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New Monomers for Fullerene-Containing Polymers

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Abstract—By reaction of 2-(acryloyloxyethyl) and (undecen-10-en-1-yl) methylmalonates with fullerene C_{60} in the system toluene–CBr_4–DBU, and also by reaction of 2-(2,2-dichloroacetoxy)ethyl acrylate with C_{60} in the system toluene–DBU the corresponding products of fullerene monocyclopropanation were synthesized.

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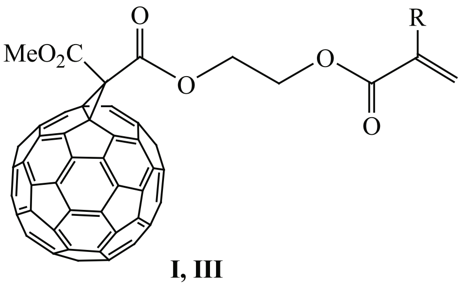
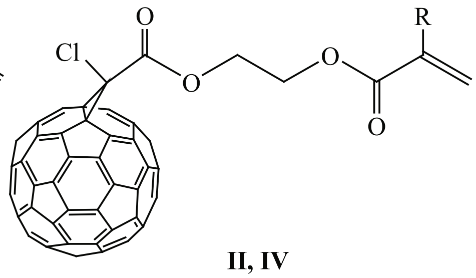
Synthesis and examination of fullerene-containing polymers is a promising trend in the search for new materials for optoelectronics, sun batteries etc. [1–3].

We formerly described [4] monomers **I, II** of methacrylate type bound by spacers with fullerene C_{60}. In extension of this research we report here on synthesized acrylates **III, IV** similar to methacrylates **I, II**, and compound **V** with an nonactivated terminal double bond.

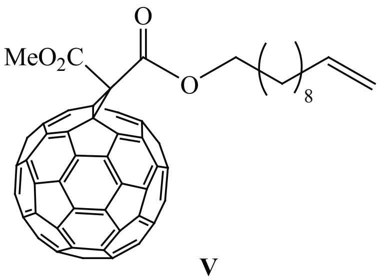
Block **VI**, the key block in the synthesis of acrylates **III, IV**, was prepared by controlled esterification of acrylic acid with ethylene glycol by procedure [5] (Scheme 1).



I, III



II, IV

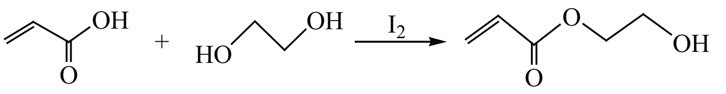


V

R = CH_3 (**I, II**), H (**III, IV**).

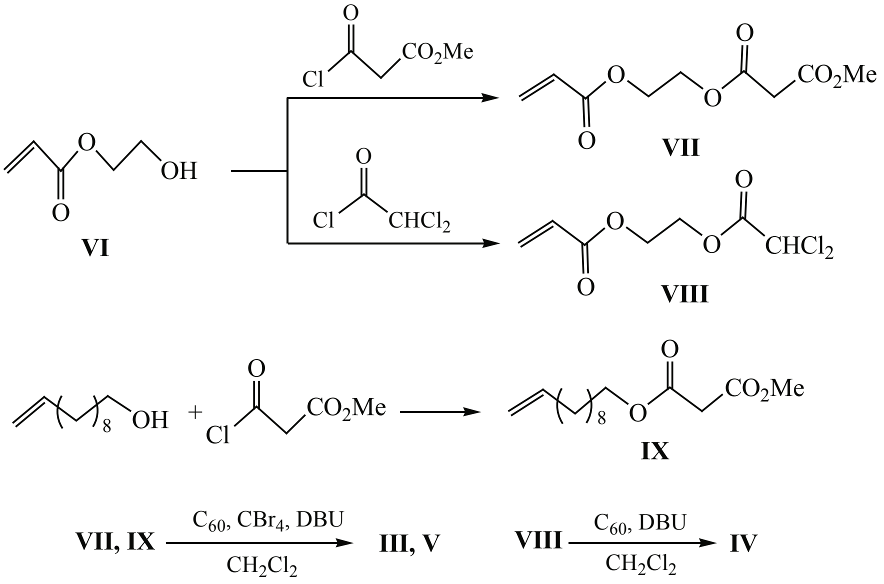
The subsequent acylation of compound **VI** with methylmalonyl and dichloroacetyl chlorides afforded in good yields acylation products **VII, VIII**. Block **IX** was obtained similarly to the synthesis of compound **VII** from undecenylene alcohol by acylation with methylmalonyl chloride in pyridine. In the final stage blocks **VII, IX** were subjected to cyclopropanation with fullerene C_{60} in conditions of Bingel–Hirsch reaction [6] to obtain

Scheme 1.



VI

Scheme 2.



monomers **III, V**; the synthesis of compound **IV**, like that of compound **II** [4], was carried out with the use of ester **VIII** without CBr_4 (Scheme 2).

As seen, compounds **III–V** contain C=C double bonds of different character providing a possibility to apply these substances to the synthesis of fullerene-containing polymers.

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer IR Prestige-21 Shimadzu from thin films. UV spectra were taken on a spectrophotometer UV-365 Shimadzu UV-VIS-NIR. ^{1}H NMR spectra were registered on a spectrometer Bruker AM-300 (operating frequency 300.13 MHz) from solutions in $CDCl_3$, internal reference TMS. ^{13}C NMR spectra were obtained on a spectrometer Bruker Avance-500 (operating frequency 125.77 MHz). Mass spectra were measured on an instrument MALDI Voyager-D STR TOF. The reaction progress was monitored by TLC on Sorbfil plates (Russia), spots visualized by thermal destruction or by wetting with alkaline solution of potassium permanganate. The synthesis products were isolated by column chromatography on silica gel (30–60 g of adsorbent per 1 g of the substance), as eluents were used mixtures petroleum ether–ethyl acetate or dichloromethane.

2-Hydroxyethyl acrylate (VI). A mixture of 12 mL (0.17 mol) of acrylic acid, 105.4 g (1.7 mol) of ethylene glycol, and 0.1 g (0.4 mmol) of iodine was boiled for 4 h (TLC monitoring). On cooling a water solution of NaCl was added to the reaction mixture, the reaction product was extracted into dichloromethane, the organic solutions were washed with 5% water solution of $Na_2S_2O_3$, with brine, and dried with $MgSO_4$. The solvent was distilled off, the residue was distilled in a vacuum. Yield 14.0 g (71%), bp 83–85°C (10 mm Hg), n_D^{23} 1.4452 {bp 83–85°C (8 mm Hg), n_D^{20} 1.4500 [7]}. IR spectrum, ν, ν, cm^{-1}: 3425, 2945, 2879, 1716, 1635, 1616, 1454, 1409, 1296, 1199, 1084, 1042, 985, 882, 812. ^{1}H NMR spectrum, δ, ppm: 3.89 t (2H, CH_2O, *J* 4.6 Hz), 4.31 t (2H, CH_2O, *J* 4.6 Hz), 5.96 d.d (1H, $=CH_2$, *J* 1.2, 10.3 Hz), 6.14 d.d (1H, =CH, *J* 10.4, 17.3 Hz), 6.50 d.d (1H, $=CH_2$, *J* 1.2, 17.1 Hz). ^{13}C NMR spectrum, δ, ppm: 60.89, 66.10 (2 OCH_2), 127.90 (=CH), 131.34 ($=CH_2$), 166.54 (CO_2).

2-(Acryloyloxyethyl) methyl malonate (VII). To a solution of 0.2 g (1.52 mmol) of compound **VI** in 3 mL of pyridine was added 0.25 g (1.83 mmol) of methylmalonyl chloride, and the mixture was stirred at room temperature till complete consumption of initial compound **VI** (TLC monitoring). Then the mixture was diluted with 30 mL of chloroform, washed with 5% HCl water solution, dried with $MgSO_4$, the solvent was distilled off. The residue was chromatographed on silica gel (eluent petroleum ether–ethylacetate, 3 : 1). Yield 0.19 g (57%). IR spectrum, ν, cm^{-1}: 2958, 1735, 1637, 1620, 1439, 1410, 1338, 1276, 1183, 1154, 1058, 1023, 989, 810. ^{1}H NMR spectrum, δ, ppm: 3.42 s (2H, CH_2), 3.72

s (3H, OCH_3), 4.36 m (4H, $2CH_2O$), 4.96 m (1H, OH), 5.85 d.d (1H, $=CH_2$, J 1.3, 10.7 Hz), 6.11 d.d (1H, =CH, J 17.5, 10.5 Hz), 6.42 d.d (1H, $=CH_2$, J 1.3, 17.3 Hz). ^{13}C NMR spectrum, δ, ppm: 41.14 (CH_2), 52.56 (OCH_3), 61.91 and 63.10 (2 OCH_2), 127.89 (=CH), 131.46 ($=CH_2$), 165.79, 166.26 and 166.69 (CO_2). Found: $[M - OCH_3]^+$ 185.0512. $C_8H_9O_5$. Calculated: $[M - OCH_3]^+$ 185.0444. Mass spectrum, m/z (I_{rel}, %): 185 $[M - OCH_3]^+$ (1), 173 (3), 156 (3), 144 (3), 117 (2), 113 (13), 101 (100), 99 (15), 86 (22), 69 (8), 59 (18), 55 (90). Found, %: C 49.81; H 5.72. $C_9H_{12}O_6$. Calculated, %: C 50.00; H 5.59.

2-(2,2-Dichloroacetoxy)ethyl acrylate (VIII). To a solution of 0.056 g (0.55 mmol) of compound **VI** in 0.5 mL of pyridine was added at cooling 0.1 g (0.68 mmol) of dichloroacetyl chloride, and the mixture was stirred for 12 h at room temperature till the complete consumption of initial ester (TLC monitoring). Then the mixture was diluted with 30 mL of chloroform, washed with 5% HCl water solution, dried with $MgSO_4$, the solvent was distilled off. The residue was chromatographed on silica gel (eluent CH_2Cl_2). Yield 0.1 g (75%). IR spectrum, ν, cm^{-1}: 3012, 2966, 1760, 1728, 1643, 1620, 1453, 1410, 1296, 1271, 1188, 1169, 1079, 1034, 985, 970, 810, 673, 666. ^1H NMR spectrum, δ, ppm: 4.43 m (2H, OCH_2CH_2O), 4.50 m (2H, OCH_2CH_2O), 5.88 d.d (1H, $=CH_2$, J 1.1, 10.5 Hz), 5.97 s (1H, $CHCl_2$), 6.12 d.d (1H, $=CH_2$, J 10.5, 17.3 Hz), 6.43 d.d (1H, =CH, J 1.2, 17.4 Hz). ^{13}C NMR spectrum, δ, ppm: 61.45 (CH_2O), 63.73 ($CHCl_2$), 64.63 (CH_2O), 127.45 (=CH), 131.65 ($=CH_2$), 164.32 and 165.58 ($2CO_2$). Mass spectrum, m/z (I_{rel}, %): 199 (0.3), 159 (1), 155 $[M - 2Cl]^+$ (3), 141 (3), 127 (9), 111 (21), 87 (8), 85 (60), 83 (100), 76 (23). Found, %: C 36.81; H 3.43; Cl 30.96. $C_7H_8Cl_2O_4$. Calculated, %: C 37.03; H 3.55; Cl 31.23.

(Undec-10-en-1-yl) methyl malonate (IX). To a solution of 0.53 g (3.10 mmol) of 10-undecenol in 3 mL of pyridine was added dropwise 0.51 mL (3.70 mmol) of methylmalonyl chloride, and the mixture was stirred at room temperature till complete consumption of initial alcohol (TLC monitoring). Then the mixture was diluted with 30 mL of chloroform, washed with 5% HCl water solution, dried with $MgSO_4$, the solvent was distilled off. The residue was chromatographed on silica gel (eluent petroleum ether–ethylacetate, 3 : 1). Yield 0.65 g (78%). IR spectrum, ν, cm^{-1}: 2974, 2926, 2855, 1741, 1641, 1435, 1418, 1362, 1240, 1198, 1171, 1117, 993, 910, 758, 723, 638. ^1H NMR spectrum, δ, ppm: 1.19 m (12H, CH_2), 1.55 t (2H, CH_2, J 7.3 Hz), 1.95 q (2H, CH_2, J 7.3 Hz), 3.30 s (2H, C^2H_2), 3.66 s (3H, OCH_3), 4.06 t (2H, OCH_2, J 6.7 Hz), 4.85 d.d (1H, $=CH_2$, J 1.0, 9.2 Hz), 4.91 d.d (1H, $=CH_2$, J 1.5, 17.1 Hz), 5.72 m (1H, =CH). ^{13}C NMR spectrum, δ, ppm: 25.73 (CH_2), 28.42, 28.88, 29.05, 29.13, 29.35, 29.40, 33.75 (CH_2), 41.38 ($CO\underline{C}H_2$), 52.41 (OCH_3), 65.69 (OCH_2), 114.12 (=CH), 139.14 ($=CH_2$), 166.54 ($\underline{C}O_2Me$), 167.03 (CO_2). Found, %: C 66.18; H 9.87. $C_{15}H_{26}O_4$. Calculated, %: C 66.64; H 9.69.

{1-Methoxycarbonyl-1-[(acryloyloxy)-ethoxycarbonyl]-1,2-methano}-1,2-dihydro-C_{60}-fullerene (III). To a solution of 0.2 g (0.277 mmol) of C_{60} in 30 mL of toluene was added 0.059 g (0.277 mmol) of ester **VII**, 0.26 g (0.277 mmol) of diazabicyclo[4.2.0]-undecen-7-ene (DBU), and 0.091 g (0.277 mmol) of CBr_4. The reaction mixture was stirred at room temperature for 5 min (TLC monitoring in toluene). Then the reaction mixture was filtered, the filtrate was washed with 5% HCl water solution, dried with $MgSO_4$, the solvent was distilled off. The residue was chromatographed on silica gel (eluent toluene). We obtained 0.158 g (61%) of monosubstituted product **III** and 0.04 g of unreacted fullerene. ^1H NMR spectrum, δ, ppm: 4.09 s (3H, OCH_3), 4.56 m (2H, CH_2O), 4.75 m (2H, CH_2O), 5.89 d (1H, $=CH_2$, J 10.5 Hz), 6.14 d.d (1H, =CH, J 10.6, 17.3 Hz), 6.48 d.d (1H, $=CH_2$, J 10.7, 17.3 Hz). ^{13}C NMR spectrum, δ, ppm: 51.73 ($C^{\mathit{1}}_{cyclopropyl}$), 54.12 ($OCH_3$), 61.87, 64.69 ($2CH_2O$), 71.31 ($C_{sp^3\text{-fullerene}}$), 127.72 (=CH), 131.88 ($=CH_2$), 138.80, 139.32, 140.98 (2C), 141.91 (2C), 142.21, 142.96, 143.04 (3C), 143.10, 143.88, 143.91, 144.59, 144.66 (2C), 144.71 (3C), 144.92, 144.93, 145.08, 145.14, 145.18, 145.20, 145.22, 145.29 (2C) ($C_{fullerene}$), 163.43 (CO_2), 163.88 and 165.74 (CO_2). Found M^+ 934.041. $C_{69}H_{10}O_6$. Calculated M 934.0477.

{1-[2-(Acryloyloxy)ethoxycarbonyl]-1-chloro-1,2-methano}-1,2-dihydro-C_{60}-fullerene (IV) was obtained similarly from 0.1 g (0.138 mmol) of C_{60}, 0.031 g (0.138 mmol) of ester **VIII** in the presence of 0.13 mL (0.138 mmol) of DBU in 30 mL of toluene. Yield 0.06 g (46%). IR spectrum, ν, cm^{-1}: 3432, 2927, 1743, 1723, 1666, 1506, 1427, 1405, 1302, 1264, 1174, 1114, 985, 826, 807, 658, 523. ^1H NMR spectrum, δ, ppm: 4.59 m (2H) and 4.81 (2H, $2CH_2O$), 5.88 d.d (1H, $=CH_2$, J 1.1, 10.4 Hz), 6.14 d.d (1H, =CH, J 10.5, 17.3 Hz), 6.46 d.d (1H, $=CH_2$, J 1.1, 17.3 Hz). ^{13}C NMR spectrum, δ, ppm: 61.82 and 65.24 ($2CH_2O$), 52.87 ($C^{\mathit{1}}_{cyclopropyl}$), 74.90 ($C_{sp^3\text{-fullerene}}$), 127.69 ($=CH_2$), 131.95 (=CH), 138.78, 139.48, 141.18 (2C), 141.82, 142.27 (3C), 142.96, 143.05, 143.13 (2C), 143.16 (2C), 143.32, 143.77, 143.90, 144.21, 144.37, 144.45, 144.63, 144.75, 144.84 (3C), 144.90, 144.98, 145.26 (2C), 145.31, 145.40($C_{fullerene}$), 163.95 and 166.78 (CO_2). Found M^+ 910.005. $C_{67}H_7ClO_4$. Calculated M 910.0033.

{1-Methoxycarbonyl-1-[(undec-10-enyloxy)-carbonyl]-1,2-methano}-1,2-dihydro-C_{60}-fullerene (V) was obtained similarly to compound **III** from 0.1 g (0.14 mmol) of C_{60}, 0.038 g (0.14 mmol) of ester **IX** in the presence of 0.13 mL (0.14 mmol) of DBU and 0.045 g (0.14 mmol) of CBr_4 in 30 mL of toluene. Yield 0.075 g (59%). ^{1}H NMR spectrum, δ, ppm: 1.29 m (8H, CH_2), 1.37 m (4H, CH_2), 1.46 q (2H, *J* 7.7 Hz), 1.83 q (2H, CH_2, *J* 7.5, 6.7 Hz), 2.04 q (2H, CH_2, *J* 7.0 Hz), 4.09 s (3H, OCH_3), 4.50 t (2H, CH_2O), 4.93 d.t (1H, =CH_2, *J* 0.9, 10.4 Hz), 4.99 d.d (1H, =CH_2, *J* 1.8, 17.1 Hz), 5.78 m (1H, =CH). ^{13}C NMR spectrum, δ, ppm: 25.99, 28.58, 28.95, 29.16, 29.22, 29.47, 29.59, 33.84 (CH_2), 52.15 ($C^{1}_{cyclopropyl}$), 54.04 (OCH_3), 67.56 (OCH_2), 71.54 ($C_{sp^3\text{-}fullerene}$), 114.24 (=$CH_2$), 125.32 (=CH), 138.95, 139.13, 139.19, 140.98 (2C), 141.92, 141.95, 142.22 (2C), 143.00, 143.04 (3C), 143.10, 143.91, 144.65 (2C), 144.71, 144.92, 145.14, 145.20 (3C), 145.29 (2C), 145.33 ($C_{fullerene}$), 163.66 and 164.18 (CO_2). Found M^+ 988.229. $C_{75}H_{24}O_4$. Calculated M 988.167.

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