Poly(ethylene glycol) Graft Copolymers Containing Carboxylic Acid Groups: Aggregation and Viscometric Properties in Aqueous Solution

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ABSTRACT: Poly(ethylene glycol) monomethyl ethers (MPEG) were grafted on copolymers of maleic anhydride and styrene, methyl methacrylate, and ethylhexyl methacrylate, respectively. Hydrolysis of the remaining anhydride residues gave graft copolymers carrying a large number of carboxylic acid groups along the main chains. The properties in aqueous solutions of these graft copolymers were studied with respect to aggregation behavior and viscometric properties. Aggregation of the polymers was examined by quasi-elastic light scattering and flow field-flow fractionation in water and KCl solution. Both methods showed that the anionic graft copolymers mainly were present as single molecules in pure water, with a minor fraction of aggregates. In KCl solution, aggregates with average sizes of approximately 30 nm were the dominant species. In aqueous solution, the polymers exhibited polyelectrolyte behavior, i.e., a dramatic increase of the viscosity upon neutralization. Graft copolymers with hydrophobic groups in the backbone had lower viscosities.

Introduction

The properties of block and graft copolymers have for a long time received much interest. Their behavior in the solid phase and in solution is affected by interactions between the chemically dissimilar segments and their surroundings. The polymers form polymolecular aggregates similar to micelles when dissolved in a solvent which is good for one block but poor for the other.[1−7] The micelle formation is driven by the phase separation of the lyophobic blocks into a core which is surrounded by a corona formed by lyophilic blocks swollen by the solvent. Amphiphilic block and graft copolymers containing hydrophobic blocks and poly(ethylene glycol) (PEG) segments show this behavior in aqueous solution.[4−7] In addition to polymolecular micelles, the block and graft copolymers may form monomolecular micellelike structures, in which single polymer chains arrange themselves with the lyophobic parts toward the center of the structure.[1−3]

In a previous paper we have reported on the preparation of graft copolymers having PEO grafts and a backbone carrying carboxylic acid groups[8] and their properties in the solid phase. The aim of the present investigation was to study the behavior of these anionic graft copolymers in aqueous solution. Because of the carboxylic acid groups attached to the main chain, the polymers may behave as polyelectrolytes, exhibiting in solution a large chain expansion on neutralization.[9,10] The polyelectrolyte behavior was studied by measurement of solution viscosity at different pH values. The aggregation properties of the polymers in aqueous solution were investigated by quasi-elastic light scattering and flow field-flow fractionation.

Experimental Section

Preparation of Anionic Graft Copolymers. Three copolymers were prepared by solution copolymerization of styrene/maleic anhydride, styrene/maleic anhydride/methyl methacrylate, and styrene/maleic anhydride/ethylhexyl methacrylate. Poly(ethylene glycol) monomethyl ethers (MPEG) of different molecular weights (550 or 2000) were grafted onto the copolymers in dimethylformamide solution by a reaction between MPEG and the anhydride residues of the copolymer backbones (see Figure 1). After termination of the reaction, the solvent was removed and the graft copolymers formed were dissolved in water and separated from unreacted MPEG through dialysis in aqueous solution (5−12 mg/mL), for 2 weeks. The aqueous solutions of the graft copolymers were kept at 8 °C until further use. Details on the preparation and characterization of the graft copolymers were published elsewhere.[8]

Methods

Viscosity Measurements. Viscosity measurements were carried out at 25 °C using a Ubbelohde viscometer. Solutions containing 0.5−8 mg/mL of graft copolymers in water or KCl solution were neutralized with LiOH or KOH to the desired pH. Before use, all stock solutions were filtered through a 0.45 μm PTFE membrane (Millipore). The errors in the viscosity measurements were less than 0.5%.

Quasi-Elastic Light Scattering. Quasi-elastic light scattering (QELS) measurements were performed using a Coulter model N4MD submicron particle analyzer. The light source was a He−Ne laser, and scattering angles of 29.8° and 90° were used. The size distribution processor (SDP) used the program CONTIN (developed by S. Provencher) for the Laplace inversion of the autocorrelation function. Measurements were carried out in a concentration range 4−10 mg/mL of the polymer solution. The solutions were filtered through a 0.2 μm filter and allowed to adopt room temperature before being transferred into the light scattering cell. The values presented for each sample are averages of at least 20 measurements at 90°.

Flow Field-Flow Fractionation. The flow field-flow fractionation (FlFFF) experiments were performed in two asymmetrical channels (I and II), both with a trapezoidal geometry.[11,12] The channel lengths were 28.5 cm. The trapezoid widths and were 2.05 cm at the

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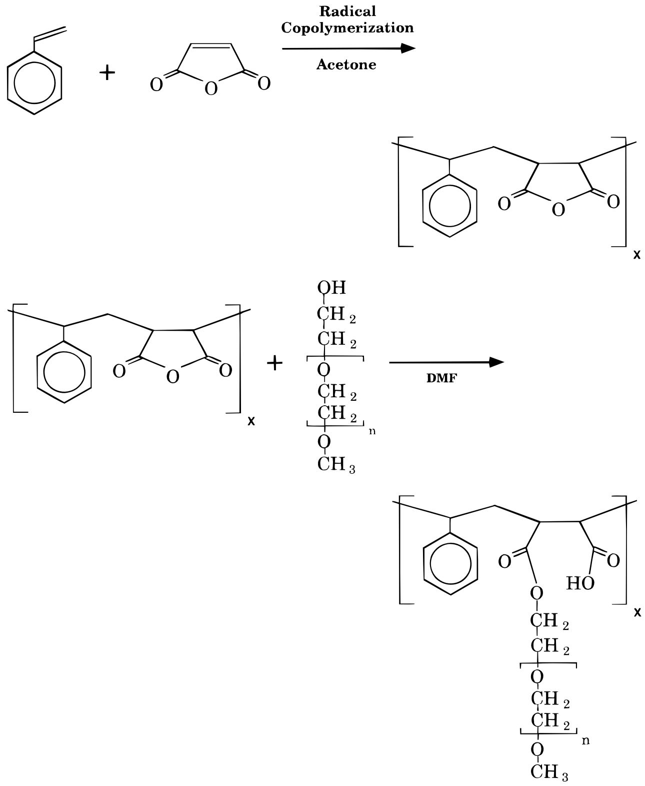

Figure 1. Reaction scheme.

inlet end and 0.48 cm at the outlet end, respectively. The area at the tapered inlet end was 2.1 cm^2 and the total area of the membrane enclosed by the spacer was 34.6 cm^2. The channel thickness was calibrated with ferritin (Pharmacia) to 0.0125 cm (channel I) and to 0.0127 cm (channel II), which gives a channel volume of 0.432 and 0.439 mL, respectively. The focusing point was determined with ferritin to be 2.3 cm. The channel assembly, the instrumental setup, and the operative procedures of the FlFFF system, were those described in previous publications.[11,12] A photometric detector (Pharmacia Monitor UV detector), using a wavelength of 254 nm, was used for sample detection.

Principles of FlFFF. FlFFF is one of the subtechniques in the family of field-flow fractionation (FFF) methods. FFF has been under development during almost 30 years and has now reached commercial status. The separation principle is common for all FFF subtechniques.[13] The sample is transported in a thin channel by a liquid flow with a parabolic velocity profile. During this transport, the sample components are exposed to a force acting perpendicular to the transport direction, driving them to one of the channel walls, the accumulation wall. Diffusion of the sample components counteracts this force, and due to the individual diffusion coefficients, the distance from the accumulation wall will be related to the size of the sample components. Thus, they will be transported through the channel at different velocities and separated in time due to differences in diffusion coefficient, i.e., hydrodynamic size. In FlFFF the perpendicular force consists of a secondary flow pumped transversally through the channel. The asymmetrical variant of FlFFF uses only one permeable wall[14] and the entering flow will therefore exit both through the accumulation wall and through the channel outlet. Changes in the inlet flow rate (V_{in}) and the ratio between the cross flow rate and the outlet flow rate (V_c/V_{out}) will influence the retention of the sample.[11,14] The theory for asymmetrical FlFFF has been well-described.[11] At sufficiently high retention levels, a linear relationship between the retention time, t_r, and the hydrodynamic diameter, d_H, can be applied:

$$d_{\mathrm{H}} = \frac{2kTV^0}{\pi\eta w^2 V_{\mathrm{c}} t^0} t_{\mathrm{r}}$$

where k is the Boltzmann constant, T the absolute temperature, V^0 the channel void volume, η the viscosity coefficient of the carrier liquid, w the channel thickness, and t^0 the void time. This equation was used to convert the retention times into hydrodynamic diameters.

Results and Discussion

The graft copolymers used in the present investigation were composed of main chains carrying pendant carboxylic groups and grafts consisting of poly(ethylene glycol) monomethyl ethers (MPEG). As backbone polymer, an alternating copolymer of styrene (S) and maleic anhydride (MAN)[8] was prepared through radical solution polymerization (Figure 1). Under similar conditions, terpolymers of S, MAN, and methyl methacrylate (MMA) or ethylhexyl methacrylate (EHMA) were prepared (Table 1). All three backbone polymers contained approximately 50 mol % of styrene, and as seen in Table 1 the methacrylate monomers were incorporated at the expense of MAN. If the backbone polymer poly(S-*co*-MAN) is kept in an aqueous solution, it becomes soluble after about 1 day when the anhydride groups have become hydrolyzed. However, neither the backbone polymer containing MMA nor that containing EHMA were soluble in water. In 0.1 M KCl solution, none of the backbone polymers was soluble.

The anhydride groups along the backbone were used as reactive sites in the grafting reaction. MPEG was grafted onto the main chain through a ring-opening reaction of the anhydride groups in which one carboxylic acid group is formed together with an ester linkage (Figure 1). A minor fraction of the anhydride groups were utilized in the grafting reaction, which left a number of anhydride groups available for other reactions, e.g., hydrolysis in water. The latter reaction gives a main chain containing a large number of carboxylic acid groups.

Properties such as hydrophobicity and chain flexibility are different for the dissimilar backbone polymers, and it can be anticipated that because of inter- and intramolecular interactions, solubility and state of solution of the graft copolymers should depend on the backbone composition. Furthermore, depending on pH, the carboxylic acid groups along the main chain may be ionized or, at low pH values, hydrogen bonded to water or to carbonyl and ether oxygens. Consequently, because of the different types of interactions, the solution behaviors of the polymers are difficult to predict.

Aggregation of the Graft Copolymers. The graft copolymers were soluble in pure water as well as in KCl solution at low ionic strengths. However, the different segments in the graft copolymers have dissimilar solubility properties. As noted above, the backbone polymers were shown to be poorly soluble in water and insoluble in KCl solution. On the other hand, the MPEG grafts are quite soluble in aqueous solution. The dissimilar polymer segments may thus phase separate and cause aggregation of the polymer molecules. In a recent paper, Eckert and Webber discuss the formation of micelles derived from poly(styrene-*alt*-maleic anhydride-*graft*-ethylene oxide), in which the carboxylic acid

Table 1. Composition of Graft Copolymers

sample	backbone composition[a,b] (mol %) S	MAN	MMA	EHMA	M_n of[c] backbone	M_n of MPEG	conversion of[a] anhydride (mol %)	MPEG in graft copolymer (% w/w)	M_n
MAN 550	50	50			83 000	550	9	20	103 000
MMA 550	50	32	18		98 000	550	22	28	135 000
EHMA 550	47	41		12	80 000	550	21	28	113 000
MAN 2000	50	50			83 000	2000	12	54	181 000
MMA 2000	50	32	18		98 000	2000	15	49	191 000
EHMA 2000	47	41		12	80 000	2000	20	59	196 000

[a] Determined by ^{1}H-NMR. [b] S = styrene, MAN = maleic anhydride, MMA = methyl methacrylate, EHMA = ethylhexyl methacrylate. [c] Determined by GPC using polystyrene standards.

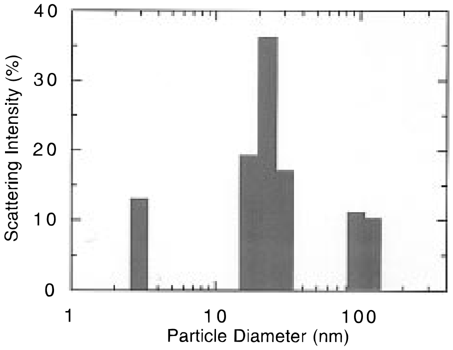

Figure 2. Distribution of particle sizes from QELS measurement of MMA 2000 in pure water.

Table 2. Hydrodynamic Sizes Measured

(a) QELS

sample	hydrodynamic diameter[a] (nm) Water 1	Water 2	Water 3	0.01 M KCl 1	0.01 M KCl 2	0.1 M KCl 1	0.1 M KCl 2
MAN 550	*b*	22 (90)	192 (10)	23 (27)	103 (73)	38 (75)	191 (25)
MMA 550	3 (4)	28 (55)	96 (41)	25 (74)	105 (26)	31 (76)	196 (24)
EHMA 550	3 (4)	36 (54)	90 (42)	23 (57)	71 (43)	35 (85)	253 (15)
MAN 2000	4 (36)	28 (33)	111 (31)	22 (80)	144 (20)	26 (85)	157 (15)
MMA 2000	4 (14)	29 (55)	118 (31)	23 (84)	114 (16)	27 (90)	161 (10)
EHMA 2000	5 (39)	32 (18)	109 (43)	20 (85)	192 (15)	29 (64)	122 (36)

(b) FlFFF

sample	H_2O 1	H_2O 2	0.01 M KCl 1	0.01 M KCl 2	0.1 M KCl 1	0.1 M KCl 2
MAN 550	3			21		
MMA 550	4	23	13	29	12	32
EHMA 550	3			23		30
MAN 2000	3			19		22
MMA 2000	3	25		21		23
EHMA 2000	3	13		23		26

[a] Values within brackets are the relative scattering intensities of the different populations. The error in the QELS measurements, based on the standard deviations, is approximately 10%. [b] One third of the measurements indicated a third population at 3 nm. [c] Peak values of FlFFF fractograms; see Figures 3 and 4. The error in the peak value is approximately 10%.

groups were converted to methyl esters.[15] The micelle diameters were determined by static light scattering, QELS, and transmission electron microscopy (TEM). In the present study the aggregation behavior of the graft copolymers was studied by analyzing aqueous solutions by QELS and FlFFF. Similarly to QELS, FlFFF is an absolute method for determination of hydrodynamic size in the sense that calibration is not necessary. The separation principle is common to all FFF techniques and is based on the relation between diffusion coefficients of the sample components and their molecular sizes. The method has been used for size determination of water soluble polymers[11,16,17] and may have some advantages over the traditionally used techniques, i.e., GPC and QELS. One of the present graft copolymers, MMA-550, has previously been carefully examined by FlFFF.[11,12]

In pure aqueous solutions of the different polymers, particles of three different populations could be detected by QELS (Figure 2, Table 2), with sizes of 3−5, ca. 30, and 90−190 nm. The relative scattering intensities of the different populations indicated that most of the polymer was present in the population centered at 3−5 nm. Large particles give rise to a strong scattering intensity because of their large mass. Even though they may represent only a minor amount of polymer, they can still be detected. The results obtained from the FlFFF fractograms confirm the QELS data (Table 2). In all fractograms, one large peak appears at 3 nm for all polymers. At approximately 25 nm, a weak signal could be detected in some samples. It seems most likely that this signal is caused by the population at 30 nm detected by QELS. The large aggregates (90−190 nm, Table 2) indicated by QELS were not analyzed by FlFFF, because the samll amounts of polymer present in this population was not expected to be detectable.

The polymer population at 3−5 nm presumably consists of single polymer chains. The diameters obtained for the is population seem quite low and have to be considered with a critical mind. The size range is very close to the lower limit of the instrument used; i.e., the precision in these diameters is poor. The conformation of these molecules is not clear, but it seems reasonable to expect that the hydrophobic groups of the macromolecule should accumulate at the center of the structure. The particular population around 30 nm should be polymolecular aggregates. A plausible model for these aggregates would be a micellelike structure where the hydrophobic parts of the backbone are oriented toward the interior of the structure and the hydrophilic MPEG grafts are oriented toward the aqueous phase. This arrangement would minimize the exposure of the backbone polymer to the aqueous phase. However, the carboxylic acid groups would prevent the backbone from forming a dense core because of their interaction with the MPEG grafts or with water. Hydrophobically modified polyelectrolytes are known to form interchain aggregates in aqueous solution.[18−20] The aggregation efficiency depends on the content and the nature of the hydrophobic groups and their distribution along the chain and on external factors such as ionic strength and pH. Quasi-elastic light scattering of flexible polyelectrolytes has indicated bimodal intensity correlation functions at an increased polyelectrolyte concentration in pure water or at low salt concentrations.[9,21,22] It has been concluded that also polyelectrolytes under specific conditions may form aggregates.

The particle population at 90−190 nm probably consists of clusters formed by secondary association of micelles. Block copolymers containing PEG are known to show this behavior in aqueous solution, although the

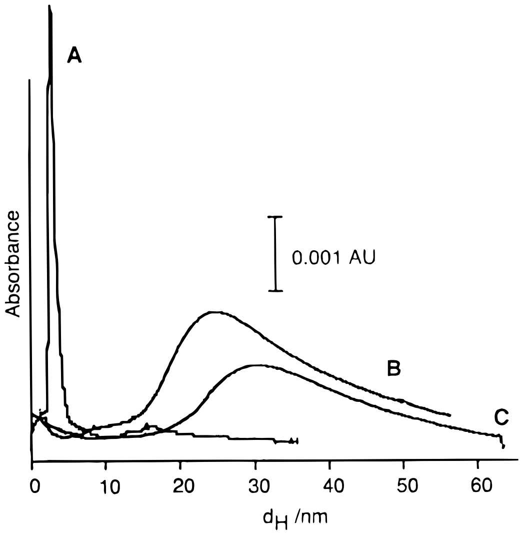

Figure 3. Fractograms of EHMA 550 in three different media: (A) water, (B) 0.01 M KCl, and (C) 0.1 M KCl (channel I). Conditions: (A) $V_{in} = 8.0$ mL/min, $V_{out} = 0.62$ mL/min, $V_c/V_{out} = 12$; (B) $V_{in} = 4.0$ mL/min, $V_{out} = 0.57$ mL/min, $V_c/V_{out} = 6$; (C) $V_{in} = 4.0$ mL/min, $V_{out} = 0.69$ mL/min, $V_c/V_{out} = 5$. Sample concentration 0.8 mg/mL. The analysis time was below 10 min.

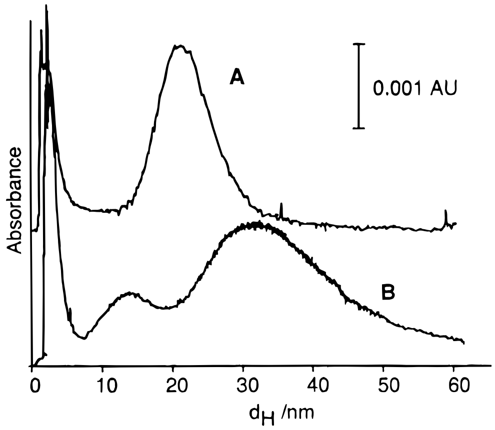

Figure 4. Fractograms of two different polymers (MMA 2000 and MMA 550) in 0.1 M KCl carrier (channel II). Conditions: (A) MMA 2000, $V_{in} = 4.0$ mL/min, $V_{out} = 0.48$ mL/min, $V_c/V_{out} = 7$; (b) MMA 550, $V_{in} = 4.0$ mL/min, $V_{out} = 0.64$ mL/min, $V_c/V_{out} = 5$. Sample concentration 0.7 mg/mL. The analysis time was below 8 min.

reasons for the cluster formation are not clear.[5,6] It has been suggested that reversible self-association of poly(ethylene oxide) in water causes the cluster formation.[6,7]

QELS and FlFFF measurements on the graft copolymers were also made in 0.01 and 0.1 M KCl solution, respectively. According to the FlFFF results presented in Figure 3 and Table 2 and the QELS data in Table 2, an increase of the ionic strength resulted in a dramatic shift toward polymer aggregates rather than single polymer chains. No single polymer chains could be detected in KCl solution by QELS, but according to the FlFFF fractograms, their presence cannot be excluded. Aggregates having diameters in the range of 19–29 nm in 0.01 M KCl and 22–38 nm in 0.1 M KCl were registered by both analytical techniques. According to the FlFFF fractograms, one of the polymers, MMA 550, also showed a minor peak corresponding to 12–15 nm in both 0.01 and 0.1 M KCl (Figure 4). For this polymer the responses were consistent and reproducible and indicated a minor population of aggregates which may be difficult to explain. Although this population may have evaded observation by QELS, an experimental artefact in the FlFFF analysis cannot be excluded.[12]

The aggregation behavior of the graft copolymers can be explained by changes in the solubility as the ionic strength changes. The solubility of the backbone decreases as the concentration of KCl increases, the anionic groups present along the backbone will be screened by the salt, and the electrostatic repulsion forces will be accordingly reduced. This effect will allow the hydrophobic groups to increasingly interact, which would lead to a more compact conformation of the main chain. Furthermore, the solubility of PEG is known to decrease with increasing salt concentration.[23,24] In order to minimize the interfacial free energy of the system the sizes of the micelles increase as the salt concentration increases, until at a certain salt concentration precipitation occurs.[12]

The polymer concentration was varied between 0.5 and 25 mg/mL; at higher concentrations turbidity became a problem for the measurements. The hydrodynamic sizes of the small aggregates were similar, independent of the polymer concentration, and the sizes of the larger aggregates only varied within the margins of error. The ratio between the populations was approximately the same throughout the measured concentration range. Poly(styrene-*block*-ethylene oxide)[6] and triblock copolymers of PEG and poly(propylene oxide)[25] have been reported to show a reversed concentration dependence, i.e., the large-sized polymer populations decreased as the concentration increased.

There are two principally different models for micelle structures. A mean density model[26–28] is the most appropriate one for micelles consisting of a large core and a relatively thin corona, and a star model[29] is most appropriate for those having a small core from which long chains protrude to form a large corona. For the present graft copolymers, the aggregates formed in aqueous solution probably have no distinct boundary between the core and corona, due to hydration and hydrogen bonding of the carboxylic acid groups. As the salt concentration increases, however, the cores of the micelles may become more dense and may thus be described by the star model.

In 0.1 M KCl solution, the micelles formed from copolymers having MPEG 2000 grafts generally had smaller diameters than the same backbone polymers grafted with MPEG 550 (Table 2 and Figure 4). The MPEG 2000 graft copolymers were more water soluble than the MPEG 550 ones, because the contained 50–60% w/w of MPEG, as compared to 20–30% (Table 1) for the latter ones, and the grafts were nearly 4 times as long. The higher degree of hydrophobicity of the MPEG 550 graft copolymers thus seems to induce an increase of the micellar size and the aggregation number. For micelles of poly(styrene-*alt*-maleic anhydride-*graft*-ethylene oxide), the aggregation numbers were found to vary inversely with the grafting density.[15] Similar behavior is well-known for block copolymers placed in a selective solvent.[30–33]

Viscometric Properties. Viscosity was measured for MMA 2000 in pure water and in 0.1 M KCl solution. The reduced viscosity was plotted against the concentration of the graft copolymer, as shown in Figure 5. In pure water, the viscosity increased as the concentration decreased. This behavior has been explained by an expansion of the polyelectrolyte chains caused by a decrease in ionic strength of the solution when the concentration of the macro-ion is reduced. For solutions

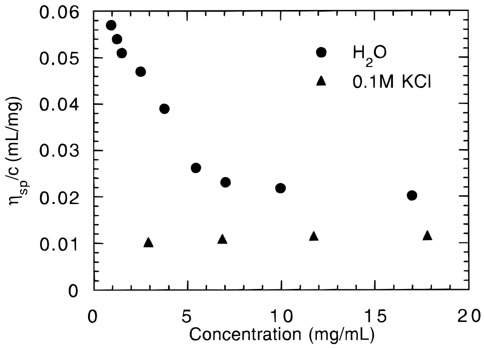

Figure 5. Reduced viscosity of MMA 2000 in water and in 0.1 M KCl.

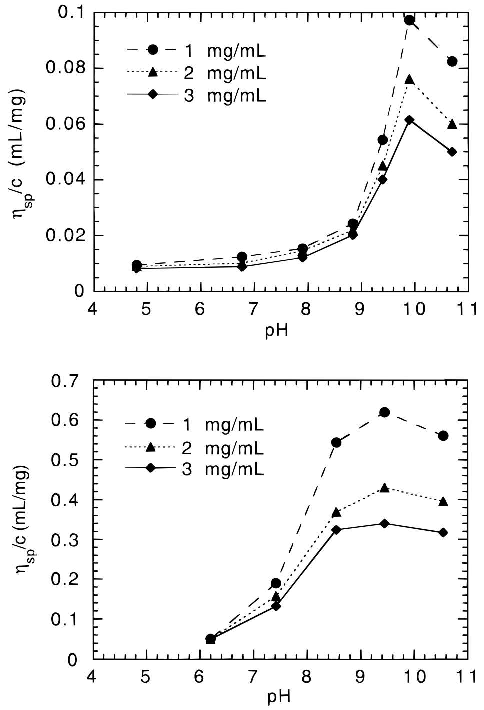

Figure 6. Reduced viscosity at different polymer concentrations in aqueous solution. The polymers were neutralized using LiOH. (a, top) EHMA 2000, (b, bottom) MAN 2000.

containing charged macromolecules without added low molar mass salt, the extrapolation of η_{sp}/c to $c = 0$ is not possible. Despite this, qualitative information can be obtained from the reduced viscosity at a constant polymer concentration. However, at high ionic strengths, i.e., in 0.1 M KCl, a linear relationship between the reduced viscosity and the concentration of the graft copolymer is obtained.

A typical feature of a polyelectrolyte is the change in conformation with polymer charge. As the degree of neutralization of the acid groups increases, electrostatic repulsion forces between the anionic centers cause the polyelectrolyte to adopt a more rodlike structure. In order to investigate the viscosity behavior of the present graft copolymers, LiOH was added to aqueous solutions of the polymers. In Figure 6 the neutralization of EHMA 2000 and MMA 2000 is shown, and as evident from the figure, the viscosity increased upon neutralizing the acid groups, due to extension of the graft copolymer. The viscosity reached a maximum when all acid groups were neutralized. Addition of an excess of LiOH caused electrostatic shielding of the carboxylate groups, and the viscosity decreased again. The concentration dependence of the reduced viscosity is shown in Figure 6. However, $\eta_{sp}/c^{0.5}$ is practically constant, which is the expected result for a classical polyelectrolyte according to Fouss' law.[34,35] Solutions of neutralized polymers in water as well as in KCl solutions were studied by QELS, but no evidence of any aggregates could be found.

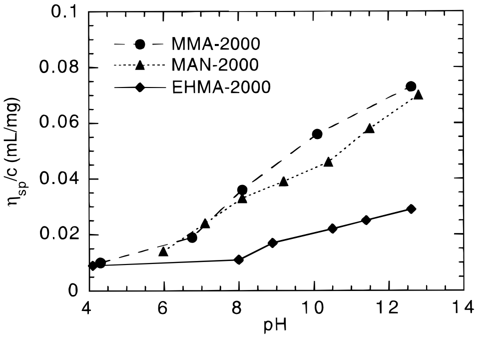

Figure 7. Reduced viscosity of graft copolymers having different backbones. The polymers (3 mg/mL in 0.1 M KCl solution) were neutralized with KOH.

By using different compositions of the backbones, the properties of the graft copolymers may be altered. Figure 7 shows results from viscosity measurements in 0.1 M KCl for three different backbone polymers grafted with MPEG 2000. The polymers all contained 50−60% w/w of MPEG and had molecular weights between 180 000 and 195 000 (Table 1). Two major differences between the polymers were found: the level of the viscosity increase at neutralization and the pH value for the onset of the increase. For graft copolymers having a backbone of poly(S-*co*-MAN), the reduced viscosity increased monotonically when potassium hydroxide was added, as seen in Figure 7. However, the graft copolymers containing MMA and, particularly, EHMA behaved differently. For these polymers, a higher electrical charge of the backbone polymer was needed to overcome the intramolecular hydrophobic interactions caused by the alkyl groups and to start the unfolding of the backbone polymer. MMA 2000 and MAN 2000 reached approximately the same level of reduced viscosity, but for EHMA 2000 the viscosity was considerably lower. The EHMA 2000 polymer contains longer alkyl groups than the other two polymers, and even at a completely charged backbone, hydrophobic interactions will cause a more compact conformation and thereby a lower viscosity. Similar results were reported from studies on solution viscosities of copolymers of maleic anhydride and alkyl vinyl ethers having varying side chain lengths.[36,37]

Polymers having the same backbone and different molecular weights of the grafts showed greatly different viscosities upon neutralization of the polymer, both in the absence and presence of salt (Figure 8). For example, at the same weight concentration, a polymer having MPEG 550 grafts generally showed a higher viscosity than the same backbone grafted with MPEG 2000, despite the fact that the latter copolymer had the higher molecular weight. The grafting densities were quite similar for both types of graft copolymers, as seen in Table 1. Typical results are presented in Figure 8 for the MMA 550 and MMA 2000 polymers. The viscosity measurements indicated that the MPEG 2000 graft copolymers had a less expanded conformation than those having MPEG 550 grafts. As mentioned previously, all graft copolymers showed an increase of η_{sp}/c in pure water upon decreasing the polymer concentration. This fact contradicts the assumption that inter-

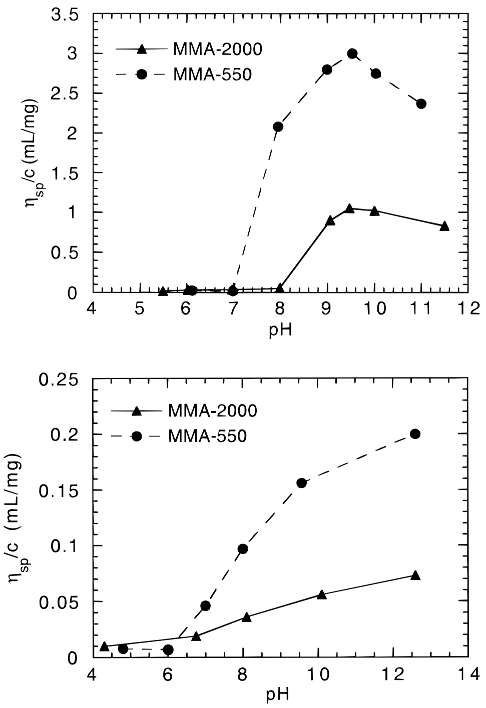

Figure 8. Reduced viscosity of poly(styrene-*co*-maleic anhydride-*co*-methyl methacrylate) grafted with MPEG 550 and MPEG 2000, respectively, and neutralized using KOH (polymer concentration 3 mg/mL): (a, top) in water, (b, bottom) in 0.1 M KCl.

molecular association of the polymers is the cause of the viscosity increase. Differences in the charge distribution around the polymer main chains may be one reason for the effects observed. In the MPEG 2000 graft copolymers, the long MPEG grafts surrounding the backbone offer an environment richer in EO units than in the corresponding MPEG 550 copolymers and, consequently, a medium of different composition and dielectric constant. Counterion solvation and charge distribution may thus be quite different for the two types of graft copolymers.

Conclusions

It was established by both QELS and FFF that the polycarboxylic acid graft copolymers in aqueous solution mainly were present as single molecules, together with a minor fraction of aggregates. In KCl solution aggregates with average sizes of approximately 30 nm were shown to be the dominant species. At increased ionic strengths of the medium, electrostatic forces will be shielded and hydrophobic interactions become more important, causing aggregation of the hydrophobic segments of the backbones. It seems likely that the graft copolymers assemble to form micellelike structures, in which the backbone forms a core which is surrounded by a corona consisting of hydrated MPEG grafts. The average sizes of the micelles were shown to increase with increasing KCl concentration.

The reduced viscosity of graft copolymers showed the typical behavior of a polyelectrolyte in aqueous solution. Graft copolymers having hydrophobic alkyl groups along the backbone were shown to need a minimum electrical charge to overcome the intramolecular hydrophobic interaction. As opposed to polymers having less hydrophobic backbones, the onset of the viscosity increase occurred at higher degrees of neutralization for these polymers, and the viscosities at full neutralization were significantly lower. Strong intramolecular hydrophobic interactions would lead to a compact conformation for the polymer molecules and, consequently, a low viscosity even at high degrees of neutralization.

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