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Solution Properties of Linear and Branched Block Copolymers Consisting of Acidic and PEO Blocks

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ABSTRACT: Double-hydrophilic block copolymers of ethylene oxide and acrylic acid or methacrylic acid have been synthesized via radical polymerization using two different methods. Depending on the synthesis method used, branched or linear structures have been obtained. Solution properties of two different kinds of block copolymers have been investigated by dynamic light scattering and viscosimetry. The effects of the solution pH, ionic strength, and temperature on the complexation of the polymers have been studied. Branching affects strongly the flow properties of the polymer solutions. Rheologically the solutions of branched polymers are Newtonian. Fast diffusion of the polymer substructures could be detected by light scattering. Linear block copolymers show shear thinning behavior, as expected. The conformations of the polymer chains have been shown to depend on the solution pH, ionic strength and temperature. Also, the structure of polyelectrolyte complexes changes with temperature at low pH.

Introduction

Block copolymers consisting of neutral poly(ethylene oxide) blocks and poly(meth)acrylic acid are interesting for several reasons. The polymers are sometimes called double-hydrophilic ones, and in these, the charged block may interact strongly, e.g., with cationic substances whereas the function of the other block is mainly to solubilize the polymer complex.[1,2] Complexation of PMAA and PAA with PEO has been extensively studied.[3−9] Also, the complexation of PEO−PMAA block copolymers with cationic low molar mass substances, as well as with polycations has recently been studied; the complexes have been defined as block ionomer complexes.[10,11] Dautzenberg has investigated the complexation of PMAA-*graft*-PEO with a polycation and shown that the PEO grafts may prevent the flocculation of an 1:1 complex.[12] Several complexes formed by PEO−PMAA block copolymers have been characterized. Also, micelle formation of PMAA−PEO block copolymer has been observed.[13] Owing to the capability of P(M)AA−PEO to complex with itself, the properties of these polymers in aqueous solutions need to be characterized in detail.

Traditionally PEO−PMAA block copolymers have been prepared by anionic polymerization.[10,11,14] Anionic polymerization, however, has its limitations, and hence, developing an efficient method for producing block copolymers via radical polymerization is of high interest. Recently, new “living”/controlled radical polymerization reactions, like atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer (RAFT) reactions have been studied intensively as methods of preparing block copolymers.[15−17] However, in ATRP and RAFT, the choice of monomers is still limited. Utilization of various macroinitiators in the radical polymerization has been studied as well. Radical polymerization of styrene and diallyldimethylammonnium chloride by PEO-based macroazoinitiators has been successful.[18,19]

In the radical polymerization of acrylic acid in the presence of PEO, chain transfer is known to occur.[20] Here we report the syntheses of PEO−PAA as well as PEO−PMAA block copolymers via radical polymerization. The former has been synthesized using a PEO macroazoinitiator (MAI) and the latter, by combining two preformed blocks. The structures and, correspondingly, solution properties of the polymers are distinctively different.

Experimental Section

Materials. 4,4′-Azobis(4-cyanopentanoic acid), ACPA, was purchased from Fluka, and it was dried under vacuum for 48 h. Phosphorus pentachloride was purchased from Fluka and used as received. Poly(ethylene oxide) monomethyl ether with $M_w = 5000$ g/mol, PEO, Polysciences, Inc., was dried in a vacuum oven at an elevated temperature, 50 °C, for 48 h. Triethylamine, dichloromethane, chloroform, hexane and diethyl ether were used as received. Acrylic acid, Fluka, was distilled under vacuum over copper turnings. Water used in purifications and measurements was distilled and deionized, Elgostat UHQPS. Tri(methyl silyl)methacrylate (TMSMA), Aldrich, was distilled in a vacuum. α-Amino-ω-methoxy-PEG, MW 5000, Shearwater Polymers, Inc., was dried under vacuum at 50 °C overnight. *N*-hydroxysuccinimide, Fluka, and 1,3-dicyclohexylcarbodiimide (DCC), Fluka, were used as received. Dioxane, acetone, and acetonitrile were dried on molecular sieves.

Syntheses. Preparation of PEO-*block*-PAA copolymers by macroazoinitiators was conducted in three steps. First, ACPA was converted to the corresponding acyl chloride, 4,4′-azobis(4-cyanopentanoyl chloride), ACPC, by the method of Smith.[21] ACPA was treated with PCl_5 in a molar ratio of 1:2 in benzene at room temperature. Second, MAI was prepared by a condensation reaction of ACPC and PEO in dichloromethane in the presence of an excess amount of triethylamine,[18,22] the reaction time being 2 days. MAI was purified by ultrafiltration in water, to remove the unreacted PEO and ACPC. The purity of MAI was ascertained by IR, NMR, and UV-spectroscopies and by SEC, which showed the absence of the molecular weight fraction 5000. The third step was the radical polymerization of acrylic acid using the MAI as an initiator. The polymerization was conducted in an aqueous solution at 65 °C for 3 h. The molar ratio of the monomer to the initiator was 250 and the monomer concentration was 7 mass %. The polymerization

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was terminated by pouring the reaction mixture into an excessive amount of cold methanol.

A reference polymerization of acrylic acid was conducted by mimicking the reaction conditions described above. Polymerization of AA was initiated with ACPA, and the reaction medium was an aqueous PEO solution, where the molar ratio of PEO and ACPA was 2:1 as in the case of using MAI.

Both product copolymers were purified by ultrafiltration (molecular weight cut off 30 000) in aqueous 0.1 M NaOH and subsequently with water, after which the polymers were in their sodium acrylate form.

In the synthesis of PEO-*block*-PMAA copolymers, TMSMA (14 mass %) was first radical polymerized using ACPA (2 mol %) as an initiator. Reaction was carried out in dioxane at 60 °C under nitrogen for 18 h. The solvent was evaporated and the polymer dried under vacuum at room-temperature overnight. The product was purified by reprecipitation from acetone to acetonitrile. It was filtered and dried under vacuum overnight. The second step of the synthesis was the activation of the carboxylic acid end groups by an excess amount of *N*-hydroxysuccinimide.[23,24] This was carried out in dioxane in the presence of DCC for 2 days. The reaction mixture was precipitated in acetonitrile, and the product was dried under vacuum. In the final step the activated PTMSMA and the amino-terminated PEO were attached to each other in a condensation reaction. The reaction was carried out in dioxane under nitrogen at room temperature in dark for 2 weeks. The product was precipitated in acetonitrile. All the reaction steps were done in dry conditions in order to prevent the hydrolysis of the protecting trimethylsilyl group. The protecting silyl groups were removed by washing the product first with 0.1 M NaOH and subsequently with water.

Methods. ^{1}H NMR (Varian Gemini 2000) and IR (Nicolet 205 FT-IR spectrometer) were used to determine the chemical compositions of the polymers. The molecular weights were determined by size exclusion chromatography, SEC, (Waters) with 0.1 M aqueous $NaNO_3$ + 3% acetonitrile as an eluent, using poly(ethylene oxide) and poly(acrylic acid) standards (Waters), and by static light scattering, SLS, (Brookhaven Instruments BI-200SM goniometer and a BI-9000AT digital correlator, Ar laser λ = 514.5 nm). The distributions the diffusion coefficient were determined by dynamic light scattering (CONTIN). Dynamic viscosities were measured by a Bohlin VOR rheometer with concentric cylinders.

Results and Discussion

Syntheses. The block copolymer of ethylene oxide and sodium acrylate synthesized by utilizing MAI, PANa-*block*-PEO, had high molecular weights as measured by SEC. Also the molecular weight of the reference polymer, which was prepared by polymerizing acrylic acid in an aqueous PEO solution, was high. After repeated purifications, all nonreacted PEO was removed, as confirmed by SEC. The ^{1}H NMR spectra of the copolymer and the reference polymer showed strong signals originating from covalently bound PEO. It was possible to estimate the molecular weights also from ^{1}H NMR spectra of the polymers because the molecular mass of the PEO segment was known. The molecular weights by NMR were much lower than those measured by SEC, indicating that each polymer contains more than one PEO block (Table 1).

Thus, the structure of the PANa-*block*-PEO copolymers is not linear but more complex. The similarity of the ratios M_n(SEC)/M_n(NMR) of the PANa-*block*-PEO and the reference polymer, 1.40 and 1.45, respectively, suggests that the structure of the polymers is determined mainly by the chain transfer to PEO.[20] Therefore, branched structures are very probable.

Linear block copolymers were obtained through preparing poly(trimethylsilyl methacrylate), PTMSMA, with a carboxyl end group originating from the initiator, and by a subsequent connection of PTMSMA to an amino-terminated PEO. Because of different termination mechanisms occurring simultaneously in the radical polymerization the linear polymer, PEO-*block*-PMANa, most probably is a mixture of di- and triblock copolymers. This assumption is supported by the M_n values shown in Table 1.

Table 1. Molecular Weights of the Copolymers[a]

polymer	M_w	M_n
PANa-*block*-PEO	278 000 (A)	115 000 (A) 82 200 (C)
ref-PANa-*block*-PEO	412 000 (A)	262 000 (A) 180 000 (C)
PMANa	56 400 (A)	22 300 (A)
PEO-*block*-PMANa	71 900 (A) 81 100 (B)	31 800 (A) 27 400, if diblock (C) 58 400, if triblock (C)

[a] Key: (A) GPC 0.1 M $NaNO_3$ + 3% ACN; (B) SLS 0.1 M $NaNO_3$; (C) ^{1}H NMR MW of PEO block = 5000.

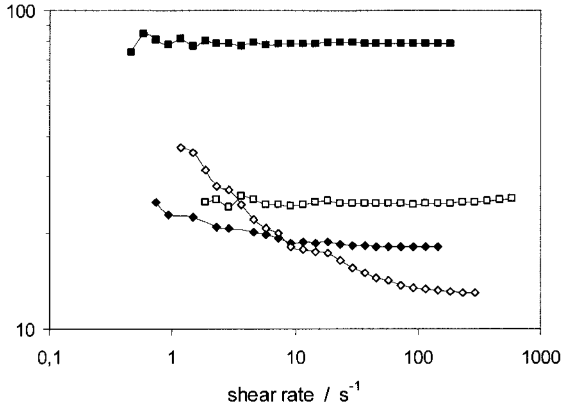

Figure 1. Steady shear viscosities of the linear PEO-*block*-PMANa, c_p = 10 wt % and c_s = 0.5 M (diamonds), and the branched PANa-*block*-PEO, c_p = 5 wt % and c_s = 1.0 M (squares), in salt-free solutions (filled symbols) and in saline solutions (open symbols).

Rheology. Results of the steady shear viscosity measurements on the salt-free and saline aqueous solutions of the branched PANa-*block*-PEO are shown in Figure 1, c_p = 5 wt % and c_s = 1.0 M $NaNO_3$. Solutions of the branched polymer exhibited Newtonian flow. Similar flow properties have been detected in solutions of dendrimers, hyperbranched polyesters, and aromatic poly(ether imide)s.[25−28] Some polyelectrolytes exhibit Newtonian viscosity in salt-free aqueous solutions as well but become shear thinning once the ionic strength is increased.[29] In the case of dendrimers, shear thinning is not observed owing to the compact structure of the solute; long chains with a capability of forming entanglements with each other do not exist. In that sense, dendrimers behave like noninteracting spheres. Generally, the explanation for the Newtonian flow of the polyelectrolyte solutions rises from the electrostatic repulsion between chains with like charges. Addition of salt screens out the charges and the polyelectrolytes start to behave like neutral polymers. PANa-*block*-PEO is a weak polyelectrolyte, which might explain the Newtonian behavior in a salt-free solution. However, increasing the ionic strength of the solution did not turn the sample shear thinning. This strongly supports the hypothesis that the structure of the block copolymer is compact due to the branching. The viscosities of the

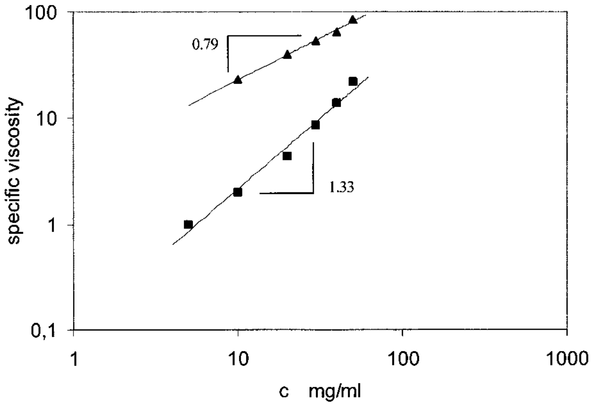

Figure 2. Specific viscosities of the branched PANa-*block*-PEO vs polymer concentration. Triangles represent the salt-free solution and squares stand for 1 M $NaNO_3$ solution.

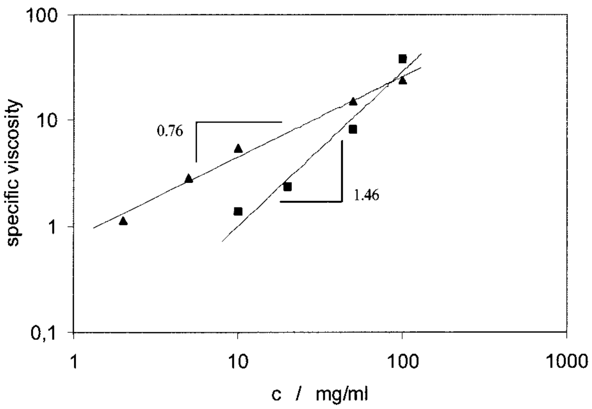

Figure 3. Zero shear viscosities of the linear PEO-*block*-PMANa vs polymer concentration. Triangles represent the salt-free solution and squares stand for 0.5 M $NaNO_3$ solution.

solutions of the reference polymer were higher due to higher molecular weight, but they exhibited Newtonian viscosities in salt-free and saline solutions as well (results not shown). This confirms the important effect of the chain transfer in the structure formation during the polymerization reaction. Comparison of the viscosities of the branched PANa-*block*-PEO and the linear PEO-*block*-PMANa confirms the conclusion as well. Shear thinning is much more pronounced in a saline solution of the PEO-*block*-PMANa, $c_p = 10$ wt % and $c_s = 0.5$ M $NaNO_3$, than in a salt-free aqueous solution. Although Coulombic interactions cause a repulsion between the charged PMANa blocks in a salt-free solution, neutral PEO blocks in the chain ends are free to coil and hence, slight shear thinning is observed. On the other hand, in PANa-*block*-PEO, the PEO blocks are tightly bound to and surrounded by PANa blocks and hence incapable of forming entanglements.

The semidilute concentration regime of a polyelectrolyte solution is generally divided into unentangled and entangled regions. In these regions, the viscosities of polyelectrolyte solutions may be predicted with equations[30]

$$\eta = \eta_s N(cb^3)^{1/2} B^{-3/2}\left(1 + \frac{2Ac_s}{c}\right)^{-3/4} \qquad (1)$$

and

$$\eta = \eta_s n^{-4} N^3 (cb^3)^{3/2} B^{-9/2}\left(1 + \frac{2Ac_s}{c}\right)^{-9/4} \qquad (2)$$

where (1) presents the unentangled solution and (2) the entangled one. η_s is the viscosity of the solvent, N the degree of polymerization, c the concentration of the repeating units, and b the monomer length. B controls the number and size of monomers in an electrostatic blob and thus depends on the quality of solvent, and A is the average number of monomer units between charges, c_s the salt concentration, and n the number of neighboring polymer chains needed for entangling. From the equations above, the zero-shear viscosity in salt-free polyelectrolyte solutions scales to the polymer concentration as $\eta \sim c^{1/2}$ in the untentangled region and $\eta \sim c^{3/2}$ in the entangled region. In saline solutions the corresponding relations are $\eta \sim c^{5/4}$ and $\eta \sim c^{15/4}$, respectively, as in the solutions of neutral polymers. In Figures 2 and 3, the specific viscosities of the semidilute solutions of branched and linear polymers are plotted against the polymer concentration. The entanglement concentration c_{ent} is not exceeded in any of the samples, and the slopes of the straight lines are in an adequate accordance with theory. Hence, neither the presence of the PEO segment in the block copolymers nor the branched structure of PANa-*block*-PEO interferes with the polyelectrolyte behavior of the polymers.

Light Scattering. The effect of the ionic strength, pH, and temperature on the dynamics of the polyelectrolyte block copolymers was studied by dynamic light scattering. In the following discussion, emphasis is on the degree of ionization on one hand, and on the hydrogen bond formation on the other. The aim is to find out the effect of branching on the properties of the polymer solutions. However, the comparison of the copolymers needs to be conducted carefully, because of the known difference in the behavior of PAA and PMAA with changing pH.

In salt-free solutions both the linear PEO-*block*-PMANa and the branched PANa-*block*-PEO showed bimodal distributions of diffusion coefficients. Same observation has been made in many preceding polyelectrolyte studies.[32,33] According to Förster et al. the concentration dependence of the diffusion coefficient is characterized by three different concentration regimes.[34] These regimes are determined by the ratio of the polymer and the salt concentrations $\lambda = c_{pe}/c_s$, but not by the absolute ionic strength of the solution. In the dilute lattice regime, $\lambda \ll 1$, only one diffusive process is observed. At very low salt and very low polymer concentrations, diffusion is determined by the electrostatic interactions rather than by hydrodynamic friction of molecules. At high salt and low polymer concentrations, polyelectrolytes are known to behave like neutral polymers. At a transition regime, $\lambda \approx 1$, the value of diffusion coefficient increases with increasing λ and it splits up into fast and slow diffusive processes. The onset of splitting is achieved either by changing the amount of salt at constant polyelectrolyte concentration or vice versa. In a semidilute regime, where $\lambda \gg 1$, both fast and slow diffusive processes are observed. The coefficient of fast diffusion D_F is independent of λ and the slow diffusion, D_S, decreases slightly with increasing λ. Origin of the slow diffusion in the transition and semidilute regimes is in the diffusion of temporal large domains.[34,35] Qualitative description is as follows. At $\lambda < 1$ each polyion is surrounded by its own ion cloud. At $\lambda > 1$, the ion clouds of neighboring polyions begin to overlap. The stabilization of the temporal aggregates

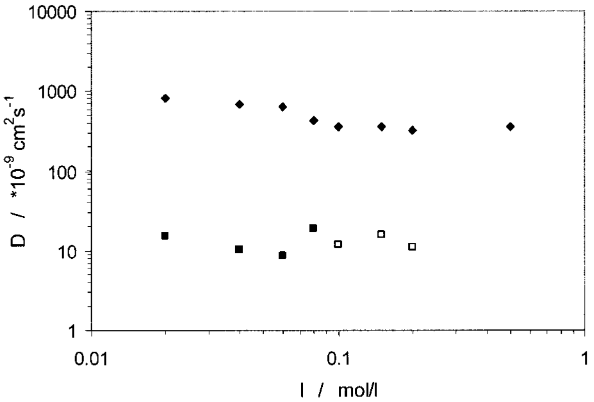

Figure 4. Diffusion coefficients D_S (squares) and D_F (diamonds) of the linear PEO-*block*-PMANa against the ionic strength of the solution, $c_p = 5$ mg/mL. (Open symbols, see text.)

occurs by fluctuating forces arising from small ions in the overlapping region shared by some neighboring polyions. Fast diffusion process taking place in the transition and semidilute regimes is attributed to thermally excited displacement fluctuations of polymer segments between entanglements. This is usually referred to as the gel mode of the transient network.

The behavior of the linear PEO-*block*-PMANa fits well to the theory described above. In a salt-free 5 mg/mL solution there is an intensive slow diffusion process observed indicating the presence of large domains. Fast diffusion is observed as well. As the salt concentration is increased the intensity of the slow process diminishes whereas the fast diffusion becomes more prominent. The block copolymers are taking a coiled conformation and starting to diffuse as single molecules. In Figure 4, the diffusion coefficients D_S and D_F of PEO-*block*-PMANa are plotted as weighted averaged values of individual distributions of diffusion coefficients against the ionic strength. With increasing ionic strength, the transition regime is reached at 0.06 M $NaNO_3$, $\lambda \approx 1$, (calculated value 0.04 M). A decrease in the D_F takes place, indicating a transition from the diffusion of chain entanglements to the diffusion of single molecules. In the dilute lattice regime, the slow diffusion process is still observed (indicated with open squares in Figure 4). The reason may be the proximity of the critical overlap concentration of the polymer itself, 7.43 mg/mL in 0.1 M $NaNO_3$, as determined by light scattering. That the slow diffusion is still observed at a salt concentration above 0.06 M may as well be due to the capability of PEO to bind some of the added salt. At a $NaNO_3$ concentration of 0.5 M, the slow diffusion has fully disappeared and a single diffusion of screened block copolymer coils is observed. In a 1 mg/mL polymer solution, as the condition $\lambda \approx 1$ was exceeded the slow diffusive process disappeared.

The behavior of the branched PANa-*block*-PEO is complicated. In Figure 5, the diffusion coefficients D_S and D_F are plotted against ionic strength. In a 1 mg/mL solution, the transition regime, $\lambda \approx 1$, was attained at an ionic strength about 0.02 M (calculated value 0.01 M). Yet through the whole studied range of the salt concentration both fast and slow diffusion processes were observed. As the ionic strength was increased and the solution conditions were approaching the transition state, the value of D_S increased and D_F stayed approximately at a constant level. As the dilute regime was reached, $I > 0.02$ M, a process of self-diffusion was observed, and the value of the fast diffusion coefficient increased discontinuously. Explanation for the very fast diffusive process is most likely seen in the branched structure of PANa-*block*-PEO. In the semidilute regime, both the D_S and D_F presumably originate from the same processes as in the case of the linear polyelectrolytes. As the transition regime is exceeded, the slower process arises from the diffusion of single molecules as in the solutions of the linear polyelectrolyte, but the origin of the fast diffusion is the gel mode. In the dilute regime, the gel mode arises from the diffusion of the substructures of the branched block copolymer.

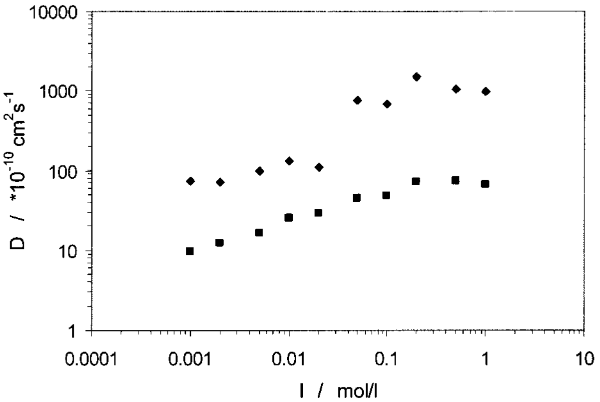

Figure 5. Diffusion coefficients D_S (squares) and D_F (diamonds) of the branched PANa-*block*-PEO against the ionic strength of the solution, $c_p = 1$ mg/mL.

Adjusting the pH of the branched PANa-*block*-PEO solution with NaOH affected the diffusion behavior of the particles in a similar manner as when increasing the ionic strength by $NaNO_3$. This was the case also when the solutions of both linear and branched block copolymers were acidified by HCl. However, decreasing pH has other effects on the polymer as well. As is known, PEO forms hydrogen bonds with PMAA and PAA. Therefore, the change observed in the diffusion processes as HCl is added has two origins. The phenomenon is well illustrated in Figure 6, which presents the distributions of diffusion coeffients at varying pH of the linear PEO-*block*-PMANa solutions. First, the addition of HCl increases the ionic strength of the solution, hence moving the system from the semidilute regime toward the transition regime. The intensity of the signal arising from the slow diffusion process decreases while the intensity of the fast process increases. Apparently, increasing the ionic strength decreases the frequency of the formation of the temporal aggregates and thereby changes the intensities of the two diffusive processes. Concurrently the degree of protonation of the acid groups increases as does the number of hydrogen bonds between the carboxylic groups and ether oxygens of PEO. Critical precipitation pHs for the mixed solutions of linear PEO/PMAA and PEO/PAA homopolymers are 3.0 and 1.9, respectively.[3] In the present case, below pH 3.8 macroscopic precipitation of PEO-*block*-PMANa occurred. At pH 4.5 only one diffusive process was observed, indicating the formation of soluble aggregate structures. Nonionized PMAA is water-soluble at low temperature and low concentration. However, at higher concentrations gelling occurs due to the intermolecular hydrogen bonding between MAA units.[36] There is an excess of MAA over the EO units in the PEO-*block*-PMANa block copolymers, thus below the critical pH the PMAA segments on the surfaces of the

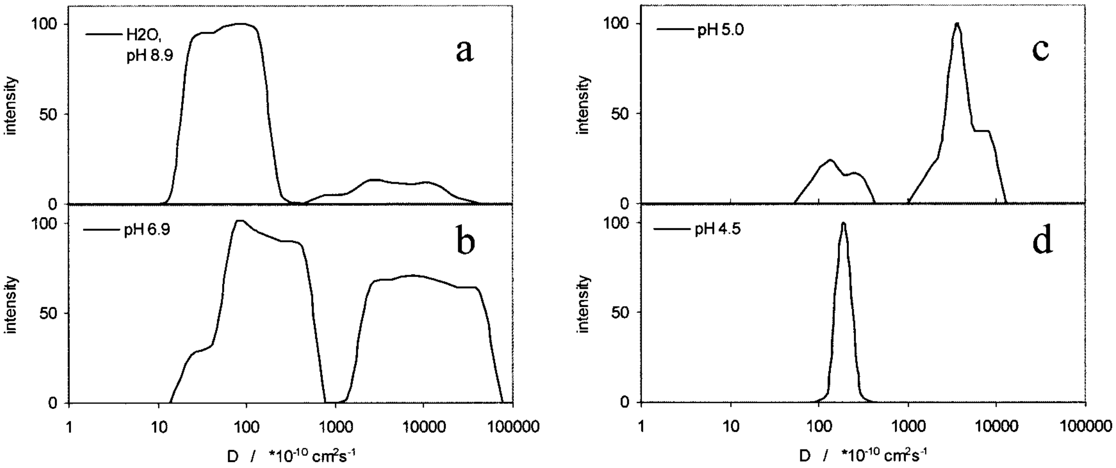

Figure 6. Distributions of diffusion coeffients with decreasing pH of the linear PEO-*block*-PMANa solutions, $c_p = 5$ mg/mL: (a) H_2O, pH 8.9; (b) pH 6.9; (c) pH 5.0; (d) pH 4.5.

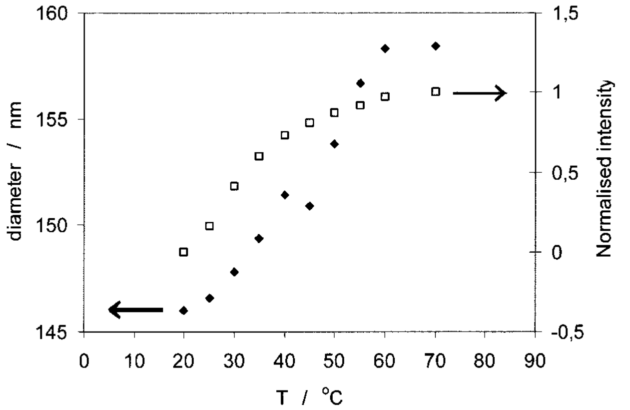

Figure 7. Effect of solution temperature on the normalized intensity of scattered light, and the hydrodynamic diameter of PEO-*block*-PMANa at pH 4.5. The diameter is calculated using the cubic cumulant fit.

micelles form intermolecular hydrogen bonds and precipitation occurs. Gohy et al. reported PMAA–PEO forming micelles at pH as low as 2.[13] In that work, the ratio of EO units to MAA units was much higher than in the present case, however.

Because the increase in temperature increases the gelling tendency of PMAA, also the temperature dependence of the solubility of PEO-*block*-PMANa ($c_p = 5$ mg/mL) was checked in pH 4.5. In Figure 7, the normalized scattered light intensity together with hydrodynamic diameter are shown against temperature. Both functions show inflection points but at slightly different temperatures. First, the increase of the normalized intensity deviates from linearity above 40 °C, and second, the increase in the particle diameter ends at 60 °C. The first inflection point coincides with the breaking down of the linear relationship observed between the $[\eta]$ and $1/T$ of the nonionized PMAA in water.[36] It may be concluded that the PMAA blocks shrink upon increasing temperature up to 40 °C. Above this temperature, most of the PEO blocks probably have been turned out from the collapsed PMAA core, and any further increase in the particle size is due to a minor change in the aggregation number. Above 60 °C, the system has stabilized as the cloud-point temperature of PMAA, ~50 °C,[37] has been exceeded. Although the number of hydrophobic PMAA units is high the polymer does not precipitate. This supports the conclusion by Gohy et al. that a transition from a hydrogen-bonded PEO/PMAA core to a hydrophobic PMAA core takes place as a consequence of the increase in temperature.[13]

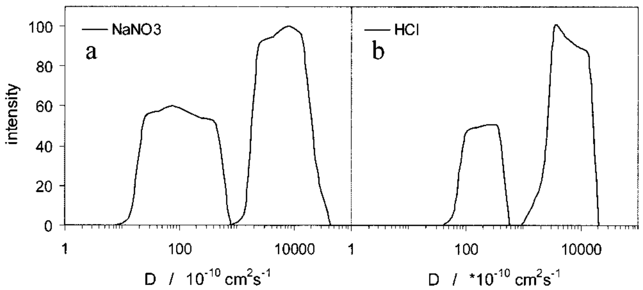

Figure 8. Comparison of the distributions of the diffusion coefficients when the ionic strength is adjusted to 0.02 M by either (a) $NaNO_3$ or (b) HCl (pH 5.7).

The more complex structure of the branched PANa-*block*-PEO was detectable also when its aqueous solution was acidified. The changes in the distributions of the diffusion coefficients arising from two origins could not be separated as clearly as in the case of the linear polymer. The disappearance of the polyelectrolyte effect was seen as a disappearance of the most slowly diffusing species. At the same time the formation of hydrogen bonds was observed as the broadening of the distribution. Finally, at pH 2.7, the range of diffusion coefficients was $(30-9000) \times 10^{-10}$ cm^2 s^{-1}. The distribution was broad due to various diffusive processes: the diffusion of both the contracted and coiled substructures of the polymer, as well as that of the whole polymers, and the diffusion of the polymer aggregates. Also, different water solubilities of PAA and PMAA contribute to the softer transition of the branched PANa-*block*-PEO.[3]

The role of the ionic strength in determining the behavior of the polymer is illustrated in Figure 8, where the distributions of the diffusion coefficients are shown for two samples. The first sample is the aqueous saline solution of PEO-*block*-PMANa with $I = 0.02$ M, the second is a sample where the same ionic strength has been obtained by adding HCl. The effect of the ionic strength is clearly seen also in Figure 9, where data on samples with either added sodium nitrate or added hydrochloric acid are combined. When the diffusion coefficients are plotted against ionic strength it turns out that the acid and the salt have a similar effect on

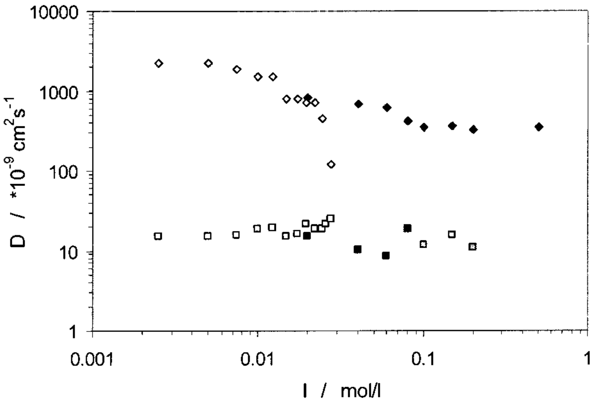

Figure 9. Diffusion coefficients D_S (squares) and D_F (diamonds) of the linear PEO-*block*-PMANa against the ionic strength of the solution. Ionic strength adjusted either by $NaNO_3$ (filled symbols) or HCl (open symbols).

the polymer, as long as the pH of the solution is kept above the critical point to avoid the precipitation of the polymer.

Conclusions

Radical polymerization of acrylic acid in aqueous solutions in the presence of PEO produces highly branched structures due to chain transfer. The branched structures are fairly compact as shown by the Newtonian viscosities of both aqueous and saline solutions. The effect of the branched structure is very well observed also in the dynamic light scattering results. Both the D_F and D_S are present through a wide range of added salt concentration due to the internal motions of the molecules.

PEO-*block*-PMANa forms soluble complexes at low pH. However, because of the high abundance of the hydrophobic PMAA, there is a critical pH below which the particles precipitate. The morphology of the aggregates may be changed upon changing the temperature. Above the cloud-point of PMAA, the particles consist of a PMAA core and a PEO shell.

References and Notes

(1) Qi, L.; Cölfen, H.; Antonietti, M. *Chem. Mater.* **2000**, *12*, 2392.
(2) Öner, M.; Norwig, J.; Meyer, W.; Wegner, G. *Chem. Mater.* **1998**, *10*, 460.
(3) Ikawa, T.; Abe, K.; Honda, K.; Tsuchida, E. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 1505.
(4) Chen, H.-L.; Morawetz, H. *Eur. Polym. J.* **1983**, *19*, 923.
(5) Bednar, B.; Li, Z.; Huang, Y.; Chang, L.; Morawetz, H. *Macromolecules* **1985**, *18*, 1829.
(6) Oyama, H.; Tang, W.; Frank, C. *Macromolecules* **1987**, *20*, 474.
(7) Iliopoulos, I.; Halary, J. L.; Audebert, R. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 275.
(8) Baranovsky, V.; Shenkov, S.; Rashkov, I.; Borisov, G. *Eur. Polym. J.* **1991**, *27(7)*, 643.
(9) Baranovsky, V.; Shenkov, S.; Rashkov, I.; Borisov, G. *Eur. Polym. J.* **1992**, *28(5)*, 475.
(10) Kabanov, A.; Bronich, T.; Kabanov, V.; Yu, K.; Eisenberg, A. *Macromolecules* **1996**, *29*, 6797.
(11) Bronich, T.; Kabanov, A.; Kabanov, V.; Yu, K.; Eisenberg, A. *Macromolecules* **1997**, *30*, 3519.
(12) Dautzenberg, H. *Macromol. Chem. Phys.* **2000**, *201*, 1765.
(13) Gohy, J. F.; Varshney, S. K.; Jerome, R. *Macromolecules* **2001**, *34*, 3361.
(14) Wang, J.; Varshney, S.; Jerome, R.; Teyssie, P. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30(10)*, 2251.
(15) Kitano, H.; Chibashi, M.; Nakamata, S.; Ide, M. *Langmuir* **1999**, *15*, 2709.
(16) Paik, H.; Teodorescu, M.; Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 7023.
(17) Le, T.; Moad, G.; Ezio, R.; Thang, S. PCT Int. Appl. WO 9801478 A1 980115.
(18) Nagamune, T.; Ueda, A.; Nagai, S. *J. Appl. Polym. Sci.* **1996**, *62*, 359.
(19) Lieske, A.; Jaeger, W. *Macromol. Chem. Phys.* **1998**, *199*, 255.
(20) Bromberg, L. *J. Phys. Chem. B* **1998**, *102*, 1956.
(21) Smith, D. A. *Makromol. Chem.* **1967**, *103*, 301.
(22) Cvetkovska, M.; Lazarevic, M.; Koseva, S.; Baysal, B.; Hamurcu, E. E.; Uyanik, N. *J. Appl. Polym. Sci.* **1997**, *65*, 2173.
(23) Cammas, S.; Suzuki, K.; Sone, C.; Sakurai, Y.; Kataoka, K.; Okano, T. *J. Controlled Release* **1997**, *48*, 157.
(24) Yamazaki, A.; Song, J.; M.; Winnik, F.; M.; Brash, J. L. *Macromolecules* **1998**, *31*, 109.
(25) Uppuluri, S.; Morrison, F. A.; Dvornic, P. R. *Macromolecules* **2000**, *33*, 2551.
(26) Rietveld, I. B.; Bedeux, D. *J. Colloid Interface Sci.* **2001**, *235*, 89.
(27) Nunez, C. M.; Chiou, B.; Andrady, A. L.; Khan, S. A. *Macromolecules* **2000**, *33*, 1720.
(28) Thompson, D. S.; Markoski, L. J.; Moore, J. S.; Sendijarevic, I.; Lee, A.; McHugh, A. J. *Macromolecules* **2000**, *33*, 6412.
(29) Tam, K.; Farmer, M.; Jenkins, R.; Bassett, D. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 2275.
(30) Dobrynin, A.; Colby, R.; Rubinstein, M. *Macromolecules* **1995**, *28*, 1859.
(31) Sartori, R.; Sepulveda, L.; Quina, F.; Lissi, E.; Abuin, E. *Macromolecules* **1990**, *23*, 3878.
(32) Sedlak, M.; Konak, C.; Stepanek, P.; Jakes, J. *Polymer* **1987**, *28*, 873.
(33) Dautzenberg, H.; Jaeger, W. *Polyelectrolytes Formation, Characterization and applications*; Hanser Press: New York, 1994.
(34) Förster, S.; Schmidt, M.; Antonietti, M. *Polymer* **1990**, *31*, 781.
(35) Schmitz, K.; Ramsay, D. J. *Macromolecules* **1985**, *18*, 933.
(36) Silberberg, A.; Eliassaf, J.; Katchalsky, A. *J. Polym. Sci.* **1957**, *13*, 259.
(37) Eliassaf, J.; Silberberg, A. *Polymer* **1962**, *3*, 555.

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