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Polymerizable Dendrimers: III. Synthesis and Polymerization of N-Methacryloyl Urea Derivatives Bearing Branched Aspartic Acid Condensates

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POLYMERIZABLE DENDRIMERS: III. SYNTHESIS AND POLYMERIZATION OF N-METHACRYLOYL UREA DERIVATIVES BEARING BRANCHED ASPARTIC ACID CONDENSATES

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ABSTRACT

A convergent synthesis was used to build up dendrimeric structures consisting of L-aspartic acid units. The bifunctional monomer N-methacryloyl-N′-succinoyl urea (*3*) was synthesized by addition of the free amino group of L-aspartic acid to methacryloyl isocyanate. Dendrimers of different generation were prepared by condensation of the branched peptides with the methacrylic monomer resulting in N-methacryloyl-N′-α,β-bis-(L-dimethoxyaspartyl)-succinoyl urea (*5*) and N-methacryloyl-N′-α,β-bis-(L-aspartyl-α,β-bis-(L-dimethoxy aspartyl))-succinoyl) urea (*6*).The monomers were homopoymerized and copolymerized with phenyl methacrylate and phenyl methacrylamide by free radical mechanism.

INTRODUCTION

In the last decade, rapidly increasing interest has been focused on the development of different types of dendrimers which are highly branched molecules. Such dendritic structures can be obtained via repeating combination of at least trifunctional molecules [1,2]. Numerous papers appeared describing cascade molecules which contain e.g. terminal oxybenzyl- [3], hydroxyl- [4-5], amino- [6,7],

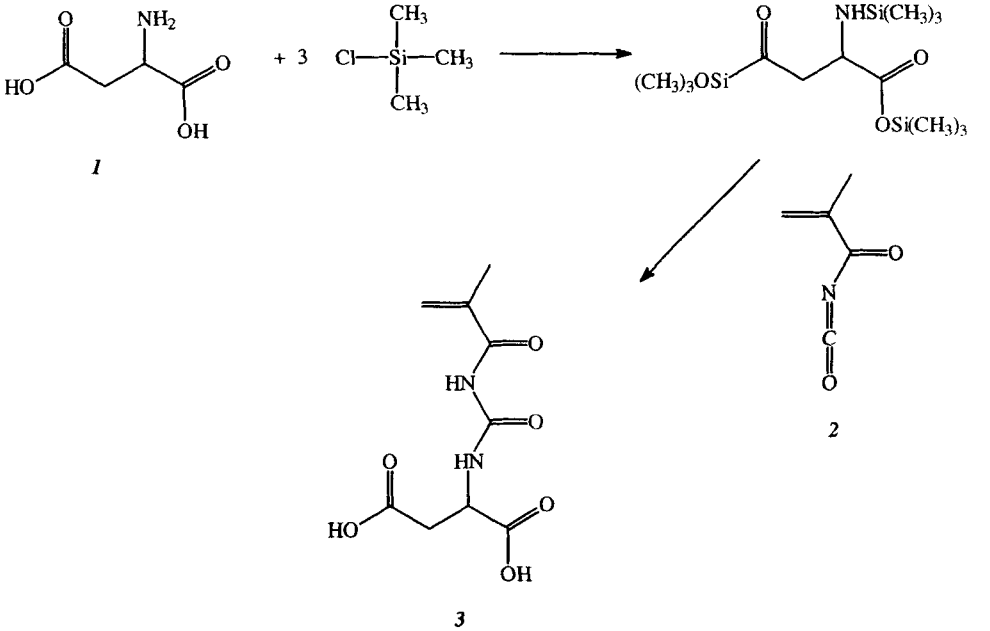
ester [8] and isopropyliden groups [9]. In addition, chiral dendrimers bearing amino-acids at the surface have recently been investigated [10-12].

In the field of polymer chemistry, the synthesis of a dendritic polyether macromonomer which contains 4-oxymethylstyrene has also been described as the first copolymerizable dendrimer [13].Further development in this area has been done recently [14].

Due to our interest in the developments of highly functionalized polymers, we investigated new branched monomers bearing up to 8 ester groups and one methacrylic function [15]. Recently, we described polymers which were derived from L-aspartic acid containing dendrimers bound to a methacrylamide spacer group [16]. The present paper illustrates the approaches of the peptide synthesis of N-methacryloyl urea derivatives, obtained by addition of L-aspartic acid to methacryloyl isocyanate. It is interesting to note that methacryloyl isocyanate was also used e.g. for synthesis of polymerizable amino-protecion groups [17].

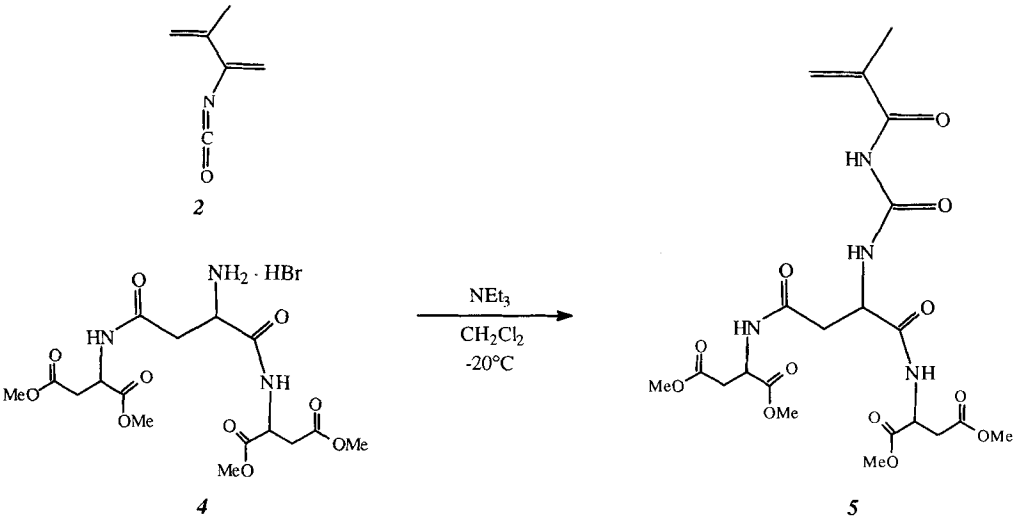
RESULTS AND DISCUSSION

The synthesis of the branched monomer N-methacryloyl-N′-succinoyl urea (*3*) was performed by the addition of L-aspartic acid to methacryloyl isocyanate. To achieve this, the carboxylic functions of L-aspartic acid had to be protected by trimethyl chloro silane. This is accompanied by an activation of the corresponding

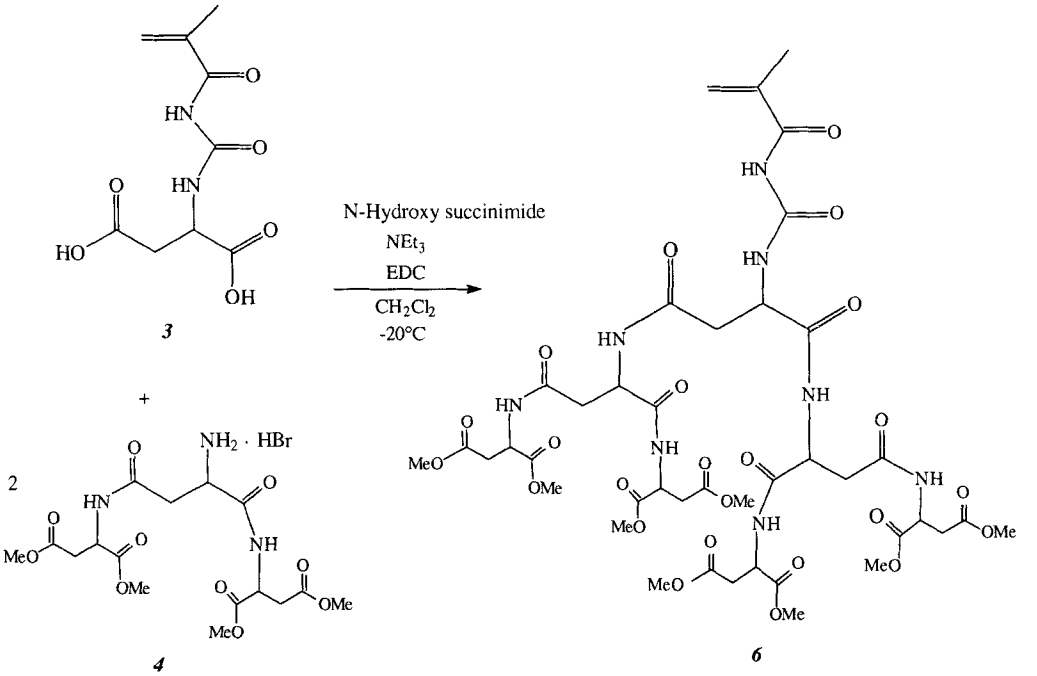


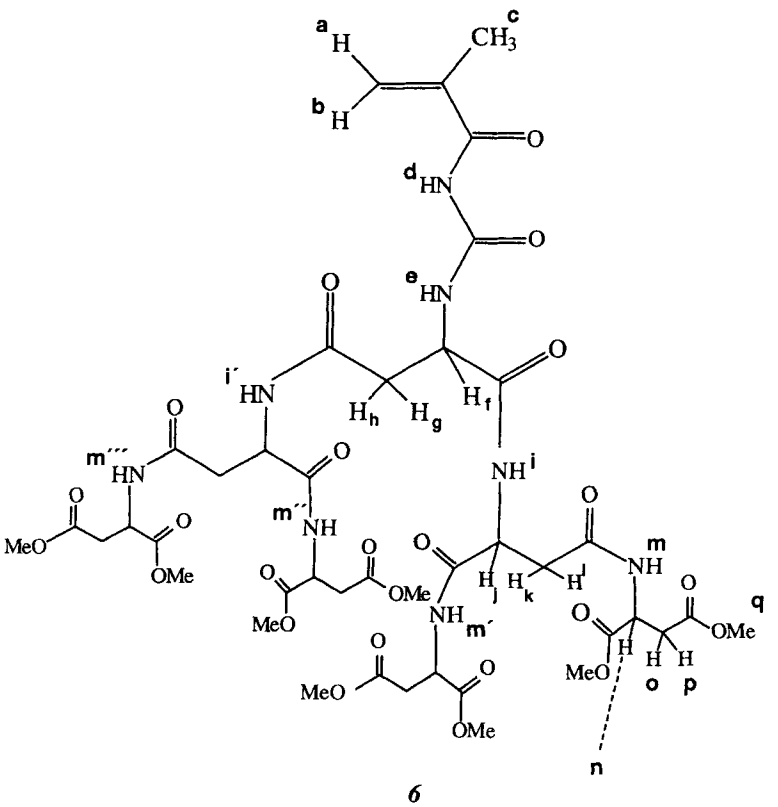
1 *2* *3*

amino group by the same reagent. The addition of α,β-bis-(L-dimethoxyaspartyl)-L-aspartic acid hydrobromide (*4*) to methacryloyl isocyanate yielded in the dendrimer N-methacryloyl-N′-(α,β-bis-(L-dimethoxyaspartyl)-succinoyl) urea (*5*) of the first generation with 4 ester groups.



In contrast to the direct addition of branched trimer *4* to methacryloyl isocyanate, condensation of *4* with the monomer *3*, with the help of EDC, resulted in the dendrimer (*6*) of the second generation.





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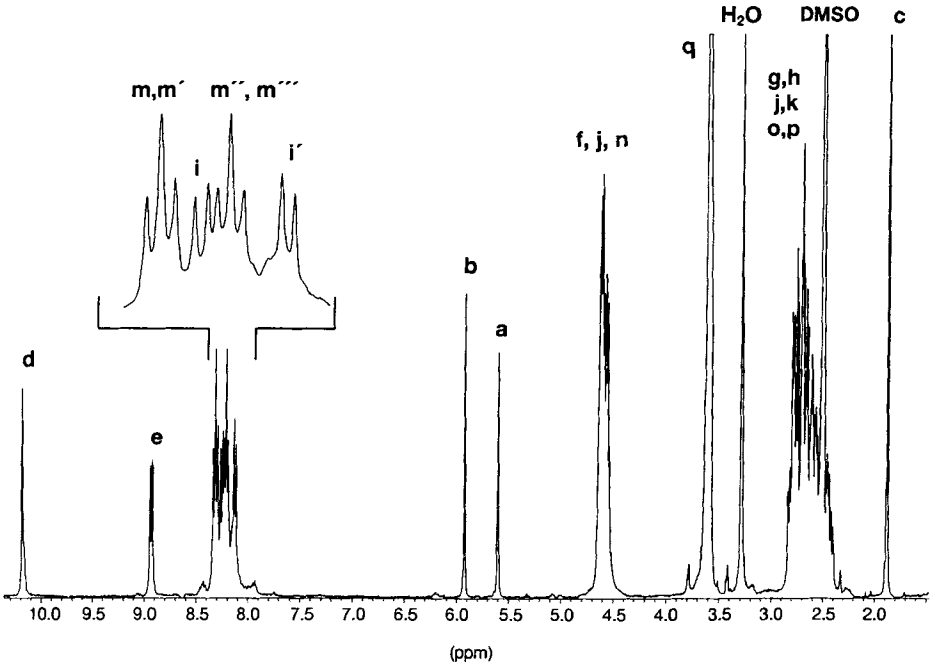


Figure 1. 400 MHz ^{1}H-NMR spectrum of monomer **6**.

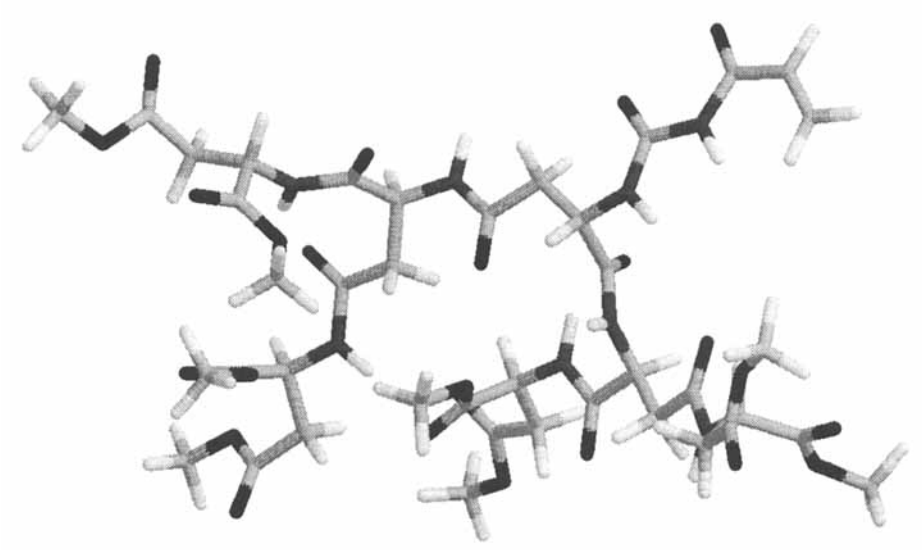


Figure 2. Molecular model of monomer **6.**

Figure 1 shows the ^{1}H-NMR spectrum of monomer ***6***. Herein, each of the NH-groups can be assigned to the corresponding signals. First, the unusually high shift of 10.19 ppm of H^d at the imide group is due to the direct neighborhood of two carbonyl groups.

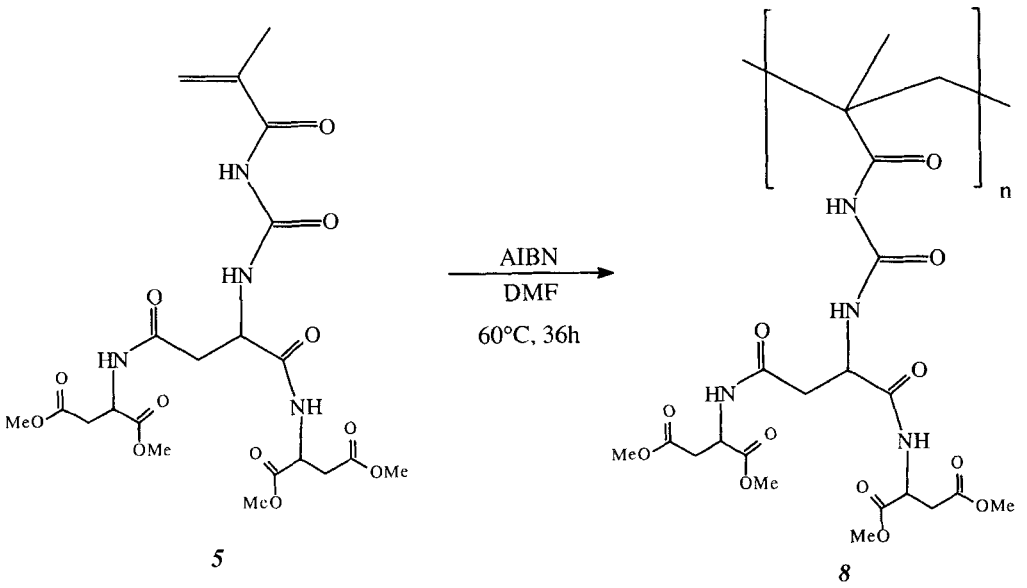
The signal of the amino hydrogen H^e of zero generation appears at 8.93 ppm. Analyzing the signals of the peptidic branches as shown in the extended part of Figure 4, we believe that the amino groups bound to the α-carboxylic group are higher shifted than the one at the β–position in the same generation. The small difference between the shift of H^m and $H^{m''}$ could be caused by the fact that the proton $H^{m''}$ is bound to the β–carbonylamide group, in contrast to H^m, which is bound to the α-position. The amide-protons $H^{m'}$ and $H^{m'''}$ can be assigned analogously.

Figure 2 shows a molecular model of monomer ***6***, which was calculated on a force field MM^+-level [18]. As illustrated from the tube model, the methacrylic function seems to be not sterically hindered, indicating the possibility of homopolymerization.

The free radical homo- and copolymerizations of monomers ***3*** and ***5*** were verified. Therefore, N-methacryloyl-N′-succinoyl urea (***3***) was homopolymerized resulting in poly-[N-methacryloyl-N′-succinoyl urea] (***7***) and copolymerized in a ratio of 1:1 with phenyl methacrylamide yielding in poly[N-methacryloyl-N′-succinoyl-urea-co-phenyl methacrylamide] in a ratio of nearly 1:5 (***9***). In both cases,

absolute DMF was used as a solvent and AIBN as initiator at a temperature of 60°C. Polymers *7* and *9* were examined by DSC measurements, but no glass transition could be detected.

Under similar conditions, dendrimer *5* was also homopolymerized yielding in polymer *8*. In the case of copolymerization of N-methacryloyl-N′-(α,β-bis-(L-dimethoxyaspartyl)-succinoyl) urea (*5*) with phenyl methacrylate in ratio of 1:5 , for this copolymer ***10***, a incorporating value of nearly 1:12 was determined and a T_g value of 113°C could be found. GPC measurements (polystyrene standard) of ***10*** indicated a molecular weight of M_n = 5,600 and a polydispersity of M_w / M_n = 3.9. Attempts to determine the molecular weights of the other polymers appeared to be difficult. GPC and MALDI measurements were not useful in characterizing these polymers satisfactorily. Viscosity measurement in solution suggests the presence of oligomers.



5 *8*

Examinations by ^{1}H-NMR spectroscopy underlined the fact that monomers *3* and *5* are incorporated into copolymers *9* and ***10***. The characteristic amide and ester groups, and also the corresponding hydrogen of L-aspartyl residues, appear as broad signals. The ratios of incorporated monomers are also calculated by ^{1}NMR spectroscopy.

EXPERIMENTAL

Materials and Methods

NMR-spectra were recorded with Bruker ARX 400. Mass spectra were performed on Varian MAT 311A and FAB at Finnigan MAT 90 (FAB). Infrared Spectra were recorded on Perkin-Elmer-Spektrometer 397 and 1420. Elemental analyses were carried out with a Perkin-Elmer 204 B elemental analyzer, polarographic measurements with a Perkin-Elmer 241 (cavity volume 1 ml, cavity length 10 cm) and melting points were measured with a Büchi melting point determinator 510.

All chemicals and solvents were obtained from Fluka and were used without further purification. Z-L-aspartic acid and L-aspartic acid dimethylester hydrochloride were synthesized according to literature.[19, 20]

Synthesis of Monomers

N-Methacryloyl-N'-succinoyl urea (3)

A mixture of 4.80 g (36 mmol) of L-aspartic acid and 125 ml of dry dichloromethane. The mixture was heated to reflux. Then11.74 ml (108 mmol) of trimethyl chloro silane were added. After the mixture was stirred for 30 minutes, 15.06 ml of triethylamine were added dropwise in such a way that the mixture still boiled without heating. Finally, the suspension was heated to reflux for 24 hours. The resulting solution was cooled to -20°C and 4.00 g (36 mmol) of methacryloyl isocyanate were added dropwise. The solution was stirred at the same temperature for 6 hours. Stirring was continued for 12 hours at room temperature. The resulting precipitate was filtered off and the filtrate was washed three times each with 80 ml of water. The organic layer was dried over sodium sulfate and the desired product was precipitated as a white powder by adding n-hexane.

yield: 4.75 g (54%).

mp: 168-169°C dec.

^{1}H-NMR (DMSO-d_6, 400 MHz): δ= 1.88 (s, 3H, C**H**$_3$), 2.69-2.85 (m, 2H, CHC**H**$_2$), 4.54-4.59 (m, 1H, C**H**CH$_2$), 5.61, 5.93 (AB system, 2H, **H**$_2$C=), 9.08 (d, ^{3}J= 8.01 Hz, 1 H, CHN**H**CONHCO), 10.26 (s, 1 H, CHNHCON**H**CO), 12.55 (2H, COO**H**)

^{13}C{^{1}H}-NMR (DMSO-d_6): δ= 18.72 (1C, **C**H$_3$), 36.94 (1C, **C**H$_2$CH(NH)COOH), 49.41 (1C, CH$_2$**C**H(NH)COOH), 123.83 (1 C, **C**H$_2$ alkene), 138.81 (1C, **C** alkene), 153.67 (1C, HN**C**ONH), 178.31, 178.71 (2C, **C**OOH)

MS (70 eV): m/z (%) 226(1) $[M\text{-}H_2O]^+$, 199(8) $[199\text{-}CO_2H]^+$, 154(5) $[199\text{-}CO_2H]^+$, 69(70) $[H_2CC(CH_3)CO]^+$, 44(100) $[CO_2]^+$, 41$[H_2CCCH_3]^+$

$C_9H_{12}N_2O_6$ (244.20). calc.: C 44.27 H 4.95 N11.48; found: C44.20 H4.96 N11.37.

N-Benzyloxycarbonyl-α,β-bis-(L-dimethoxyaspartyl)-L-aspartic acid

10 g (37 mmol) N-benzyloxycarbonyl-L-aspartic acid (*1*), 14.62 g (74 mmol) L-aspartic acid dimethylester hydrochloride (*2*) and 8.51 g (74 mmol) N-hydroxysuccinimide were suspended in 150 ml of dry dichloromethane. The suspension was cooled to -20°C and treated with 10.3 ml (74 mmol) of triethylamine. Then 15.3 g (74 mmol) dicyclohexylcarbodiimide were added and the mixture was stirred for 4 hours at -20°C. Stirring was continued for 12 hours at room temperature. The resulting precipitiate was filtered off and washed with 80 ml of warm dichloromethane. The filtrate was washed three times, each with 100 ml of diluted aqueous solution of citric acid, 100 ml saturated potassium hydrogencarbonate solution and 100 ml of water. The organic phase was dried over sodium sulfate. The solvent was removed in vacuum and the crude product was recrystallized from methanol, yielding (*5*) in thin needles.

yield: 11.3 g (55%)

mp: 161°C

α_D^{20} = 63.0 ±0.5 (c = 1 in CH_2Cl_2)

^{1}H-NMR (DMSO-d_6, 250 MHz): δ = 2.47-2.93 (m, 6H, CHC**H**$_2$), 3.67, 3.69 (s, 12H, OC**H**$_3$), 4.46, 4.72 (m, 3H, C**H**CH$_2$), 5.09 (s, 2H, OC**H**$_2$C$_6$H$_5$), 7.43 (ps, 5H, aromatic), 7.48 (ps, 1H, N**H**COOCH$_2$), 8.44-8.49 (m, 2H, CON**H**CH)

^{13}C{^{1}H}-NMR (DMSO-d_6): δ = 35.45, 35.69 (3 C, CH**C**H$_2$), 48.51, 48.59, 51.75 (3C, **C**HCH$_2$), 52.20, 52.25 (4C, O**C**H$_3$), 65.54 (1C, O**C**H$_2$C$_6$H$_5$), 127.75, 127.85, 128.37 (1C, **C**H phenyl; 2C, **C**H phenyl; 2C, **C**H phenyl), 136.91 (1C, **C** phenyl), 155.68 (1C, HN**C**OOCH$_2$), 169.15, 170.44, 170.50, 171.06, 171.14, 171.24 (6C, **C**ONH and **C**OOCH$_3$)

IR(KBr): 3320 cm^{-1} (NH, sec. amide), 3070, 3030 (CH, aromatic), 2940 (CH, aliphatic), 1730 (C=O, ester), 1675 (amide I), 1640 (C=C, aromatic), 1550 (amide II), 1430 (CH), 1370 (CH_3), 1180-1220 (C-O, ester), 755, 695 (monosubst. aromate).

MS (70ev): m/z (%) 553(3) $[M]^+$, 522(3) $[M\text{-}OCH_3]^+$, 393(3) $[M\text{-}Asp(OMe)_2]^+$, 365(11) $[393\text{-}CO]^+$, 160(70) $[Asp(OMe)_2\text{-}H]^+$, 108(3) $[C_6H_5CH_2OH]^+$, 91(100) $[C_7H_7]^+$, 77(9) $[C_6H_5]^+$, 65(30) $[C_5H_5]^+$

$C_{24}H_{31}N_3O_{12}$ (553.52) calc.: C 52.08 H 5.64 N 7.59; found: C 52.25 H 5.77 N 7.76

α,β-Bis-(L-dimethoxyaspartyl)-L-aspartic acid hydrobromide (4)

5.0 g (9 mmol) of *3* were treated with 9 ml of a mixture of 33% hydrobromic acid in acetic acid. The solution was stirred for one hour at 25°C. Then 150 ml of dry diethyl ether were added and the mixture was stored several hours at -20°C. The resulting precipitate was collected on a filter and washed with dry diethyl ether. The obtained yellowish solid material was dried over potassium hydroxide.

yield: 4.1 g (91%)

mp.: 68-72°C

α_D^{20} = 4.2 ±0.5 (c=1 in MeOH)

^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 2.62-2.86 (m, 6H, CHC**H**$_2$), 3.62, 3.63, 3.64, 3.65 (s, 12H, OC**H**$_3$), 4.12 (1H, CH_2C**H**(NH_2*HBr), 4.62-4.71 (m, 2H, CH_2C**H**(NH)), 8.11 (s, 3H, N**H**$_2$***H**Br), 8.79 (d, ^{3}J = 7.77 Hz, 1 H, N**H**), 8.92 (d, ^{3}J = 7.71 Hz, 1 H, N**H**)

^{13}C{1H}-NMR (DMSO-d_6): δ = 36.10, 36.24, 36.46 (3 C, CH**C**H$_2$), 49.54, 49.59, 49.68 (3C, **C**HCH$_2$), 52.61, 52.67, 53.13, 53.26 (4C, O**C**H$_3$), 168,88, 169.29 (2C, **C**ONH), 171.17, 171.22, 171.33, 171.60 (4C, **C**OOCH$_3$)

IR (KBr): 3350 cm^{-1} (NH, sec. amide), 3050 (NH_3^+), 2950, (CH, aliphatic),1735- 1750 (C=O, ester), 1660-1680 (amide I), 1520-1550 (NH_3^+ and amide II), 1435 (CH), 1370 (CH_3), 1200-1280 (C-O, ester)

MS (FAB): m/z (%) 442(9) $[M\text{-}HBr+Na]^+$, 420(100) $[M\text{-}HBr+H]^+$, 259(11) $[420\text{-}Asp(OMe)_2]^+$, 231(38) $[259\text{-}CO]^+$, 162(41) $[Asp(OMe)_2\text{-}H]^+$, 146(23) $[162\text{-}NH_2]^+$, 70(48) $[HNCHCH_2CO]^+$

$C_{16}H_{26}BrN_3O_{10}$ (500.28) calc.: C 38.41 H 5.24 N 8.40; found: C 38.17 H 5.16 N 8.23

N-Methacryloyl-N'- (α,β-bis-(L-dimethoxyaspartyl)-succinoyl) urea (5)

3.00 g (6 mmol) of α,β-bis-(L-dimethoxyaspartyl)-L-aspartic acid hydrobromide (*4*) were dissolved in 20 ml of dry dichloromethane and treated with 0.84 ml (6 mmol) triethylamine. At -20°C 0.67g (6 mmol) methacryloyl isocyanate were added dropwise to this solution. After 12 hours stirring at room temperature, the reaction mixture was washed two times each with 20 ml of diluted acetic acid,

20 ml of a saturated potassium hydrogen carbonate solution and 20 ml of water. After drying the organic layers over sodium sulfate, the desired product was solidified by adding n-hexane.

yield: 1.95 g (61%)

mp.: 216(C

^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 1.88 (s, 3 H, C**H**$_3$), 2.55-2.81 (m, 6H, CHC**H**$_2$), 3.59, 3.60, 3.61,3.62 (s, 12H, OC**H**$_3$), 4.60-4.64 (m, 3H, C**H**CH$_2$), 5.61, 5.93 (AB system, 2 H, **H**$_2$C=), 8.46 (pt, 2H, **H**NCOCH$_2$CH(NH)CON**H**), 8.90 (d, ^{3}J = 7.87 Hz, 1H, HNCOCH$_2$CH(N**H**)CONH), 10.23 (s, 1 H, NHCON**H**CO)

^{13}C{^{1}H}-NMR (DMSO-d_6): (δ =18.96 (1C, **C**H$_3$), 36.28, 36.52, (2C,H$_3$COOC**C**H$_2$CH(NH)COOCH$_3$), 38.48 (1C, NHCO**C**H$_2$CH(NH)CONH), 49.30,49.50 (2C, H$_3$COOCCH$_2$**C**H(NH)COOCH$_3$), 50.49 (1C, NHCOCH$_2$**C**H(NH)CONH), 52.46, 52.50, 52.99, 53.06 (4C, O**C**H$_3$), 124.02 (1C, **C**H$_2$ alkene), 139.11 (1C, **C** alkene), 153.87 (1C, HN**C**ONH), 169.84, 170.03(2C, N**H**CCH$_2$ u. CH**C**ONH), 171.28, 171.37, 171.76, 171.85 (4C, COOCH$_3$)

IR (KBr): 3300 cm^{-1} (NH, sec. amide), 3060 (CH, alkene), 2850 (CH, aliphatic), 1740 (C=O, ester), 1660 (amide I), 1635 (C=C, alkene), 1530 (amide II), 1435 (CH), 1370 (CH$_3$), 1175-1300 (C-O, ester).MS (FAB): m/z (%) 553(100) [M+Na]$^+$, 531(90) [M+H]$^+$, 468(71) [M- 2OCH$_3$]$^+$, 420(10) [Asp(Asp(OMe)$_2$)Asp(OMe)$_2$+H]$^+$, 370(15) [M- Asp(OMe)$_2$]$^+$, 162(9) [Asp(OMe)$_2$+H]$^+$

$C_{21}H_{30}N_4O_{12}$ (530.49). calc.: C 47.55 H 5.70 N 10.56. found: C 47.37 H 5.85 N 10.85

*N-Methacryloyl-N′-(α,β-bis-(L-aspartyl-α,β-bis-(L-dimethoxyaspartyl))-succinoyl) urea (**6**)*

1.00g (4.10 mmol) of prepared N-methacryloyl-N-succinoyl urea (***3***),4.10g (8.20 mmol) of α,β-bis-(L-dimethoxyaspartyl)-L-aspartic acid hydrobromide(***4***) and 0.94 g (8.2. mmol) N-hydroxysuccinimide were dissolved in 20 ml of dry dichlormethane. After cooling the solution to -20°C 0.83 g (8.20 mmol) tri-ethylamine were added, followed by an amount of 1.57g (8.20 mmol) N-(3-dimethyl-aminopropyl)-N′-ethylcarbodiimide hydrochloride. The suspension was shaken at -20°C for 6 hours. After additional stirring at room temperature for 24 hours, the reaction mixture was washed two times each with 20 ml of diluted citric acid, 20 ml of a saturated sodium hydrogen carbonate solution and 20 ml of water.

After drying the organic layers over sodium sulfate, the crude product was evaporated to dryness and recrystallized from methanol.

yield: 0.75 g (17%)

mp.: 194-196°C

^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 1.87 (s, 3 H, C**H**$_3$), 2.43-2.80 (m, 14H, CHC**H**$_2$), 3.59, 3.60, 3.61,3.62 (s, 24H, OC**H**$_3$), 4.54-4.64 (m, 6H, C**H**CH$_2$), 5.60, 5.92 (AB system, 2 H, **H**$_2$C=), 8.12-8.34 (m, 6H, **H**NCOCH$_2$CH(NHCONH)CON**H** a. H$_3$COOCCH(N**H**)CH$_2$COOCH$_3$), 8.93 (d, ^{3}J= 7.50 Hz, 1H, HNCOCH$_2$CH(N**H**CONH)CONH), 10.19 (s, 1 H, NHCON**H**CO)

^{13}C{^{1}H}-NMR (DMSO-d_6): δ = 18.65(1C,**C**H$_3$), 36.02,36.27,(6C, H$_3$COOC**C**H$_2$CH(NH)COOCH$_3$), 37.49 (1C, NHCO**C**H$_2$CH(NH)CONH), 49.09, 49.26, 49.32, 50.01, 50.24 (6C, H$_3$COOCCH$_2$**C**H-(NH)COOCH$_3$), 50.92 (1C, NHCOCH$_2$**C**H(NHCONH)CONH), 52.22, 52.71 (8C, O**C**H$_3$), 123.68 (1C, **C**H$_2$ alkene), 138.86 (1C, **C** alkene), 153.65 (1C, HN**C**ONH), 169.78, 169.85, 169.96 (6C, N**H**COCH$_2$ u. CH**C**ONH), 171.03, 171.14, 171.20, 171.45, 171.63 (8C, **C**OOCH$_3$)

MS (FAB): m/z (%) 1069(80) [M+Na]$^+$, 1047(20) [M+H]$^+$, 984(25) [M-2 OCH$_3$]$^+$, 420(23) [Asp(Asp(OMe)$_2$)Asp(OMe)$_2$+H]$^+$, 162(100) [Asp(OMe)$_2$+H]$^+$

$C_{41}H_{58}N_8O_{24}$ (1046.95). calc.: C 47.04 H 5.58 N 10.70. found: C 46.90 H 5.62 N 10.73

Synthesis of Polymers

Poly-[N-methacryloyl-N′-succinoyl -urea] (7)

A solution of 1000 mg (4.1 mmol) of N-methacryloyl-N′-succinoyl-urea and 34.5 mg (0.21 mmol, 5 mol.%) AIBN in 2 ml of dry and oxygen-free DMF was stirred vigorously at 60°C for 24 hours. The polymeric solution was dropped into acetone, yielding a crude product that was dried and reprecipitated twice, again from a DMF solution that was poured into acetone.

yield: 700 mg (70%)

mp: > 250°C

^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 0.81-1.30 (CH$_2$ u.CH$_3$), 2.55-2.88 (6H, CHCH$_2$), 4.51 (1H, CHCH$_2$), 8.93 (1H, CH$_2$CHNH), 12.60 (COOH)

$(C_9H_{12}N_2O_6)_n$ $(244.20)_n$. calc.: C 44.27 H 4.92 N11.48. found: C 43.40 H 5.06 N 11.31

Poly [N-methacryloyl-N'-(α,β-bis-(L-dimethoxyaspartyl)-succinoyl)-urea] (8)

500 mg (0.94 mmol) of N-methacryloyl-N'-α,β-bis-(L-dimethoxyaspartyl)-succinoyl)-urea were dissolved with 15.4 mg (0.094 mmol, 10 mol%) AIBN and 9.5 mg (0.047 mmol, 4 mol%) dodecanthiol in 1.5 ml of dry DMF. Treating the suspension with nitrogen was followed by stirring the solution for 24 hours at 60°C. It was then put into 70 ml of a mixture of methanol/water (ratio 1:2). The resulting solid phase was treated twice in the same manner.

yield: 192 mg (39%)

viscosity: (η_{red} = 1.84x10^{-2} l/g (±0.17x10^{-2} l/g)

^{1}H-NMR (DMSO-d_6, 400 MHz): (= 0.85-1.23 (3H, C**H**$_3$), 2.55-2.89 (8H, C**H**$_2$), 3.60 (s, 12H, OC**H**$_3$), 4.57-4.66 (3 H, C**H**CH$_2$), 8.19-8.89 (4H, N**H**)

IR (KBr): 3330-3360 cm^{-1} (NH, sec amide), 2950, 2850 (CH, aliphatic), 1650-1760 (C=O, ester and amide I), 1510-1550 (amide II), 1420 (CH), 1370 (CH$_3$), 1170-1300 (C-O, ester).

$(C_{21}H_{30}N_4O_{12})_n$ $(530.49)_n$ calc. C 47.55 H 5.70 N 10.56 found: C 47.57 H 5.88 N 10.35

Poly[N-methacryloyl-N'-succinoyl-urea-co-phenyl methacrylamide] (9)

500 mg N-methacryloyl-N'-succinoyl-urea (2 mmol) and 322 mg (2 mmol) phenyl methacrylamide were dissolved in 2 ml of abs. DMF. After treating the solution with nitrogen, 35 mg (0.2 mmol, 5 mol%) AIBN were added and the mixture was stirred for 48 hours at 60°C. The crude copolymer was solidified by dropping the solution in acetone. The polymer was purified by dissolving it in DMF and solidifying it twice from acetone.

yield: 500 mg (60%)

mp: 240°C dec.

^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 0.85-1.33 (C**H**$_2$ u.C**H**$_3$), 2.01-2.22 (CHC**H**$_2$), 4.52 (C**H**CH$_2$), 6.59-7.46 (aromatic), 8.92 (N**H**)

$(C_9H_{12}N_2O_6)_1 \cdot (C_{10}H_{11}N0)_{4.97}$ $(1045.36)_n$. calc.: C 67.44 H 6.43 N 9.35. found: C 60.06 H 6.60 N 9.15

Poly[N-methacryloyl-N'-(α,β–bis-(L-dimethoxyaspartyl)-succinoyl)-urea-co-phenoxy-methacrylic acid]

465 mg (0.88 mmol) N-methacryloyl-N'-(α,β-bis-(L-dimethoxyaspartyl)-succinoyl-urea and 714 mg (4.40 mmol) phenyl methacrylate were dissolved in 5 ml DMF. The solution was treated with nitrogen and after that, 44 mg (26.80 mmol, 5 mol%) AIBN were added. The suspension was shaken for 48 hours at 60°C, followed by pouring the solution into a mixture of ethanol/water (ratio 2:3).

The product was purified in the same manner.
yield: 760 mg (64%)
mp: >250°C
^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 1.19-1.43 (CH_2 and CH_3), 2.33-2.49 (CH_2CHNH), 3.61-3.64 (OCH_3), 4.57 (CH_2CHNH), 7.08-7.33 (aromatic)

$(C_{21}H_{30}N_4O_{12})_1$ $(C_{10}H_{10}O_2)_{12.67}$ calc.: C 67.59 H 6.19 N 2.35. found: C 68.63 H 6.07 N 2.21

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