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Molecular mass characterization of polymers with strongly interacting groups using gel permeation chromatography–light scattering detection

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Abstract

This work is aimed at studying dilute solution behavior and developing techniques for the proper M_r characterization of polymers with strongly interacting groups. In particular, we have studied ionomers based on poly(dimethylcarbosiloxane) with carboxylic groups and hydrophobically modified polyacrylamide and its charged terpolymer. Gel permeation chromatography–light scattering (GPC–LS) study of organosilicon ionomers allowed us to follow molecular mass distribution evolutions during approximately a week that evidenced the gradual dissolution of clusters formed in bulk polymers. The rate of this process depends on the polymer composition and its preliminary treatment. Observed aggregates are found to be stable during the procedure of chromatographic analysis. For characterization of hydrophobically modified polyacrylamide and its charged derivatives, we have used aqueous NaNO_3 –acetonitrile mixed solvent. Fluorescence spectroscopy with pyrene as a probe did not reveal any hydrophobic association in this solvent in contrast to aqueous solutions. Reversed-phase retention as well as polyelectrolyte exclusion were suppressed at GPC analysis. GPC–LC and classical LS methods gave consistent results for uncharged and weakly charged polymers. In the case of highly charged and highly hydrophobic terpolymers LS results evidenced association, while GPC–LC gave credible M_r values. We can conclude that in the last case, the observed association was weak enough to be disrupted in the course of chromatography.

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1. Introduction

Polymers with strongly interacting groups are of great interest due to their unusual properties caused by the ability to microphase segregation in bulk and in solution. This peculiarity leads to high probability of self-organization with the formation of various

types of nanostructures [1]. At present, associative polymers are studied both for fundamental research and for practical purposes as biologically important macromolecules, potential polymeric surfactants, thickening fluids, and precursors for high modulus fibers. Among the polymers of this type, one can mention ionomers—non-polar polymers with small amount of ionogenic groups. Dipole–dipole interactions between ionic pairs in non-polar media are the main driving force leading to the formation of regular multiplet structures [2]. Ionomers usually

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show extremely low critical micellar concentration and critical gelation concentration [3,4].

Another type of amphiphilic associative polymer is hydrophobically modified hydrophilic polymers and polyelectrolytes. These polymers are able to associate due to hydrophobic interactions of long side chains. The structure of solutions and gels of these polymers is the result of the balance between hydrophobic interactions, electrostatic repulsion, counterion entropy contribution and H-bond formation [1,5]. The features mentioned above cause many difficulties in M_r characterization of associative polymers. In most cases, polymers with strongly interacting groups are formed by chemical modification of polymeric precursors and M_r characterization of precursors is usually performed. In particular, this is the case with various ionomers [6,7]. Sometimes, chemical modification of strongly interacting side chains leading to a suppression of their interaction allows one to perform M_r characterization [7,8].

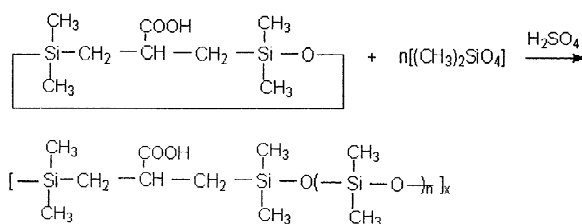
The aim of this work was to study dilute solution behavior and develop techniques for the proper M_r characterization of some associative polymers of the two types mentioned above. In particular, we have studied ionomers based on poly(dimethylcarbosiloxane) with carboxylic and metalcarboxylate groups which were synthesized [3,9–13] by cationic copolymerization. The second object of our study was copolymer of acrylamide with hydrophobic monomers, containing long alkyl side chain and ternary copolymer with charged sodium acrylate units. These polymers are known as hydrophobically associating polymers [14].

The most popular methods of M_r characterization, gel permeation chromatography (GPC) and static light scattering (SLS) can be essentially disturbed in the case of associative polymers. At present, there is a possibility of coupling GPC with M_r -sensitive detection, such as LS detection [15]. This approach is, in our opinion, the most promising for characterization of polymers with strongly interacting groups, because it is very sensitive to the presence of large particles, which can be distinguished from the molecular species even at very low content, it does not require M_r calibration with standard polymers, and it can give true weight-average molecular mass M_w values even in the case of distorted size exclusion mechanism of separation.

2. Experimental

2.1. Materials: siloxane based ionomers

The synthesis of poly(dimethylcarbosiloxanes) containing small amount of side carboxyl groups was performed by cationic copolymerization of 1,1,3,3-tetramethyl-1,3-disila-5-2-oxacyclohexane with octamethylcyclotetrasiloxane according to the following scheme [9–13]:



Random copolymers with 1.7 and 3.3 mol.% of monomer units containing carboxylic groups were obtained. The content of carboxylic groups was determined by titration. Copolymers were isolated from the reaction mixture by precipitation into methanol and dried at 60–70 °C under vacuum for 8 h. Ionomers with metal carboxylate groups were obtained by neutralization of these copolymers with nickel or zinc acetate in toluene–ethanol mixtures as described in Ref. [16].

The following designations are assumed in this work: 3.3-COOH(r) denotes copolymer with 3.3 mol.% of –COOH groups freshly reprecipitated from the mixture toluene–isopropanol (9:1) into methanol and dried under vacuum at 60 °C for 8 h; 3.3-COOH(d) denotes dried copolymer, i.e. the same copolymer stored during 6 months or a year (specified in the text) over molecular sieves; 1.7-COOH(d) is copolymer with 1.7 mol.% of –COOH groups stored for ~6 months over molecular sieves; 1.7-Zn is Zn-containing ionomer based on 1.7-COOH stored for ~6 months in air.

2.2. GPC study of siloxane based ionomers

GPC was performed on a Waters chromatograph consisting of an M600 pump with He degassing system, an M410 RI detector, a UK-6 injector, a U-Styragel linear column in a thermostatic oven and Maxima software. Toluene (pure for analysis) was used as an eluent at 30 °C at 1 ml/min flow-rate.

Polymer solutions (25 μl) of 3 mg/ml concentration were injected for analysis. Universal calibration with polystyrene (PS) standards (Waters) was performed using the following Mark–Houwink–Sakurada equations: $[\eta] = 11 \cdot 10^{-5} M_r^{0.725}$ (PS) and $[\eta] = 20 \cdot 10^{-5} M_r^{0.66}$ (poly(dimethylsiloxane), PDMS). The adsorption effect of $-\text{COOH}$ groups at these conditions was investigated by testing the columns with $-\text{COOH}$ containing telechelic PDMS [17]. Therefore, calculated molecular masses were underestimated and should be considered as apparent values.

Solutions of 3-mg/ml concentration were prepared under stirring with magnetic stirrer at room temperature or at 50–60 $^{\circ}\text{C}$ during 2–6 h up to formation of transparent solution. Solutions were filtered through Fluoropore 0.45- μm membrane (Millipore).

2.3. GPC–low angle laser light scattering (LALLS) study of siloxane based ionomers

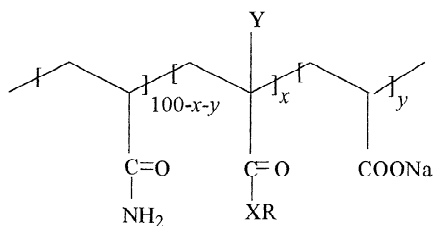
GPC–LALLS experiments were performed on a Waters M501 pump equipped with an M410 refractive index detector and a Chromatix CMX-100 (Milton Roy) LALLS photometer, a Rheodyne injector with 200- μl sample loop, two $\mu\text{Bondagel}$ linear columns (Waters) at room temperature and 1 ml/min flow-rate. The mixture toluene–isopropanol (9:1) was used as an eluent. Data processing was performed with the PC LALLS program (Milton Roy).

Solutions with concentration of 2 mg/ml were prepared by dissolving dry polymer in toluene–isopropanol at room temperature and by stirring with magnetic stirrer up to formation of transparent solutions. This takes from 0.5 to ~ 8 h depending on the sample nature. In the case of metal containing ionomers with 3.3% of $-\text{COOX}$ containing units, we could not reach complete dissolution at all: the samples contained lightly swollen gels.

The value of the refractive index increment determined with Chromatix KMX-16 (Milton Roy) differential refractometer was equal to $dn/dc = -0.115 \pm 0.001$ at $\lambda = 633$ nm for the two $-\text{COOH}$ containing copolymers mentioned above.

2.4. Materials: binary and ternary polymers of acrylamide

Binary and ternary polymers of the following structure



where $R = -(\text{CH}_2)_n\text{CH}_3$, $n = 8, 11$; $X = -\text{O}, -\text{NH}$; $Y = -\text{H}, -\text{CH}_3$, were prepared by free-radical copolymerization of monomers in aqueous micellar media using the known [18–21] technique. n -Nonylmethacrylate (NMA) and n -dodecylmethacrylate (DDMA) were used as hydrophobic monomers. The hydrophobic monomer was solubilized within micelles of surfactant, sodium dodecylsulfate (SDS), whereas hydrophilic monomers acrylamide (AAm) and sodium salt of acrylic acid (SA) (in the case of terpolymers) were dissolved mainly in aqueous medium. Ammonium persulfate was used as initiator. In most of the syntheses, the following experimental parameters were kept constant: the overall concentration of monomers was 3% (w/w), the concentration of ammonium persulfate was $4.4 \cdot 10^{-3} \text{ mol l}^{-1}$, the temperature was 50 $^{\circ}\text{C}$ and the time of reaction was 6 h. The main variable parameters were the concentrations of hydrophobic monomer and SDS (in the case of copolymers) or the concentrations of hydrophobic monomer, charged monomer SA and SDS (in the case of terpolymers).

AAm, ammonium persulfate, and SDS were purchased from Aldrich. Acrylic acid (AA) was purchased from Fluka. Hydrophobic monomers, NMA and DDMA, were obtained from the Institute of Polymer Chemistry (Dzerzhinsk, Russia). Nonylacrylamide (NAAm) and dodecylacrylamide (DDAAm) were synthesized in Nesmeyanov Institute using the method described in Ref. [18]. Water was of Millipore quality.

The typical experimental procedure of the synthesis of polymer was as follows. The reaction vessel consisted of a 100–150-ml flask fitted with a water condenser, an inlet/outlet of inert gas (argon), a thermometer, a magnetic stirrer and a thermostated water jacket (or heating stirrer mantle). First 3 g ($4.22 \cdot 10^{-2} \text{ mol}$) of AAm, 4.1 g ($1.42 \cdot 10^{-2} \text{ mol}$) of SDS and 0.045 g ($0.021 \cdot 10^{-2} \text{ mol}$) of NMA in 94.4 ml of water were placed into the reactor. Reaction mixture was purged with argon during 15 min, heated to 50 $^{\circ}\text{C}$ under stirring and stirred at this

temperature under a flow of argon until the hydrophobic comonomer was completely solubilized in SDS micelles (usually for 30–45 min). When the mixture became homogeneous, a solution of 0.098 g ($0.042 \cdot 10^{-2}$ mol) of ammonium persulfate in 4 ml of water was injected into the reactor with a syringe. The reaction was allowed to proceed for 6 h. Then a 5-fold excess of methanol was squirted into the cooled reaction mixture. The precipitate thus obtained was recovered by filtration, washed with methanol and dried first at room temperature and then under vacuum at 60 °C for 5 h.

The yield of polymer was 92% (w/w) as determined by gravimetric analysis.

To determine the content of the residual surfactant, elemental analysis of the prepared polymer for sulfur was performed. The content of sulfur was determined by X-ray fluorescence (XRF). The content of the residual SDS was 4.5% (w/w). After reprecipitation from water–methanol (7:3) into methanol, it decreased to 1% (w/w). The yield became 83% (w/w). The amount of sodium acrylate groups was calculated as the difference between the total content of sodium in polymer sample (determined by atomic absorption spectroscopy) and the content of sodium present in the residual amount of SDS (corresponding to the content of sulfur obtained by XRF). The content of hydrophobic monomer units could not be determined quantitatively, because of its small value.

Rheological and fluorescence properties of these copolymers detected the presence of hydrophobic domains.

The following designations are assumed in this work: 0.5C9(MA) denotes copolymer with 0.5 mol.% of NMA units, 0.5C12(Am)/5SA denotes terpolymer with 0.5 mol.% of DDAAm units and 12 mol.% of SA units.

2.5. GPC–multiangle laser light scattering (MALLS) of acrylamide copolymers

GPC measurements were made with a Waters liquid chromatograph equipped with a M501 pump, a UK6 injector and a differential RI M410 (DRI) detector. A purge with He was applied to degas the eluent. Maxima software was used for data processing. For GPC–MALLS experiments, a Waters M501 pump, a UK6 injector with an M410 DRI detector

coupled with a Dawn-F light scattering photometer (Wyatt Technology) was used. The ASTRA 2.01 program was used for data processing.

As hydrophilic columns, either laboratory-made column packed with 7- μm spherical particles of hydrolyzed copolymer of glycidylmethacrylate with ethylene dimethacrylate [22], G-gel, or Ultrahydrogel 2000 and 1000 (Waters) were used. An 0.05–0.1 M NaNO_3 –MeCN (8:2) mixture was used as an eluent at a flow-rate of 0.5–1 ml/min. Eluent was filtered through 0.22- μm Durapore membrane (Millipore).

Samples were dissolved in eluent, concentration of probes was 1–1.5 mg/ml and the volume was 100 μl . Sample solutions were filtered through 0.45- μm Durapore membrane (Millipore).

2.6. Static light scattering of acrylamide copolymers

The multiangle SLS measurements were performed with an FICA 50 goniometer at $\lambda = 546$ nm. Solutions with a concentration of ~ 1 –2 mg/ml were prepared in the chosen solvent (deionized water or aqueous solution of low-molecular-mass salt or their mixture with acetonitrile) and cleaned by filtration through Durapore 0.22- or 0.45- μm membrane (Millipore) into optical cuvette. The dilution was performed into the cuvette through Durapore 0.22- μm membrane. Zimm double extrapolation method [23] providing M_w , z -average root mean square radius of gyration R_z and second virial coefficient A_2 was used to treat the data.

Refractive index increment dn/dc at $\lambda = 546$ nm was measured using a laboratory-made Pulfrich differential refractometer. For copolymer with 1% of hydrophobic units, the measured value of dn/dc was equal to that of PAAm within the limits of experimental error. Therefore, the value obtained for PAAm [$dn/dc = 0.175 \pm 0.005$ in the mixture 0.05 M NaNO_3 –acetonitrile (8:2 v/v)] was taken for all the copolymers. $dn/dc = 0.161 \pm 0.002$ at $\lambda = 633$ nm was determined for the above mentioned copolymer in the same mixture using a Chromatix KMX-16 (Milton Roy) differential refractometer.

2.7. Fluorescence spectroscopy studies of acrylamide copolymers

The fluorescence spectroscopy measurements were

performed with an Hitachi MPF-3 spectrofluorimeter using 5- and 1.5-nm bandpass settings for excitation and emission, respectively. The excitation wavelength was 338 nm. Pyrene was used as fluorescent probe. Pyrene obtained from Fluka was recrystallized three times from absolute ethanol. Solutions for fluorescence measurements were prepared by first pipetting 0.012 ml of pyrene stock solutions ($2 \cdot 10^{-4}$ mol l^{-1} in ethanol). Then 3 ml of polymer solution of a given concentration was added to the flask and stirred for 1 day before the fluorescence measurements were made.

3. Results and discussion

3.1. Siloxane based ionomers

The gradual decrease of the value of intrinsic viscosity $[\eta]$ of siloxane based ionomers studied in this work was observed earlier [16] in non-polar solvent. This decrease could occur for as long as a month depending on the nature of the metal and the content of $-COOX$ groups. The storage of bulk samples over molecular sieves also affected this process. A similar behavior was reported for poly(isopropylene carboxylate) [24].

Our attempts to characterize these copolymers by GPC showed [17] great variations of apparent M_r values of one and the same copolymer depending on its pretreatment and dissolution history. Fig. 1 demonstrates typical GPC results of carboxy-containing copolymer 3.3-COOH. Most of its metalcarboxylate ionomers were hardly soluble in non-polar solvents (toluene and chloroform) and mixtures with polar isopropanol.

Table 1 shows M_w values obtained from these measurements. $M_w = 7800$ should be considered as underestimated due to the adsorption effect of $-COOH$ groups that was evidenced using telechelic polysiloxanes [17]. However, the increase of M_w by a factor of 10–30 arises from the temperature treatment of bulk sample or from its storage over drying agents. This large increase of M_w measured at the same GPC conditions as a result of bulk sample history could point to changes in the nature of species dispersed in solution from macromolecules to aggregates. One can suppose that adsorption active $-COOH$ groups are located inside the aggregates and

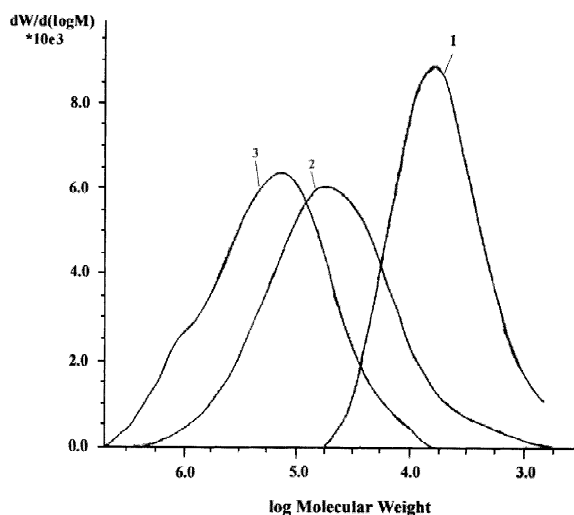


Fig. 1. GPC traces of polydimethylcarbosiloxanes: (1) 3.3COOH(r); (2) 3.3COOH; (3) 3.3COOH(d).

therefore cannot interact with the surface of sorbent. Otherwise the increase of aggregation number should be accompanied by an increase in the number of adsorption active sites.

It should be pointed out that this influence of storage conditions and temperature treatment on the apparent M_r values correlates with thermomechanical and mechanical properties [16] of bulk copolymers.

Similar effects of pretreatment on bulk properties of siloxane based dizwitterionomers can be found in another paper [25].

To see whether the above mentioned behavior of $[\eta]$ and variations of apparent M_r values are connected with conformational reorganizations in solution or they reflect real changes in masses of species (supermolecular or molecular) we studied siloxane based ionomers by GPC with LS detection.

The dissolution of 1.7-COOX and 3.3-COOX polydimethylcarbosiloxanes with carboxylic and metalcarboxylate groups was studied by GPC-LALLS in a mixture of toluene–isopropanol. 3.3-COOZn, 3.3-COONi and 1.7-COONi ionomers were found to remain insoluble during 2 weeks. 1.7-COOZn gave transparent solution as well as all copolymers with $-COOH$ groups.

Fig. 2 demonstrates typical time evolutions of GPC-LALLS traces of 3.3-COOH copolymer stored over molecular sieve during a year. These evolutions show a gradual ~ 5 -fold decrease of M_r of species.

Table 1
Apparent molecular masses of polycarbosiloxanes from GPC data in toluene

Sample	M_n	M_w	M_w/M_n	Dissolution temperature
3.3-COOH(r)	3700 (25 000)	7800 (87 000)	2.1 (3.5)	Room (measured in chloroform)
3.3-COOH	15 100	106 000	7.0	50–60 °C
3.3-COOH(d)	84 000	351 000	4.2	50–60 °C
3.3-Ni	12 000	32 000	2.7	Room

M_n , number average molecular mass.

Table 2 shows the results of M_w determination during several days. It shows that freshly reprecipitated –COOH containing samples are dissolved to molecules over hours, whereas samples dried over molecular sieves come to molecular species in several days through the stage of aggregates. One should emphasize that aggregates are not disrupted in the course of chromatographic analysis. The aggregates originate in multiplet-cluster structure [2,26] of bulk samples. Variations in the rate of dissolution

correlate with the variations in mechanical properties. The storage over drying agents promotes the remove of polar molecules such as water and alcohol playing a role of plastisizer in multiplets. These conditions are favorable for the development of a well-organized structure with strong microsegregation. The microsegregation in metalcarboxylated ionomers is much stronger, so that if the content of these groups is large enough, they cannot form dilute solutions at all. Theoretical consideration of ionomers led to the concept of superstrong microsegregation [2]. This segregation regime can explain the rather high stability of physical intermolecular bonding in ionomers.

In Ref. [27], similar conclusions about the origin of aggregates and microgels in solutions of block copolymer ionomers were drawn on the basis of static and dynamic light scattering data that evidenced slow dissolution of large supermolecular species.

One can mention that in dilute solutions of

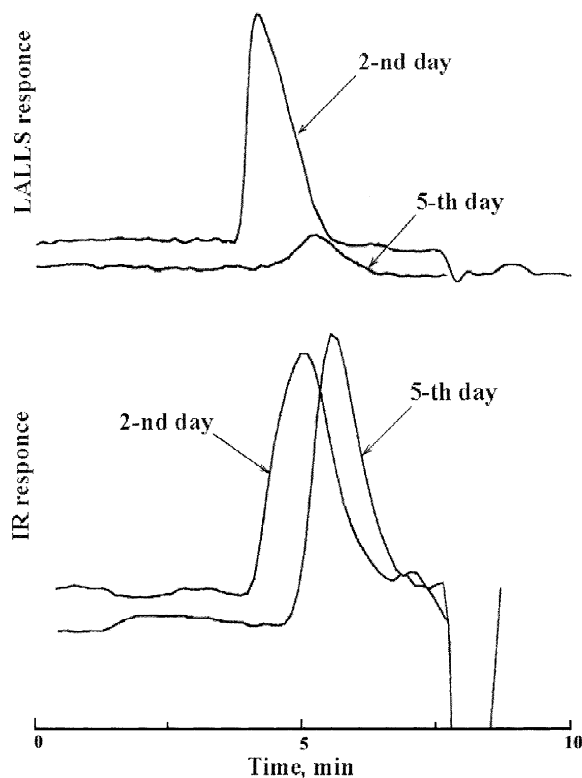


Fig. 2. Time evolutions of GPC–LALLS chromatograms of polydimethylcarbosiloxane 3.3COOH(d).

Table 2
Results of the study of polydimethylcarbosiloxane by CPG–LALLS

Sample	Dissolution time	GPC–LALLS	
		$M_w \cdot 10^{-3}$	M_w/M_n
3.3-COOH(d)	1 Day	116	2.5
	2 Days	62	2.0
	5 Days	21	1.8
3.3-COOH(r)	0.5 h	35	1.9
	2 Days	22	1.6
	5 Days	21	1.6
1.7-COOH(d)	2 h	66	1.7
	2 Days	37	1.8
	5 Days	38	1.8
1.7-Zn	2 h	52	2.4
	5 Days	39	3.0

telechelic siloxane ionomers, we have found [3] an opposite tendency. The aggregation process developed with time from micellar solutions to larger secondary aggregates. This behavior is consistent with that reported for carbochain telechelic ionomers [28].

3.2. Binary and ternary polymers of acrylamide

Our studies of aqueous solutions of hydrophobically modified binary and ternary polymers of AAm (HM PAAm) using pyrene as a fluorescence probe evidenced hydrophobic association of macromolecules [29]. Typical dependence of polarity parameter of pyrene in aqueous solution of terpolymer based on HM PAAm is presented in Fig. 3. It is seen that the polarity parameter of pyrene decreased with polymer concentration from the characteristic value to that for pyrene in pure water ($I_1/I_3=2.0$) up to values of ~ 1.1 , which are characteristic for pyrene solubilized in hydrophobic aggregates in aqueous solutions of different associative polymers [30,31]. Fig. 3 shows that hydrophobic aggregates appear in dilute solution of polymer.

It is clear from the above consideration that we should search for an appropriate solvent for M_r characterization of HM PAAm which eliminates the

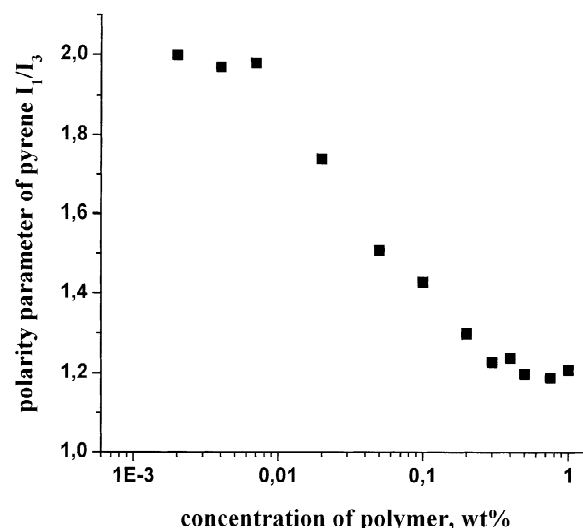


Fig. 3. Polarity parameter of pyrene I_1/I_3 as a function of polymer concentration for 0.5C12(Am)/4SA terpolymer.

association and which can be used both for LS and GPC.

In our case, HPGPC has the following disadvantages: the first one is connected with the absence of appropriate standard polymers for M_r calibration, especially in the high- M_r region, and the second one is as follows: HPGPC columns based on $-OH$ containing acrylic sorbents, which have been used in our work, demonstrate irreversible retention of all the copolymers in aqueous eluents due to reversed-phase interaction with sorbents. The addition of 20% (v/v) of acetonitrile to the eluent led to elimination of the retention and well defined GPC chromatogram were obtained for binary copolymers. However, chromatograms of charged terpolymers were distorted due to repulsions of charges. Therefore, eluent containing 80% (v/v) of 0.05–0.1 M $NaNO_3$ and 20% (v/v) of acetonitrile was chosen as an optimum. Water–acetonitrile mixtures are widely used as a mobile phase in liquid chromatography because of their low viscosity, low refractive indices and UV transparency. These mixtures are recommended in particular for use for GPC of various water-soluble polymers on stationary phases based on hydrophilic acrylic copolymers containing hydroxylic groups [32].

The fluorescence probe study of several binary and ternary polymers [0.2C12(MA), 0.5C9(Am)/2SA] performed in the mixed solvent at polymer concentrations of 0.1% (w/w), which we usually use for M_r analysis, gave the values of polarity parameter of pyrene of 1.8–1.9 that corresponded to its values in pure solvent without polymer that evidenced the absence of hydrophobic aggregates at these conditions.

As to the advantages for LS analysis, our solvent mixture, besides low viscosity and low refractive index providing high value of dn/dc , has one more advantage: refractive indices of its components are close to each other ($n_{H_2O}=1.333$, $n_{MeCN}=1.344$, $n_{mix}=1.343$). This fact allows us to use the mixed solvent for LS study without preliminary dialysis of solutions since errors arising from preferential adsorption of one of the components of the mixture would be within the limits of usual experimental error [33].

A series of binary and ternary copolymers was studied by GPC–MALLS at the chosen conditions

Table 3
Results of GPC–MALLS and SLS study of acrylamide copolymers

Copolymer	GPC–MALLS		SLS		
	$M_w \cdot 10^{-5}$ ($\text{g} \cdot \text{mol}^{-1}$)	M_w/M_n	$M_w \cdot 10^{-5}$ ($\text{g} \cdot \text{mol}^{-1}$)	$A_2 \cdot 10^4$ ($\text{ml} \cdot \text{mol} \cdot \text{g}^{-2}$)	R_g (nm)
<i>Binary copolymers</i>					
0.5C9(MA)	5.0	2.8	5.1	0.6	47
1C9(MA)	5.0	1.9	–	–	–
1C9(Am)	6.2	2.0	6.0	6.3	70
0.2C12(MA)-1	8.3	2.1	–	–	–
0.2C12(MA)-2 ^b	8.8	4.2	14 ^a	1.7 ^a	105 ^a
<i>Ternary copolymers</i>					
0.5C9(MA)/2SA	9.3	2.2	9.3	1.7	72
0.7C9(MA)/7SA	10	4.3	–	–	–
1C9(Am)/2SA	10	1.9	–	–	–
0.4C12(MA)/2.3SA	10	1.8	–	–	–
0.5C12(Am)/4SA	8.5	6.5	7.3	4.6	58
1C9(MA)/12SA	8.5	6.5	120	0.74	260
1.5C12(MA)/13SA	10	9.3	170	0.8	300

^a Measured in the mixture water–acetonitrile (8:2) without salt.

^b Synthesized at lowered concentration of SDS (2%, w/w).

and the results were compared with those of conventional SLS. These results are shown in Table 3. An example of a GPC–MALLS chromatogram is shown in Fig. 4. One can see from the table that M_w obtained by two methods are consistent for binary and ternary polymers with C9 side chains and some C12 polymers. However, copolymers and terpolymers with the highest content of long C12 side chains [1C12(MA)/12SA and 1.5C12(MA)/13SA] demonstrate great discrepancies in M_w . Zimm plots of these samples can look quite regular (Fig. 5), but the obtained M_w values reflect aggregates rather than

macromolecules. The ability of these terpolymers to hydrophobic association in aqueous solutions in the presence of salt, which is shown by the limiting solubility of pyrene and by the rheological study [34], is essentially higher as compared with others. These polymers contain large amount of hydrophobic groups and their solubility in water is connected with the repulsions of charges. The screening action of salt causes enhancement of hydrophobic interactions. The addition of acetonitrile weakens these interactions but cannot prevent the association in every case. In some cases, we obtained twisted diagrams or

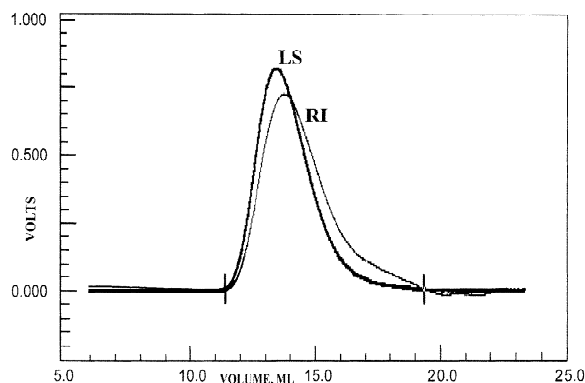


Fig. 4. GPC–MALLS chromatograms of 0.5C12(Am)/4SA terpolymer: RI and LS at 90° traces.

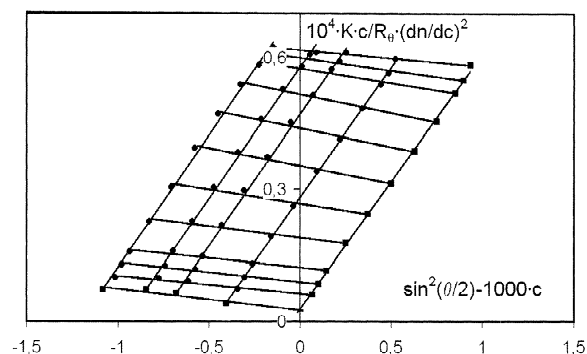


Fig. 5. Zimm plot of 1C9(MA)/12SA terpolymer in 0.1 M NaNO₃–acetonitrile (8:2) mixture.

regular diagrams that led to negative $1/M$ values at extrapolation to $c=0$ and $\theta=0$.

The influence of added salt can be seen in an example of 0.2C12(MA)-2 polymer, which is more hydrophobic than its analogue 0.2C12(MA)-1 due to the difference of amounts of surfactant taken for the synthesis (2 and 4% (w/w), respectively). It is known [20] that the less is the ratio surfactant to hydrophobe, the longer are hydrophobic blocks and the higher is hydrophobicity of polymer. The attempt to measure M_r by SLS in our usual mixed solvent containing salt led to twisted Zimm diagram, but in the absence of salt, it was normal, slightly curved and gave an M_w close to that obtained by GPC–MALLS. The last method gave the same results in both solvents (with and without NaNO_3) used as eluents.

One can conclude that association, which can be observed in our mixed solvent by conventional SLS, is rather weak and is disrupted in the course of chromatography, so that GPC–MALLS in water–acetonitrile mixtures is the preferential method for M_r characterization of hydrophobically modified polyacrylamide.

One can mention that A_2 values are typical for coils in thermodynamically good solvent for all studied copolymers despite the fact that acetonitrile is a poor solvent for these polymers.

4. Conclusions

It has been shown using GPC and GPC–LALLS that the dissolution of siloxane based ionomers occurs through the stage of supermolecular species. These aggregates are not disrupted during chromatography. The rate of their dissolution depends on the nature of interacting groups and the history of bulk sample and correlates with mechanical properties of bulk polymers. The origin of the observed aggregates is the multiplet-cluster structure of bulk polymers.

It has been shown that hydrophobically associating binary and ternary polymers of acrylamide can be successfully characterized by GPC–MALLS in water–acetonitrile mixtures. The aggregates that can be observed in the case of highly charged and highly hydrophobic copolymers by conventional SLS in the

used mixed solvent are not stable and can be disrupted during the procedure of chromatographic analysis.

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