Macromol. Symp. ***161****, 87–96 (2000)*

Novel Polyelectrolytes with Regular Structure – Synthesis, Properties and Applications

Werner Jaeger*[a], Ulrich Wendler[a], Antje Lieske[a], Jörg Bohrisch[a],
Christine Wandrey[b]

[a] Fraunhofer-Institut für Angewandte Polymerforschung, Kantstrasse 55,
D-14513 Teltow, Germany
[b] Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

SUMMARY: Cationic polyelectrolytes and polymeric betaines with narrow molecular weight distribution as well as block copolymers containing charged and uncharged blocks of different hydrophilicity/hydrophobicity were synthesized by different routes of radical polymerization. The cationic polyelectrolytes were characterized with respect to solution properties and electrolyte behaviour. The block copolymers serve as powerful stabilizers in precipitation and emulsion polymerization processes.

Introduction

Polyelectrolytes with well defined molecular architecture and molecular parameters, in particular ionically charged polymers with regular structure, are required for investigation of their interactions with oppositely charged ionic surfactants or macroions in solution, with colloidal particles and with macroscopic solid surfaces1). These interactions make a large number of polyelectrolyte applications in both daily life and industrial processes. Polymers of interest are cationic polyelectrolytes with narrow molecular weight distribution, cationic block copolymers and polymeric betaines. In this paper we summarize results concerning synthesis, properties and applications of these polymers.

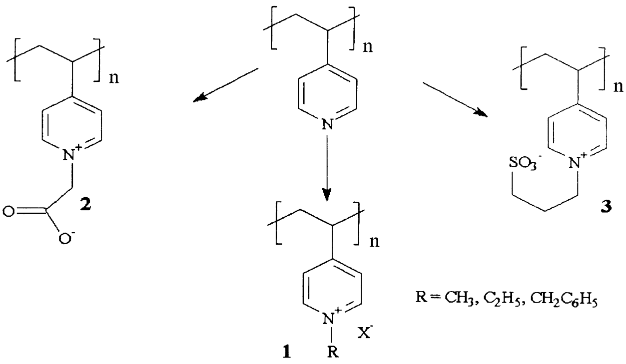
Results and Discussion

Controlled radical polymerization became a common way to obtain both polymers with low polydispersities and block copolymers2). Using N-oxyls as terminators, polymers of vinylbenzyl chloride (VBC) and 4-vinylpyridine (4-VP) with polydispersities lower than 1.5 as well as block copolymers of these monomers with styrene are available3,4). These polymers serve as reactive precursors in the synthesis of functionalized macromolecules. They can readily be converted into ionically charged polymers with narrow molecular weight distribution3,4).

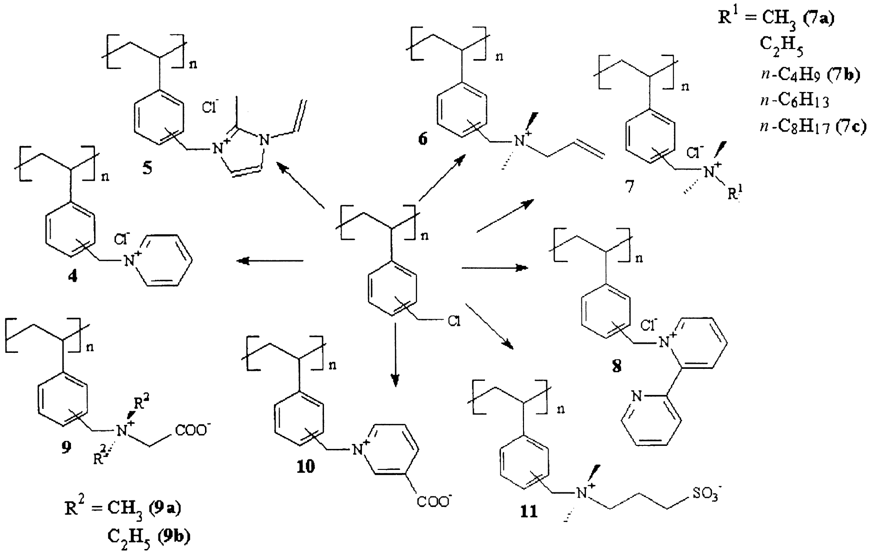
CCC 1022-1360/00/$ 17.50+.50/0

1. Cationic polyelectrolytes and polycarbobetaines

Quaternization of poly(4-VP) with alkyl halogenides leads to cationic polyelectrolytes **1** (Scheme 1). Reaction of poly(VBC) with various tertiary amines results in cationic polyelectrolytes **4-8** (Scheme 2). Poly(4-VP) and poly(VBC) can easily be converted to polybetaines **2**, **9** and **10** and to poly(sulfobetaine)s **3** and **11**, mostly with a degree of substitution 90-100% (by NMR spectroscopy). As expected, no change in the chain length takes place as proved by GPC with selected samples[3,5].



Scheme 1 Functionalization of poly(4-VP) leading to cationic polyelectrolytes **1**, polybetaines **2** and polysulfobetaines **3**



Scheme 2 Functionalization of poly(VBC) leading to cationic polyelectrolytes **4 - 8**, polybetaines **9**, **10** and polysulfobetaines **11**

The polymers listed in Schemes 1 and 2 serve as model compounds for basic investigations of solution properties and interactions of ionically charged macromolecules. Polymer **1** as well as polymers **4 - 8** are cationic polyelectrolytes with a wide variety of charge density and hydrophilic/hydrophobic properties of the monomer units, and with an equal degree of polymerization (low polydispersity). Therefore, they offer the possibility of precise investigation of structure - property relations. An example is the determination of the exponent α of the Mark-Houwink equation, $[\eta] = K \cdot M_w^{\alpha}$: α increases from 0.65 (**7b**, R = Bu) to 0.77 (**4**) and 1.00 (**8**). This is probably caused by the increased chain stiffness due to the more bulky substituents. A pronounced influence on α was observed with polymer **7a** (R = Me) by varying both counter-ion and ionic strength. With decreasing ionic strength, the coil expansion leads to higher α values. In particular, at ionic strengths higher than 0.02 M, an influence of the counter-ion radius is detectable (Table 1).

Table 1 Dependence of α on the counter-ion and ionic strength for **7a**

[Br$^-$]		[Cl$^-$]			[F$^-$]		
0.5 M	0.02 M	0.5 M	0.1 M	0.02 M	0.5 M	0.1 M	0.02 M
0.68	1.02	0.76	0.88	1.01	0.87	0.91	1.02

Density measurements of the polymers in aqueous solution give additional information about the state of solution. Table 2 gives the measured and calculated values of the partial molar volume $\bar{v}_{mol}$ of some of the newly synthesized polycations and the polycarbobetaine **9a**.

Table 2 Measured and calculated partial specific and molar volumes of various charged polymers

Polymer	$\bar{v}$	$\bar{v}_{mol}$	$\bar{v}_{mol\ calc}$ 6)	Difference	
	cm^3/g	cm^3/mol	cm^3/mol	cm^3/mol	%
4	0.788	182.6	180.4	-2.2	-1.22
6	0.853	202.8	207.1	4.3	2.08
7a.Cl^-	0.836	177.0	181.1	4.1	2.26
7a.NO_3^-	0.796	189.7	192.3	2.6	1.35
7b	0.884	224.4	229.4	5	2.18
7c	0.932	288.8	293.8	5	1.70
9a	0.787	172.6	177.9	5.3	2.98

The calculated data are obtained by the method of Durchschlag6) and are in good agreement with the measured values. Using the theoretical values, it is possible to estimate the ring formation of polybetaine structures in solution because of the strong influence of the ring size in the increment system of Durchschlag. In contrast to some other experimental data of polyanions[7)], no influence of the molecular weight on the partial molar volume is detectable (Fig. 1).

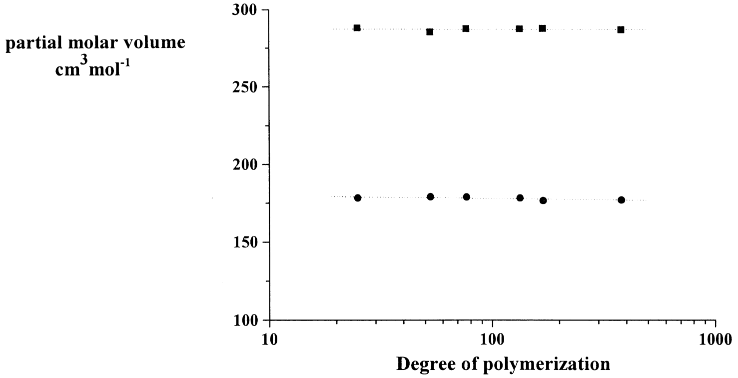


Fig. 1 Partial molar volume in dependence on the degree of polymerization (■ **7a**, ● **7c**)

Electrochemical properties of cationic polyelectrolytes have been studied by measurement of the equivalent conductivity Λ and the counter-ion activity coefficient f_a (for definitions, see[8)]). Both Λ and f_a increase with dilution and decrease with the molecular weight of the polymers (Fig. 2). The correlation of Λ with the ratio of the polymer concentration c_p to the overlap concentration c* is in good agreement with theoretical considerations[9)].

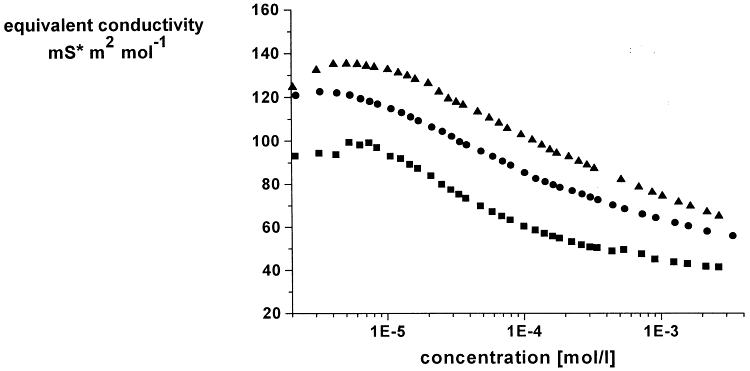


Fig. 2 Equivalent conductivity of polycation **7b** for different DP depending on the polymer (concentration (■ DP = 27, ● DP = 56, ▲ DP = 182)

Additionally, for the first time, a correlation of f_a with the ratio c_p/c^* could be presented[9)]. These findings support the approach that the dependence of the equivalent conductivity on the molecular weight results mainly from changes in the polyion - counter-ion interaction. On the basis of all experimental results, quantitative model calculations have been performed[9)]. Both f_a and Λ depend on the chemical structure of the polyelectrolytes. At equal chain length of **7**, f_a increases with increasing size of the substituent of the ionic groups (Fig. 3), but Λ decreases with increasing chain radius.

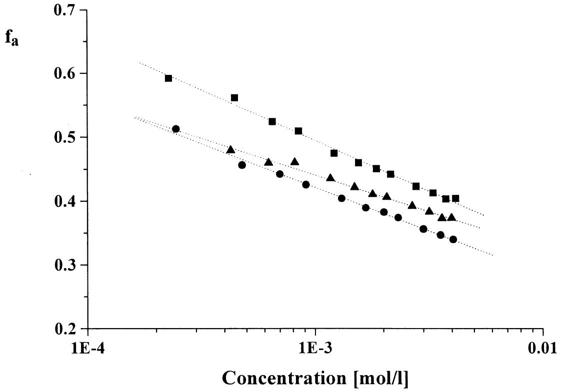


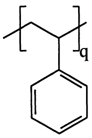
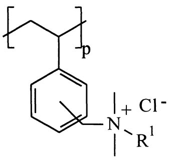
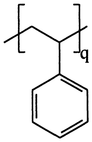
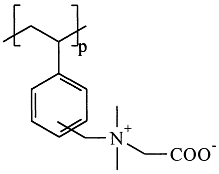
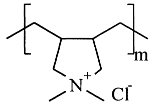
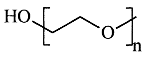
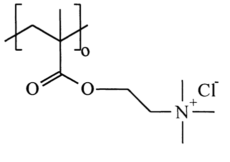
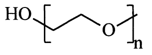
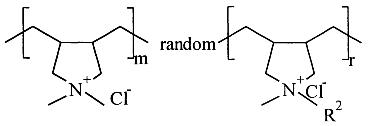
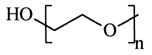
Fig. 3 Influence of the structure on the counter-ion activity coefficient f_a ($P_n = 56$) (● **7a**, ▲ **7b**, ■ **7c**)

Investigation of solution properties of polybetaines indicates different degrees of intramolecular betaine formation depending on the chemical structure[5)]. This leads to only 10 % of titratable COOH groups with **2**, but 14 – 75 % with **9b** depending on the molecular weight (12 000 – 88 000, 0.5 M NaCl). This finding is supported by electrophoretical measurements, which prove the expected strong dependence of the electrophoretic mobility of the polymeric betaines on the H^+ concentration[10)].

2. Block copolymers

Block copolymers containing cationic blocks as listed in Table 3 were synthesized following different routes. Controlled radical polymerization using VBC macromonomers of different molecular weights and styrene leads to block copolymers with variable block length ratio (polydispersity ~ 1.3). The reactive VBC block can readily be quaternized with tertiary amines leading to **I**[4)]. In a similar manner, block copolymers containing betaine blocks **II** were synthesized for the first time by modification of the precursor polymer with ethyl *N*,*N*-dimethylglycinate and subsequent alkaline hydrolysis. Amphiphilic block copolymers **Ia** with adjustable length and ratio of strongly hydrophilic and strongly hydrophobic blocks are soluble as micelles in toluene as well as in aqueous solution.

Table 3 Synthesized cationic block copolymers

Polymer	Hydrophobic block	Cationic block	Hydrophilic nonionic block
I		 $R^1 = CH_3$ (**Ia**), n-C_4H_9 (**Ib**	–
II			–
III	–		
IV	–		
V	–	 $R^2 = n$-C_8H_{17} (**Va**), n-$C_{12}H_{25}$ (**Vb**)	

Static light scattering and ultracentrifugation measurement of micellar block copolymer solutions of **Ia** in 0.1 M NaCl solution indicate an increase in both sedimentation coefficient s_0 and aggregation number Z with increasing length of the hydrophobic block while keeping constant the length of the hydrophilic block (Table 4).

A similar behaviour was found for structure **II**. Again, the aggregation increases with increasing ratio of the hydrophobic to hydrophilic part.

Table 4 Composition and properties of block copolymers **Ia**

Copolymer	p	q	q/p	M_w/M_n	s_0 (s)	Z	Size[a] (nm)
Ia/1	27	31	1.1	1.25	5.6	150	130
Ia/2	27	57	2.1	1.23	13.6	460	171
Ia/3	27	75	2.8	1.22	28.9	1300	222
Ia/4	63	47	0.7	1.29	8.8	220	116
Ia/5	63	56	0.9	1.31	18.0	480	121

[a] PS particle size when used in emulsion polymerization of styrene

Another successful method for the preparation of block copolymers by radical polymerization uses macroinitiators already containing one of the components of the desired block copolymers[11]. By polymerization of a diallylammonium chloride or methacrylate and acrylate monomers containing quaternary ammonium groups with poly(ethylene glycol) (PEG) macroinitiators, block copolymers consisting of PEG and cationic blocks of nearly equal block length are obtained (Table 3, **III**, **IV** and **V**). The reaction of the diallyl compounds generally proceeds as cyclopolymerization leading to linear polymers containing pyrrolidinium rings as structure units of the cationic polymer chain. With diallyl(dimethyl)ammonium chloride (DADMAC), the structure of diblock copolymer **III** was verified extensively by different analytical methods[12]. Polymerization of monomers with long alkyl substituents (octyl, dodecyl) leads to block copolymers **Va** and **Vb** containing polysoap blocks, a new type of polymeric surfactants. Some typical examples are listed in Table 5.

Table 5 Analytical data for block copolymers **III** and **V**, and corresponding polysoaps **Va**, n=0 and their application as stabilizers in styrene emulsion polymerization

Block copolymer	Molar ratio of monomer units[a]		[Stabilizer]	PS particle size distribution	
or polysoap	r / m	n / r + m	wt.%[b]	size, nm	polydispersity
III	0:100	0.8:1.0	0.2	208	0.062
Vb/1	13:87	2.3:1.0	0.2	514	0.455
			0.5	397	0.250
			5.0	336	0.314
Vb/4	18:82	1.6:1.0	0.2	208	0.159
Va/5	39:61	1.0:1.0	0.2	442	0.221
Va, n=0	41:59	0:1.0	-	-	-
Va, n=0	12:88	0:1.0	0.2	190	0.073
-	-	-	0.2[c]	192[c]	0.064[c]

[a] determined by ^{1}H NMR; [b] relative to styrene; [c] CTAB used as a stabilizer

Water solubility of these polymers requires the design of the cationic block as a random copolymer of DADMAC and its long-alkyl-substituted (C_8 or C_{12}) analogue (**Va** and **Vb**)[13]. Viscosity measurements proved a rise in intra- as well as intermolecular aggregation with decreasing content of PEG as well as with growing content and alkyl chain length of the surface-active component of the polysoap block. The novel polymers may form micelles with lower polarity and higher solubilization capacity (Table 6) compared with the pure polysoap, **Va,** n=0, and with the copolymer with the DADMAC middle block, **III**.

Table 6 Properties of block copolymers **III, Va** and of the respective polysoap, **Va,** n=0

	III	Va/5	Va, n=0
λ_{max} [nm]	469	434	459
Solubilization capacity[a)]	0	0.317	0.062

[a)] Decanol/alkyl (mol/mol)

3. Emulsion polymerization using block copolymer stabilizers

The synthesized block copolymers were tested for their efficiency in stabilizing different heterophase polymerizations. Block copolymers **IV** are powerful stabilizers in the precipitation polymerization of water-soluble monomers in aqueous systems of high ionic strength[14)]. Block copolymers **I** and **V** were tested in the styrene emulsion polymerization. With the amphiphilic block copolymer **I,** latices of excellent stability even at high salt concentrations were obtained, probably due to the formation of highly charged particles, stabilized by a corona of cationic chains in the dispersion medium[5)]. The particle size increases with increasing length of the hydrophobic polystyrene block (Table 4)[15)]. Emulsion polymerizations using block copolymers **V** as stabilizers were carried out following a standard recipe with the type and amount of the stabilizer as the only variations. The results are summarized in Table 5. The particle size distribution of the resulting latices is a reliable property indicating the stabilizing effect: small and narrowly distributed particles show a high stabilizing efficiency.

Emulsion polymerization in the presence of a conventional cationic surfactant, cetyl(trimethyl)ammonium bromide (CTAB), led to a latex possessing a narrow particle size distribution with a mean particle diameter of about 200 nm. Similar results were obtained using pure **Vb**, n = 0 and block copolymer **III** (cationic block without polysoap properties). We propose the following stabilization mechanism (Figs 4a and b). The PEG blocks of the block copolymer and the long alkyl chains of the polysoap are able to adsorb on polystyrene particles via hydrophobic interactions. Due to the initiation with a cationic initiator, 2,2'-azobis(isobutyrimidamide) dihydrochloride (V50), the surface of polystyrene particles is positively charged. As the cationic block of **III** and the backbone of the polysoap are also positively charged, repulsion occurs between the particle surface and the charged parts of the polymers. These parts reach into the aqueous phase leading to both electrostatic and steric stabilization of the particles.

Block copolymers **V** do not bring about an efficient stabilization. The resulting polystyrene particles are predominantly relatively large with a broad distribution. Increasing the stabilizer concentration shows only a small effect. To understand these findings, the “bifunctional” character of the substances has to be considered: they are block copolymers with additional polysoap properties. Both the PEG blocks and the alkyl chains of the polysoap blocks possess the ability to adsorb on the particle surface. In addition, repulsion occurs between the particle surface and cationic polysoap backbone. Combination of these three factors may cause steric hindrance to adsorption of some of the alkyl chains or PEG blocks. Consequently, besides hydrophilic parts of the stabilizers, also some hydrophobic parts may reach into the aqueous phase leading to hydrophobic interactions of the particles and, therefore, to large particles of broad distribution (see Fig. 4c). An efficient polymeric stabilizer based on block copolymers with ethylene glycol units, resulting from these studies, should employ a tail-end polysoap instead of the described head polysoap for the cationic block. This should prevent additional hydrophobic interactions because of the hydrophilic conformation of tail-end polysoaps. Investigation of the polymerization behaviour and stabilization efficiency in emulsion polymerization using (acryloyloxyundecyl)trimethylammonium chloride as a polymerizable surfactant for the charged block is in progress.

Experimental

Polymerizations were carried out in a stirred tank reactor under nitrogen. Functionalization of poly(4-VP) and poly(VBC) proceeds by the known procedures[3,4)]. Isolation and purification of the polymers as well as characterization by NMR spectroscopy, viscometry, SEC, ultracentrifugation and SLS were performed as described earlier[16)]. Measurement of partial molar volumes followed the procedure published by Wandrey[7)].

Emulsion polymerization: 16.4 g of styrene, 190.0 g of water and a chosen amount of stabilizer were placed in a thermostatted batch reactor, purged with nitrogen for 1 h and then thermostatted at 80 °C. The stirrer speed was maintained at 300 rpm. 0.16 g of V50 was dissolved in 6 g of water and added to the reactor. The polymerization time was 6 h.

Acknowledgment

The authors gratefully acknowledge financial support of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

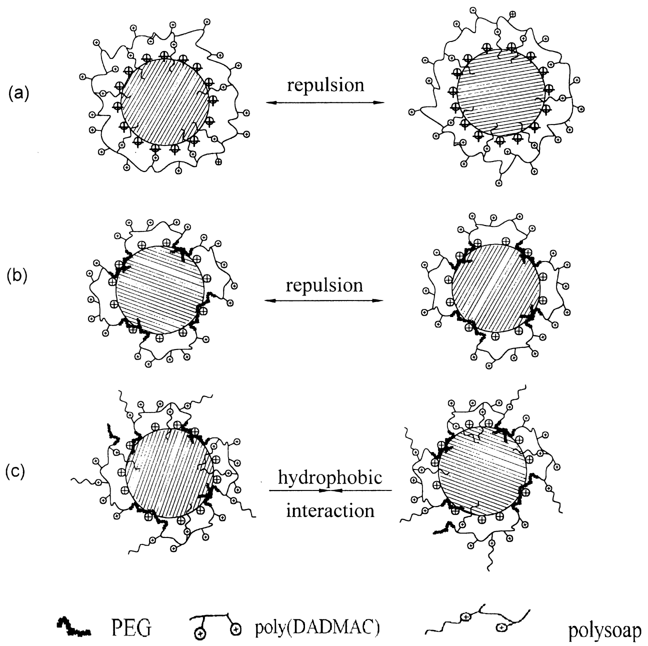


Fig. 4 Stabilization of polystyrene particles with (a) polysoap, **Va** or **Vb**, n=0, (b) block copolymer **III**, (c) block copolymers **V**

References

1. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philipp, Ch. Seidel, D. Stscherbina, Polyelectrolytes - Formation, Characterization, Application, Carl Hanser Publ., Munich 1994, p. 65 ff, 166 ff, 328 ff
2. H. Frey, J. Kressler, W. Richtering, R. Mülhaupt, Acta Polym. **48**, 107 (1997)
3. J. Bohrisch, U. Wendler, W. Jaeger, Macromol. Rapid Commun. **18**, 975 (1997)
4. U. Wendler, J. Bohrisch, W. Jaeger, G. Rother, H. Dautzenberg, Macromol. Rapid Commun. **19**, 185 (1998)
5. W. Jaeger, U. Wendler, A. Lieske, J. Bohrisch, Langmuir **15**, 4026 (1999)
6. H. Durchschlag, P. Zipper, Prog. Coll. Polym. Sci. **94**, 20 (1994)
7. C. Wandrey, A. Bartkowiak, D. Hunkeler, Langmuir **15**, 4062 (1999)
8. C. Wandrey, Polyelektrolyte – Makromolekulare Parameter und Elektrolytverhalten, Cuvillier Verlag, Göttingen 1997
9. C. Wandrey, U. Wendler, W. Jaeger, D. Hunkeler, in preparation
10. O. Grosche, J. Bohrisch, U. Wendler, W. Jaeger, Macromol. Chem. Phys. **201**, 447 (2000)
11. M. K. Mishra, Ed., Macromolecular Design - Concept and Practice, Polymer Frontiers Int., New York 1994, p. 229 ff, 265 ff, 313 ff
12. A. Lieske, W. Jaeger, Macromol. Chem. Phys. **199**, 255 (1998)
13. A. Lieske, W. Jaeger, Tenside Surfactants Deterg. **36**, 155 (1999)
14. a) W. Jaeger, B.-R. Paulke, A. Zimmermann, A. Lieske, U. Wendler, J. Bohrisch, Polym. Prepr. **40**, 980 (1999); b) A. Zimmermann, W. Jaeger, K.-H. Reichert, Polym. News **22**, 390 (1997)
15. U. Wendler, Herstellung von Modellpolyelektrolyten mit Hilfe der kontrollierten radikalischen Polymerisation, Mensch & Buch Verlag, Dissertation, Berlin 1998
16. H. Dautzenberg, E. Görnitz, W. Jaeger, Macromol. Chem. Phys. **199**, 1561 (1998)