Probing the effects of external species on poly(acrylate acid) chain dynamics by using cationic AIE-active fluorophore

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We report here our results on the investigation of the chain dynamics of poly(acrylic acid) in aqueous solution. The concentration of poly(acrylic acid) was approximately 3.8×10^{-4} mol/L, two orders of magnitude higher than that reported in the literature. The pH value of the solution was 3.9, and the hydrogen bonds between the intrinsic and ionized carboxylic acid groups formed dynamic networks, which captured aggregation-induced emission-active molecules (a tetra-quaternary ammonium modified tetraphenylethene derivative) inside the polymer coils and induced fluorescence emission. The hydrogen bonds can be classified as intra- or intermolecular; both can be probed based on the emission change of the tetra-quaternary ammonium modified tetraphenylethene probes. The effects of different external stimuli on the polymer chain dynamics were investigated using different metal cations (including Na^+, Li^+, Zn^{2+}, Ni^{2+}, Ca^{2+}, and Co^{2+}), different cation concentrations (1×10^{-6} to 4×10^{-4} mol/L), different poly(acrylic acid) molecular weights (5, 240, and 450 kDa), and different copolymers. The experimental results indicate that the long poly(acrylic acid) chains (high molecular weight) tend to form dense globular coils and exclude the probe molecules outside, which are robust and unsusceptible to water-soluble metal cations. However, the shorter poly(acrylic acid) chains tend to form intermolecular hydrogen bonds, which are helpful in capturing more probe molecules inside the networks, thus inducing stronger emission. Because of the dual functions of forming hydrogen bonds with carboxylic groups and acting as an acceptor of protons from the carboxylic acid group to form cationic species, copolymerization with acrylate amide [poly(acrylic acid)-*co*-poly(acrylamide)] can greatly affect the chain dynamics of poly(acrylic acid) segments, which is reflected by the drastically decreased emission intensity from the fluorescent probes.

polymer dynamics, concentrate solution, aggregation-induced emission, metal cation, hydrogen bonding.

1   Introduction

The chain dynamics of polyelectrolytes in aqueous solution is one of the fundamental topics in polymer science. From the biological viewpoint, this topic involves understanding the process of DNA replication and RNA message transport. In real industrial applications, it relates to the design and preparation of better agents of food additives, flocculants, slurry stabilizers, etc. Recently, fluorescence spectroscopy has been widely used in the investigation of polymer chain dynamics [1–3], and fluorescent probes with their

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aggregation-induced emission (AIE) property have attracted great attention from researchers in this field because of their unique emission mechanism [4–8].

Heparin, for example, is a typical polyelectrolyte with negatively charged sulfate side groups. It plays an important role in some biological processes, and also acts as an anti-coagulant agent and regulator of cell growth and differenti-ation. Cationic AIE-active fluorescent probes have been used for the quantitative and sensitive detection of heparin. Wang *et al.* [9] reported a cationic silole derivative exhibit-ing the ability to sense the presence of heparin. Because of the fluorescence "turn-on" mechanism of AIE-active probes, this silole-based fluorescent probe exhibited high detection sensitivity. However, the specificity was not de-sirable because of the nonspecific binding of the probe molecules to proteins. Kwok *et al.* [10] improved the selec-tivity and sensitivity using a specially designed cationic fluorene-based AIE-active probe. Moreover, the compara-tive investigation results revealed that the AIE-active fluo-rescent probe performed better than the probe possessing an aggregation-caused quenching property. AIE-active fluo-rescent probes have been employed in DNA-related studies. For example, Hong *et al.* [11] reported monitoring the for-mation and disintegration of G4 using a tetra-pod cationic tetraphenylethene (TPE) derivative. The fluorescence turn-on detection of DNA with AIE-active probes was also demonstrated by other researchers [12–15].

In our previous work [16], a TPE-based cationic AIE-active fluorescent probe was successfully utilized in the investigation of the chain dynamics of poly(acrylic acid) (PAA, Scheme 1) in a sub-concentrated solution. It has been observed that the solution pH can affect the conformation of polymer chains. Under acidic conditions, PAA chains take the conformation of compact polymer coils via inter-/ intramolecular hydrogen bonds, which hold the AIE-active probe molecules inside the coils and restricts the intramo-lecular rotations of phenyl groups in the TPE derivative. Thus, an enhancement of fluorescent emission can be rec-orded [4,8]. Under alkaline conditions, the PAA chains take an extension conformation; the ionized carboxylic groups prevent the polymer chains from collapsing into compact coils. The cationic AIE-active probes are released into the aqueous solution, and accordingly, a weak fluorescent emission can be recorded.

Despite the progress, further scientific issues need to be addressed. In the practical application of PAA, some metal cations co-exist in the aqueous solution. Sometimes, PAA is used together with other polymer species, for example, with polyacrylamide (PAM). Therefore, evaluating the effects of other co-existing species such as metal cations and other types of polymers on the chain dynamics is an important task. Herein, we report our recent work on these topics. To decrease the possible hydrophobic interaction between the aromatic core of the AIE-active probe and the alkyl polymer chain, a tetra-quaternary ammonium modified TPE deriva-tive (TATPE, Scheme 1) was selected as the fluorescent probe. It was observed that TATPE possesses the typical AIE properties [11]. Moreover, because of the four quater-nary ammoniums, TATPE exhibits higher water solubility than the previously used dicationic TPE derivative [16].

2   Experimental

PAA samples with molecular weights of 5 kDa (25 wt% in H_2O), 240 kDa (25 wt% in H_2O), and 450 kDa (solid) were purchased from Sigma-Aldrich (USA). Copolymers of PAA-*co*-PAM and PAA and maleic anhydrate [P(AA-*co*-MAL)] were purchased from Sigma (USA) and used as re-ceived. The molecular weights of PAA-*co*-PAM and P(AA-*co*-MAL) were 52 and 30 kDa, respectively. Sodium acetate, lithium acetate, calcium acetate, zinc acetate, cobalt acetate, nickel acetate, and manganese acetate were pur-chased from Sinopharm (China). All of these salts were an-alytical reagents and used directly. The AIE-active fluores-cent probe TATPE was prepared as reported previously [11]. Fluorescence (FL) spectra were recorded on a Perkin-Elmer LS 55 spectrofluorometer (USA). The details of the solution preparation and FL measurements are provided in the Sup-porting Information online.

3   Results and discussion

3.1   Effect of metal cations

PAA is a common polyelectrolyte bearing a large variety of carboxylic groups on the side chains, and it can undergo complexation with metal cations in an aqueous solution. To attenuate the effect of anions on the polymer chain dynam-ics as much as possible, different acetates were used to evaluate the complexation of PAA and metal cations. Usu-ally, Na^+ is the most abundant cation in various water sources; thus, the effect of the Na^+ concentration on the conformational change of the PAA chain is important. PAA
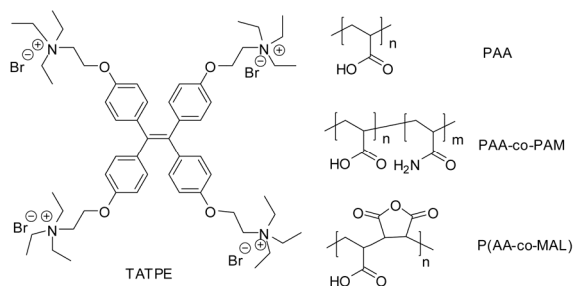

Scheme 1   Molecular structures of the tetra-quaternary ammonium-modified tetraphenylethene (TATPE) derivative: poly(acrylic acid) (PAA), block copolymer of poly(acrylic acid) and polyacrylamide (PAA-*co*-PAM), and random copolymer of poly(acrylic acid) and polyacrylamide [P(AA-*co*-MAL)].

with an average molecular weight of 240 kDa was first used for the estimation. The molar concentration was 3.8×10^{-4} mol/L (or 1.26 mol/L calculated based on an acrylic acid segment). This concentration can be converted into a weight concentration of approximately 92.0 mg/mL, which is approximately two orders of magnitude higher than that reported in classical works using fluorescent probes [17–20].

Figure 1 shows the [Na$^+$]-dependent changes in the FL intensity of a PAA aqueous solution containing 2×10^{-4} mol/L TATPE; the data were acquired from a typical experimental run. The concentration of metal cations, PAA or TATPE, is described using square brackets for conciseness. Without Na$^+$, the aqueous solution of PAA and TATPE itself displays a moderate FL emission with an emission peak at approximately 477 nm. The carboxylic acid side group of PAA can be ionized by H$_2$O molecules, and the solution is in a weakly acidic state. As elucidated by our previous work, under acidic conditions, intra- and intermolecular hydrogen bonds construct dynamic networks, which hold some TATPE molecules and result in FL emission from these probes. The emission features only exhibit slight changes when [Na$^+$] increases from 4.0×10^{-10} to 4.0×10^{-3} mol/L, over seven orders of magnitude. The plot of the variation of the peak FL intensity versus [Na$^+$] provides more details.

For example, using the intensity at 477 nm as a reference, the highest and lowest intensities were recorded to be
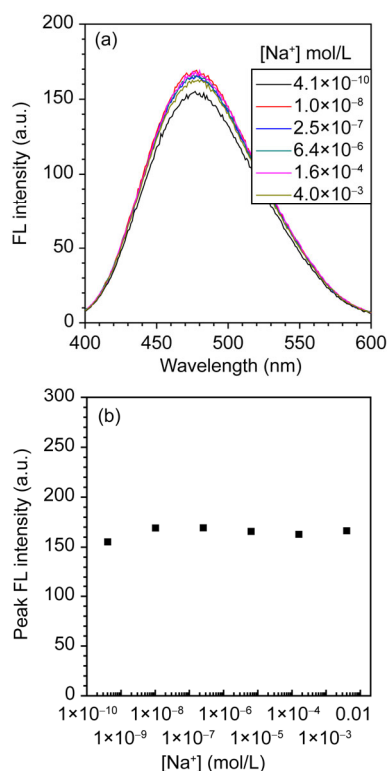
Figure 1 (a) Effect of Na$^+$ concentration ([Na$^+$]) on the FL intensity change of PAA aqueous solution in the presence of TATPE probe; (b) variation of the peak FL intensity versus [Na$^+$]. [PAA]=1.26 mol/L; [TATPE]=2×10^{-4} mol/L; pH 4; excitation wavelength=380 nm (color online).

169.1 and 154.5; thus, the absolute difference in the FL intensity over the entire concentration range is only 8.6%, which falls into the experimental error of the spectrofluorometer. These data indicate that the PAA chain dynamics in the mixture solution of PAA and TATPE can sustain a large range of [Na$^+$]. This observation is reasonably understood because the emission intensity would not undergo a detectable change if the added Na$^+$ species could not affect the structure of the dynamic hydrogen-bonding systems. It is well known that the complexion between Na$^+$ and ionized –COO$^-$ groups is much weaker than that between H$^+$ and –COO$^-$. Consequently, the addition of Na$^+$ into a PAA aqueous solution has little effect on the dynamic hydrogen-bonding systems and can hardly induce the emission changes.
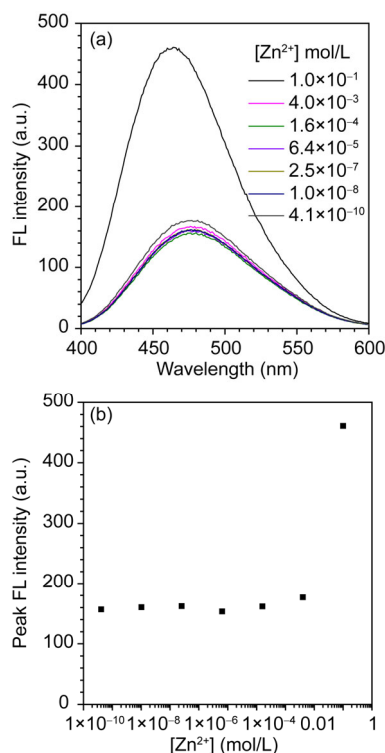
According to the above analysis, the addition of Li$^+$ into PAA aqueous solution should have a similar effect on the emission features of the system. This hypothesis was confirmed by experimental results, as observed in Figure S1 (Supporting Information online). Considering that divalent cations such as Zn^{2+}, Co^{2+}, and Ni^{2+} have stronger coordinating abilities than Na$^+$ and Li$^+$, we examined the effect of [Zn^{2+}], [Co^{2+}], and [Ni^{2+}] on the emission features of the aqueous solutions of PAA and the respective cations, and the data are summarized in Figures 2, 3, S2 and S3. For Zn^{2+}, the fluorescent responses of this system are nearly identical to that observed for the PAA and Na$^+$ mixture solution in the concentration range from 4.0×10^{-10} to 4.0×10^{-3} mol/L (Figure 2). The emission intensity only underwent a very small change. The same trend is valid when adding Ni^{2+} or Co^{2+} cations into the PAA aqueous solution. When PAA with an average M_w of 240 kDa was used, similar results were obtained (Figure 3).

These data indicate that highly water-soluble metal cations such as Zn^{2+}, Ni^{2+}, and Co^{2+} have no significant effect on the PAA chain dynamics in the concentration range 0–4.0×10^{-3} mol/L. This finding is understandable because H$^+$ has a higher affinity to carboxylic anion than Zn^{2+} or Ni^{2+}, although Zn^{2+} or Ni^{2+} has a higher affinity than that of Na$^+$ or Li$^+$. If this deduction is true, it would correlate with the hydrogen-bonding system when [Zn^{2+}] is high enough to compete with H$^+$. To confirm this deduction, we introduced 0.1 mol/L Zn^{2+} into the PAA and TATPE mixture solution, and as expected, the FL intensity steeply increased to 2.8-fold of that of the mixture solution with a lower [Zn^{2+}]. A synthetic analysis of all the above data suggests that water-soluble mono- and divalent metal cations have a weak influence on the chain dynamics of PAA in aqueous solution and that the inter/intramacromolecular hydrogen bonding interaction dominates the chain dynamics when the concentration of the metal cations is lower than 10^{-3} mol/L.
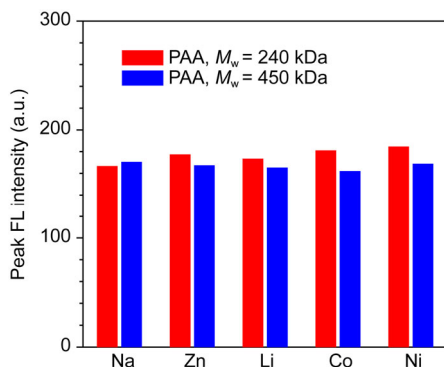
3.2   Effect of molecular weight

Dynamics involve the extension and collapse of a polymer

chain, thereby the chain length or the molecular weight is an important parameter in the evaluation of chain dynamics. In general, a longer polymer chain can be viewed as a series connection of shorter chains, and the self-similarity property of polymer chains predicts that PAAs with different molecular weights will exhibit similar FL responses. However, in fact, the longer and shorter chains will behave differently because of the different treacliness corresponding to the

different chain length.

To verify the expected similarities and differences, we first examined the pH-dependent FL responses of the PAA and TATPE mixture solutions containing PAA aqueous solution with 2×10^{-4} mol/L TATPE and 3.8×10^{-4} mol/L PAA of different molecular weights. Noting that a small molecular weight difference cannot lead to an evident change in the dynamic behaviors because of the self-similarity of polymer chains, we used PAA with molecular weights of 5 and 450 kDa as comparative samples, which are evidently smaller and larger than the previously studied PAA sample (240 kDa), respectively. The recorded FL spectra are presented in Figure 4. It can be observed that the trend of the FL intensity with variation of the pH value of the solution is identical for the two samples. In the pH region from 1.8 to approximately 3.9, the FL intensity increases monotonously with the pH value, and then, it decreases steeply with increasing of the pH value. For neutral and basic aqueous solutions, the systems are non-emissive. These observations are similar to that previously observed for the PAA sample with an average molecular weight of 240 kDa, and such a pH-dependent FL intensity change can be rationally attributed to equilibrium between the dynamic hydrogen-bonding entities and the electrostatic interaction of the TATPE and PAA chains [16].

An evident difference in the FL intensity at the same pH

Figure 2   (a) Effect of [Zn²⁺] on the FL intensity change of PAA aqueous solution in the presence of a TATPE probe; (b) variation of the peak FL intensity versus [Zn²⁺]. M_w of PAA is 450 kDa; [PAA]=3.8×10^{-4} mol/L; [TATPE]=2×10^{-4} mol/L; pH 4; excitation wavelength=380 nm (color online).
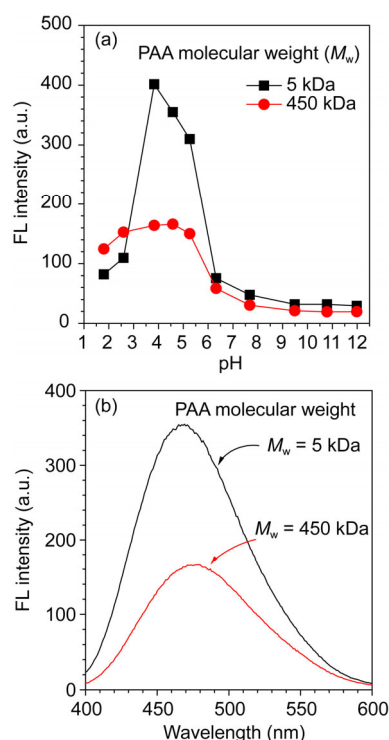

Figure 3   Effect of different metal cations on the FL intensity change of PAA aqueous solution in the presence of a TATPE probe. Concentration of the metal cations=4.0×10^{-3} mol/L; PAA samples with molecular weights of 450 and 240 kDa were used in the detections. [PAA]=3.8×10^{-4} mol/L; [TATPE]=2×10^{-4} mol/L; pH 4; excitation wavelength=380 nm (color online).

Figure 4   Molecular-weight- and pH-dependent FL changes. (a) FL intensity variation with pH value ranging from 1.8 to 12.0; (b) difference in the peak FL intensity of PAA with molecular weight of 450 and 5 kDa. [PAA]=3.8×10^{-4} mol/L; [TATPE]=2×10^{-4} mol/L; excitation wavelength=380 nm.

value can be observed for the two samples. For example, at pH 3.9, the FL intensity recorded for the mixture containing the PAA sample with a molecular weight of 5 kDa is approximately 2.4 times of that recorded for the PAA sample with a molecular weight of 450 kDa. These comparative results imply that in an appropriate acidic solution, the shorter PAA chains have a larger capacity to capture more TATPE probe molecules than the longer ones. In fact, in acidic solution (e.g., at pH 3.9), the hydrogen bonding can be divided into two types: intramolecular and intermolecular. For a longer PAA chain, the carboxylic acid side groups have a larger probability to form intramolecular hydrogen bonds, and the polymer tends to form a dense globular shape; thus, most of the TATPE probes are excluded from the polymer blob. Consequently, FL is mainly contributed by TATPE probing molecules captured in the intermolecular hydrogen-bonding networks. In contrast, for shorter PAA chains, the carboxylic acid side groups on the same polymer backbone are less likely to form intramolecular hydrogen bonds. Instead, they have a larger probability of forming intermolecular hydrogen bonds, and a dynamic intermolecular hydrogen-bonding network can be generated, which is helpful for capturing more probe molecules inside the networks. Because the portion of the emissive TATPE species is relatively larger, the induced FL intensity is stronger. Based on a series of PAA samples with different molecular weights, it is expected that the threshold molecular weight at which the intramolecular hydrogen bonding outnumbers the intermolecular bonding can be determined. This work is on-going in our laboratory.

According to the principles of polymer physics, a dense globular polymer coil held together by intramolecular hydrogen bonding is more stable than a loose coil connected with intermolecular hydrogen bonding. In other words, the FL emission of a PAA/TATPE system with high molecular weight will exhibit low responses to external stimuli, whereas the system with low molecular weight will be highly responsive to external stimuli. To verify this idea, we used Ca^{2+} cations as an external stimulus because it is well accepted that Ca^{2+} has a strong complexation capacity to carboxylic acid groups on a PAA chain. The FL intensity changes upon the addition of various Ca^{2+} concentrations into the PAA/TATPE mixture solutions are shown in Figure 5. For PAA with a molecular weight of 450 kDa, the FL intensity maintains the same level when $[Ca^{2+}]$ increases from 0 to 1×10^{-3} mol/L. A small enhancement of the FL intensity was recorded when $[Ca^{2+}]$ increased to 0.01 mol/L. In contrast, for PAA with a molecular weight of 5 kDa, the FL intensity of the system begins to decrease when $[Ca^{2+}]$ is 1×10^{-4} mol/L, and the FL intensity decays to approximately 56.8% of its original value ($[Ca^{2+}]=0$). As $[Ca^{2+}]$ increases to 0.01 mol/L, the residual emission is only approximately 8% of its original FL intensity. A similar trend is observed for the addition of $[Zn^{2+}]$, $[Ni^{2+}]$, and $[Na^+]$ cations into the PAA/TATPE systems. As demonstrated in Figures S4–S6,
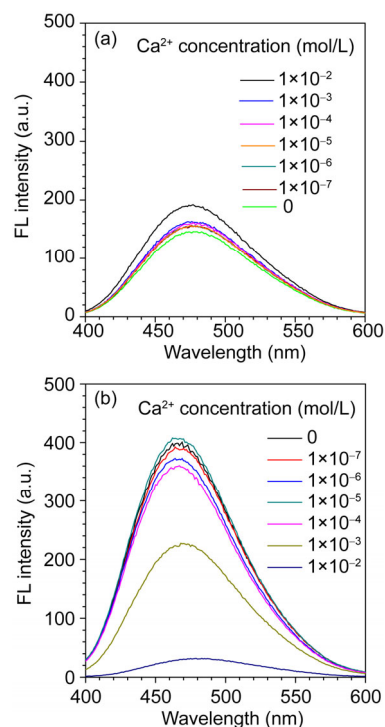
Figure 5 Effect of $[Ca^{2+}]$ on the FL intensity of PAA aqueous solutions in the presence of a TATPE probe. The M_w of PAA is 450 (a) and 5 kDa (b), respectively. [PAA]=3.8×10^{-4} mol/L; [TATPE]=2×10^{-4} mol/L; pH 4; excitation wavelength=380 nm (color online).

the concentration-dependent FL intensity change exhibits an order of $[Zn^{2+}]<[Ni^{2+}]<[Na^+]$. These results indicate that a higher concentration of metal cations is necessary to disturb the hydrogen-bonding networks in the sequence of $[Na^+]$, $[Ni^{2+}]$, and $[Zn^{2+}]$. This finding is reasonable because the capability of coordinating with carboxylic group is in the order of $[Na^+]<[Ni^{2+}]<[Zn^{2+}]$. Overall, the experimental data are consistent with the expectation of the principles of polymer science.
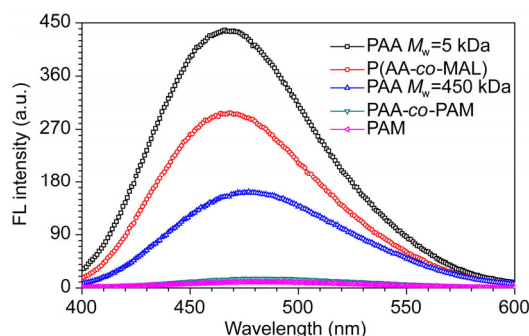
3.3 Effect of copolymerization

As described in the above discussion and our previous work [11,16], the electrostatic interaction between the cationic quaternary ammonium and anionic carboxylic groups and the inter-/intramolecular hydrogen bonds plays a crucial role in elucidating PAA chain dynamics with a fluorescent TATPE probe. The electrostatic interaction attracts the cationic TATPE probes approximating the anionic PAA chains. The hydrogen bonds construct dynamic cross-linking networks, which restrict the movement of the TATPE probes and induce the fluorescent emission. In PAA/TATPE solution, the polymer chains take dense globular conformation because of the high density of hydrogen bonds and low density of negative charge at low pH values (e.g., pH<3). In this situation, TATPE molecules have a low probability of entering into the dense polymer coils; thus, the system exhibits low FL intensity. At high pH values

(e.g., pH>6), the density of hydrogen bonds decreases, and the density of negative charges increases; thus, the PAA chains possess an extension conformation. Consequently, the highly soluble TATPE probes cannot be effectively held by the loosely arranged PAA chains, and the system emits weak fluorescence. The maximum FL intensity is observed at an appropriate pH value, and this trend was confirmed by PAA samples with various molecular weights (Figure 4).

According to these analyses, decreasing the density of the negative charge on the polymer chain is disadvantageous to capturing positively charged probe molecules. In addition, increasing the density of intramolecular hydrogen bonds to a certain degree should help to freeze out the probe molecules of the hydrogen networks. Both these factors result in the decrease of the FL intensity of the mixture. PAM is a highly water-soluble polymer that can form hydrogen bonds with carboxylic groups. In addition, the amide group is a weak organic base that can act as an acceptor of protons from a carboxylic acid group to form a cation. Introducing PAM units will bestow the polymer with both a decreased density of negative charge and increased density of hydrogen bonds. Therefore, an evidently decreased FL intensity should be recorded if PAM units are introduced into a polymer chain. We validated this assumption using a random copolymer containing both PAA and PAM segments with an average molecular weight of 52 kDa, and the experimental results are presented in Figure 6. For the PAM homopolymer, the PAM/TATPE mixture solution was almost nonemissive because of the absence of electrostatic attraction between PAM and TATPE species despite the existence of hydrogen bonding in PAM polymer coils. In comparison with PAA homopolymers, the FL intensity of the PAA-*co*-PAM/TATPE mixture solution was much lower, and only approximately 1/20th and 1/8th of that recorded for the PAA (5 kDa)/TATPE and PAA (450 kDa)/TATPE mixture solutions, respectively, were measured.

The emission behaviors of the copolymer of P(AA-*co*-Mal) provide further validation of the assumption. As displayed in Figure 6, for a P(AA-*co*-Mal) sample with an average molecular weight of 30 kDa, the FL intensity of the P(AA-*co*-Mal)/TATPE mixture solution is much stronger than that of the PAA-*co*-PAM/TATPE system, stronger than that of the PAA (450 kDa)/TATPE system, and weaker than that of the PAA (5 kDa)/TATPE system. These observations can be explained as follows. P(AA-*co*-Mal) is a water-soluble polymer carboxylic acid group containing highly polar anhydrate moieties. Unlike the amide group, however, the MAL moiety cannot serve as a proton acceptor; thus, it does little help in the formation of hydrogen bonds. In addition, the MAL unit is an uncharged moiety. Therefore, the incorporation of MAL units into the polymer chain is equivalent to reducing the molecular weight of PAA to a certain degree. Consequently, the emission behavior in Figure 6 is observed, which agrees well with the explanation for the PAA-*co*-PAM system.

Figure 6   Effect of copolymerization of acrylic acid monomer with maleic acid and acrylate amide on FL intensity in their aqueous solutions in the presence of a TATPE probe. The M_w values of P(AA-*co*-MAL), PAA-*co*-PAM, and PAM are 52, 30, and 200 kDa, respectively. [TATPE]=2×10^{-4} mol/L; pH 4; excitation wavelength=380 nm (color online).

4   Conclusions

In summary, we successfully obtained a better understanding of the polymer chain dynamics of PAA in concentrated aqueous solution using an AIE-active fluorescent probe TATPE. Under acidic conditions (pH 3.9), the hydrogen bonds between the intrinsic and ionized carboxylic acid groups construct dynamic networks and capture TATPE probes inside the polymer coils. The mixture solutions thus emit fluorescence in moderate intensity. The changes in the FL intensity upon the addition of different metal cations (including Na^+, Li^+, Zn^{2+}, Ni^{2+}, Ca^{2+}, and Co^{2+}) in a broad concentration range (1×10^{-6} to 4×10^{-4} mol/L) are unobvious, except for the introduction of a high concentration (>0.01 mol/L) of divalent metal cations such as Ca^{2+} and Zn^{2+} into the solution. These observations indicate that the hydrogen-bonding networks are robust and unsusceptible to water-soluble metal cations. The hydrogen bonding can be classified into two types: intra- or intermolecular. Long PAA chains (with high molecular weight) form dense globular shapes and exclude the TATPE probes from the polymer coil, thus decreasing the FL intensity. In contrast, shorter PAA chains have a larger probability of forming intermolecular hydrogen bonds, which are helpful in capturing more probe molecules inside the networks, thus inducing stronger FL emission. The dense coils linked with intramolecular hydrogen bonds are more insusceptible to external stimuli compared with the short polymer chains. Unlike the metal cations, the PAM segments can greatly affect the chain dynamics of PAA segments because of their dual functions of forming hydrogen bonds with carboxylic groups and acting as acceptors of proton from a carboxylic acid group to form a cation. A pronounced decrease in the FL intensity was recorded for the PAA-*co*-PAM system. These understandings of PAA chain dynamics are helpful to guide applications of water-soluble polymers in the areas of flocculating agents; thickening materials; gene-transfection vehicles; and dynamic behaviors of heparin, DNA, and RNA.

Conflict of interest   The authors declare that they have no conflict of interest.

Supporting information   The supporting information is available online at http://chem.scichina.com and http://link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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