 1733, 1460, 1380, 1151, 971, 727, 520. The polymer does not melt or decompose when heated up to 350 °C. Found (%): C, 85.28; H, 2.78. Calc. for $C_{83}H_{26}O_8$ (%): C, 86.60; H, 2.28.

Copolymer **8**. Compound **5** (0.018 g, 0.0434 mmol) and Grubbs catalyst **6** (0.99 mg, 0.00124 mmol) were added to a solution of compound **1** (0.05 g, 0.0434 mmol) in 30 ml of CH_2Cl_2 in argon atmosphere. The reaction mixture was stirred for 24 h, then 1 ml of ethyl vinyl ether was added and the product was precipitated with 20 ml of methanol. The precipitated copolymer was filtered, washed with toluene until the filtrate grew colourless and then dried *in vacuo*. Yield (conversion) of copolymer was 0.05 g (73%). Solubility in $CHCl_3$ is 60 mg cm^{-3}, in *o*-$C_6H_4Cl_2$ – 84 mg cm^{-3}. IR (ν/cm^{-1}): 2956, 2927, 1729, 1420, 1169, 970, 757, 550. ^{1}H NMR ($CDCl_3$), δ: 3.40 (br. s, CH_2-malonate), 4.10–4.50 (m, CH_2O), 5.10–5.50 (m, CH=CH). The copolymer does not melt or decompose when heated up to 350 °C. Found (%): C, 79.66; H, 3.92. M_w = 25100, M_w/M_n = 1.50.