Macromolecular design of new cationic polyelectrolytes

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Methods were elaborated for the synthesis of new monomers, derivatives of diallylguanidine and macromers, which contain fragments of polytetrahydrofuran and diallylic nitrogen-containing end groups (diallylamine, alkyldiallylammonium, diallylguanidine both in base and acetate forms). Alkylation of a macromer with a diallylamine end group was carried out with methyl iodide in various organic solvents. The possibility of synthesis of diallylguanidine acetate homopolymer as well as its statistical copolymer with diallyldimethylammonium chloride was shown. For the first time, block copolymers based on synthesized macromers were obtained.

Key words: diallylguanidine, diallyl dimethyl ammonium chloride, macromers, macroinitiator, cationic and radical polymerization and copolymerization, polyelectrolytes, macromolecular design.

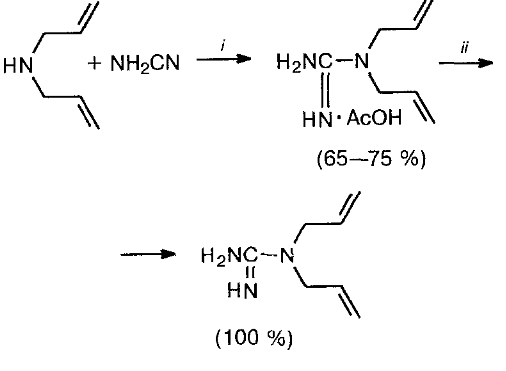
The present report opens a series of articles on the macromolecular design of new polyelectrolytes (both cationic and anionic): formation by methods of polymer chemistry and elaboration of synthetic pathways leading to new generation of water soluble and water swelling polymeric systems with valuable set of physical chemical and applied properties.

Results and Discussion

Syntheses of monomers and macromers. Several ionogenic (cationogenic in nature) monomers, derivatives of diallylguanidin (DAG), were synthesized by reaction of diallylamine and cyanamide in presence of acetic acid (acetonitrile as a solvent) (Scheme 1).

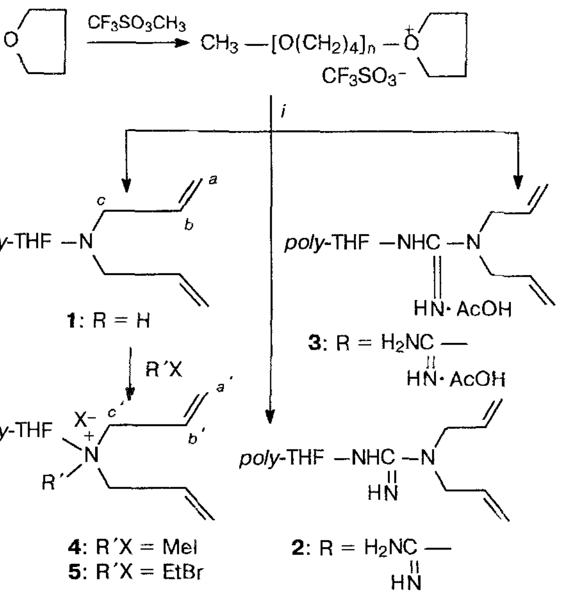
Macromers with different end groups (EG) and various molecular masses (MM) were obtained on the basis of polytetrahydrofuran (poly-THF) derivatives (Scheme 2).

Scheme 1



i. AcOH, Δ, MeCN; *ii.* EtONa, EtOH

Scheme 2



i. Excess of termination agent $RN(CH_2CH=CH_2)_2$.

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Table 1. Synthesis of macromers

Entry	THF:MTF:TA ratio[a]	τ min	Product	K(%)[b]	MM(×10^3)			
					^{1}H NMR	GPS		
					$\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
1	1000:1:5	70	**1**	15	12.0	12.6	14.1	1.12
2	1000:2:10	55	**1**	30	6.0	8.4	9.6	1.15
3a	1000:4:20	22	**1**[c]	20	4.3	4.5	5.0	1.11
3b					2.5	2.8	3.2	1.15
4	1000:2:10	35	**2**	22	4.4	3.4	6.4	1.87
5	1000:2:10	50	**2**	28	5.2	4.2	7.2	1.72
6	1000:4:12	45	**3**	41	5.9	5.5	6.9	1.23

[a] Molar, TA — termination agent. [b] THF conversion. [c] The sample with greater MM (3a) was isolated by precipitation from cooled methanol (0—3 °C); the second sample (3b) was isolated by precipitation of the residue from cold (0—5 °C) water. Weights of fractions 3a and 3b were nearly equal.

Table 2. Alkylation of macromers **1** with methyliodide

Entry	MM(**1**)[a] (×10^3)	$\bar{M}_w/\bar{M}_n$[a]	τ h	Solvent	MM(**4**)[a] (×10^3)	$\bar{M}_w/\bar{M}_n$[a]	Q[b]
1	2.8	1.15	0.8	THF:MeOH 4:1	2.3	1.25	50
2	7.4	1.13	1.7	THF	6.2	1.13	20
3	12.6	1.12	0.7	THF	11.8	1.09	0
4	12.6	1.12	69.0	THF	10.2	1.21	100
5	12.6	1.12	76.0	THF:MeOH 1:2	12.8	1.06	84
6	2.8	1.15	0.8	MeOH	2.7	1.15	14

[a] According to GPC data ($\bar{M}_n$). [b] Quaternization degree (%), according to ^{1}H NMR data for allyl group protons (see Table 3).

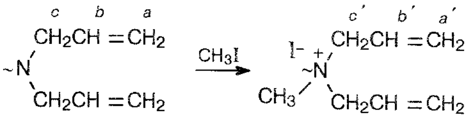
Cationic polymerization of THF (of "living chains" type) initiated by methyltriflate (MTF) was carried out in bulk at ~20 °C, followed by addition of a termination agent (TA). The MM and conversion degree are determined by the concentration of initiator added and duration of the reaction (Table 1). As was shown earlier[1—3], by regulating these parameters it is rather easy to vary the MM of poly-THF being obtained and the degree of conversion of monomer into polymer.

The MM was determined by ^{1}H NMR (comparision of the integral intensity of EG and that of poly-THF chain) and gel permeation chromatography (GPC) methods. These methods give similar results.

Alkylation of macromers **1** was carried out with a 5—10-fold excess of alkyl halides in THF, methanol or their mixture at ~20 °C. The choice of the solvent was determined by solubility of the polymer sample. Degree of alkylation was determined by the ^{1}H NMR method (Table 2). It was shown that a decrease in MM of the sample to be alkylated (Table 2, entries 1—3) or THF addition to methanol (Table 2, entries 6 and 1, as well as 5 and 4) accelerate the alkylation reaction.

After obtaining macromer **4**, with structure similar to that of diallyl dimethyl ammonium chloride (DADMAC) (fragment of poly-THF instead of methyl group), we studied quaternization reaction of tertiary aminogroup of macromer **1** with methyl iodide at ~20 °C. According to ^{1}H NMR data, alkylation in methanol was completed after 63 hour (Table 3).

After quaternization of macromer **1** signals of allyl protons are shifted down-field (see Fig. 1):



Signals of H_c are observed at 3.1 ppm, while those of H'_c do at 4.0—4.3 ppm. Integral intensity of the former decreases and that of the latter increases with an increase in the degree of quaternization. Moreover, the total sum is 4 protons. All signals of the protons of double bonds are observed at 5.0—6.0 ppm, and the

Table 3. Dependence of quaternization degree upon time[a]

τ/h	Q (according to ^{1}H NMR)[b]	
	$H'_c/H_c + H'_c$	$H'_c/H_a + H_b + H'_a + H'_b$
0.8	10	14
1.4	13	16
2.1	18	20
4.5	34	38
5.8	56[c]	50
24.0	79[c]	80
48.0	93[c]	95
63.0	100	100

[a] Temperature 20—22 °C, solvent CD$_3$OD, $\bar{M}_n$(**1**) = 2.8 · 10^3. [b] Quaternization degree (%). [c] H_c signals are partially overlapping with other signals.

total sum is 6 protons. Therefore, equations for the calculation of the degree of quaternization (1 and 2) are as follows:

$$Q = \frac{I(H'_c)\cdot 100\%}{\Sigma I(H_c),(H'_c)} \qquad (1)$$

$$Q = \frac{6I(H'_c)\cdot 100\%}{4\Sigma I(H_a),(H_b),(H'_a),(H'_b)} \qquad (2)$$

where Q is quaternization degree (%), I is integral intensity of the corresponding signals.

It is also possible to calculate quaternization degree using integral intensity of signal of Me group (H_d) (peak at 3.0—3.1 ppm) (Eq. 3). However it is near polymer chain signals and end MeO group of polymer chain signal; in some cases it is hard to isolate it from the

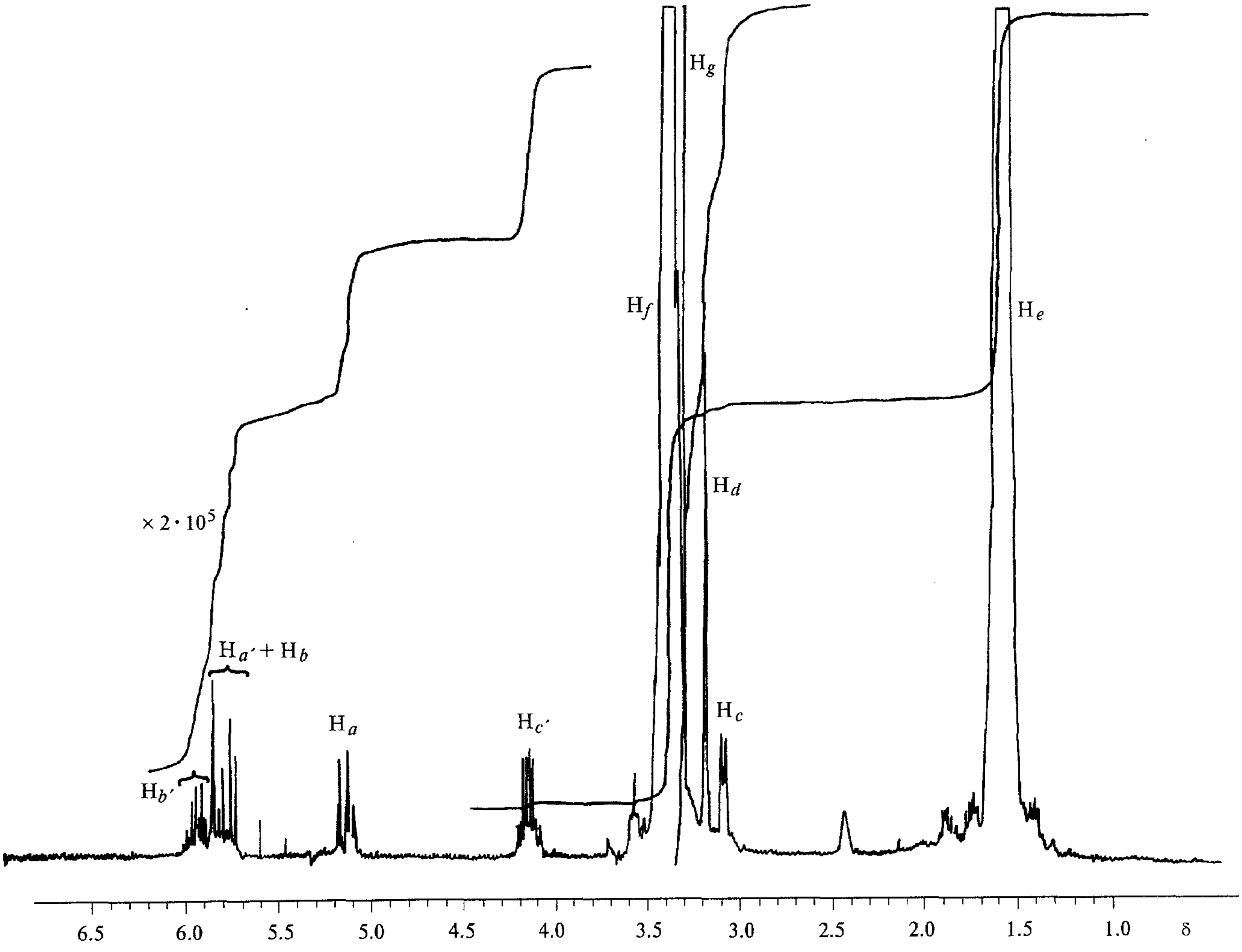
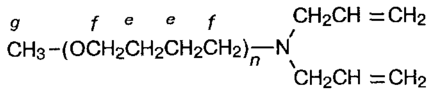
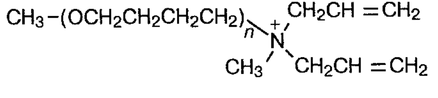


Fig. 1. ^{1}H NMR spectrum (CDCl$_3$, δ) of the mixture of non-methylated (**1**) and methylated (**4**) macromers.



$$\overset{g}{CH_3}-(O\overset{f}{CH_2}\overset{e}{CH_2}\overset{e}{CH_2}\overset{f}{CH_2})_n-N(\overset{c}{CH_2}\overset{b}{CH}=\overset{a}{CH_2})_2$$

(**1**)



$$\overset{g}{CH_3}-(O\overset{f}{CH_2}\overset{e}{CH_2}\overset{e}{CH_2}\overset{f}{CH_2})_n-\overset{+}{N}(CH_3)(\overset{c'}{CH_2}\overset{b'}{CH}=\overset{a'}{CH_2})_2$$

(**4**)

spectrum (sometimes this is the case for H_c protons of Equation 1).

$$Q = \frac{6I(H'_d)\cdot 100\%}{3\Sigma I(H_a),(H_b),(H'_a),(H'_b)} \qquad (3)$$

Using the spectrum of the mixture of macromers **1** and **4** (Fig. 1) as the example, it is possible to demonstrate the acceptability of this method for determining the degree of polymerization, and consequently the MM of macromers.

The integral intensity of signals of vinyl protons H_a, H_b, H'_a, H'_b (in the case of 1 only H_a and H_b, for **4** — H'_a and H'_b) corresponds to 6 protons, while the integral intensity of signals of protons H_e or H_f of polymer chain corresponds to 4 protons of one repeating unit. However they were measured with different amplification. For the former group of signals, the determination of one proton integral requires that the total integral be divided by the coefficient of amplification (k). However, for determining the integral of the polymer chain, the degree of polymerization (n) should be taken into account. Hence, we have equation

$$I_1/6k = I_2/4n,$$

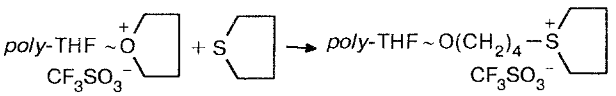
and as a consequence equation (4), allowing the calculation of the degree of polymerization and $\bar{M}_n$ of macromers (MM of THF and MM of one unit of polymer chain are equal):

$$n = 1.5kI_2/I_1, \qquad (4)$$

where n is degree of polymerization, k is coefficient of amplification of EG signals in comparision with integration of polymer chain protons (usually it is 2^m, where m = 3—6 depending on MM macromers), I_1 is value of integral of H_a, H_b, H'_a, H'_b protons, I_2 is value of integral of H_e or H_f poly-THF protons.

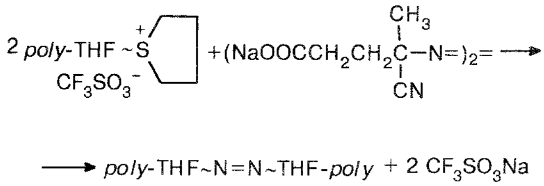
A macroinitiator with MM = $15 \cdot 10^3$ was synthesized by polymerization of THF in bulk with MTF as initiator, followed by substitution of oxonium EG on thiolanium EG (thiolane was added in 10-fold excess), which stabilized EG so that it is possible to isolate this product in pure form (Scheme 3).

Scheme 3



A polymer solution was added dropwise to the aqueous solution of disodium 4,4′-dicyano-4,4′-azodivalerate, the macroinitiator thus forming precipitates (Scheme 4).

Scheme 4



The study of cationic polymerization of THF described above, which includes termination of growing chain by various reagents, has shown that the "living-chain" type mechanism of polymerization operates over a rather wide interval of reaction conditions and molecular mass distribution, and parameter $\bar{M}_w/\bar{M}_n$ is within 1.1—1.4 ($\bar{M}_w$ is a mean-mass MM, $\bar{M}_n$ is an average MM). Some increase in $\bar{M}_w/\bar{M}_n$ up to 1.5—1.8 is observed only when DAG is used.

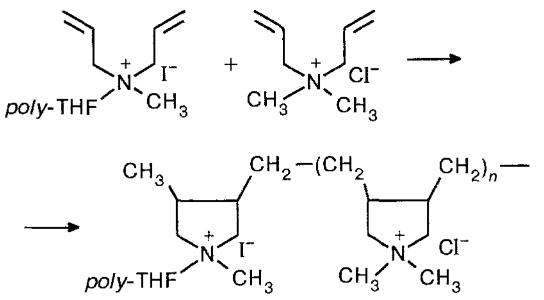
On the possibility of polimerization and copolymerization of synthesized monomers and macromers. Some reactions of homopolymerization and copolymerization with participation of synthesized mono(macro)mers were investigated. In particular, a homopolymer of DAG acetate with intrinsic viscosity [η] = 0.05 dL g^{-1} (0.1 *N* aqueous solution of NaCl, 25 °C) was prepared. A statistical copolymer of DAG acetate with DADMAC was prepared. The molar ratio of monomer units in copolymer chain is 1:1 (according to ^1H NMR and elemental analysis data). The copolymer has [η] = 0.09 dL g^{-1} (0.1 N NaCl water solution, 25 °C). Processes of homo and copolymerization were carried out in water at 60 °C with ammonium persulfate (APS); [M] = 3 mol L^{-1}, ratio [M]:[I] = 100 ([M] is monomer concentration, [I] is initiator concentration); for copolymerization initial molar ratio was $[DAG]_0 : [DADMAC]_0$ = 1:1. The relatively low MM of obtained polymers and copolymers can be ascribed probably to the considerable contribution from reaction of chain transfer on the monomer, which is characteristic of polymerization of allylic monomers.[4]

Copolymerization of several macromers with nitrogen containing diallyl monomers promoted by APS was carried out. Thus, macromer **4** ($\bar{M}_n = 3.5 \cdot 10^3$) was copolymerized with DADMAC (initial molar ratio EG:DADMAC = 1:20) in a methanol/water mixture to give a block copolymer with $\bar{M}_n = 4.3 \cdot 10^3$ (GPC data). The absence of formation of a homopolymer, poly-DADMAC, under investigated copolymerization conditions was shown (Scheme 5).

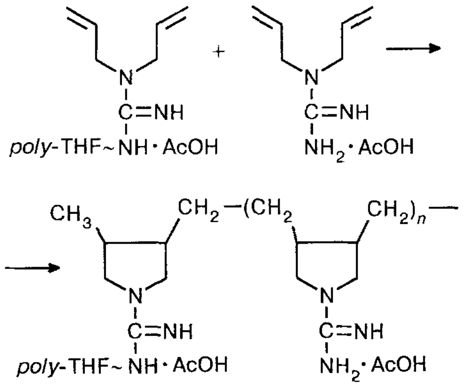
The block copolymer with $\bar{M}_n = 6.7 \cdot 10^3$ was obtained by copolymerization of macromer **3** ($\bar{M}_n = 5.6 \cdot 10^3$) with DAG acetate in DMSO (EG:DAG acetate = 1:20) (Scheme 6).

The MM of the forming block copolymers does not substantially increase in comparision with initial macromers, owing probably to non-optimal reaction conditions: co-monomers ratio, initiator concentration and selection of the solvent. Nevertheless, the principal pos-

Scheme 5



Scheme 6



sibility of preparation of new cationogenic block copolymers and simultaneous modificattion of hydrophilic-hydrophobic properties of the copolymers were shown.

Experimental

^1H NMR spectra were recorded using a Bruker WH 360 instrument in $CDCl_3$, D_2O, CD_3OD at ~20 °C.

GPC measurements were carried out with a Spectra Physics instrument, model SP 4100 with Waters differential refractometer and UV detectors and Polymer Laboratories TSK columns (10^3 Å and 10^5 Å). Dry THF was used as the eluent. The MM was determined using polystyrene standards (17000, 5100 and 1770; 128000, 39000 and 11800). The GPC data were recalculated using the coefficient k = $MM_{macromer}/MM_{standard}$ = 0.6.

Tetrahydrofuran was dried over sodium and benzophenone and used freshly distilled. Acetone was refluxed and distilled over P_2O_5. Diethyl ether was dried over $CaCl_2$. Methyl iodide and ethyl bromide were distilled before use.

Diallylamine (DAA) was distilled prior to use over NaOH under dry nitrogen, b.p. 109.0—109.5 °C. ^1H NMR ($CDCl_3$, δ, ppm): 1.12 (s, 1 H, NH), 3.19—3.29 (m, 4 H, CH_2), 5.03—5.17 (m, 4 H, CH_2=) 5.80—5.93 (m, 2 H, CH=).

Synthesis of DAG acetate. Glacial acetic acid (67 mL, 70 g, 1.17 mol) was added with stirring to cooled DAA (119.0 g, 1.22 mol) in an one-neck flask (0.5 L). Then to the resulting DAA acetate a solution of 49 g (1.17 mol) of cyanamide in acetonitrile (60 mL) was added. After this the reaction mixture was stirred for 10 min. The prepared mixture was added dropwise to refluxing acetonitrile (250 mL) in a three-neck flask (1.0 L) with a reflux condencer and dropping funnel during 1h 45 min, then the resulting mixture was refluxed for an additional 1h 45 min. Crystals of the product appeared after addition of half of the mixture. The precipitate was filtered off, washed many times with acetonitrile, *n*-butanol and acetone, and dried *in vacuo* at ~20 °C to give 168.9 g (yield 73 %) of DAG acetate, m.p. 214—217 °C. ^1H NMR (D_2O, δ, ppm): 1.90 (s, 3 H, Me), 4.03—4.06 (m, 4 H, CH_2), 5.25—5.37 (m, 4 H, CH_2=), 5.84—5.94 (m, 2 H, CH=).

Synthesis of DAG. Sodium (2.5 g, 0.109 mol) was dissolved in 30 mL of anhydrous ethanol. To the resulting solution of sodium ethylate a solution of 21.7 g (0.109 mol) of DAG acetate in 30 mL of dry ethanol was added with stirring. The reaction mixture was stirred for 90 min, then kept 12 hours. Precipitate of sodium acetate was filtered off and the filtrate was evaporated on a rotary evaporator, yielding 15.1 g (100 %) of DAG, m.p. 166—169 °C. ^1H NMR (D_2O, δ, ppm): 3.84—3.90 (m, 4 H, CH_2), 5.13—5.23 (m, 4 H, CH_2=), 5.75—5.86 (m, 2 H, CH=).

Homopolymerization of DAG acetate. A thrice degassed solution of 4.18 g (21 mmol, 3 mol L^{-1}) of DAG acetate and 0.048 g (0.21 mmol, 0.03 mol L^{-1}) of APS in 7 mL of distilled water was sealed in an ampule *in vacuo* and subsequently heated at 60 °C for 52 h. Then the ampule was opened and the reaction mixture was transferred to a dropping funnel and added to 75 mL of dry acetone. The polymer precipitate was filtered off and rinsed with 10 mL of dry acetone and dried *in vacuo* at ~20 °C, yielding 0.9 g (21 % conversion) of homopolymer with [η] = 0.05 dL·g^{-1} (0.1 *N* aqueous solution of NaCl, 25 °C). ^1H NMR (D_2O, δ, ppm): 1.85 (s, $\underline{CH_3}COOH$).

Copolymerization of DAG acetate with DADMAC. A thrice degassed solution of DAG acetate (2.39 g, 12 mmol), DADMAC (1.94 g, 12 mmol) (total concentration of monomers 3 mol L^{-1}) and APS (0.055 g, 0.24 mmol, 0.03 mol L^{-1}) in 8 mL of distilled water was sealed and heated at 60 °C for 52 hours. After opening the ampule, the reaction mixture was added dropwise to 100 mL of dry cold acetone (5 °C, crushed ice). The polymer precipitated as an oil. After decantation it was dissolved in 5 mL of methanol and added dropwise to 100 mL of dry ether at 5 °C (crushed ice). The precipitate was filtered off, rinsed on a glass filter with ether and dried at room temperature *in vacuo*, yielding 1.12 g (26 % conversion) of copolymer with [η] = 0.09 dL g^{-1} (0.1 *N* aqueous solution of NaCl, 25 °C). ^1H NMR (D_2O, δ, ppm): 1.85 (s, $\underline{CH_3}COOH$) and 2.90 (s, one of Me groups of DADMAC), ratio of integral of these signals is 1:1.

Syntheses of macromers 1—3. Cationic polymerization of THF was carried out in bulk at 20 °C in a dry nitrogen atmosphere with stirring on a magnetic stirrer. Calculated quantities of freshly distilled THF and MTF were used, and the initiator was added under dry nitrogen stream with a syringe through a septum; freshly distilled DAA was added in a similar way. DAG derivatives were added under nitrogen stream either as a solid or as a solution in dry THF (DAG base). After completion of the reaction, part of THF was evaporated (up to a concentration of ~50 %) and a concentrated solution of macromer was added dropwise to vigorously stirred cooled methanol or water (0—5 °C). The precipitated macromer was filtered off, rinsed on a glass filter and dried at ~20 °C *in vacuo*. Calculations and results are listed in Table 4 (see also Table 1; numbers of entries correspond to those in Table 4).

Table 4. Initial substances and products in syntheses of macromers

Entry	Initial substances			τ_p[b]	Products, g	K(%)[c]	Solvent
	THF mL (mol)	MTF μL (mmol)	TA[a] mL (mmol)	min			
1	100 (1.23)	142 (1.23)	DAA 0.75 (6.15)	70	**1**, 12.0	15	MeOH
2	150 (1.85)	450 (3.70)	DAA 2.28 (18.50)	55	**1**, 39.5	30	H_2O
3a	100 (1.23)	560 (4.93)	DAA 3.03	22	**1**, 7.7	20	MeOH
3b			(24.66)		8.8		H_2O
4	150 (1.85)	450 (3.70)	DAG 2.62[d] (18.50)	35	**2**, 28.9	22	H_2O
5	150 (1.85)	450 (3.70)	DAG 2.62[d] (18.50)	50	**2**, 36.9	28	H_2O
6	100 (1.23)	560 (4.93)	DAG acetate 3.06[d] (15.36)	45	**3**, 36.4	41	H_2O

[a] Termination agent; [b] τ is polymerization time; [c] K is THF conversion; [d] quantity in grams.

Quaternization of macromer 1. Macromer **1** (3.65 g, 1.46 mmol with respect to EG : $\bar{M}_n$ = 2.8 · 10^3; Tables 1 and 4, sample 3b) was dissolved in a mixture of 20 mL of THF and 5 mL of methanol, and then freshly distilled methyl iodide (0.45 mL, 1.04 g, 7.3 mmol) was added. The mixture was stirred with a magnetic stirrer at ~20 °C for 50 min. Macromer **4** was isolated in the usual manner as described for the synthesis of macromer **1**, yielding 3.46 g of product with $\bar{M}_n$ = 2.3 · 10^3 and $\bar{M}_w/\bar{M}_n$= 1.25 (according to GPC data) and quaternization degree 50 % (according to ^{1}H NMR data). The other experiments of alkylation were carried out in the same manner with varying of solvent and alkylation time (see Table 2 for data).

Investigation of alkylation of macromer 1 depending on time of reaction was carried out in deuterated methanol CD_3OD. Macromer **1** (0.54 g, 0.216 mmol with respect to EG: $\bar{M}_n$ = 2.8 · 10^3, sample 3b in Tables 1 and 4) was dissolved and a 5-fold excess of methyl iodide (0.067 mL, 1.08 mmol) was added. The reaction mixture was stirred and aliquots (0.4 mL) were taken after definite time intervals, and their ^{1}H NMR spectra were recorded. Calculation of the degree of alkylation was carried out using signals of allyl protons (data are given in Table 3).

The macroinitiator was synthesized according to the known method.[5] An aqueous solution of NaOH (1 *N*, 70 mL, 0.070 mol) was added to the suspension of dicyanoazodivaleric acid (13.34 g, 0.035 mol, Aldrich, content of main product is 75 %) in 200 mL of distilled water; the mixture was stirred for 90 min until dissolution of the acid. The resuling solution was evaporated on a rotary evaporator and the residue was dried *in vacuo* at ~20 °C, yielding 11.50 g of disodium 4,4′-diciano-4,4′-azodivalerate. THF (100 mL, 1.23 mol) was polymerized in the presence of MTF (0.139 μL, 1.23 mmol) for 55 min as usual, then 1 mL (11.36 mmol) of thiolane was added, the mixture was stirred for 150 min and left for 12 h. To the vigorously stirred solution of 2.1 g (6.45 mmol) of disodium salt prepared earlier in 700 mL of cold (0—3 °C) distilled water a half (50 mL) of the solution of polymer with thiolanium EG was added dropwise. The second part of the reaction mixture was treated in the same manner. The precipitate of macroinitiator was filtered off from both portions and dried on a glass filter connected to an aspirator pump, then *in vacuo* at ~20 °C, yielding 15.53 g (17 % THF conversion) of product with $\bar{M}_n$ = 15.6 · 10^3 and $\bar{M}_w/\bar{M}_n$ = 1.11 (according to GPC data), containing one azo function per molecule.

Copolymerization of macromer 4 with DADMAC. An ampule was charged with 1.52 g of macromer **4** (0.434 mmol with respect to EG: $\bar{M}_n$ = 3.5 · 10^3 and $\bar{M}_w/\bar{M}_n$ = 1.38 according to GPC data, 5.4 · 10^{-2} mol · L^{-1}), 1.32 g (8.71 mmol, 1.1 mol · L^{-1}) of DADMAC (molar ratio **4** : DADMAC = 1:20) and 0.026 g (0.169 mmol, 21 mmol · L^{-1}) of APS in a mixture of 3 mL of methanol and 5 mL of distilled water. The mixture of reagents as a suspension was thrice degassed, sealed *in vacuo* and kept at 60 °C for 18 h and at 50 °C for 27.5 h. After opening the ampule, the solid fraction was filtered off and dried *in vacuo* at ~20 °C, yielding 1.52 g of block copolymer with $\bar{M}_n$ = 4.3 · 10^3 and $\bar{M}_w/\bar{M}_n$ = 1.33 (according to GPC data).

Copolymerization of macromer 3 with DAG acetate. The reactor was charged with 6.34 g of macromer 3 (1.13 mmol with respect to EG: $\bar{M}_n$ = 5.5 · 10^3 and $\bar{M}_w/\bar{M}_n$ = 1.23 according to GPC data, 8.8 · 10^{-2} mol L^{-1}), 4.51 g (22.66 mmol, 1.51 mol L^{-1}) of DAG acetate (molar ratio **3** : DAG acetate = 1:20) and 0.20 g (1.3 mmol, $8.7 \cdot 10^{-2}$ mol L^{-1}) of APS in 15 mL of DMSO. The reaction mixture was purged by dry nitrogen to remove oxygen and heated at 50 °C for 4 days with stirring on a magnetic stirrer. After this, one-third of solvent was removed; the resulting precipitate was filtered off, washed with DMSO, dried *in vacuo* at 50 °C, yielding 6.21 g block copolymer with $\bar{M}_n = 6.7 \cdot 10^3$ and $\bar{M}_w/\bar{M}_n = 1.17$ (according to GPC data).

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References

1. Y. Tezuka and E. J. Goethals, *Eur. Polym. J.*, 1982, **18**, 991.
2. E. J. Goethals, *Makromol. Chem.*, Macromol. Symp., 1986, **6**, 53.
3. F. D. Haese and E. J. Goethals, *British Polymer Journal*, 1988, **20**, 103.
4. D. A. Topchiev, G. T. Bikasheva, A. I. Martynenko, N. N. Kaptsov, and V. A. Kabanov, *Vysokomol. soed. B*, 1980, **22**, 269 [*Polym. Sci. USSR*, 1980, **22** (Engl. Transl.)].
5. F. D.Haese and E. J. Goethals, *Makromol. Chem., Rapid Commun.*, 1986, **7**, 165.

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