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ORIGINAL CONTRIBUTION

Studies on the conformational behavior of acenaphthylene-labeled poly (acrylamide-*co*-acryloyl-6-deoxy-6-amino-β-cyclodextrin)

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Abstract An acenaphthylene (ACE)-labeled, β-cyclodextrin (β-CD)-modified poly(acrylamide) (PAM), (P(AM-*co*-β-CD)/ACE), was prepared in the present study. The conformational behavior of the ACE-labeled polymer in aqueous solution was studied by employing various fluorescence techniques, including fluorescence anisotropy and fluorescence quenching with different quenchers. It was demonstrated that the copolymer is partially hydrolyzed even though the charge density of the copolymer might be low, and the intra- and intermolecular complexation occurs in the copolymer solution due to the host–guest interaction between β-CD and ACE appended on the polymer backbone. The supramolecular interaction also exists in solid state as confirmed by the studies of the solid samples, which were obtained by freeze–drying the solution samples, by using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. It is expected that this kind of copolymers may be used as building blocks for the construction of novel supramolecular structures and for the preparation of smart soft solid like stimuli-responsive hydrogels.

Keywords Fluorescence · Acenaphthylene · β-Cyclodextrin · Supramolecular structures · Host–guest systems

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Introduction

Compared with polymers and traditional polymerization processes, small-size molecules are accessible in high purity, and their supramolecular polymerization can be accomplished at room temperature in a reversible and predictable manner. These advantages have made the programmed supramolecular organization ("self-assembly") of the components (building blocks) become a new way for the construction of polymers and even superpolymers (polymers with advanced structures) in which the building blocks are connected by physical interactions or supramolecular interactions [1–6]. From this point of view, the physical interactions play crucial roles in the formation of supramolecular structures and, thereby, the investigation of them is of great importance in supramolecular chemistry. Host–guest interaction, hydrophobic interaction, electrostatic interaction, coordination, and hydrogen bonding are the most important physical interactions which are commonly found in supramolecular structures.

Based upon the principles of supramolecular chemistry, design and construction of smart molecular materials like stimuli-responsive hydrogels, stimuli-responsive viscous solutions, etc. are possible. Actually, the relevant research has become one of the most exciting and most rapidly growing areas of chemical research [7–9]. Like building a house, to build a required supramolecular structure, some building blocks of specific structures are needed. The blocks could be small molecules, macromolecules, or even microparticles containing functional structures, which guarantee the physical interactions between different blocks. Research in this field has significantly advanced and has led to a wide variety of exciting discoveries [10–12]. Recent reports describing the mechanism of formation, properties, and possible applications of supramolecular structures have been critically reviewed [13].

Host–guest interaction seems to be particularly attractive for this goal, as it combines selectivity and solvent sensitivity, and with relatively high binding constants. In particular, by proper choice of a host–guest combination, it is possible to realize ideal conditions for self-assembly, i.e., formation of kinetically labile but nevertheless thermodynamically stable bonds. Accordingly, it is not surprising that host–guest supramolecular structures, which are processable in solution, have gained considerable attention in the past few years [14–16]. The properties of host–guest supramolecular structures can be widely varied due to the availability of a multitude of hosts and guests, both having effect on binding strength, reversibility, and solubility. A kind of hosts which has been of particular importance for the construction of supramolecular structures is cyclodextrins (CDs), which are cyclic oligomers having six, seven, eight or even more glucopyranose units. When CDs exist in water, their inside cavities are considerably hydrophobic, and they are capable of binding a lipophilic molecule, like acenaphthalene (ACE), within them. Due to this kind of remarkable host–guest interactions, the chemistry of CDs and modified CDs has been studied extensively [17–20]. On this basis, it is expected that when both CD and ACE were copolymerized into a polymer backbone, it was possible to form intra- or intermolecular CD–ACE inclusion complexes, and it would result in physical cross-linking within a polymer chain or between polymer chains. No doubt, this kind of studies will become the bases for the construction of three-dimensional network structures and other advanced structures maintained by physical interactions.

In this study, β-CD and ACE were copolymerized with acrylamide (AM), and a water-soluble polymer, P(AM-*co*-β-CD)/ACE, was obtained. The conformational behavior of the polymer and the host–guest interaction within the polymer in aqueous solution and at solid state were studied systematically. The details of the studies are reported in this article.

Experimental part

Materials

β-CD (AR) was purified by recrystallization from water. AM (AR) was purified by recrystallization from acetone. ACE (85%, Aldrich) was purified by triple recrystallization from ethanol followed by sublimation.

The derivatives of β-CD, including 6-*o*-tosyl-β-CD (Tosyl-CD), 6-deoxy-6-amino-β-CD (β-CDNH$_2$), and acryloyl-6-deoxy-6-amino-β-CD, which is a polymerizable monomer, were prepared according to literature methods [21–24].

ACE-labeled PAM (PAM/ACE) was prepared by free radical copolymerization using AIBN as initiator in ethyl acetate at 60 °C. Polymerization was conducted in a three-neck round-bottom flask equipped with a magnetic stirrer, thermometer, condenser, and nitrogen purge. Conversion was controlled to less than 20%. Purification was accomplished by multiple reprecipitation from aqueous solution into methanol.

ACE-labeled P(AM-*co*-β-CD) (P(AM-*co*-β-CD)/ACE) was also prepared by free radical copolymerization, but the initiator used was $(NH_4)_2S_2O_6$ and the solvent employed was a mixture of THF and water (1:9, *v*:*v*). Purification was accomplished by multiple reprecipitation from aqueous solution into ethanol. The β-CD content in the labeled polymer was determined by ^{1}HNMR method, and the result was about 10 mol%. The water used throughout was purified by deionization and then double distillation.

β-CD-modified PAM (PAM/CD) can also be prepared by the same method in water. The β-CD content was about 8 mol%.

Sample preparation

Polymer solutions used in the measurements were prepared from their stock solutions. The concentrations of the stock solutions for PAM/ACE and P(AM-*co*-β-CD)/ACE were 3 and 1 wt%, respectively.

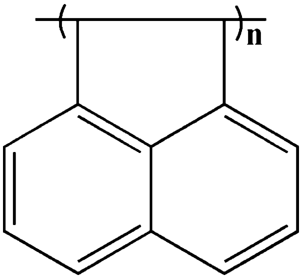
For the fluorescence anisotropy measurements, all samples of different polymer concentrations (0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.40, and 0.50 wt%) were prepared in a similar manner. The preparation can be described by using a solution containing 0.1 wt% PAM/ACE and 10 mmol/l β-CD as an example. To make this solution, 0.1 ml of PAM/ACE stock solution (3 wt%) and 2.5 ml of β-CD stock solution (12 mmol) were added to a 5-ml flask. The mixture was diluted to 3 ml with water. The P(AM-*co*-β-CD)/ACE and PAM/ACE solutions can be prepared by replacing the above β-CD solution with water.

For fluorescence quenching experiments, three kinds of quenchers, including CH_3NO_2, $TlNO_3$, and KI, have been used in the studies. The concentration of CH_3NO_2 in its stock solution was 0.9 mol/l. $Na_2S_2O_3$ was introduced into the stock solution of KI to prevent the oxidation of I^{-1} by air. In the stock solution, the concentrations of KI and $Na_2S_2O_3$ were 0.9 and 4×10^{-3} mol/l, respectively. The solution must be prepared freshly for each set of experiments (again, due to the instability of I^{-1} in air.). For $TlNO_3$, a stock solution of 0.18 mol/l was prepared. The concentration of polymer in the samples was 0.1 wt%.

The 0.1- and 0.5-wt% solutions of P(AM-*co*-β-CD)/ACE were prepared respectively and laid aside for 7 days. After freeze–drying the solutions, the white powders were obtained, which were studied by using XRD and SEM techniques.

Analytical methods

All fluorescence measurements were conducted on a time-correlated single photon counting fluorescence spectrometer (Edinburgh Instruments FLS 920) and on a Perkin-Elmer LS-50B fluorescence spectrometer. It can be imagined that the segmental mobility of the polymer in the complexation state, in particular that of the segments existing in direct contact with another polymer chain, would be lower than that in the bulk solution. Therefore, the comparison of the segmental motions of polymers in the complexation state with that in the bulk solution should allow reasonably detailed conclusions to be drawn. Like the fluorescence polarization measurement, the fluorescence anisotropy measurement is a direct measure of the segmental mobility of polymers. In the determining process, a plane-polarized light is used as a light source, and the fluorophore labeled on the polymer chain is excited to its exited state. It is true that depolarization can occur via the well-known excitation diffusion mechanism along a polymer chain or across many polymer chains [25]. This means that the excitation energy is not necessarily bound to the original absorbing molecule but is instead able to migrate over much larger distances than those associated with the induced dipole–dipole interaction. Phillips [26] found that the energy migration efficiency is strongly dependent on the mole fraction of chromophore labeled on the polymer chain. When the mole fraction of chromophore exceeds 0.5%, the down-chain energy transfer can occur. Due to this reason, the ACE content was intentionally restricted (0.5 mol% as determined), and the concentration of the polymer was also limited at 0.1 wt%. In this way, depolarization via excitation diffusion may be avoided, or, at least, the affect can be minimized. If the label has no movement within its excited state lifetime, the emission from the label will be fully polarized. However, the emission from such kinds of labels is partially or fully depolarized because of segmental motions of the polymer. In the present study, ACE was chosen as a label because it has no motion independent of the polymer chain on which it was attached (cf. Scheme 1). The rate of depolarization of a label can be determined by examination of the intensities of fluorescence emitted in planes parallel, I_{vv}, and perpendicular, I_{vh}, to that of the vertically polarized excitation. In the steady-state measurement, the anisotropy, *r*, is a measure of the extent to which fluorescence polarization is retained within the excited state lifetime and is constructed according to Eq. 1 [27]:



Scheme 1 Schematic representation of the labeling of a polymer chain with acenaphthylene (ACE)

$$r = \frac{I_{vv} - GI_{vh}}{I_{vv} + 2GI_{vh}} \tag{1}$$

where *G* is the instrumental correction factor. Furthermore, it is defined by Eq. 2,

$$G = I_{hh}/I_{hv} \tag{2}$$

where I_{hh} and I_{hv} are the fluorescence intensities emitted in planes parallel and perpendicular to that of the horizontally polarized excitation, respectively. By employing the polarization accessory and software of the machine, the parameters *G* and *r* can be determined automatically. However, as a normal practice, the *r* values are determined for more than 80 times for a given sample at a given condition. The data shown in the results are average values. It is clear that *r* is determined by both the nature of the label and the segmental mobility of the polymer. For a given fluorophore, a larger *r* value corresponds to a lower segmental mobility of a polymer, and vice versa.

Bruker AV 300 (300 MHz) NMR spectrometer, Elementar Analysensysteme GmbH VarioEL elemental analyzer, Brucher Equinox 55 FTIR spectrometer, Japan Rigaku D/max-III diffractometer, and Quanta 200 Scanning Electron Microscopy spectrometer were employed for the characterization of the samples and for the studies of the conformational behavior of polymers.

Results and discussion

Fluorescence anisotropy studies

Considering the fact that complexation will reduce the flexibility of polymer chain, our approach to the determination of the complexation within or between P(AM-*co*-β-CD)/ACE was determined to focus on the segmental mobility of P(AM-*co*-β-CD)/ACE. The fluorescence anisotropies of P(AM-*co*-β-CD)/ACE and its control systems containing PAM/ACE and PAM/ACE + β-CD, respectively, were measured as a function of time. The results are shown in Fig. 1. In reference to the figure, it is revealed that the fluorescence anisotropies of PAM/ACE in the two control systems did not change very much with time under the experimental conditions and within the experimental time scale, indicating that there were no significant changes in the segmental motions of the polymers. In contrast, however, for the system of P(AM-*co*-β-CD)/ACE, its *r* values increased gradually till day 6 and were significantly greater than those of the control systems. After that, there was no more significant change in the value for the system, suggesting that the segmental mobility of this polymer decreased along with time and reached equilibrium around day 6. The rate of complexation process is well related to the concentrations of the components taking part in the process. In addition, steric hindrance is also an important factor to affect the rate of the process. For example, Tato et al. [28] reported that a trimer of β-cyclodextrin (β-CD) forms an inclusion complex with sodium deoxycholate (NaDC) as a ditopic guest. It had been demonstrated that the morphology of the aggregates changes along with elongation of the aggregation time (90 days). The result had been rationalized by considering that it is the steric hindrance that slows down the supramolecular growth. Similarly, Kobayashi and his colleagues [29] studied the host–guest complexation between γ-cyclodextrin (γ-CD) and pyrene, and they found that a few hours are needed for γ-CD to include two pyrene molecules. The reason has been also attributed to steric inhibition. Based upon these references, and the results of our experiment, it might be reasonable to conclude that for the system of P(AM-*co*-β-CD)/ACE, the slow formation of the host–guest complex might be a result of two reasons, that is, the low concentrations of the host and the guest (ACE 2.81×10^{-5} mol/l, CD 5.62×10^{-4} mol/l), and the steric hindrance from the polymer chains. The increase of *r* value may be rationalized by considering the conformational changes of the polymer induced by the host–guest interaction of β-CD and ACE within or between the polymer chains. It is believed that at the beginning, the polymer chains are likely to adopt loose coil conformations because of their good solubility in water and their low concentration in the medium. The loose coil conformations must be characterized by greater segmental mobility and small *r* values. Along with elongation of time, however, β-CD appending on the polymer backbone started to associate ACE due to the host–guest interaction between them, resulting in intra- and/or interchain cross-linking of the polymers. The cross-linking must reduce the segmental mobility of the polymer chains and increase the *r* value of the polymer. This argument was supported by the results from similar studies for the control systems, in which the *r* values are time independent within the measurement errors and are much smaller than those for the system containing P(AM-*co*-β-CD)/ACE. This is because in the control systems, there are no structural bases for the cross-linking, and thereby PAM/ACE can only exist in linear chain state even though β-CD is there.

The *r* values for the systems of PAM/ACE, PAM/ACE + β-CD, and P(AM-*co*-β-CD)/ ACE in aqueous phase and P (AM-*co*-β-CD)/ACE in ethanol were measured at different concentrations after the solutions had been prepared for 6 days. The results are shown in Fig. 2. It can be seen that the *r* values of the four systems did not change very much along with the increase in concentration. The *r* values for P (AM-*co*-β-CD)/ACE in water are much greater than those for the corresponding systems, including the same polymer in ethanol, indicating that host–guest interaction between β-CD and ACE might have occurred within the whole concentration range studied. It is not surprising that there was no indication of host–guest interaction in the system of P(AM-*co*-β-CD)/ACE in ethanol. This is because the polarity of ethanol is close to that of the cavity of β-CD (see the paper of Wang et al. [10]). Therefore, there is no

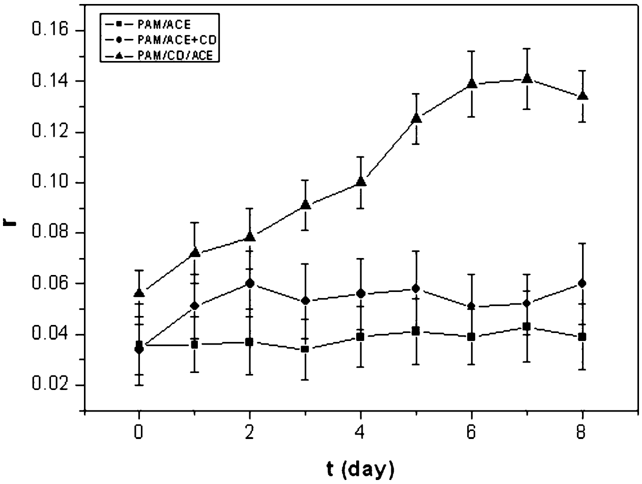


Fig. 1 Plots of the fluorescence anisotropy (*r*) of each system vs time

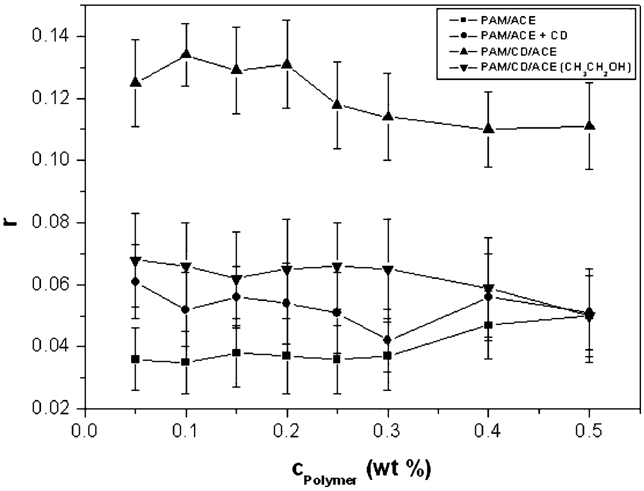


Fig. 2 Plots of fluorescence anisotropy (*r*) of each system vs sample concentration

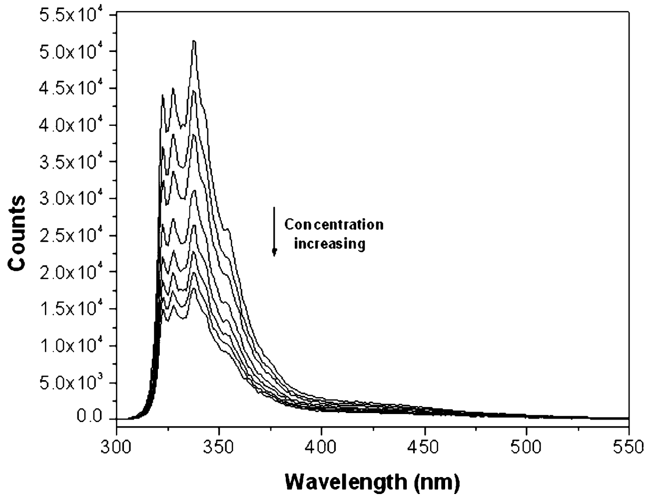


Fig. 3 Steady-state fluorescence emission spectra of PAM/ACE as a function of KI concentration (λ_{ex}=290 nm)

reason for ACE to be included in the cavity of the β-CD, and there will be no intra- or interchain cross-linking. This may be the reason why the *r* values of P(AM-*co*-β-CD)/ACE in ethanol are low.

Fluorescence quenching studies

Fluorescence quenching has been widely studied both as a fundamental phenomenon and in the application of fluorescence to biochemical and synthetic polymer problems [30]. For the study of water-soluble polymers, fluorescence quenching measurements can reveal the accessibility of fluorophores to quenchers and the localization of a fluorophore either covalently bound to a polymer chain or dispersed in a polymer solution as a probe. In principle, information regarding polymer conformation and details such as coil compactness, charge density, and coil size may be assessed through the efficiency of quenching by a given low-mass fluorescence quencher.

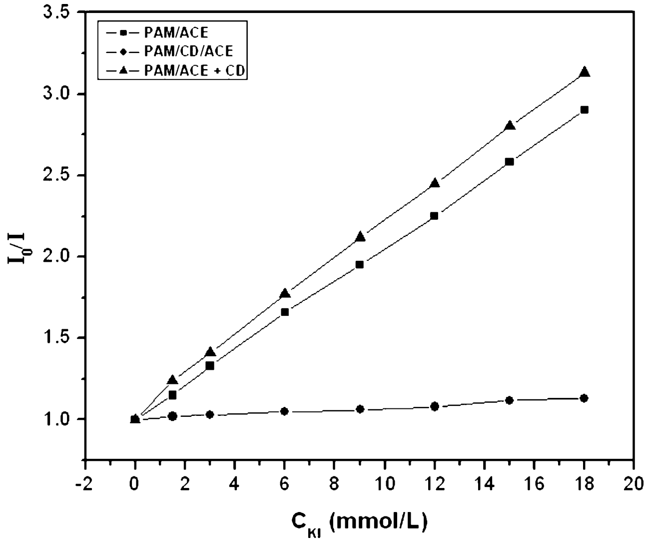


Fig. 4 Stern–Volmer plots for ACE-labeled polymer systems, with KI as a quencher, ($\lambda_{ex}/\lambda_{em}$=290/340 nm)

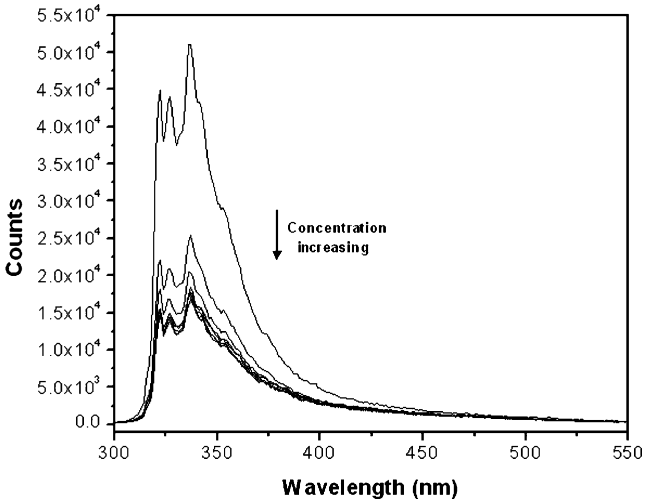


Fig. 5 Steady-state fluorescence emission spectra of P(AM-*co*-β-CD)/ACE as a function of $TlNO_3$ concentration (λ_{ex}=290 nm)

In the current studies of ACE-labeled AM-based polymers in dilute aqueous solutions, one neutral (CH_3NO_2) and two charged (KI and $TlNO_3$) species were employed as quenchers.

Potassium iodide as a quencher

For the systems in which KI was used as a quencher, the steady-state fluorescence emission spectra of PAM/ACE are presented in Fig. 3 as a function of the concentration of KI (The fluorescence spectra of the PAM, the PAM-*co*-CD, and the PAM-*co*-CD with free ACE and the PAM-*co*-CD-*co*-ACE were displayed in supplementary material). Clear-

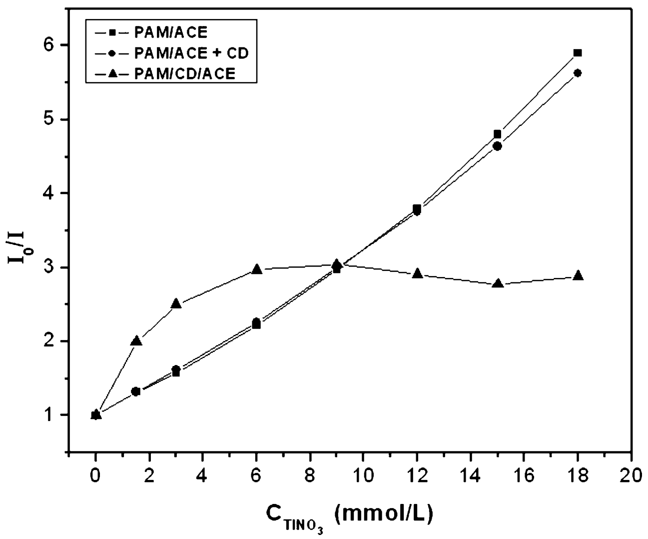


Fig. 6 Stern–Volmer plots for ACE-labeled polymer systems, with $TlNO_3$ as a quencher, ($\lambda_{ex}/\lambda_{em}$=290/340 nm)

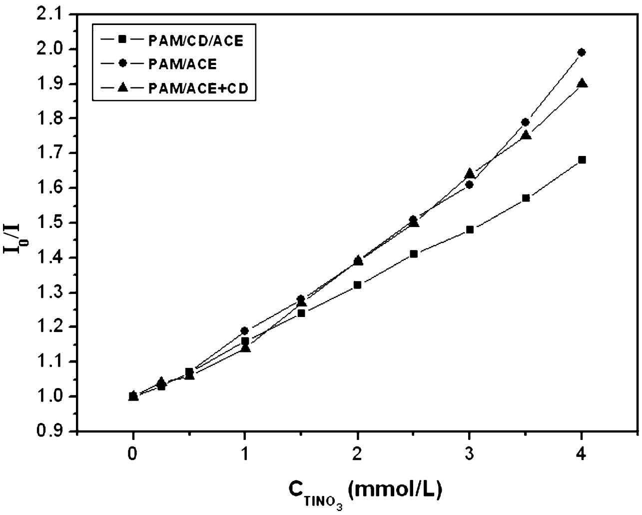


Fig. 7 Stern–Volmer plots for ACE-labeled polymers in the presence of 0.1 M NaCl, with $TlNO_3$ as a quencher ($\lambda_{ex}/\lambda_{em}$=290/340 nm)

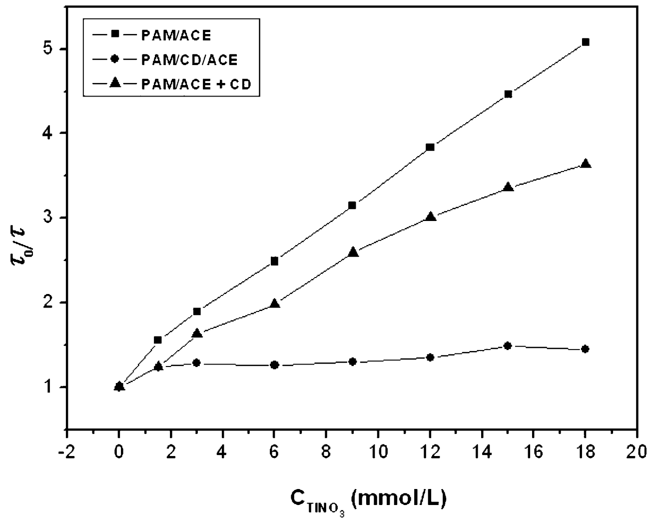


Fig. 9 Stern–Volmer plots for the PAM systems, with $TlNO_3$ as a quencher. Data from lifetime measurements ($\lambda_{ex}/\lambda_{em}$=290/340 nm)

ly, for the system of PAM/ACE, the emission intensity of the polymer decreased along with the increasing concentration of KI. The data were analyzed with Stern–Volmer equation, and the plot is shown in Fig. 4. Similarly, the Stern–Volmer plots for the systems of PAM/ACE + β-CD and P(AM-*co*-β-CD)/ACE are also shown in the figure. It can be seen that the quenching efficiencies for the two control systems are much greater than that for P(AM-*co*-β-CD)/ACE, and the bimolecular quenching constants for the two control systems are 3.2×10^9 and 3.7×10^9 M^{-1} s^{-1}, respectively, which are typical values for diffusion-controlled quenching processes, in support of the results from the fluorescence anisotropy measurements, that is, that the polymers in the two systems may adopt loose coil conformations. For the PAM/ACE + β-CD system, the β-CD is in a free state, and the polymers, similar with PAM/ACE, may adopt loose coil conformations; thereby, diffusion of KI in the system is scarcely affected even though the host–guest complex between ACE and β-CD is formed. In contrast, for the system containing the copolymer, P(AM-*co*-β-CD)/ACE, the bimolecular quenching constant is only 1.6×10^8 M^{-1} s^{-1}, at least 10 times lower than that expected for diffusion-controlled quenching systems, suggesting that ACE in this system may exist in a state with lower accessibility. Actually, the low accessibility might be originated from both network formation (cross-linking due to host–guest complexation) and electrostatic repulsion. The fact that the polymer is negatively charged has been experimentally confirmed (see the part of “Thallium nitrate as a quencher” in the next section).

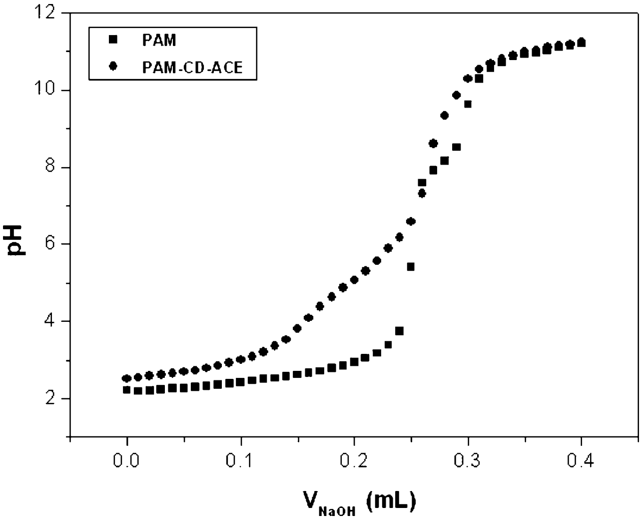


Fig. 8 Titration curves of PAM and P(AM-*co*-β-CD)/ACE

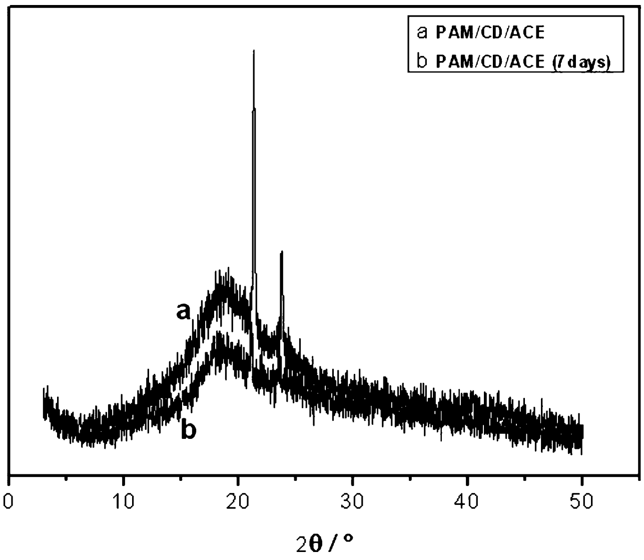
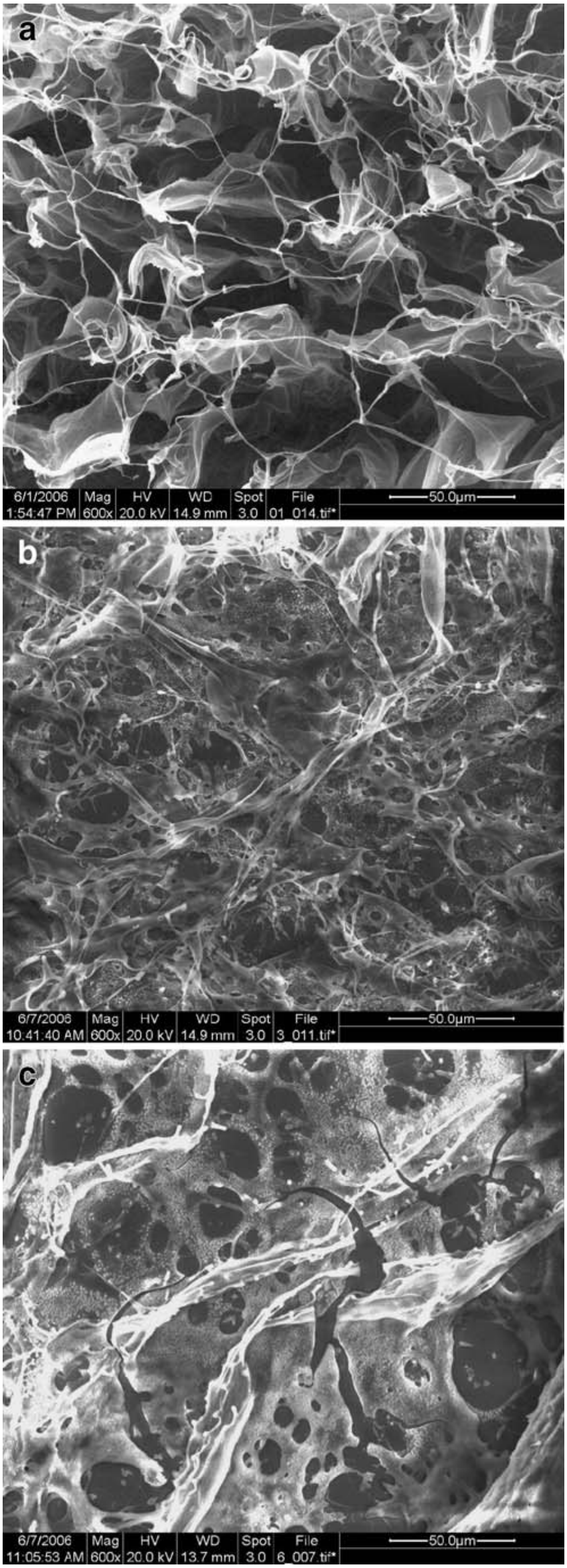


Fig. 10 XRD of P(AM-*co*-β-CD)/ACE



◀ **Fig. 11** SEM images of P(AM-*co*-β-CD)/ACE (**a**), PAM/ACE (**b**), and PAM/CD (**c**)

Thallium nitrate as a quencher

Similar to KI, the quenching efficiency of $TlNO_3$ for PAM/ACE and PAM/ACE + β-CD systems is also very high. The bimolecular quenching constants for the two systems are 7.3×10^9 and 7.2×10^9 M^{-1} s^{-1}, respectively. These values are also typical for diffusion-controlled quenching processes, supporting the tentative conclusion from fluorescence anisotropy and KI quenching studies. For P(AM-*co*-β-CD)/ACE system, however, the quenching behavior is totally different from those of the two control systems (cf. Figs. 5 and 6). At the beginning, the fluorescence intensity decreased rapidly with addition of the quencher. Once the concentration of the quencher, however, exceeds 6 mmol/l, further increase in the concentration of the quencher does not induce any further significant reduction in the fluorescence intensity. The abnormal great quenching efficiency of $TlNO_3$ at low concentration to the fluorescence emission of P(AM-*co*-β-CD)/ACE must be caused by special association of the polymer to the quencher. This is because only in this way the local concentration of the quencher can be significantly higher than that in the bulk phase, thereby causing greater reduction of the fluorescence emission of the polymer. The association could be originated from the electrostatic interaction between the polymer and the quencher (Tl^+). This is because hydrolization of PAM can produce some carboxyl groups on the polymer chains, which has been proved to be highly possible [31, 32]. This elucidation is supported by the results from a series of similar quenching experiments with $TlNO_3$ as a quencher conducted in the presence of 0.1 mol/l NaCl. The results are shown in Fig. 7. In reference to the figure, it can be observed that the presence of 0.1 mol/l NaCl shows great effect upon the quenching behavior of the quencher to the polymer. Actually, the presence of NaCl has screened the association between the polymer and the quencher, and it thereby decreased the quenching efficiency of the quencher to the emission of the polymer. Considering the ionic nature of the salt, it is no doubt that the association should be electrostatic in nature. It is to be noted that in the presence of 0.1 mol/l NaCl, the quenching experiments could only be conducted in a concentration range much narrower than that employed before due to precipitation of the quencher in the system. It might be surprising that similar hydrolization did not occur in the two control systems, which are also PAM-based polymers. The difference might be understood by considering that P(AM-*co*-β-CD)/ACE and PAM/ACE were prepared in different conditions. The solvent used for the preparation of PAM/ACE was ethyl acetate, but that used for P(AM-*co*-β-CD)/

ACE was a mixture of THF and water (1:9, *v*:*v*). Considering the facts that PAM is not very stable in polar medium [31] and that the polymerization for the preparation of the polymer in aqueous phase was conducted at relatively high temperature, it is not surprising that the polymer might be partially hydrolyzed. To prove the statement, a pH titration experiment has been conducted, and the results are shown in Fig. 8. In reference to the figure, it can be seen that for the PAM system, it is a typical strong acid to strong base titration curve. For the system of P(AM-*co*-β-CD)/ACE, however, the result is different: it is characterized by a titration of a weak acid titrated by a strong base, a strong evidence of hydrolysis of P(AM-*co*-β-CD)/ACE. Of course, the hydrolysis might have occurred during the synthesis of the copolymer. In contrast, the polymer used in the control systems was produced in a nonpolar medium, and thereby the possibility for the hydrolization of this polymer should be very low. Furthermore, it is not difficult to deduce that the charge density on the backbone of P(AM-*co*-β-CD)/ACE should be low because saturation was reached at quite low $TlNO_3$ concentration. The negative charge nature of P(AM-*co*-β-CD)/ACE should be also an important reason that explains why the quenching efficiency of KI to the emission of this polymer is so low.

Further examination of the Stern–Volmer plot for the system containing P(AM-*co*-β-CD)/ACE and $TlNO_3$, the emission intensity of the polymer, did not change very much with the further increase of the concentration of the quencher. A result can be easily explained by recognizing that the label was included in the inner cavity of its host on the polymer chain, supporting the tentative conclusion proposed from former studies. It should be easy to understand that the presence of β-CD might prevent the diffusion contact of the quencher to the fluorophore, suggesting that the quenching in this system might be dominated by static quenching. To confirm this expectation, fluorescence quenching experiments through lifetime measurements were conducted, and the results are depicted in Fig. 9. It is clear that an increase in the concentration of the quencher had little effect upon the fluorescence lifetime of the label in this polymer. In contrast, however, the increase showed significant effects upon the fluorescence lifetimes of the fluorescence labels in the other two systems. These are strong evidences to support the tentative conclusion that the polymer, P(AM-*co*-β-CD)/ACE, is partially hydrolyzed, and the label stays in the inner cavity of its host, β-CD. In other words, intra- and/or interpolymer complexation exists in this copolymer solution.

Nitromethane as a quencher

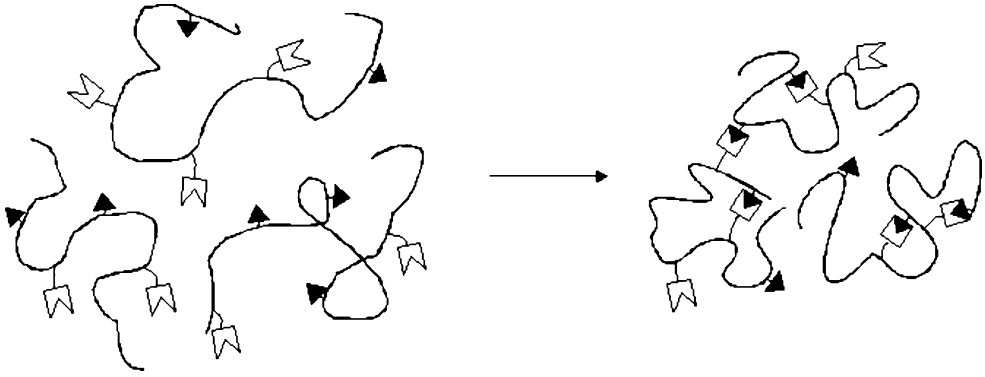
In addition to KI and $TlNO_3$, nitromethane was also employed as a quencher to investigate the conformational behaviors of the polymers in the three systems. It has been revealed that the bimolecular quenching constants of this quencher to the systems of PAM/ACE, P(AM-*co*-β-CD)/ACE, and PAM/ACE + CD are 3.9×10^9, 2.8×10^9, and 3.5×10^9 M^{-1} s^{-1}, respectively. These are the results being expected because this quencher is a neutral quencher; the charge on the polymer backbone should have little effect upon the diffusion of it, and also the quencher is relatively hydrophobic, thereby it can get into contact with the β-CD-modified copolymer.

XRD studies

The powder XRD patterns of the solid sample of P(AM-*co*-β-CD)/ACE and the powders derived from the solution laid aside for 7 days were displayed in Fig. 10. The solid sample (a) has a diffractogram consistent with its nature, while the powders obtained from the solution (b) gives a different pattern especially in the 20–25° (2θ) area where peaks associated with crystalline ACE have almost disappeared. This result may be rationalized by considering the conformational changes of the polymer induced by the host–guest interaction of β-CD and ACE within or between the polymer chains.

SEM studies

Figure 11 shows the SEM imagines of the solid samples of P(AM-*co*-β-CD)/ACE, PAM/ACE, and PAM/CD, respec-



Scheme 2 Schematic representation of the structures of P(AM-*co*-β-CD)/ACE in dilute aqueous solution

tively. The solid samples were obtained by freeze-drying the aqueous solutions of the polymers, which had been maintained at room temperatures for more than 6 days before the freeze-drying. A comparison of the images reveals that the morphologies of P(AM-*co*-β-CD)/ACE are structurally distinct from the isolated components. They are characterized by three-dimensional networks (cf. Fig. 10a), while those of PAM/ACE and PAM/CD are typical route solids. Such differences in microstructures are direct evidences for the presence of physical cross-linking within a P(AM-*co*-β-CD)/ACE chain or between P(AM-*co*-β-CD)/ACE chains [33].

Conclusion

An ACE-labeled and β-CD-modified PAM was prepared as an example copolymer to study the intra- and intermolecular complexation induced by host–guest interaction between β-CD and ACE, which had been affixed on the side chains of the polymer backbone. Fluorescence techniques and XRD and SEM studies demonstrated that the complexation does exist in the system containing P(AM-*co*-β-CD)/ACE. The intra- and/or intermolecular complexations proposed can be schematically represented by Scheme 2. On the basis of this finding, it is expected that the copolymers like the one studied may be used as building blocks for the construction of novel supramolecular structures and even for the preparation of smart soft solid like stimuli-responsive hydrogels. These kinds of studies are in progress.

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