

## Synthesis of C<sub>60</sub>-capped vinyl ether oligomers by living cationic polymerization technique

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### SUMMARY:

This study concerns the synthesis of C<sub>60</sub>-capped vinyl ether (VE) oligomers with well-defined structure by living cationic polymerization technique. The VE oligomers bearing C<sub>60</sub> at the chain end were prepared by addition reaction between mono-octynylfulleride anions and living cationic VE oligomers. Living oligo(isobutyl vinyl ether) (IBVE) and oligo(methyl vinyl ether) (MVE) were synthesized using CH<sub>3</sub>CH(OiBu)Cl/ZnI<sub>2</sub> as initiating system. The C<sub>60</sub>-capped VE oligomers were obtained as dark brown gummy solid in 28% for IBVE and 34% for MVE. The UV/VIS and <sup>13</sup>C NMR spectra indicated the formation of C<sub>60</sub>-capped oligomers via 1,2-addition reaction. It was also found that the films of blends of C<sub>60</sub>-capped oligomers with poly(IBVE) and polystyrene (5 wt.-% C<sub>60</sub>) are homogeneous on a micron scale and transparent, resulting from a good dispersion of C<sub>60</sub> in the polymer matrix.

### Introduction

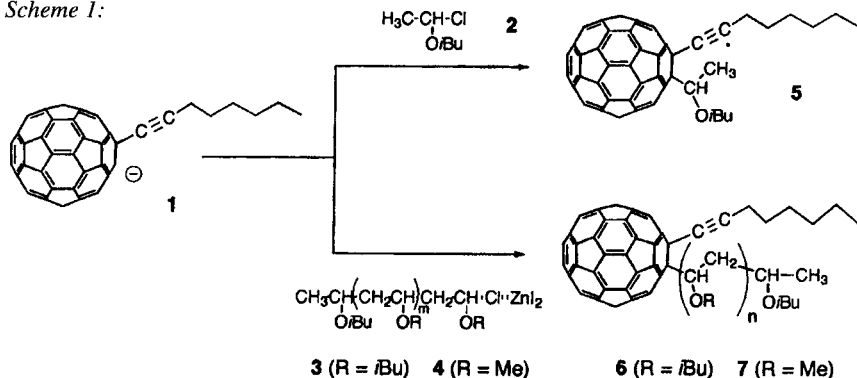
In recent years, much attention has been paid to the chemical transformation of fullerene C<sub>60</sub> because of its applicabilities to advanced materials<sup>1,2</sup>. Incorporation of the C<sub>60</sub> molecules into polymer chains is gaining interest as one of the effective methods for improving the processability of fullerene<sup>3–7</sup>.

Fullerene-containing polymers reported so far can be classified into four types. The first type is the polymers with fullerene units incorporated into the main chain (in-chain type)<sup>3</sup>. The second is the polymers bearing pendant fullerene (on-chain type)<sup>4</sup>. The third is the fullerene-incorporating polymer networks (cross-link type), where fullerene acts as a cross-linking site<sup>5</sup>. The fourth is the fullerene-terminated telechelic polymers, i.e., polymers having one or two fullerene end groups (end-chain type)<sup>6,7</sup>. The fullerene is prone to undergo nucleophilic reactions<sup>8</sup>. However the addition of nucleophiles to C<sub>60</sub> molecules sometimes results in the formation of a mixture of polyadducts, which are different in both the number of addends and the positions of addition. Thus, it is of great importance and interest to prepare fullerene-containing polymers with well-defined structures<sup>6</sup>.

Recently Murata et al. reported the synthesis and full characterization of a stable carbanion, 1-octynyl-C<sub>60</sub><sup>-</sup> (1), derived from 1-octynyl-1,2-dihydro[60]fullerene<sup>10</sup>. This carbanion can be generated quantitatively from its precursor, and was shown to react with various carbon electrophiles. These results have motivated our present study. The aim of this study is to prepare the end-chain type oligomers with well-defined structure using living cationic polymerization technique<sup>9</sup>.

Thus, in the present study, 1-octynyl- $C_{60}$  anion **1** was reacted with living vinyl ether oligomers obtained by living cationic polymerization of vinyl ethers (VEs)<sup>10,11</sup> using appropriate initiating systems.

Scheme 1:



## Results and discussion

### Synthesis of $C_{60}$ -capped oligomers

1-Octynyl- $C_{60}$  anion **1** was prepared by deprotonation of 1-octynyl-1,2-dihydro[60]fullerene, which was obtained by reacting  $C_{60}$  with 1-octynyllithium in THF<sup>10</sup>.

Two types of vinyl ether oligomers were prepared by the use of living cationic polymerization technique. The combination of HCl and  $\text{ZnI}_2$  is one of the best studied initiating systems suitable for the living cationic polymerization of vinyl ether (VE) monomers<sup>9</sup>. Living oligo(isobutyl vinyl ether) (IBVE) (**3**)<sup>11</sup> and oligo(methyl vinyl ether) (MVE) (**4**)<sup>12</sup> were prepared by the above-mentioned initiating system. For the purpose of comparison, an adduct of monomeric isobutyl vinyl ether (IBVE) and HCl, i.e.,  $\text{CH}_3\text{CH}(\text{O}/\text{iBu})\text{Cl}$  (**2**) was also prepared in hexane as reported<sup>11</sup>.

The addition reactions of 1-octynyl- $C_{60}$  carbanion **1** to these living cationic species were carried out in THF at  $0^\circ\text{C}$ . In the case of adduct **2**, 6 equivalents of a hexane solution of adduct **2** was added to a vigorously stirred solution of carbanion **1** in THF, which exhibited a characteristic dark green color, at  $0^\circ\text{C}$  over 3 min. After reaction of 3 h, the resulting brownish solution was quenched with methanol and subjected to the chromatographic separation. The pure product **5** was isolated as dark brown powder in 33% yield. The addition reaction of carbanion **1** to the living oligo(IBVE) (**3**) was conducted in a similar way for 3 h in THF at  $0^\circ\text{C}$ . The reaction solution gradually turned from deep green to brown, indicating that the addition reaction proceeded. Unreacted  $C_{60}$  and other monomeric  $C_{60}$  derivatives were separated by column chromatography. The separation of product **6**, herein referred to as  $C_{60}$ -capped oligo(IBVE), from unreacted oligo(IBVE) was made by fractional precipitation using benzene/methanol system. The pure product **6** was isolated in 28% yield as a dark brown gummy solid. Product **7**, i.e.  $C_{60}$ -capped oligo(MVE), was similarly prepared by addition reaction of carbanion **1** to the living oligo(MVE) in

34% yield as a dark brown gummy solid, after purification in the same way as described above.

### Structural identification

The structure of the products was determined by UV and NMR analyses. Fig. 1 shows the <sup>1</sup>H NMR spectrum of C<sub>60</sub>-capped oligo(IBVE) (**6**), together with that of C<sub>60</sub>-IBVE monoadduct **5** for comparison. Assignment of each signal is given in the figure.

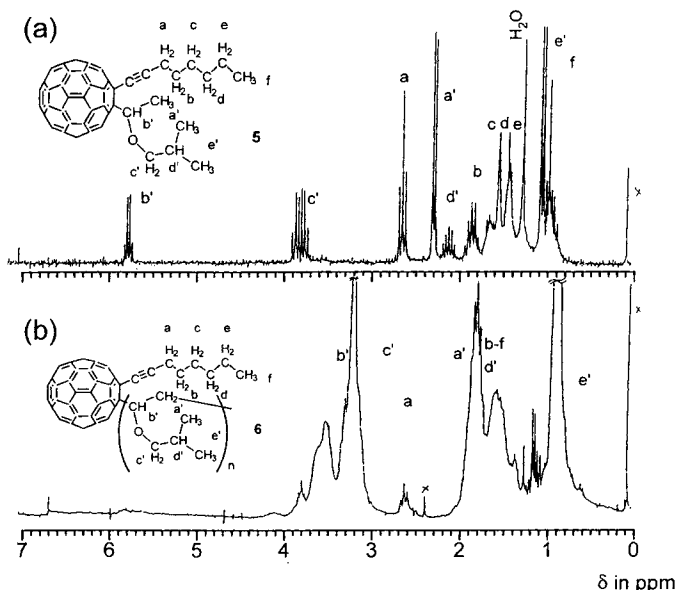


Fig. 1. <sup>1</sup>H NMR spectra of (a) IBVE-capped C<sub>60</sub> (**5**) and (b) C<sub>60</sub>-capped oligo(IBVE) (**6**) in CDCl<sub>3</sub>

At first glance, the two spectra appear quite different, but by close examination it is found that the <sup>1</sup>H NMR spectrum of **6** is composed of weak signals for a 1-octynyl group and an oligo(IBVE) moiety.

The <sup>13</sup>C NMR spectra of **5** and **6** shown in Fig. 2 more clearly indicate that compound **6** contains the C<sub>60</sub> core, 1-octynyl groups, and an oligo(IBVE) moiety.

The signals for the sp<sup>2</sup>-carbons of the C<sub>60</sub> core are somewhat broadened reflecting the non-homogeneity of the molecular weight of the oligomer.

The comparison of the NMR data of **6** with those of **5** and also the UV/VIS spectral data (see below) indicate that compound **6** is a C<sub>60</sub> derivative with two organic groups added at the 1,2-positions of the 6,6-junction bond<sup>a)</sup>.

a) The C<sub>60</sub> derivatives with two different addends at the 6,6-junction bond are normally supposed to have a C<sub>s</sub> symmetry and exhibit 30 <sup>13</sup>C NMR signals for the sp<sup>2</sup> carbons of the C<sub>60</sub> core. However, compound **5** having two addends at the 6,6-junction bond exhibits partially overlapped 54 signals due to the presence of a chiral addend, i.e. the 1-alkoxy-1-ethyl group, at one of the 1,2-positions<sup>13)</sup>.

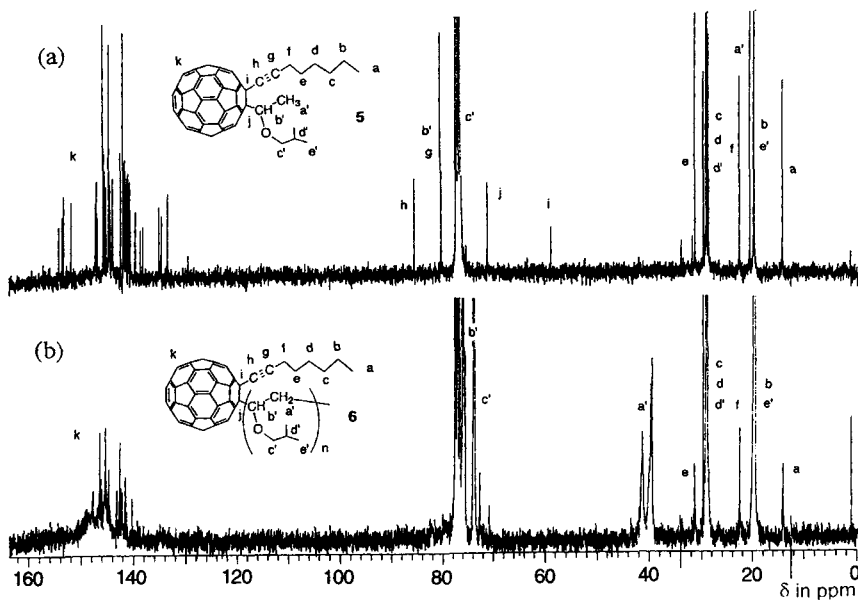


Fig. 2.  $^{13}\text{C}$  NMR spectra of (a) IBVE-capped  $\text{C}_{60}$  (5) and (b)  $\text{C}_{60}$ -capped oligo(IBVE) (6) in  $\text{CDCl}_3$

Although the accuracy is low due to the considerably large error in peak area integration, the number-average degree of polymerization ( $\overline{\text{DP}}_n$ ) of oligo(IBVE) segments in the product was estimated from comparison of the peak intensity of the peaks of the octynyl group with that of the peaks b' and c' in the IBVE moiety. The  $\overline{\text{DP}}_n$  value of oligo(IBVE) segments in product 6 was found to be 19.7 in reasonable agreement with that of the precursor. The precursor was obtained as a reference compound by quenching living oligo(IBVE) with methanol, and its  $\overline{\text{DP}}_n$  value was determined, similarly by  $^1\text{H}$  NMR spectroscopy, to be 16, which accidentally agreed with the polystyrene-calibrated SEC value. We also note that the weight- to number-average molecular weight  $\overline{M}_w/\overline{M}_n$  ratio of the precursor estimated by the SEC analysis was 1.08.

In Fig. 3, the UV/VIS spectrum of the  $\text{C}_{60}$ -capped oligomer 6 is compared with that of monomer adduct 5. Both spectra exhibit a sharp absorption at around 430 nm which is diagnostic of the  $\text{C}_{60}$  derivatives with two addends at the 6,6-junction bond. The  $\overline{\text{DP}}_n$  of IBVE segments can be also estimated from the spectrum of 6 using the absorbance at 256 nm with the assumption that the extinction coefficient is the same for these two compounds. The  $\overline{\text{DP}}_n$  value was found to be 15.8 in good agreement with that of the precursor oligomer described above.

The essentially same results were obtained on the addition of the living oligo(MVE) (4) to the 1-octynyl- $\text{C}_{60}$  anion (1) affording  $\text{C}_{60}$ -capped oligo(MVE) (7). Namely, the structure of the product was proved to be 1,2-adduct on the 6,6-junction bond of  $\text{C}_{60}$ . On the other hand, the  $\overline{\text{DP}}_n$  values of MVE segments in 7 esti-

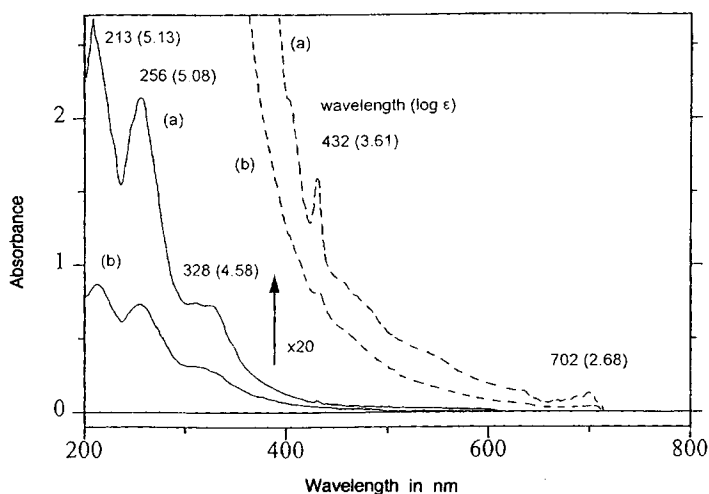


Fig. 3. UV/VIS spectra of (a) IBVE-capped C<sub>60</sub> (**5**) ( $2.04 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ ) and (b) C<sub>60</sub>-capped oligo(IBVE) (**6**) ( $6.98 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ ). The  $\lambda_{\text{max}}$  and  $\log \epsilon$  values are those of **5**

mated from <sup>1</sup>H NMR and UV/VIS spectra were 10.9 and 10.3, respectively. These values are much lower than that of the precursor ( $\overline{\text{DP}}_n = 18$ ). This discrepancy is attributed to the water solubility of the C<sub>60</sub>-capped oligo(MVE) (**7**). It was found that the higher-molecular-weight fractions of **7** are partially soluble in water, just as poly(MVE) dissolved in water. Therefore, it is possible that the higher-molecular-weight fractions were lost during the purification of the sample by washing with water.

### Redox properties

The redox properties of the newly obtained derivatives were examined by the use of cyclic voltammetry in benzonitrile. Fig. 4 demonstrates an example of the voltammograms obtained. Although some weak bumps are observed in the voltammograms with a wide sweeping range, the only reproducible waves were a single irreversible oxidation peak and three reversible waves as in the case of C<sub>60</sub>. The numerical values obtained are summarized in Tab. 1. The reduction potentials of C<sub>60</sub>-capped oligo(VE) were more negative by slightly larger than 0.1 V, probably reflecting the electropositivity of the substituted groups. Similar results were observed on 1-alkynyl-2-hydrodihydrofullerene<sup>10</sup>.

### Dispersion of C<sub>60</sub> in polymer matrix

As already mentioned, one of the major disadvantages of fullerene C<sub>60</sub> for the applications as advanced materials is its poor processing properties. Figs. 5a and b show typical examples of the dispersion of C<sub>60</sub> molecules and 1-octynyl-2-hydro-

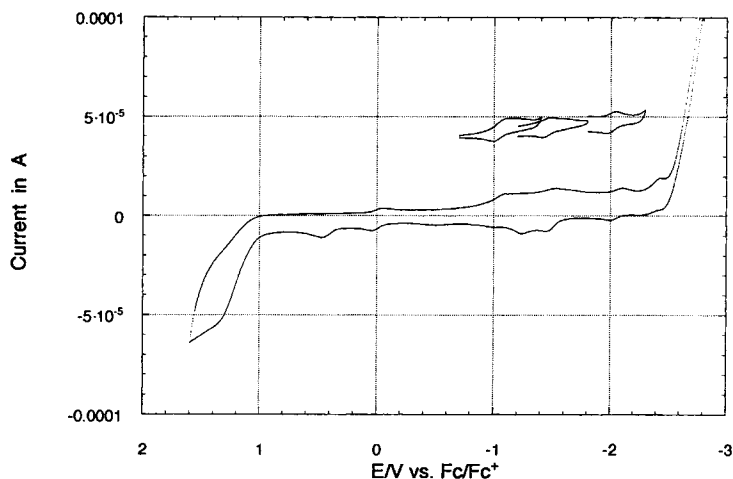


Fig. 4. Cyclic voltammogram of  $C_{60}$ -capped oligo(IBVE) (**6**). In the insets are shown the individual reduction waves measured separately. Potential in volts vs. ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate (0,05 M) as a supporting electrolyte; scan rate,  $0,1 \text{ V} \cdot \text{s}^{-1}$

Tab. 1. Results of cyclic voltammetry measurements<sup>a)</sup>

Compound	Reversible, $E_{1/2}/\text{V}$		
	$E_{\text{red}}^1/\text{V}$	$E_{\text{red}}^2/\text{V}$	$E_{\text{red}}^3/\text{V}$
$C_{60}$	-0,93	-1,36	-1,85
<b>6</b>	-1,06	-1,46	-2,03
<b>7</b>	-1,04	-1,47	-2,03

<sup>a)</sup> Potential in volts vs. ferrocene/ferrocenium measured in benzonitrile with tetrabutylammonium tetrafluoroborate ( $0,05 \text{ mol} \cdot \text{L}^{-1}$ ) as a supporting electrolyte; scan rate:  $0,1 \text{ V} \cdot \text{s}^{-1}$ .

1,2-dihydro[60]fullerene (octynyl- $C_{60}$ )<sup>10)</sup> in poly(IBVE) matrix, examined using an optical microscope. It can be seen that  $C_{60}$  molecules tend to form comparatively large aggregates or clusters, due to the immiscibility with the polymer matrix. As shown in Fig. 5c, on the other hand, in the case of  $C_{60}$ -capped oligo(IBVE), the film is homogeneous on a micron scale at the same content of  $C_{60}$  molecules as the above two (5 wt.-%  $C_{60}$ ) and transparent, apparently this resulted from a better dispersion ability of the  $C_{60}$ -capped oligomer in the poly(IBVE) matrix.

Poly(MVE) is known to be compatible with polystyrene. Next we examined the dispersion of  $C_{60}$ -capped oligo(MVE) in the polystyrene matrix. Fig. 6 shows the optical micrographs of polystyrene composite films blended with  $C_{60}$  molecules, octynyl- $C_{60}$  and  $C_{60}$ -capped oligo(MVE). It is obvious that the  $C_{60}$  molecules modified with oligo(MVE) results in a better dispersion of  $C_{60}$  in the polystyrene matrix.

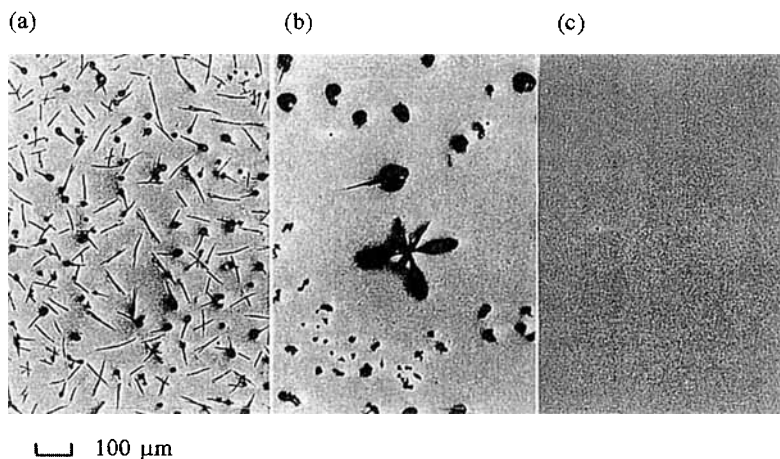


Fig. 5. Optical microscopic images of blend films of (a) C<sub>60</sub>, (b) 1-octynyl-2-hydro-1,2-dihydro[60]fullerene and (c) C<sub>60</sub>-capped oligo(IBVE) (6)

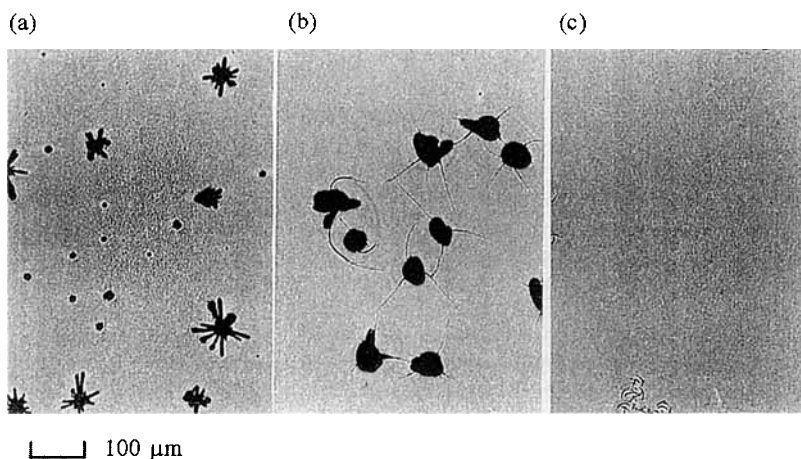


Fig. 6. Optical microscopic images of blend films of (a) C<sub>60</sub>, (b) 1-octynyl-2-hydro-1,2-dihydro[60]fullerene and (c) C<sub>60</sub>-capped oligo(MVE) (7)

## Experimental part

### Materials

Commercial isobutyl vinyl ether (IBVE) (from Tokyo Kasei) was washed with 10% aqueous sodium hydroxide solution and then with water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride before use. Commercial methyl vinyl ether (MVE) (Tokyo Kasei; purity >99%) was dried by passing the gaseous monomer through columns packed with calcium chloride and calcium hydride. Toluene, hexane, dichloromethane and carbon tetrachloride were purified by the usual methods and distilled over calcium hydride prior to use. Diethyl ether (Dojin, anhydrous) was distilled in the presence of calcium hydride before use. ZnI<sub>2</sub> (Aldrich; purity >99,99%) was used as

received. Trifluoroacetic acid, *t*-BuOK, 1-octyne (Tokyo Kasei) and *n*-butyllithium ( $1,6 \text{ mol} \cdot \text{L}^{-1}$  in hexane, Aldrich) were used without further purification.  $\text{C}_{60}$  was separated from a commercial mixture of  $\text{C}_{60}$  and  $\text{C}_{70}$  (ca. 4:1 by weight, Term Co.) by the use of a Norit carbon-silica gel column eluted with toluene. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. The IBVE-HCl adduct **2** was prepared by bubbling HCl gas into a hexane solution of IBVE.

### Measurements

NMR spectra were taken at 300 MHz for  $^1\text{H}$  and 75 MHz for  $^{13}\text{C}$  on Varian XL-300 spectrometer. UV/VIS spectra were taken on Shimadzu UV-2100. MS spectra were measured with Finnigan TSQ 7000 spectrometer.

Cyclic voltammetry was conducted on a BAS electro-analyzer CV-50W using a three-electrode cell with a glassy carbon working electrode, a platinum counter electrode, and a  $\text{Ag}/0,01 \text{ M AgNO}_3$  reference electrode. The potential was corrected against ferrocene used as an internal standard added immediately after each measurement.

Medium-pressure liquid chromatography (MPLC) was carried out using silica gel 60 (E. Merck, particle size 0,040–0,063 mm, 230–400 mesh ASTM) as a stationary phase.

Size exclusion chromatography (SEC) was carried out in tetrahydrofuran on a TOSOH HLC-802UR chromatograph equipped with polystyrene gel columns (TOSOH G2500H6 + G3000H6 + G4000H6; exclusion limit =  $1,0 \times 10^6$ ; 8,0 mm i.d.  $\times$  60 cm each) and refractive index/ultraviolet dual-mode detectors. The number-average molecular weight ( $\bar{M}_n$ ) and the polydispersity index ( $\bar{M}_w/\bar{M}_n$ ) of the precursor oligo(IBVE) were estimated on the basis of a polystyrene calibration.

The samples for the microscopic observation were prepared by the following procedures; for the poly(IBVE) matrix films,  $\text{C}_{60}$  (1,00 mg), octynyl- $\text{C}_{60}$  (1,15 mg) and  $\text{C}_{60}$ -capped oligo(IBVE) (**6**) (3,20 mg) were dissolved in toluene (1 mL) and 19 mg, 18,85 mg and 16,80 mg of poly(IBVE) ( $\bar{M}_w = 2,34 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n = 2,7$ ) were added respectively. The films were prepared to contain the same concentration of  $\text{C}_{60}$  component, i.e., 5 wt.-% in the polymer matrix. For polystyrene matrix films,  $\text{C}_{60}$  (1,00 mg), octynyl- $\text{C}_{60}$  (1,15 mg) and  $\text{C}_{60}$ -capped oligo(MVE) (**7**) (1,80 mg) were dissolved in toluene (1 mL), and 19 mg, 18,85 mg and 18,20 mg of polystyrene ( $\bar{M}_w = 1,01 \times 10^5$ ,  $\bar{M}_w/\bar{M}_n = 1,47$ ) were added, respectively (ca. 5 wt.-% for polystyrene matrix).

Each solution was applied on a slide glass and allowed to air-dry at room temperature. Optical microscopic images were obtained on a Nikon AFX-II optical microscope.

### Oligomerization procedures

Oligomerization was carried out at  $-40^\circ\text{C}$  under dry nitrogen in a vessel equipped with a three-way stopcock. The reaction was initiated by sequential addition of chilled solutions of IBVE-HCl (**2**) as an initiator and of  $\text{ZnI}_2$  under dry nitrogen. For the reference sample, the reaction mixture was terminated with prechilled ammoniacal methanol, washed with 10% aqueous sodium thiosulfate solution, and then with water to remove the initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to yield the product.

### Addition reactions

#### 1-Octynyl-2-(1-isobutoxyethyl)-1,2-dihydro[60]fullerene (**5**)

A solution of 1-octynyl- $\text{C}_{60}$  anion **1** was prepared by adding 0,16 mL (0,0144 mmol) of  $0,0881 \text{ mol} \cdot \text{L}^{-1}$  solution of *t*-BuOK in THF to a stirred solution of 1-octynyl-2-



hydro-1,2-dihydro[60]fullerene<sup>10)</sup> (12,33 mg, 0,0144 mmol) in 20 mL of THF at room temperature and stirring the mixture for 15 min at 0 °C. To a solution of **1** was added a 1,4 mol · L<sup>-1</sup> hexane solution of 1-isobutoxyethyl chloride (**2**) (0,06 mL, 0,084 mmol) dropwise over 2 min under vigorously stirring. After the reaction of 2 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane. From the second fraction was isolated product **5** (4,33 mg, 39%) as dark brown solid.

#### 1-Octynyl-2-(oligoIBVE)-1,2-dihydrofullerene (**6**)

The reaction conditions for the preparation of living IBVE oligomer **3** were as follows; [M]<sub>0</sub> = 0,5 mol · L<sup>-1</sup>, [2]<sub>0</sub> = 25 mmol · L<sup>-1</sup>, [ZnI<sub>2</sub>]<sub>0</sub> = 0,50 mmol · L<sup>-1</sup> in toluene at -40 °C. The living oligo(IBVE) with a molecular weight of 1 600, which was prepared in the reaction time of 40 min (monomer conversion of ca. 80%), was used for the subsequent coupling reaction. To a solution of **1** (9,02 × 10<sup>-5</sup> mol) was added oligo(IBVE) (**3**) (2,5 mL, 6,25 × 10<sup>-5</sup> mol) dropwise over 2 min under vigorous stirring at 0 °C in THF. After the reaction of 3 h, the resulting brown solution was evaporated under vacuum. The crude product was separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane-benzene to remove decomposed C<sub>60</sub> products. The product eluted with benzene was subjected to fractional precipitation using the benzene/methanol system to give pure product **6** (42,0 mg, 28% based on **3**) as a dark brown powder.

#### 1-Octynyl-2-(oligoMVE)-1,2-dihydro[60]fullerene (**7**)

The reaction conditions for the preparation of living MVE oligomer **4** were as follows; [M]<sub>0</sub> = 1,0 mol · L<sup>-1</sup>, [2]<sub>0</sub> = 50 mmol · L<sup>-1</sup>, [ZnI<sub>2</sub>]<sub>0</sub> = 5,0 mmol · L<sup>-1</sup> in dichloromethane at -40 °C. The living oligo(MVE) with a molecular weight of 1 050, which was prepared with a reaction time of 2 h (monomer conversion of ca. 90%), was used for the subsequent addition reaction. To a solution of **1** (1,40 × 10<sup>-4</sup> mol) was added oligo(MVE) (**4**) (2,0 mL, 1,00 × 10<sup>-4</sup> mol) dropwise over 2 min under vigorous stirring at 0 °C in THF. After reaction of 4 h, the resulting brown solution was evaporated under vacuum. The crude product was washed with water to remove unreacted oligo(MVE) and was then separated by medium-pressure liquid chromatography on silica gel 60 (Merck) eluted with hexane-benzene to remove monomeric derivatives of C<sub>60</sub>. The pure product **7** (59,6 mg, 34% based on **4**) was obtained from the benzene fraction as a dark brown gummy solid after evaporation.

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