Colloid Polym Sci (2004) 282: 209–214
DOI 10.1007/s00396-003-0869-2

ORIGINAL CONTRIBUTION

Edita Mazoniene
Rima Jule Zemaitaitiene
Gintaras Buika
Algirdas Zemaitaitis

Interaction of polyquaternary ammonium salt and persulfate

Received: 25 October 2002
Accepted: 13 January 2003

E. Mazoniene · R.J. Zemaitaitiene
G. Buika · A. Zemaitaitis (✉)
Kaunas University of Technology,
Faculty of Chemical Technology,
Radvilenu pl. 19, 3028 Kaunas,
Lithuania
E-mail: alzem@ctf.ktu.lt
Tel.: +370 37 456081
Fax: +370 37 456081

Abstract An interaction between poly(diallyldimethylammonium chloride) and ammonium persulfate in aqueous solutions has been detected and studied by methods of turbidimetry and viscometry. Investigations were carried out with the cationic polymer of different molecular weight. It was shown that association between low-molecular-weight polyquaternary ammonium salt polycations and persulfate anions was predominant over the chemical (redox) reaction with counterions Cl^-. Appreciably stable interaction products (gels, suspensions, solids) were prepared by mixing aqueous solutions of poly(diallyldimethylammonium chloride) and ammonium persulfate. The phenomenon was associated with structural complementarity of both reagents and capacity of the divalent persulfate ions to bind two charged polymer groups by intra- and interchain bridges. Stoichiometry of complexes and their thermal stability in water were examined.

Keywords Persulfate · Poly(diallyldimethylammonium chloride) · Association · Complex · Thermal properties

Introduction

Cationic polyquaternary ammonium salt, poly(diallyldimethylammonium chloride) (PDADMAC), is a water-soluble polymer and interacts with anionic high- and low-molecular-weight substances present in aqueous solutions. For this reason it is an object of a lot of scientific designs [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. However, the preparation of stable species through the interaction of ammonium persulfate (APS) and polyquaternary ammonium salt in the form of chloride was unexpected for us, bearing in mind the well-known intense redox reactions between peroxo compounds and inorganic halides releasing hazardous halogen gases. GDR patent no. 158783 [14] claimed that the slightly soluble polymer peroxodisulfate had been obtained either by dropwise addition of $Na_2S_2O_8$ to PDADMAC solution or during the polymerization of the monomer, diallyldimethylammonium chloride (DADMAC), initiated with APS in great excess.

Inorganic persulfates are known to form ionic pairs with simple quaternary ammonium salts [15, 16, 17, 18]. Such systems decompose at very fast rates in organic solvents and are often used for initiation of radical polymerization of various monomers in phase transfer conditions.

The cationic quaternary ammonium monomer exhibits a similar behavior. According to the accepted view [19, 20], $S_2O_8^{2-}$ interacts with DADMAC itself and forms ion pairs, if synthesis of poly(diallyldimethylammonium chloride) initiated by ammonium persulfate is carried out in aqueous solution. Activated decomposition [19, 20] of these pairs in water is more rapid compared with that of uncomplexed persulfate ions. According to the proposed mechanism, two primary parallel reactions proceed almost at the same rate:

activated decomposition of the mentioned ion pairs resulting in the formation of sulfate ion radicals (1) and redox reaction between PS and Cl^- associated to the monomer cations leading to the formation of sulfate anion radicals and chlorine atoms (2). Unstable and water-soluble monomer/persulfate associates cannot be easily isolated to examine their properties. To our knowledge, no more systematic investigations of the polymer/persulfate complexes have been reported.

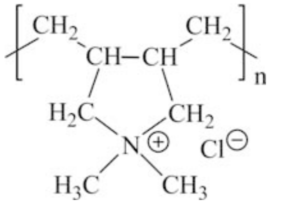
This article intends to present a proof of the electrostatically driven association between PDADMA and PS, to discuss complementarity of binding sites, thermal properties of the complexes, and to show an influence of the molecular weight of the polymer on stoichiometry. We hope that our findings will stimulate further discussion on the kinetics of the free radical polymerization of diallyldimethylammonium chloride and will be especially interesting as an example of self-assembly phenomena for polymer complex studies.

PDADMAC is a large-scale product and has many industrial and environmental applications, e.g., as a retention aid, flocculant, antistatic, dye fixation agent, electroconductive coating, and biocide [21, 22]. On the other hand, peroxides are donors of free radicals, excellent bactericides, and bleaching agents. It was thus of interest to obtain polymeric species with some oxidizing ability or peroxo compounds of the desired consistence, variable solubility, and stability. Taking into account that the usual methods of their synthesis are more or less complicated, we hope that the methodology based on simple mixing of aqueous solutions of two reagents at room temperature should attract attention.

Experimental

Experiments were carried out with poly(diallyldimethylammonium chloride) of different molecular weight. A structural formula of the polymer is presented in Scheme 1. All polymer samples were tested by means of viscometry using Ubbelohde viscometer with capillary diameter of 0.54 mm, and M_n was determined according to the published procedure [23]. Low-, medium-, and high-molecular-weight PDADMAC as 20% aqueous solutions were obtained from Aldrich ($M_n = 15\,000$, 65 000, and 100 000, respectively) and that of low-molecular-weight ($M_n = 5000$) as 40% aqueous solution from Allied Colloids. Super low-molecular-weight pure polymer sample was purchased from Reachim (Russia). It was additionally purified by precipitation in acetone-ether mixture (4:1) from its solution in methanol. Its molecular weight after purification was approx. 2000. Ammonium persulfate, Mohr salt, and potassium permanganate were Reachim reagents of the analytical grade and used without purification.

Turbidimetric measurements were performed using a photocolorimeter KFK-3 (Russia). The turbidity of the mixtures was characterized by optical density measured at $\lambda = 365$ nm, $l = 1.0$ cm. Concentrations of the polymer and persulfate, as well as a molar ratio anion/polycation n^-/n^+, were expressed using base units of ionogenic groups (1/2 mol of APS and 1 mol of repeating unit of PDADMAC, respectively).



Scheme 1 Structure of poly(diallyldimethylammonium chloride)

Decomposition of persulfate in PDADMA/PS complexes or individual APS in water solutions was examined in a thermostated (±0.2 °C) laboratory reactor made from glass at a mixing rate 100 min^{-1}. The suspensions of the complex were prepared by mixing equal volumes of 5×10^{-3} mol/L solution of the polymer ($M_n = 2000$) and 2.5×10^{-3} mol/L solution of ammonium persulfate and diluting 5 times. Distilled water of the 3rd level of quality according to EN ISO 3696:1995 was used. Any contact with metals was avoided. The PS content in the complexes and its residue after decomposition were checked by treatment of the probe with the solution of Mohr salt; the excess was retitrated with 0.01 N $KMnO_4$. The end point was detected by potentiometry using a platinum electrode.

Charge distances in both persulfate ion and diallyldimethylammonium chloride dimer were calculated by computer modeling using Hyper Chem 5 program. For geometry optimization in molecular mechanics calculations, the MM+ method was used, as well as PM3 method in vacuo in semiempirical computation. In both methods Polak-Ribiere algorithm was applied with the termination condition of 0.01 kcal/Å mol.

Results and discussion

Turbidimetric measurements of reaction mixtures gave an evidence of interaction between poly(diallyldimethylammonium) cations and persulfate anions. Figure 1 shows the dependence of the turbidity on the molar ratio n^-/n^+ at various polymer concentrations (a) and different molecular weight (b). This ratio was changed only by varying the APS amount added, the concentration of the polymer in mol of repeating unit/L being constant in the separate experiment series. At first, PDADMAC solution became white on addition of the first portions of APS solution, but transparency returned quickly on stirring. Further, above the certain range of n^-/n^+, corresponding to the polymer concentration, turbidity did not disappear and increased on adding new amounts of the divalent salt (Fig. 1a). The inflection point in the curves probably indicates the beginning of the reformation process within particles caused by intercomplex aggregation. When a more concentrated initial PDADMAC solution (1.25×10^{-3} mol/L) was used, formation of floccules (dotted segment of the curve of triangles) and their sedimentation was observed. The precipitate obtained by adding great excess of APS was insoluble in water and common organic solvents.

Concerning the influence of the molecular weight of the polymer on the turbidity (Fig. 1b), it could be stated that the formation of an insoluble phase starts

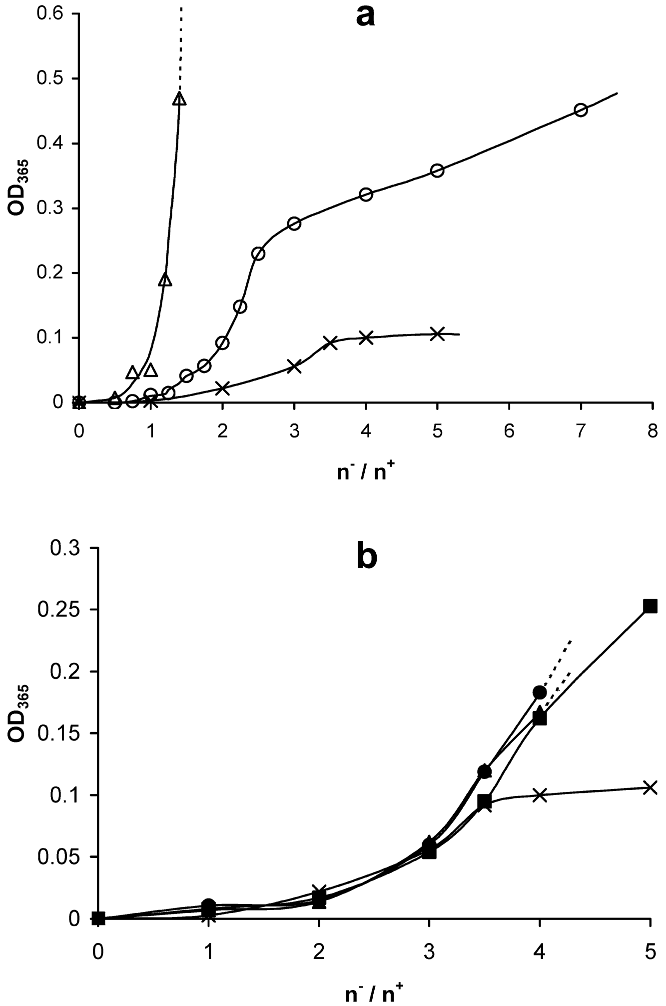


Fig. 1a–b Dependence of the optical density OD_{365} obtained for mixtures of APS and PDADMAC on the molar ratio anion/polycation. **a** C_p of PDADMAC ($M_n = 2000$) equals 3×10^{-4} mol/L (×), 6×10^{-4} mol/L (○), and 1.25×10^{-3} mol/L (Δ). **b** M_n of the polymer equals 2000 (×), 15 000 (■), 65 000 (●), and 100 000 (▲) at $C_p = 3\times10^{-4}$ mol/L

approximately at the same n^-/n^+ ratio for all polymers investigated. Solutions with higher molecular weight PDADMAC show increased turbidity. However, from these data it is impossible to compare quantitatively the amount of formed insoluble complexes due to their rapid sedimentation.

Interaction of the polycation with PS ions is followed by conformational changes of the macromolecules, which seem to be more intense than in the case of added NH_4Cl or $(NH_4)_2SO_4$. Figure 2 represents the reduced viscosity data of the polyelectrolyte in solutions as a function of the nature of an inorganic salt and its concentration. PDADMAC concentration was kept constant 1.62×10^{-2} g/dL. One may notice that in the solutions of higher ionic strength, the impact of various anions on the reduced viscosity of PDADMAC at the same salt concentration follows the sequence: $S_2O_8^{2-} > SO_4^{2-} > Cl^-$.

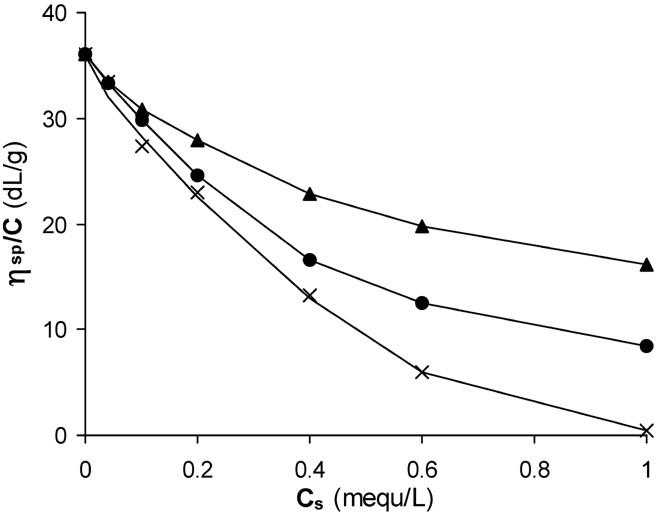


Fig. 2 Variation of reduced viscosity (η_{sp}/C) of PDADMAC ($M_n = 100\,000$) with salt concentration (C_s): NH_4Cl (▲), $(NH_4)_2SO_4$ (●), and $(NH_4)_2S_2O_4$ (×). $C_p = 1\times10^{-3}$ mol/L

It is known [24, 25] that at high dilution, reduced viscosity of a polyelectrolyte in water passes through a maximum and decreases rapidly when the external salts are added. The drop in viscosity values with the addition of monovalent salt could be attributed to shrinkage of the polyion chain owing to the screening of the charged groups [23, 24, 25, 26, 27, 28]. At a high salt concentration, polyelectrolytes behave like neutral macromolecules. PDADMAC in NaCl solutions at high ionic strength is near to the Θ-state, but the molecular weight dependencies of the radius of gyration, the second virial coefficient, and the intrinsic viscosities are somewhat contradictory and cannot be explained by the excluded volume theory [26]. The properties of polyelectrolytes, even in solutions of monovalent inorganic salts, are not well understood taking into consideration theories based on oppositely charged ion pairing [25, 28]. Counterion binding by cationic polyelectrolytes in halide series is nonspecific [29]. By mixing KI and PDADMAC solutions slightly soluble poly(diallyldimethylammonium iodide) can be obtained [30]. Theoretical interpretation of the performance of PDADMAC in the presence of di- and polyvalent ions is naturally even more complicated.

Greater changes of the viscosity caused by addition of sulfate can be understood, bearing in mind the capacity of this counterion to bind two quaternary ammonium groups of some polyelectrolytes by inter- or intrachain bridges [29]. Probably, these possible bridges are sparse, and interaction between PDADMA and sulfate anions does not lead to the formation of insoluble products. Obviously, more quaternary ammonium groups, including neighboring ones, can be involved into interaction

Table 1 Characterization of various PDADMA/PS water compositions

PDADMAC (wt%)	APS (wt%)	n^+/n^-	State
0.02	0.01	1.4	Suspension
0.02	0.02	0.7	Solution with white precipitate
2.8	0.2	9.8	Clear solution
5.0	2.5	1.4	Solution with white precipitate
8.0	4.0	1.4	Solution with white precipitate
13.0	6.5	1.4	Paste
14.9	7.5	1.4	Paste
19.7	9.9	1.4	Gel
29.0	14.6	1.4	Gel

Table 2 Data on the constitution of PDADMA/PS complexes

PDADMAC		APS	n^+/n^-	
$M_n \times 10^{-3}$	wt%	wt%	Reaction mixture	Complex
2	10	4.7	1.5	1.6
5	10	4.7	1.5	2.3
2	10	7.0	1.0	1.3
5	10	7.0	1.0	1.9
15	10	7.0	1.0	1.5
2	10	8.8	0.8	1.3
5	10	8.8	0.8	1.6
2	1	0.7	1.0	1.5
5	1	0.7	1.0	1.5
15	1	0.7	1.0	1.4
65	1	0.7	1.0	1.6

with persulfate anions. Such an expectation will be discussed further. The stronger association results in more intense schrinkage of the polyion chain due to the persulfate added.

Further experiments performed using a polymer of $M_n = 2000$ revealed the possibility for preparation of gels, pastes, or suspensions consisting of PDADMA/PS complexes in water (Table 1). The consistency of the products depended on the concentrations and ratio of both reagents. These findings show the capacity of the divalent persulfate ions to bind two quaternary ammonium groups by interchain bridges at definite conditions. Using a medium- or high-molecular-weight polymer, in most cases a curds-like mass was obtained. If the content of PS did not exceed 9–11 wt% of the polymer, the mixtures remained clear.

Another question was the stoichiometry of more saturated PDADMA/PS complexes. Various complexes were prepared:

a. using theoretically checked amounts of both reagents needed for the equivalent ion exchange
b. adding APS less than needed
c. adding APS in excess compared with PDADMAC

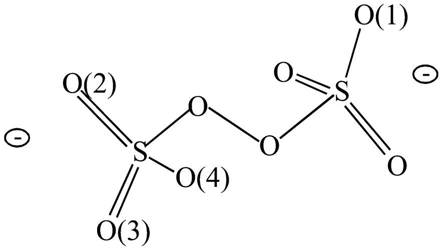
Data in Table 2 on the insoluble complexes purified by washing with water show that the molar constitution of the products differs from that in the reaction mixture. In all cases, PDADMA/PS complexes exhibited surplus cationicity (more than two PDADMAC monomer units per one bound PS ion). This behavior can be attributed to the limited accessibility of some sites on the polymer chains, probably due to the steric hindrance and kinetic reasons. Complexes prepared in more concentrated solutions with participation of the super low-molecular-weight polymer had minimum excess of free cationic groups. Moreover, a side reaction of oxidation of chloride ions to chlorine was observed when higher-molecular-weight polymers ($M_n \geq 5000$) were used. Obviously, PS that cannot achieve the cationic groups of the polymer acts in the way natural for this strong oxidizer. An influence of the molecular weight on PDADMA/PS complex formation in diluted solutions was not observable.

It may be assumed that the property of PDADMAC and PS to form the complexes is due to chemical and structural complementarity of both reagents. This expectation was preliminarily well satisfied by computer modeling of PS ion (in *trans*-configuration) and diallyldimethylammonium chloride dimer with the aid of Hyper Chem 5 program. The calculated distance between two positive charges in DADMAC dimer is in good agreement with the published values of 0.5 nm [31] and 0.55 nm [32] for PDADMAC.

Data given in Table 3 and Scheme 2 show an evident similarity of the values related to the distances between O atoms from the opposite sides of the PS ion and those between two N atoms in DADMAC dimer. An assumption can be made that there is no evident steric hindrance for the divalent PS ion to bind two neighboring ammonium groups in the macromolecular chain. Moreover, no changes in PS ground state structure (*trans*-configuration) are needed for its interaction with the polymer, while for the formation of ion pairs with low-molecular-weight quaternary ammonium salt, trioctylmethylammonium chloride, PS undergoes restructuring and adopts near *cis*-configuration due to the

Table 3 Distances between charged atoms

Atom pair	Charge distance (nm)		Calculation method
	$S_2O_8^{2-}$	DADMAC dimer	
O(1)–O(2)	0.40	0.58	MM+
O(1)–O(3)	0.56		
O(1)–O(4)	0.57		
O(1)–O(2)	0.41	0.54	PM3
O(1)–O(3)	0.56		
O(1)–O(4)	0.52		



Scheme 2 Atom numbering in $S_2O_8^{2-}$

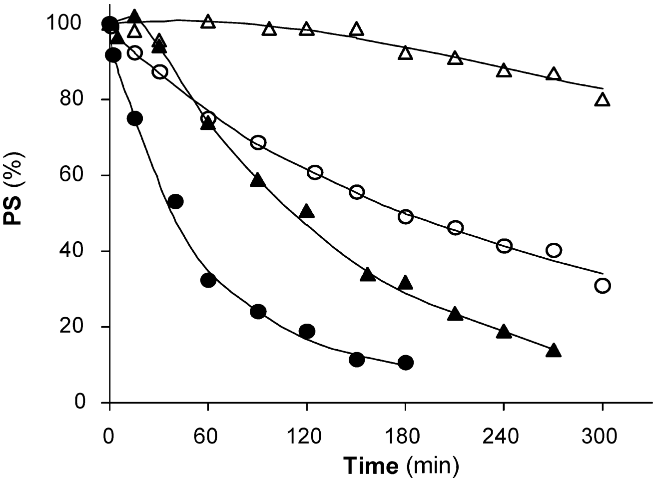


Fig. 3 Decomposition of PS in APS aqueous solution (○, ●) and in suspension of the preformed PDADMA/PS complex (Δ, ▲) at different temperatures: 60 °C (○, Δ) and 70 °C (●, ▲)

stretching of the O–O bond, resulting in the greater solvation in the activated state and the reduced activation energy of the decomposition [16, 17]. Therefore, one may expect unchanged or increased thermal stability of PS bound to the polymer. This was well satisfied by the thermal stability data.

Figure 3 shows that PS ions included into complexes with PDADMAC exhibit higher thermal stability than free ions in aqueous solution. Decomposition of peroxo groups in the complexes delayed for ≅150 min at 60 °C and ≅30 min at 70 °C. It is worth noting that such a feature can be attributed to the insoluble species, because the decomposition proceeded at a similar rate as in APS solutions, when the systems on heating had lost their maximal turbidity.

All we have already noticed permits us to consider the structure of the insoluble particles as a tangle with the tightly packed persulfate and ionic PDADMAC groups inside, and highly hydrophobic hydrocarbon chains outside. Such an arrangement creates a protective coating for persulfate ions against external influencing factors and isolates from Cl^- ions pushed to the solution. Obviously, orderliness in nanoarchitecture of the particles decreases if the macromolecular chains are longer. Unreacted polymer groups remain on the loops, and the systems with persulfate become more permeable for low-molecular-weight substances.

Further studies on the formation of PDADMA/PS complexes and their properties, such as an unusual sorption behavior, are in progress.

Conclusions

An intense interaction has been detected between persulfate ions and poly(diallyldimethylammonium chloride) cations in aqueous solutions, predominant over the redox reaction with counterions. Appreciably stable products (gels, solids, suspensions) have been obtained by mixing aqueous solutions of both reagents, owing to the capability of divalent persulfate ions to bind two quaternary ammonium groups by inter- or intrachain bridges. The stoichiometry of the complexes depended on the molar ratio of the components and the molecular weight of the polymer. The most complete interaction proceeded if low-molecular-weight poly(diallyldimethylammonium chloride) was used. In water, the insoluble species exhibited a higher thermal stability of peroxo groups than those of ammonium persulfate.

At the present stage of the research, we see possible future applications of poly(diallyldimethylammonium chloride) and ammonium persulfate complexes in textile finishing and treatment of effluents.

Acknowledgements Financial support from the Lithuanian Science and Studies Foundation is gratefully acknowledged.

References

1. Philipp B, Hong LT, Linow KJ, Dawydoff W, Arnold K (1980) Acta Polym 31:654
2. Philipp B, Linow KJ, Schleicher H (1981) Papier 35:570
3. Hartmann J, Philipp B, Dautzenberg H, Tiersch B, Purz HJ (1987) Acta Polym 38:203
4. Dautzenberg H, Linow KJ, Rother G (1990) Acta Polym 41:98
5. Xia J, Dubin PL, Dautzenberg H (1993) Langmuir 9:2015
6. Li Y, Dubin PL, Spindler R, Tomalia DA (1995) Macromolecules 28:8426
7. Petzold G, Buchhammer HM, Lunkwitz K (1996) Colloids Surf A 119:87
8. Buchhammer HM, Lunkwitz K (1996) Ber Bunsenges Phys Chem 100:1039
9. Antonietti M, Wenzel A, Thunemann A (1996) Langmuir 12:2111
10. Dautzenberg H, Lukanoff B, Eckert U, Tiersch B, Schuldt U (1996) Ber Bunsenges Phys Chem 100:1045

11. Petzold G, Nebel A, Buchhammer HM, Lunkwitz K (1998) Colloid Polym Sci 276:125
12. Buchhammer HM, Petzold G, Lunkwitz K (2000) Colloid Polym Sci 278:841
13. Kasaikin VA, Litmanovich EA, Zezin AB, Kabanov VA (1999) Dokl Akad Nauk (in Russian) 367:359
14. Ballschuh D, Rusche J, Ohme R (1979) Pat. DD 158783
15. Rasmussen JK, Smith HK (1981) Makromol Chem 182:701
16. Ghosh NN, Gupta GN, Mandal BM (1986) Makromol Chem 187:2097
17. Gupta GN, Mandal BM (1990) J Polym Sci Part A Polym Chem 28:2729
18. Simionescu C, Michailescu C, Bulacovschi V (1987) Acta Polym 38:502
19. Hahn M, Jaeger W (1992) Angew Makromol Chem 198:165
20. Hahn M, Jaeger W, Wandrey C, Reinisch G (1984) Acta Polym 35:350
21. Wandrey C, Jaeger W, Starke W, Wotzke J (1984) Wasserwirtschaft-Wassertechnik 34:185
22. Jaeger W, Hahn M, Wandrey C (1988) Mitteilungsbl Chem Ges DDR 35:151
23. Wandrey C, Jaeger W, Reinisch G (1982) Acta Polym 33:156
24. Roure I, Rinaudo M, Milas M (1996) Ber Bunsenges Phys Chem 100:703
25. Förster S, Schmidt M (1995) Advanc Polym Sci 120:51
26. Dautzenberg H, Görnitz E, Jaeger W (1998) Macromol Chem Phys 199:1561
27. Xia J, Dubin PL, Edwards S, Havel H (1995) J Polym Sci Part B Polym Phys 33:1117
28. Rice SA, Nagasawa M, with a contribution by Morawetz H (1961) Polyelectrolyte solutions: A Theoretical Introduction. In: Kaplan NO, Scheraga HA (eds) Molecular biology, vol 2. Academic Press, New York
29. Ghimici L, Dragan S (2002) Colloid Polym Sci 280:130
30. Barkauskaite J, Zemaitaitiene RJ, Zemaitaitis A (2000) Chemine technologija (in Lithuanian) 15:70
31. Wandrey C (1996) Ber Bunsenges Phys Chem 100:869
32. Dautzenberg H, Hartmann J, Grunewald S, Brand F (1996) Ber Bunsenges Phys Chem 100:1024