

Feature article

Multi-stimuli responsive amine-containing polyethers: Novel building blocks for smart assemblies



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ABSTRACT

Smart assemblies have been widely studied in recent years for their capability to respond to the environment. As a series of building blocks of smart assemblies, multi-stimuli responsive polymers have also attracted a great deal of attention. In this article, notable recent advances in the fields of synthesis and assembly of amine-containing polyethers are summarized. Amine-containing polyethers, which combine the excellent biocompatibility and temperature responsive behaviour of polyethylene glycols with the pH responsive behaviour and ease of functionality of amines, are ideal building blocks for fabricating smart assemblies. 0-D, 1-D, and 2-D smart assemblies have already been obtained from assembly of amine-containing polyethers, and they show much promise in the areas of disease diagnosis and targeting, drug delivery system, molecular recognition and separation, polymeric templates, and more.

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1. Introduction

Molecular self-assembly is ubiquitous in nature and daily life

[1]. For example, membranes of living cells are formed by the self-assembly of phospholipids. Scientists and technicians have long recognized the concept of the “bioinspired” assembly approach for building large structures from small objects. Assembly, as a “bottom-up” fabrication method, provides simple and low-cost processes to make large-area periodic nanostructures [2–5]. As a part

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of assembly, the assembly of polymers has been studied for many decades. Various morphologies including spherical micelles (spheres), lamellae, vesicles, cylindrical micelles (cylinders), nanotubes, and nanosheets have been observed in aqueous solutions [6–12].

Chemical building blocks used for assembly, such as surfactants, polymers, and nanoparticles, can spontaneously assemble into ordered structures [13–15]. In the past decades, assembly has attracted great interest because of its potential use in a diverse range of applications, such as drug delivery, fabrication of nano-products, and surface modification. Compared to small-molecule aggregates, polymer assemblies exhibit higher stability and durability due to their advantageous mechanical and physical properties.

Recently, stimuli-responsive polymers have been increasingly adopted for the fabrication of self-assembling architectures, endowing traditional assemblies with the “smart” capability to respond to the environment [16,17]. Such smart assemblies are capable of conformational changes and transitions, or in some cases disassembly, upon exposure to an external trigger (e.g., a change in temperature, pH, or chemical composition; irradiation of light; or application of an electrical field), which has aroused tremendous attention and brought to the forefront their potential utility in a broad range of emerging applications [18–23]. Therefore, smart assemblies have attracted considerable attention for their potential application across diverse areas of research spanning biomedicine, biomaterials, microelectronics, photoelectric materials, and catalysis, to name a few.

To fabricate smart assemblies in solution, smart or multi-responsive amphiphilic polymers are required. All of the polymers used for fabricating smart assemble assemblies consist of one or more hydrophobic and hydrophilic parts. Compared with the large number of hydrophobic building blocks available, the most frequently used hydrophilic building blocks are more limited, with popular examples being poly(*N*-isopropylacrylamide) (PNIPAM), polyethylene glycol (PEG, also known as polyethylene oxide (PEO)), poly(hydroxyethyl methacrylate) (HEMA), poly(vinyl pyrrolidone) (PVP), and various amines [14,24,25]. Among them, PEG is one of the most ubiquitous and promising components for assembly [21,26]. PEG is employed as a common component for a wide range of products in the pharmaceutical and cosmetic industries because it exhibits (i) high solubility in water and most organic solvents, (ii) no immunogenicity, antigenicity, or toxicity (also known as “stealth” property), and (iii) high flexibility and hydration of the main chain [27]. On the basis of Davis and Abuchowski's works [28,29] on the covalent conjugation of PEG to pharmaceutical agents, now known as “PEGylation”, many possible applications of PEG, ranging from a biocompatible additive for healthcare applications to a powerful drug modification tool, have been developed [30,31]. The consequences of PEGylation permit us to overcome many deficiencies, including increased water solubility of hydrophobic drugs, protection toward degrading enzymes, and reduced immunogenicity and antigenicity [31–33].

A major limitation of PEG is its lack of functional groups. This is especially the case for linear PEGs, which are commonly synthesized via anionic ring-opening polymerization of ethylene oxide or condensation polymerization of ethylene glycol, and possess only one or two hydroxyl groups at the chain ends. Because building blocks of smart assemblies often require tailored functionalities, various efforts have focused on the synthesis of PEGs with different terminal functional groups, including carboxylic acids, amines, thiols, epoxides, and more [32,34]. Various end-group-functionalized PEGs are already commercially available, including amine-functional PEGs (e.g., Jeffamines) and epoxy-functional PEGs. Furthermore, various methods have been introduced to

improve the functional group density of the PEGs. One such method is to introduce functional groups to the main chain; another is to develop PEGs with multiple chain-ends (branched, hyperbranched, and dendrimers) [35–37].

Among the many available functional groups, amino groups are perhaps the most widely studied as they possess both interesting pH responsiveness and high reactivity [38–40]. The pH response of amine-containing polymers is caused by the fact that amino groups are deprotonated at higher pH, resulting in a decrease in hydrophilicity. Furthermore, amino groups can react effectively with carboxyl, carbonyl, aldehyde, and epoxy groups. The easy functionalization of amino groups provides a huge platform for further modification. Amine-containing polyethers, which consist of both polyether and amine groups, combine the biocompatibility of polyethers and the high reactivity of amino groups. Frey's group has devoted much attention to and developed a library of amine-containing polyethers [32,35,41–43]. Furthermore, their multi-responsive behaviour makes these amine-containing polyethers ideal components for smart assemblies [44–46].

The click chemistry between epoxy and amine groups is a robust way to prepare amine-containing polymers. The poly(ether amine)s (PEA) [47–52] developed by our group are a series of amphiphilic polymers synthesized by the click reaction of poly(ethylene glycol) diglycidyl ether and amines. In addition to the previously mentioned advantages, PEAs also benefit from ease of synthesis and tailoring of the polymer structure, and can be functionalized sequentially through the different chemistries of amino and hydroxyl groups. Furthermore, PEA can self-assemble into nano-structured objects having different morphologies in water, which exhibit a sharp response to changes in their environment.

Several recent reviews discuss the building blocks of assembly [16,53,54], but few have focused on amine-containing polyethers. In this feature article, we have reviewed recent advances in the synthesis and assembly of amine-containing polyethers. The combination of amines and polyethers endows the resulting assemblies with biocompatibility, multi-stimuli responsiveness, and easy functionalization. 0-D, 1-D, 2-D smart assemblies have already been obtained via the assembly of amine-containing polyethers, and they show great promise in the areas of dispersion and controlled release of drugs; sensors; templates; and recognition and separation of guest molecules.

2. Synthesis of amine-containing polyethers

2.1. Chain polymerization

2.1.1. Radical polymerization

Free radical polymerization is a widely used method for the synthesis of polymers. The discovery and development of controlled radical polymerization techniques make it possible to control molecular weight precisely and to prepare block copolymers and other polymers having complex architectures. As one of the most extensively studied controlled/living radical polymerizations, atom transfer radical polymerization (ATRP) has been used to obtain many desirable polymers [55]. ATRP has been used to prepare a variety of amine-containing polyethers having different structures, such as grafted copolymers [56,57] and star-shaped polymers [58] based on PEG macroinitiator and DMAEMA. Wang et al. reported a series of amphiphilic block copolymers PEO-*b*-P(*R*₁-*r*-*R*₂) synthesized via ATRP (Fig. 1), where CuBr acted as catalyst to activate the carbon–Br bond of a brominated PEO macroinitiator, resulting in reversible deactivation of the propagating macro-radicals [44,59,60]. The obtained copolymers were ultra-pH-sensitive with finely tunable hydrophobicities and pK_as.

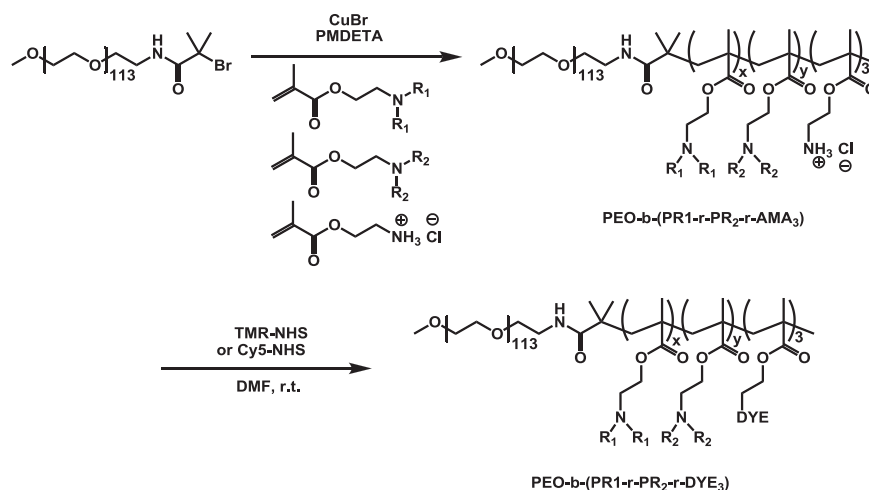


Fig. 1. Schematic illustration of the synthesis of PEO-*b*-P(PR1-*r*-R2) and dye-conjugated di-block copolymers. Reproduced with permission from Ref. [60]. Copyright 2011 John Wiley & Sons.

2.1.2. Ionic polymerization

In addition to radical polymerization, ionic ring-opening polymerization is also a powerful strategy for generating amine-containing polyethers. Lynd et al. copolymerized *N,N*-diisopropyl ethanolamine glycidyl ether (DEGE) with ethylene oxide (EO) and allyl glycidyl ether (AGE) via anionic ring-opening polymerization to develop physiologically relevant and pH-responsive block copolymers (Fig. 2) [61]. A series of amine containing polyether block copolymers were developed by using amine-terminated mPEG (mPEG₄₅-NH₂) as a macro-initiator for anionic ring-opening polymerization, thus broadening the strategies available for preparing thermo-sensitive copolymers [62–64].

Frey's group [41–43,65,66] has prepared many primary amine functionalized polyethers. The representative anionic ring-opening copolymerization strategy for preparation of these block copolymers is shown in Fig. 3a. During the copolymerization, epoxide monomers and amine-containing epoxide monomers bearing two protecting groups (R₂ = butyl, hexyl, octyl or benzyl) are randomly distributed along the copolymer backbone. The protecting groups must withstand the strongly basic conditions of anionic ring-opening polymerization, and can be further removed by catalytic hydrolysis to liberate the primary amino groups. Taking the benzyl-protected polymer as an example, Pearlman's catalyst was used to achieve full deprotection of P(EG-co-DBAG)s, resulting in the P(EG-co-AG) via the cleaving of *N*-benzyl groups (Fig. 3b).

Oxanyon-initiated polymerizations have also extended the synthetic methods available for fabrication of diblock copolymers

having different chemical structures, especially for the polymerization of methacrylate derivatives with potassium alkoxide based macro-initiators [67–69]. As shown in Fig. 4, the donor group at the β-position in the ester moiety of methacrylate monomers can activate alcoholate initiation by chelation with an alkali metal, resulting in an increased nucleophilicity of the oxanyon. Several methacrylate monomers were polymerized using potassium alkoxide as the initiator [70,71].

One of the advantages of oxanyon-initiated polymerization, when compared with traditional anionic polymerization, is that the former does not require strict experimental conditions. Oxanyon-initiated polymerization provides an efficient approach for synthesizing block copolymers with controlled molecular weights and narrow molecular weight distributions, and facilitates the incorporation of polyethers and poly(tertiary amine methacrylate) blocks. Diblock copolymers of PEO-*b*-DMAEMA [72], ABA triblock copolymers of cationic PDMAEMA(A blocks) and PPO (B blocks) [73], and even a DMAEMA-*b*-PEO-*b*-PPO-*b*-PEO-*b*-DMAEMA five block polymer [74] were successfully obtained through oxanyon-initiated polymerization. These block copolymers were evaluated as potential polymeric drug delivery systems.

Cationic ring-opening polymerization has also been adopted to obtain amine containing polyethers. Zhang et al. [75] synthesized a series of methoxy poly(ethyleneglycol)-*b*-poly(ε-caprolactone-co-γ-dimethyl maleamic acid-ε-caprolactone) (mPEG-*b*-P(CL-co-DCL)), which contained varying amounts of acid-labile β-carboxylic amides on the polyester backbones, via cationic ring-opening

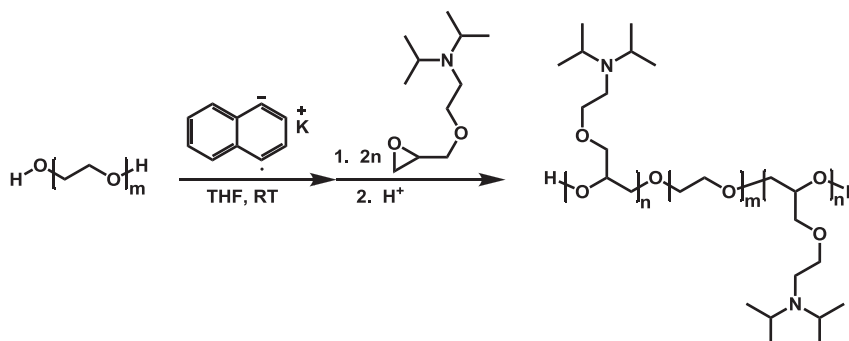


Fig. 2. Synthesis of PDEGE-*b*-PEO-*b*-PDEGE via anionic polymerization. Reproduced with permission from Ref. [61]. Copyright 2013 Royal Society of Chemistry.

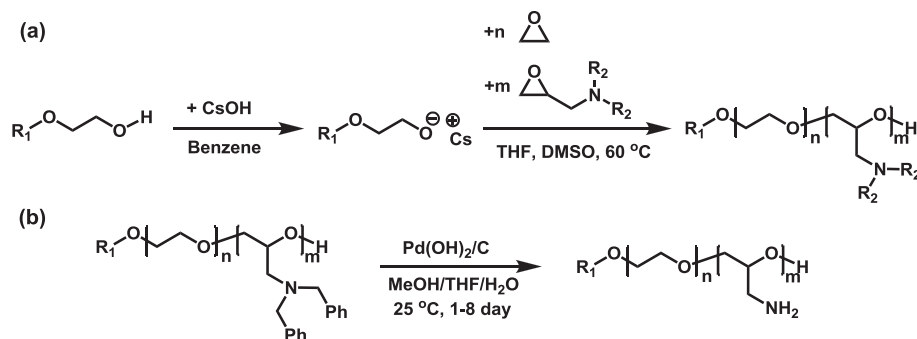


Fig. 3. (a) Polymerization strategy of amine-functional polyethers. Reprinted with permission from Ref. [42]. Copyright 2013 American Chemical Society. (b) Typical catalytic hydrolysis reaction where $R_2 = \text{benzyl}$. Reprinted with permission from Ref. [32]. Copyright 2010 American Chemical Society.

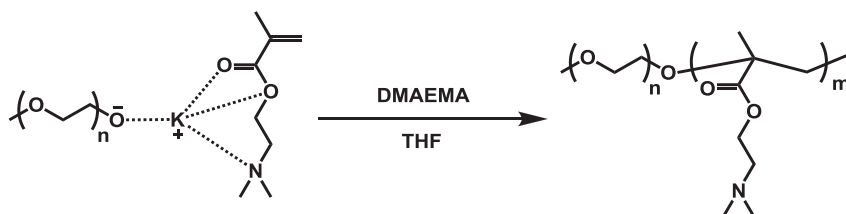


Fig. 4. Synthesis of Polyether-PDMAEMA block copolymer via oxyanion-initiated polymerization at room temperature. Reproduced with permission from Ref. [71] Copyright 1997 John Wiley & Sons.

polymerization catalysed by stannous octoate. Following hydrolysis of the β -carboxylic amides, polyethers with primary amino groups were obtained. The primary amino groups can be easily functionalized for further applications.

2.2. Step polymerization

2.2.1. Condensation polymerization

Condensation polymerizations, an important class of step polymerization, have been used to obtain amine-containing polyethers [76,77]. In one example, Zhang et al. established an approach for the generation of an adipic acid/amine-terminated polyether (D230)/diethylenetriamine copolymer (AA/AT/DE) by the condensation reaction of adipic acid with amine-terminated polyether D230 and diethylenetriamine (Fig. 5) [78]. The obtained AA/AT/DE copolymer showed potential in preventing aggregation of colloidal silica in aqueous solutions.

2.2.2. Click chemistry

Several noteworthy methods have been established to obtain amine-containing polyethers which based on click chemistry

including the epoxy-amine [79–81], azide-alkyne [82,83], thiol-ene [83,84] and epoxy-thiol [46,85] reactions.

In 2008, we developed a novel family of multi-stimuli responsive poly(ether amine) (PEA) polymers using the epoxy-amine click reaction [48]. Di-epoxy (DE) and amine monomers were copolymerized effectively under reflux conditions in ethanol. Different types of DE and amines can be chosen to design the structure and tune the properties of the resulting PEAs. As shown in Fig. 6, linear [86,87] and graft [47–49,88–92] PEAs can be obtained through click reaction of DE and di-functional amines, while hyperbranched PEAs (hPEA) [51] were achieved by reaction of DE and tri-functional amines using an initial mole ratio of 1:1. The peripheries of the hPEAs possess a large amount of reactive amino groups which can be further functionalized by epoxy-containing functional monomers. Additionally, the hydroxyl group generated by the click reaction of epoxy and amine can be further functionalized with carboxyl groups. Taking advantage of the amino and hydroxyl groups available in hPEA, a variety of functional monomers was introduced onto the hPEA backbone through sequential functionalization reactions to achieve the desired properties (Fig. 7) [93–98].

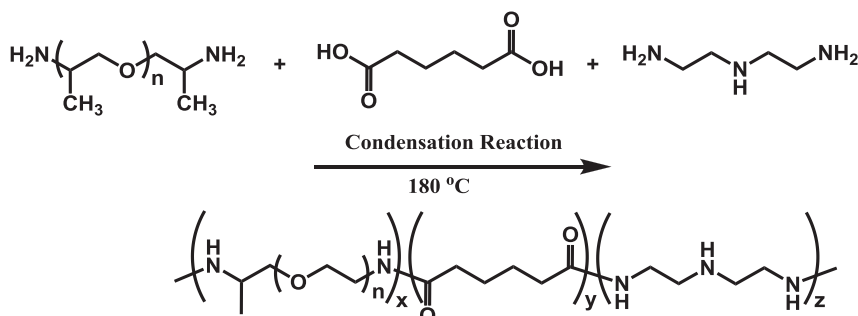


Fig. 5. Synthesis of AA/AT/DE via condensation reaction. Reprinted from Ref. [78], with permission from Elsevier.

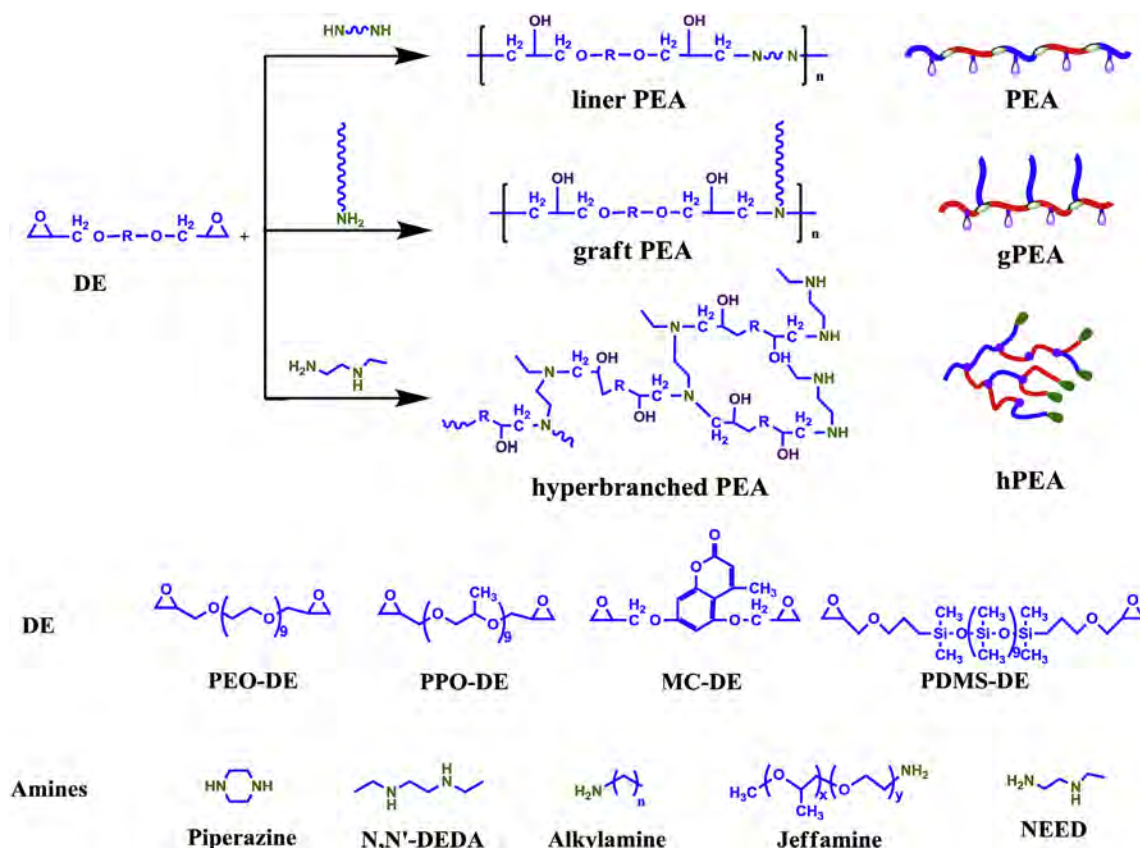


Fig. 6. One step synthetic route of PEAs under mild conditions via epoxy-amine click reaction, and the structure of Di-epoxy and amines [47–49,51,86,88–92].

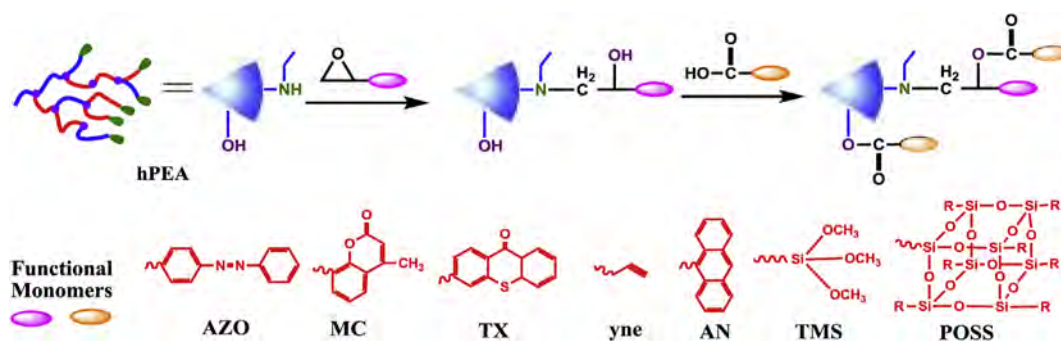


Fig. 7. Sequential functionalization of hPEAs via epoxy-amine click reaction and esterification, and a list of Functional Monomers [50,52,93–103].

Through this strategy of epoxy-amine click chemistry, Khan creatively introduced “clickable” functional groups onto the backbone of PEA in 2012 [104]. As shown in Fig. 8, the obtained polymers contained up to 4 chemically distinct reactive sites and could

be sequentially modified in the following manners: (1) via quaternisation of amine units in the backbone; (2) via azide-alkyne click chemistry; (3) via thiol-ene click chemistry; and (4) via esterification of hydroxyl groups. The structure and properties of

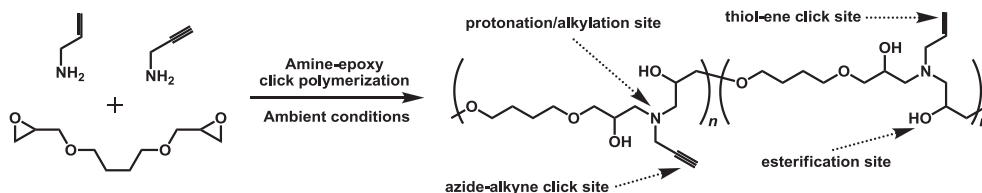


Fig. 8. One-step preparation of poly(β-hydroxyl amine)s at ambient conditions via epoxy-amine click reaction and sequential modification. Reprinted with permission from Ref. [104]. Copyright 2012 American Chemical Society.

the obtained polymers can easily be tuned to increase the range of possible applications.

2.3. Supramolecular strategy

A new strategy based on supramolecular chemistry has enriched the methods available for the preparation of amine-containing polyethers having complex architectures [105–108]. As shown in Fig. 9, Zhu et al. [109] presented a typical example to fabricate supramolecular nanoparticles via host–guest interactions between cyclodextrin (in the form of β -CD-grafted branched polyethylenimine (PEI-CD)) and adamantane (in the form of AD-functionalized polyethylene glycol (PEG) derivative, (mPEG-AD), adamantane-functionalized calcein (CA-AD) and AD-functionalized folate (FA-AD)). An advantage of supramolecular strategies is that the mixing ratios of each component can be easily tuned, resulting in the tunable morphologies and performances. The obtained supramolecular assemblies displayed excellent fluorescent properties, improved physiological stability, and long-term systemic circulation times, as well as smart targeting capabilities for cancer-specific delivery.

Naturally, it is a good choice to combine several of the methods mentioned above for fabrication of amine-containing polyethers. Several varieties of amine-containing polyethers have been synthesized by combining ionic ring-opening reactions with click chemistry [110–112], as well as via other combinations [113–115]. As shown in Fig. 10, Zhou and coworkers prepared a series of amphiphilic PEHO-g-PDMAEMAs copolymers with hydrophobic poly(3-ethyl-3-(hydroxymethyl)-oxetane) (PEHO) cores and variable lengths of PDMAEMA arms [116]. PEHO was synthesized via

cationic polymerization, with the degree of branching of PEHO increasing with increasing reaction temperature. Linear, hyper-branched, and dendrimeric PEHO could be obtained by using different reaction temperatures. Finally, PEHO-g-PDMAEMA copolymers were obtained via ATRP of DMAEMA monomers with PEHOs-Br macroinitiators (i.e., 2-bromoisobutryl bromide-modified PEHOs). These copolymers exhibited good buffering ability, low cytotoxicity and could be used for gene transfection.

3. Assemblies of amine-containing polyethers and their applications

The assembly of amphiphilic polymers has been thoroughly studied for many decades, and various morphologies have been observed in bulk and in aqueous solutions. Amine-containing polyethers, which exhibit a sharp response to temperature, pH, and ionic strength due to the presence of large amounts of ether groups and amino groups, are ideal components for assembly.

3.1. 0-D smart assemblies

Linear PEA [48], which is synthesized via epoxy-amine click chemistry of PPG-DE, PEG-DE, and piperazine, exhibits a typical phase transition behaviour of other linear amine-containing polyethers. As shown in Fig. 11b, a sharp phase transition occurs around the cloud point (CP). With increasing PEG content in the PEAs, the phase transition temperature increases. Interestingly, the CPs of PEA micelle solutions form a linear relationship with the PEG content, indicating a well-tunable CP. The tertiary amino groups in the polymer chain, which can be protonated and deprotonated at

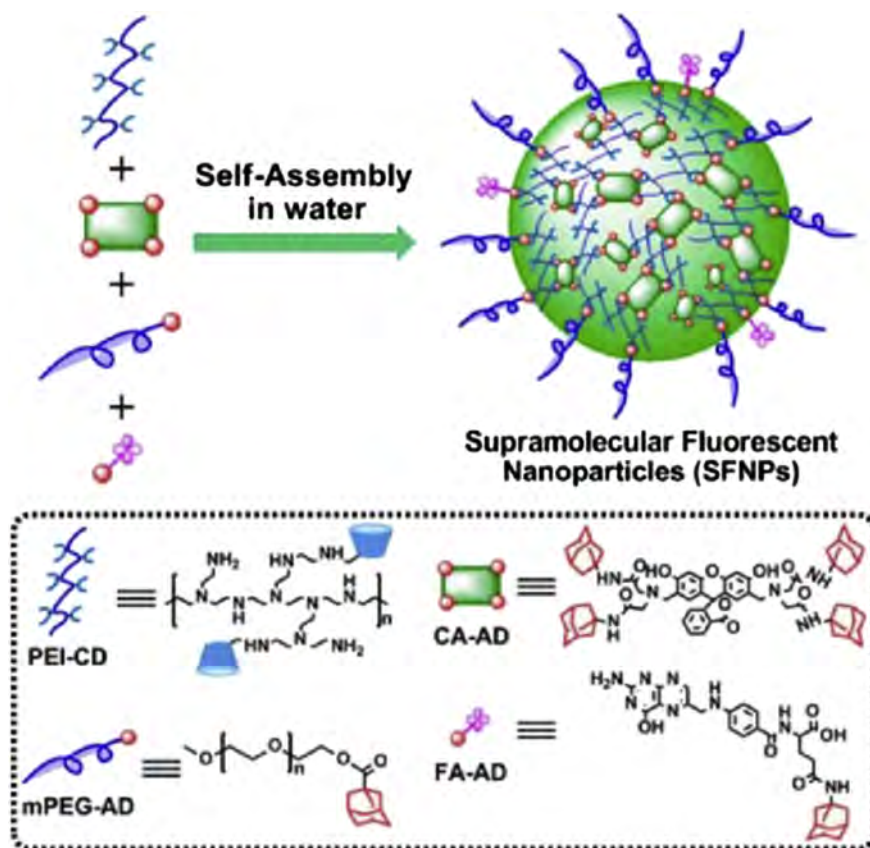


Fig. 9. Schematic Representation of Calcein-Based Supramolecular Fluorescent Nanoparticles (SFNPs) Self-Assembled in Water via Host–Guest Interactions of β -Cyclodextrin (β -CD) and Adamantane (AD). Reprinted with permission from Ref. [109] Copyright 2012 American Chemical Society.

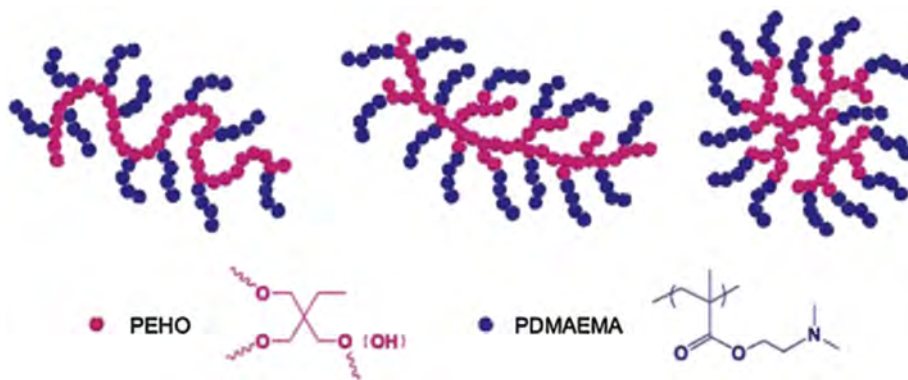


Fig. 10. The different topological architectures of PEHO-g-PDMAEMA copolymers obtained from combination of cationic polymerization of 3-ethyl-3-hydroxymethyl-oxetane and ATRP of DMAEMA with 2-bromoisobutryl bromide modified PEHOs. Reproduced from Ref. [116] with permission of the Royal Society of Chemistry.

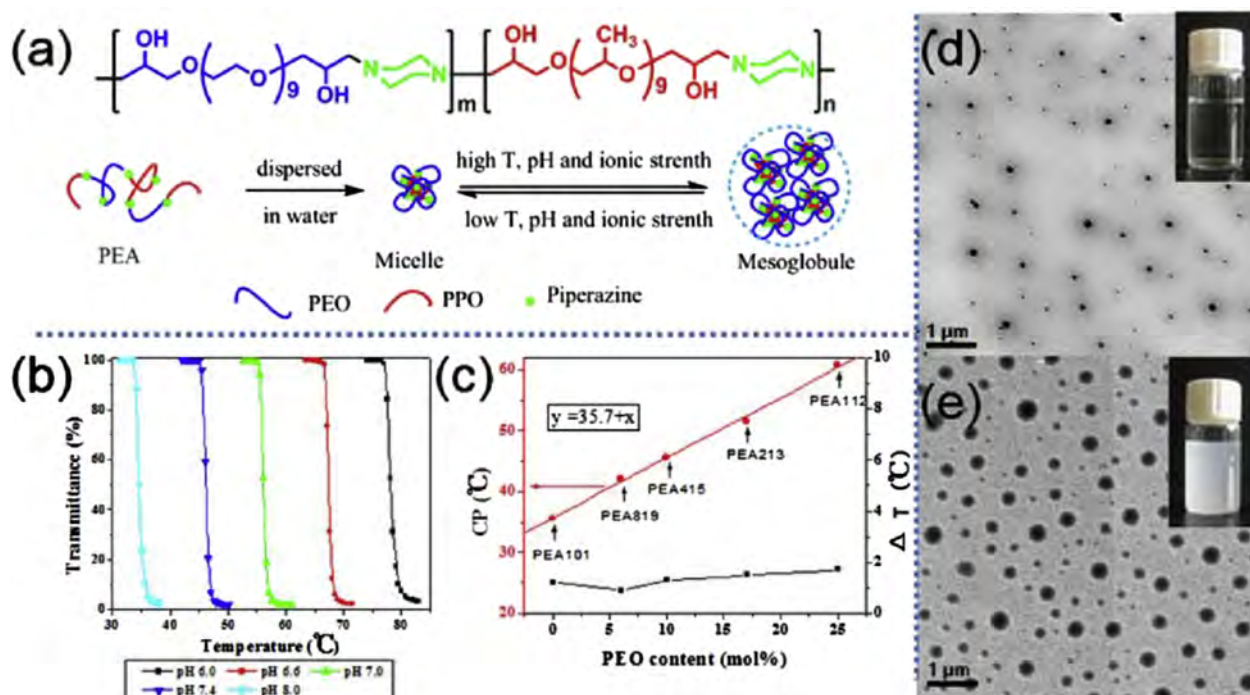


Fig. 11. Typical response behaviour of amine-containing polyethers. (a) Typical structure of linear PEA and the scheme of response behaviour. (b) The phase transition behaviour of PEA micelle solutions at pH 7.4. (c) The phase transition behaviour of PEA micelle solutions at different pH values. TEM images of PEA micelles before (d) and after (e) aggregation. Reproduced with permission from Ref. [48]. Copyright 2009 John Wiley & Sons.

different pH, can also lead to pH responsiveness. As shown in Fig. 11c, for all PEAs, increasing the increasing pH value led to a lower CP. This is caused by the fact that amine groups become less protonated at higher pH, which results in a lower hydrophilicity. As ionic strength has a significant effect on the formation of hydrogen bonds between PEG chains and water molecules, PEAs also exhibited a response to ionic strength.

Smart nanoparticles are widely studied for their potential in pharmaceutical and industrial applications. Gao and co-workers have developed a series of ultrasensitive pH-responsive nanoparticles based on the supramolecular self-assembly of PEO-*b*-(PR-*r*-DYE) [44,59,60]. PR refers to the tertiary amine containing segment, while DYE represents a pH-insensitive fluorophore. As shown in Fig. 12, at higher pH values, neutral PR segments self-assemble into the hydrophobic cores of micelles, thus resulting in the aggregation of fluorophores and quenching of fluorescent

signals through mechanisms of Fluorescence Resonance Energy Transfer (FRET) between DYE molecules and Photoinduced electron Transfer (PeT) from tertiary amines to DYE. At lower pH values, PR segments become protonated and positively charged, thus leading to micelle disassembly and dramatic increase in fluorescence emission owing to the increasing distance between TMR units and the decrease in PeT. By changing the PR segment to adjust the pKa values of ammonium groups, the transitions can be tuned from pH 5.4 to 7.4 accurately. When utilized *in-vivo*, the stealth properties of PEG can suppress protein adsorption, thus avoiding potential interference by foreign body reactions [32,117]. While reaching the acidic tumours, the polymeric micelles will disassemble, thus emitting strong fluorescence. These nano-assemblies offer many exciting opportunities for diagnostic imaging and drug delivery applications at acidic tumour sites or in specific intracellular organelles upon uptake by targeted cells. As an extension, A-PEGs

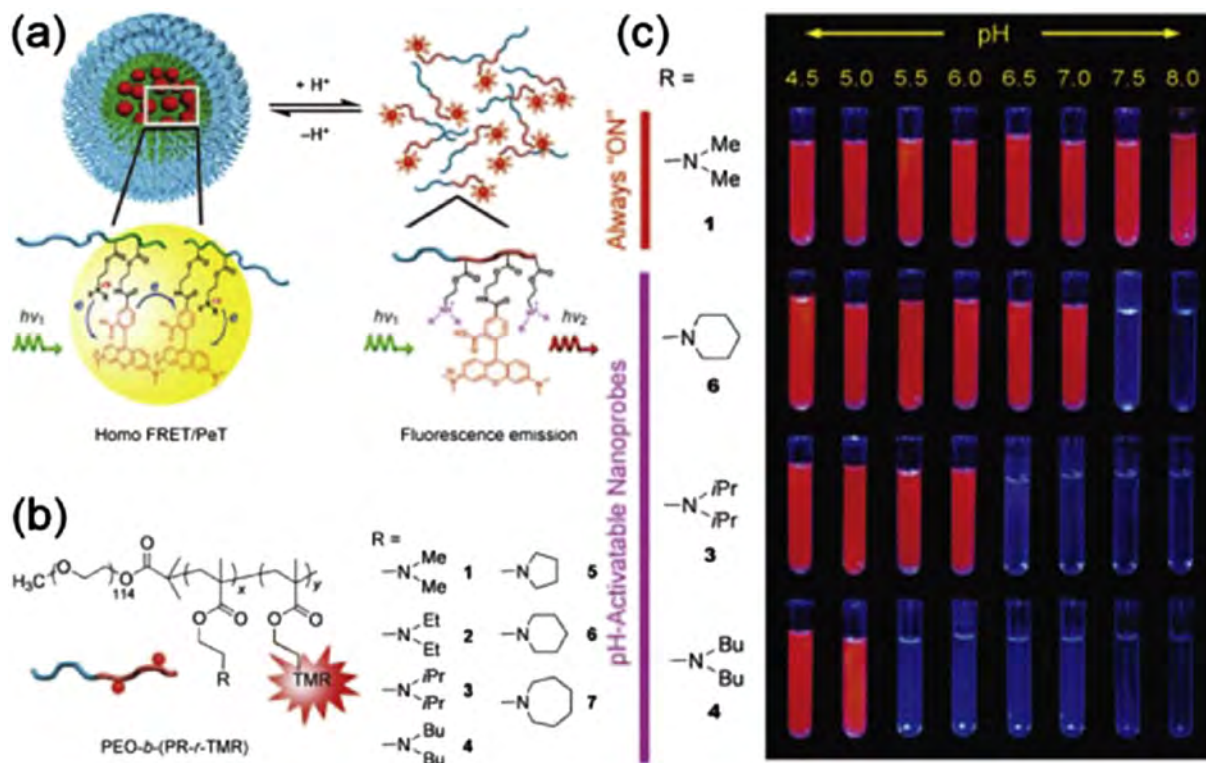


Fig. 12. (a) Schematic design of pH-activatable micellar (pHAM) nanoprobe and their mechanism of pH-dependent fluorescence emission and quenching. (b) Structures of the PEO-*b*-(PR-*r*-TMR) copolymers in the dialkyl and cyclic series. (c) Representative fluorescence images of different nanoprobe solutions at the same polymer concentration but different pH values. Reproduced with permission from Ref. [60]. Copyright 2011 John Wiley & Sons.

with pH-cleavable linkers such as hydrazone-bonded or oxime-bonded drugs can release effectively at acidic tumour sites via a pH trigger [118,119]. These efforts have been driven to a large extent by the need to improve biological specificity in diagnosis and therapy through precise spatiotemporal control over agent delivery.

The un-crosslinked micelles may disassemble under extreme conditions, resulting in the early release of encapsulated drugs, which can limit their application in certain conditions. Through creative introduction of trimethoxysilyl (TMS) groups to the side chain of PEA, we achieved the preparation of self-crosslinked micelles (Fig. 13a) [101,120]. Amphiphilic TMS-gPEA copolymers self-assemble in water to form hybrid core-shell nanoparticles, with the hydrophobic PPG and TMS forming the core and the hydrophilic L100 as the shell. The hydrophobic core can be further crosslinked through hydrolysis and condensation of the TMS moieties. Due to the existence of amino groups in TMS-gPEAs, there is no need to add additional catalysts to promote hydrolysis of the TMS moieties. The morphology of obtained hybrid nanoparticles remained intact even in organic solvents such as tetrahydrofuran (THF). The sizes of the nanoparticles were approximately 20 nm with low polydispersity index (PDIs). Interestingly, hybrid nanoparticles of TMS-gPEA possessed a great talent in recognizing of guest molecules by virtue of its multi-responsive nature to temperature, pH and ionic strength. As shown in Fig. 13a, when Rose Bengal (RB) and Rhodamine 6G (R6G) were both dissolved in the aqueous phase in the presence of TMS-gPEA nanoparticles, only the RB transferred to the toluene phase with high efficiency while R6G was left in the aqueous phase after heating. The proposed mechanism for separation is illustrated in Fig. 13a(2). The PEA nanoparticles could precipitate from water or transfer to the toluene phase at temperatures higher than the CP due to their thermal responsiveness. RB

encapsulated by the TMS-gPEA nanoparticles could be transferred to toluene phase, while R6G remained behind in the aqueous layer. This smart separation ability was also evaluated for several other dyes and similar phenomena were observed. These results indicated that the TMS-gPEA nanoparticles possessed the unique ability to selectively encapsulate dyes in water.

PEA assemblies can even recognize and separate guest molecules of similar structure [100,101,121]. hPEA microgels were added to mixed solutions of fluorescent dyes having similar structures (Fig. 13b: Fluorescein(FR)/RB, Fig. 13c: Calcein(Cal)/Erythrosin B(ETB)). It could be seen with the naked eye that most of the RB precipitated along with the hPEA-mGel (hPEA microgel) after heating and centrifugation; the supernatant was yellow, which is the typical colour of FR (Fig. 13b). A similar phenomenon was found for the Cal/ETB mixture. These experiments proved that the hPEA-mGels exhibit strong interactions with ETB and RB, but weak interactions with FR and Cal, even if their respective structures are very similar. To quantify the host-guest interaction between PEA and the dyes, we defined the “distribution coefficient” (*K*) [101] for partitioning of dyes between hPEA nanoparticles and water, as shown in Eq. (1):

$$K = \frac{[\text{Dye}]_{\text{NP}}}{[\text{Dye}]_{\text{aq}}} = 100 \times \frac{[\text{Dye}]_0}{[\text{Dye}]_{\text{aq}}} - 99 \quad (1)$$

where $[\text{Dye}]_{\text{NP}}$ is the molar concentration of dye in the PEA nanoparticle, and $[\text{Dye}]_{\text{aq}}$ is the molar concentration of dye in the aqueous phase. *K* values can be calculated for different dyes via UV-vis spectra; several of these *K* values are summarized in the Ref. [101]. It is easily understood that *K* can reflect the strength of host-guest interactions between PEA nanoparticle and dyes, with a large value of *K* implying a strong host-guest interaction, and a low

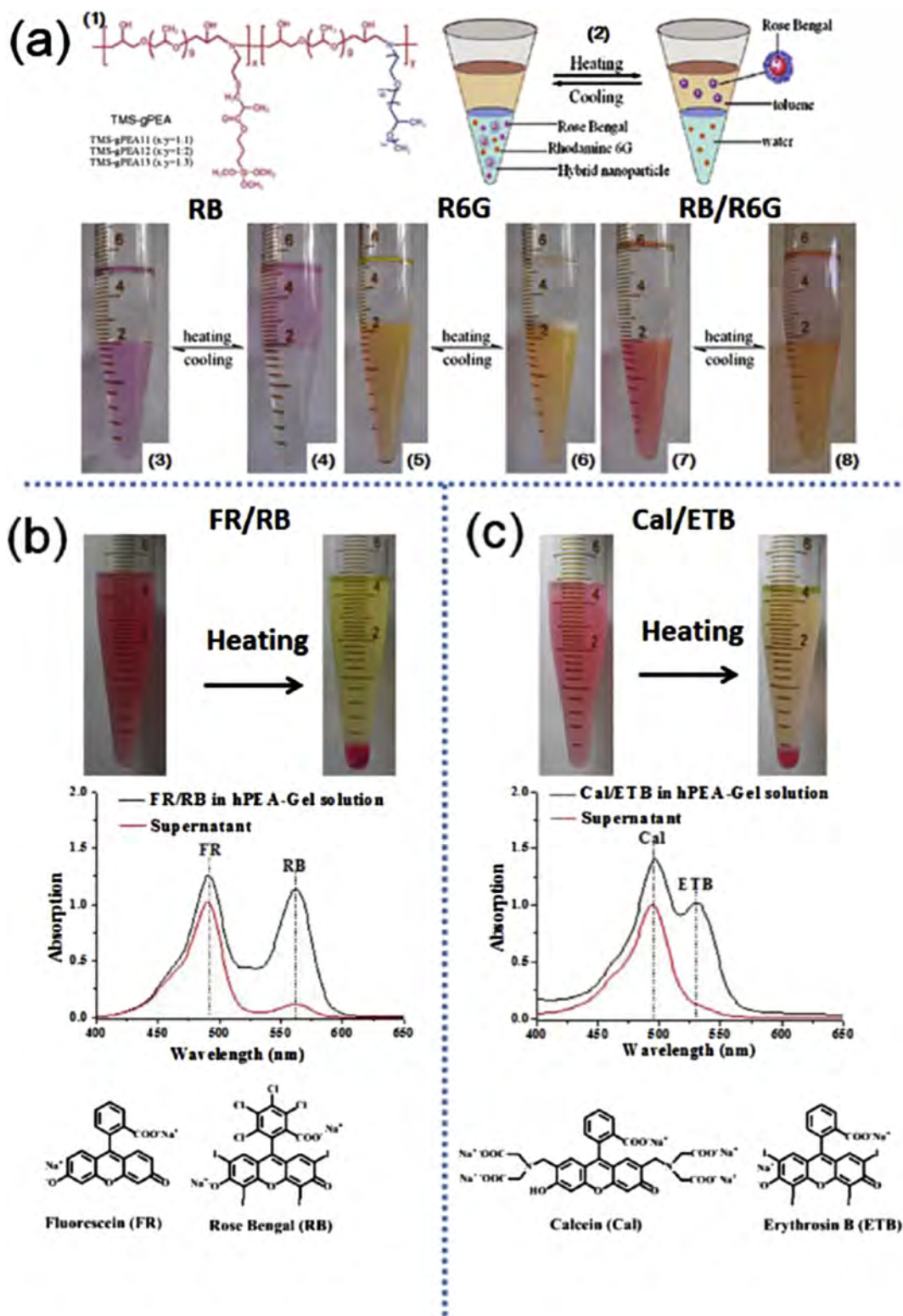


Fig. 13. (a) Chemical structure (1), scheme (2) and photographs of the dye transferring between toluene and water phases at low temperature ((3) (5) (7)) and at high temperature ((4) (6) (8)). Reprinted with permission from Ref. [120] Copyright 2010 American Chemical Society. (b) and (c) Photograph and UV-vis spectrum for separation of dyes having similar structures. Reproduced from Ref. [100] with permission from The Royal Society of Chemistry.

value of K representing a low affinity between the PEA nanoparticles and the dye. Furthermore, based on the K values obtained, the concentration of dye in the supernatant after heating and centrifugation can be calculated [101]. The heating and

centrifugation times necessary to obtain a desired purity of the dyes can then be predicted.

Compared with other crosslinking methods, photocrosslinking possesses the advantage of ease of control. Taking advantage of the

photodimerisation behaviour of coumarins (MC), coumarin-containing PEA (PEA-MC) assemblies could be photocrosslinked [86,99]. After dispersion in water, PEA-MC can self-assemble into nanoparticles with coumarin molecules located in the core. The morphology of the obtained nanoparticles was maintained even in organic solvents after crosslinking via UV irradiation. After heating above the CP, the nanoparticles aggregated to form a unique plum pudding-like microparticle structure. The obtained microparticles can be further photo-crosslinked via the reaction of residual coumarin molecules.

Anthracene (AN), another photodimerizable moiety that is widely studied, also possesses strong fluorescence behaviour. We reported a series of anthracene-containing amphiphilic hyperbranched poly(ether amine)s (hPEA-ANs), which was synthesized by introducing anthracene moieties into the periphery of hPEA through a nucleophilic addition/ring-opening reaction between the epoxy and amino groups [52]. Amphiphilic hPEA-AN could self-assemble into polymer particles in aqueous solution, wherein the hydrophobic anthracene moieties and PPG chains formed the core and the hydrophilic PEG chains formed the shell. The core of the obtained hPEA-AN particles was further crosslinked through photodimerisation of the anthracene moieties, while residual unreacted anthracene moieties rendered the core crosslinked hPEA-AN particles fluorescent. The size of assemblies, as well as the fluorescence intensity, decreased with the increasing temperature and pH. These phenomena can be ascribed to the fluorescence of anthracene being quenched by tertiary amine groups, and the fluorescence quenching effect being weakened when the amino groups are protonated or restricted. Another interesting phenomenon observed was the decrease in the fluorescence emission intensity of the particles in response to loading of Methyl Orange (MO). The quenching of fluorescence may be attributed to FRET between the dye molecules. Such phenomena can be utilized to trace the release of guest molecules.

The photoresponsive behaviour of assemblies have also been enthusiastically studied. Azobenzene is a suitable photo responsive molecule which can influence the polarity within a polymer upon light irradiation in a reversible manner [22,23]. For this reason, the azobenzene plays an important role in light-responsive polymers [54,122,123]. Through introduction of azobenzene groups into the periphery of hyperbranched poly(ether amine)s, amphiphilic azobenzene-containing hPEA (hPEA-AZOs) was obtained by our group [50]. The residual amines in the periphery of hPEA were easily modified with epoxy-functionalized azobenzenes via click chemistry. hPEA-AZOs could be directly dispersed in water to form photoresponsive polymer nanoparticles (Fig. 14). Because the isomerization of azobenzene is accompanied by a change in the dipole moment of the molecule, the CP of the hPEA-AZO nanoparticles changed upon irradiation with UV light. The polarity change may strongly influence the amphiphilicity and the CP of the assemblies, which affects their final properties [124]. However, unlike single molecules of AZO in water, the CP decreased after irradiation using 365 nm light. Usually, the *cis*-form of azobenzene is much more polar than the *trans*-form, resulting in a higher hydrophilicity and CP. However, the CP of hPEA-AZO nanoparticles decreased by more than 5 °C after irradiation. This may be ascribed to the fact that hPEA-AZOs are dispersed as nanoparticles instead of as single polymer chains in water. Accordingly, light-induced aggregation of hPEA-AZO nanoparticles was also feasible within the temperature range between the CP-*cis* (*cis*-form, after UV irradiation) and CP-*trans* (*trans*-form, before irradiation). As shown in Fig. 15, transparent hPEA-AZO solution turned turbid after 300 s of irradiation.

The co-assembly of amphiphilic polymers and inorganic components has also been widely used to fabricate hybrid materials

which combine the unique physical properties of inorganic components with the excellent processability of polymers. By changing the feed ratio or the co-assembly method, the morphology of co-assemblies and the location of inorganic components within a polymer matrix can be easily tuned [125–127]. Generally, the interaction between two components plays an important role in co-assembly. Motivated by the strong π – π conjugation of AN moieties, we fabricated core–shell microspheres (CSM) through the co-assembly of amphiphilic hPEA-AN and POSS-AN (Fig. 15a) [128]. POSS-AN was synthesized by introducing eight anthracene groups to the periphery of octa-amino POSS. The obtained assemblies were found to have a core–shell structure with low PDI (Fig. 15b), wherein hPEA-AN comprised the hydrophilic shell and POSS-AN formed the core. The size of the obtained CSMs was uniform and could be tuned from 616 to 930 nm by increasing the feed ratio of hPEA-AN and POSS-AN.

Further studies [129] have shown that AN-POSS can be dispersed in polymer matrix of hPEA-AN on the molecular scale, although the obtained core–shell microspheres (CSMs) exhibited a microphase-separated structure. In other words, the CSMs are thermodynamically unstable and can transfer to a homogenous structure under certain conditions. Thus, we made the assumption that, upon thermal annealing at a temperature higher than the melting point of POSS-AN, the microphase-separated core–shell structure may spontaneously undergo a transition to a more stable homogeneous structure with a change of distribution of POSS NPs (Fig. 15c). After heating above the melting point of POSS-AN, migration began. The migration is a typical heat-induced diffusion, and can be verified by TEM (Fig. 15d) and simulated by both Fick's law and DPD. Furthermore, the existence of AN can allow the assemblies to crosslink, thus locking in the transition state during the annealing process and preventing disassembly in organic solvents. Thus, control over the distribution of the hybrid content in the assemblies was successfully achieved in this manner. Generally, for a phase-separated system with two compatible components, this process can be used to fabricate hybrid materials with controlled location of nanoparticles in micro-assemblies, including that of core–shell spheres and other heterogeneous structures that are kinetically trapped. The location of nanoparticles within hybrid assemblies greatly affects their properties. This concept for the dynamical control of nanoparticle location by diffusion can provide new guidelines for the design and preparation of hybrid co-assemblies with desired functions and properties.

Polymer vesicles have attracted increased attention because of their low permeability, superior stability and toughness, in addition to the numerous possibilities for tailoring physical, chemical and biological properties [9]. Fortunately, polymeric vesicles can be obtained by dispersing CSMs into a hydrofluoric acid (HF)/THF solution. After treatment with HF, the hydrophobic POSS core was removed and polymeric hollow microspheres (PHMs) were obtained (Fig. 15b). The PHMs were responsive to temperature and pH, and could be used to capture and controlled release of model molecules.

Co-assembly of amphiphilic polymers and inorganic components is also an effective way to produce vesicles (Fig. 16) [130]. Amphiphilic acrylated graft poly(ether amine) and octamercaptopropyl polyhedral oligomeric silsesquioxane (POSS-SH) were chosen as the building blocks to fabricate the hybrid vesicles. After co-assembly in water, the vesicles were crosslinked through effective thiol-ene click reactions. The obtained hybrid vesicles were responsive to temperature, and could be used to control the dispersion of both hydrophilic and hydrophobic dyes in water (Fig. 16e).

In addition to responsive behaviour, the uniform structure, large amount of amino groups, and well dispersibility of amine-

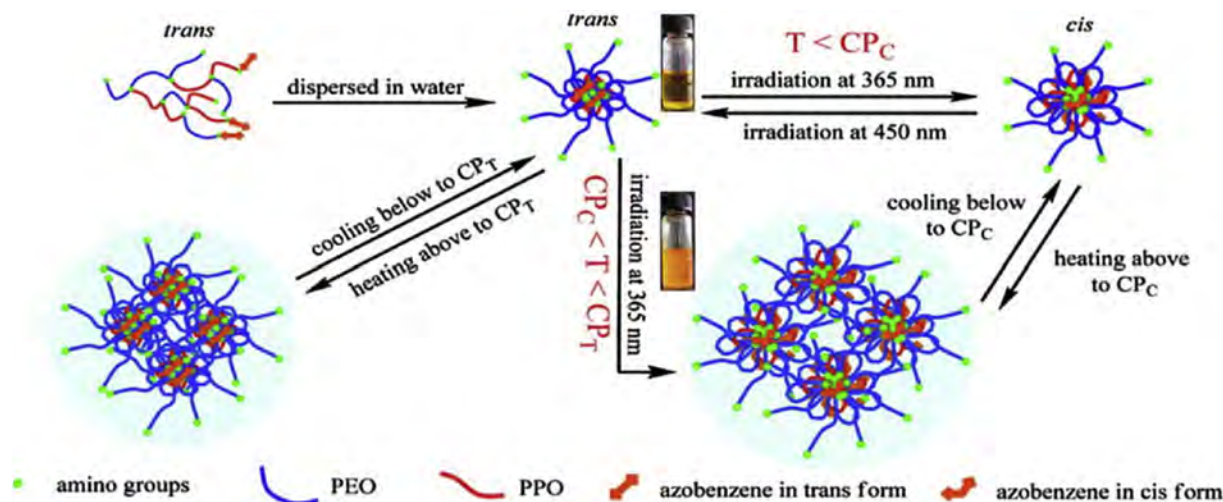


Fig. 14. Mechanism of the light response of hPEA211-AZO in aqueous solution. Reprinted with permission from Ref. [50] Copyright 2010 American Chemical Society.

containing polyether makes them ideal templates for inorganic materials. Nakashima and co-workers developed an effective way to synthesize porous hollow nanospheres using soft templates of polymeric micelles formed by an amine-containing polyether [131,132]. As shown in Fig. 17, the asymmetric ABC tri-block polymer poly(styrene-*b*-[3-(methacryloylamino)propyl] trimethylammoniumchloride-*b*-ethylene oxide) (PS-PMAPTAC-PEO) self-assembled in water to form core-shell-corona micelles. The hydrophobic PS segment formed the core and the hydrophilic PEO segment formed the corona, while the amine-containing block formed the shell. The existence of a large amount of amines in the shell makes these particles an ideal template for producing inorganic materials. The cationic shell attracted the anionic precursors tetramethoxysilane (TMOS), WO_4^{2-} and MoO_4^{2-} effectively through electrostatic interaction while the PS core and PEO corona cannot. After calcination at 500 °C for 4 h in air, the polymeric template was removed. TEM images of the resulting material confirmed the formation of highly uniform hollow particles. Such nanometer-sized hollow capsules constitute an important class of materials that are employed in diverse technological applications, ranging from drug delivery systems to lightweight composite materials.

3.2. 1-D smart assemblies

High dimensional smart assemblies such as 1-D or 2-D assemblies have attracted much attention for their unique size-dependent electronic and optical properties. Usually, it is not easy to prepare high dimensional smart assemblies due to the difficulty of restricting assembly in one or two dimensions. Crystallization-driven assembly is an effective way to prepare high dimensional smart assemblies.

1D nanostructures of fullerene can be prepared by solvent evaporation [133] and liquid-liquid interfacial precipitation (LLIP) [134]. The poor solubility and instability of C_{60} nanostructures, however, limit their applications, especially in aqueous solutions. To obtain water-soluble nanostructures containing C_{60} , much effort has been focused on modifying C_{60} derivatives with hydrophilic groups or polymeric chains. We demonstrated a simple and robust way to fabricate photocrosslinked supramolecular nanorods based on the co-assembly of two components: hPEA-AN and pristine C_{60} [135]. The whole process can be divided into two steps: formation of 1-D fullerene nanorods covered with single layer of hPEA-AN, and assembly of aforementioned nanorods and hPEA-AN

(Fig. 18e). Fullerene and AN can undergo dynamic π - π interactions, thus the introduction of hPEA-AN will not restrict the formation of the fullerene nanorods. After crosslinking of the AN moiety, amphiphilic nanorods were finally obtained (Fig. 18a-c). The diameter of the nanorods can be tuned from 50 to 90 nm by simply increasing the C_{60} content. It should be highlighted that besides the common temperature-induced aggregation of assemblies, the 1-D assemblies exhibited interesting temperature-enhanced fluorescence (Fig. 18d). Further study based on quantum yield and lifetime measurements indicate that the fluorescence lifetime of the assemblies becomes shorter at higher temperatures, while the fluorescent quantum yield increased with increasing temperature. The abnormal temperature-dependent fluorescence behaviour can be explained as follows: the charge transfer complex (CTC) of AN and fullerene tends to decompose at higher temperature, resulting in an increased number of excited AN. As a result, the fluorescence was enhanced in response to increasing temperature. Such properties make these materials useful for potential applications as fluorescence probes and sensors.

Another interesting example deserves to be mentioned here is an amine-containing polythioether. The thiol-ene click chemistry used here has proven to be an extremely effective and versatile approach for functionalization of allyl groups [83]. Zhou et al. developed a novel alternating copolymer through the click reaction of a dithiol and di-epoxide. This strategy provided an effective way to introduce functional groups (e.g., amine groups, carboxyl groups or peptides) into the nanotubes resulting from the self-assembly of the obtained amphiphilic alternating copolymers [46]. The amphiphilic polymer poly(2,3-dihydroxy butylene-*alt*-butylene dithioether) (P(DHB-*a*-BDT) could self-assemble into straight nanotubes (Fig. 19a, b). The diameters of the tubes were approximately 25–35 nm, with a 1.2 nm periodic layer, according to both XRD and AFM analyses. Differential scanning calorimetry (DSC) data suggested that a crystalline structure exists in the as-prepared nanotubes with a melting point of 52.3 °C, which can be attributed to the highly ordered packing of alkyl chains in the nanotubes. Functionalized nanotubes could also be prepared through self-assembly of functionalized derivatives via the introduction of carboxyl groups, amine groups, or peptides onto the copolymers using click copolymerization (Fig. 19c-f). Overall, the chemistry provides a facile method to construct well-defined nanostructures with tunable surface functionalities.

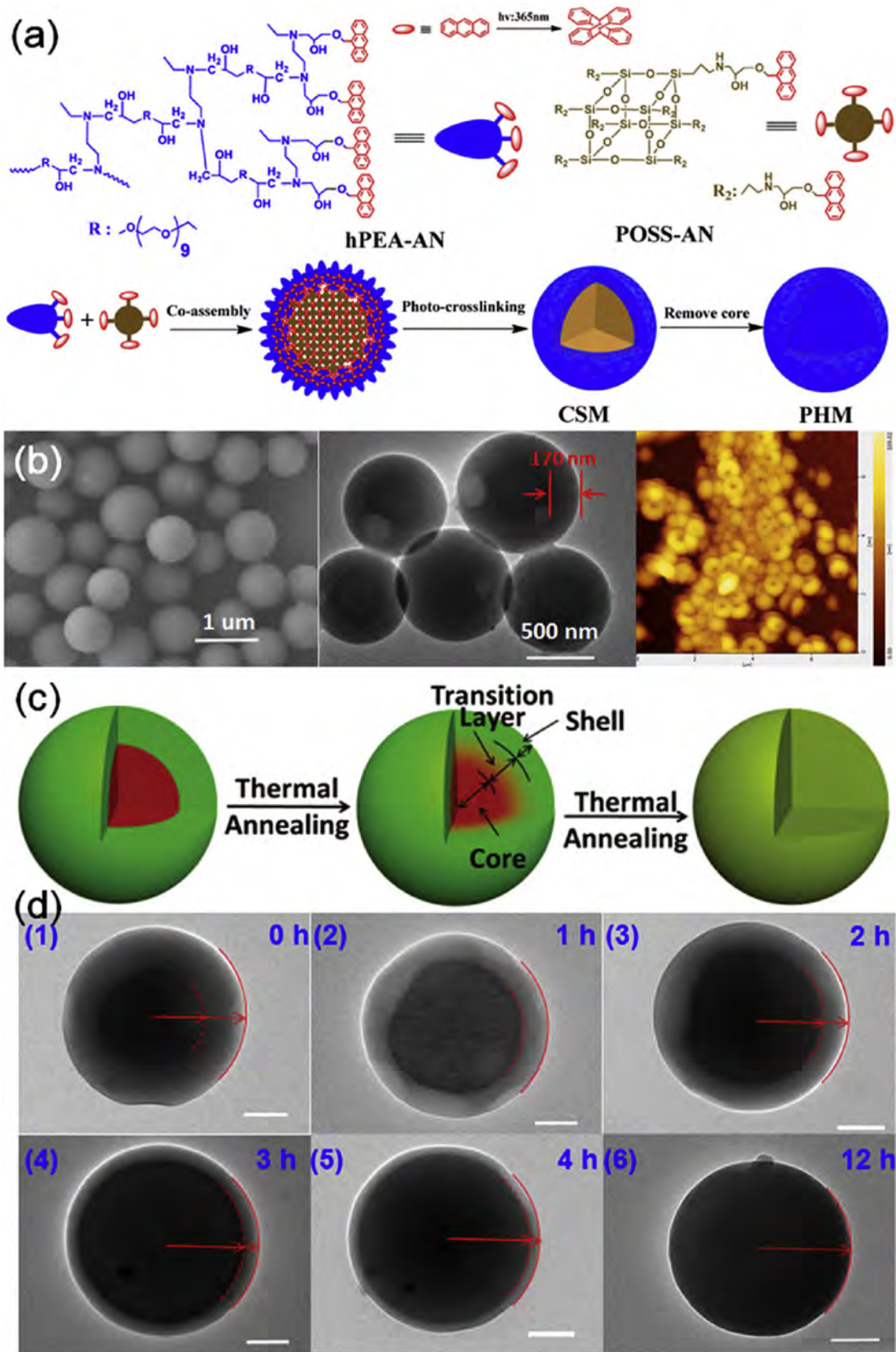


Fig. 15. (a) Scheme for co-assembly of hPEA-AN and POSS-AN; (b) typical morphologies of the obtained CSMs and PHMs; (c) scheme for the thermal annealing of CSMs; (d) TEM tracing of thermal annealing. (a) and (b) were reprinted with permission from Ref. [128] Copyright 2013 American Chemical Society. (c) and (d) were reproduced from Ref. [129] with permission of The Royal Society of Chemistry.

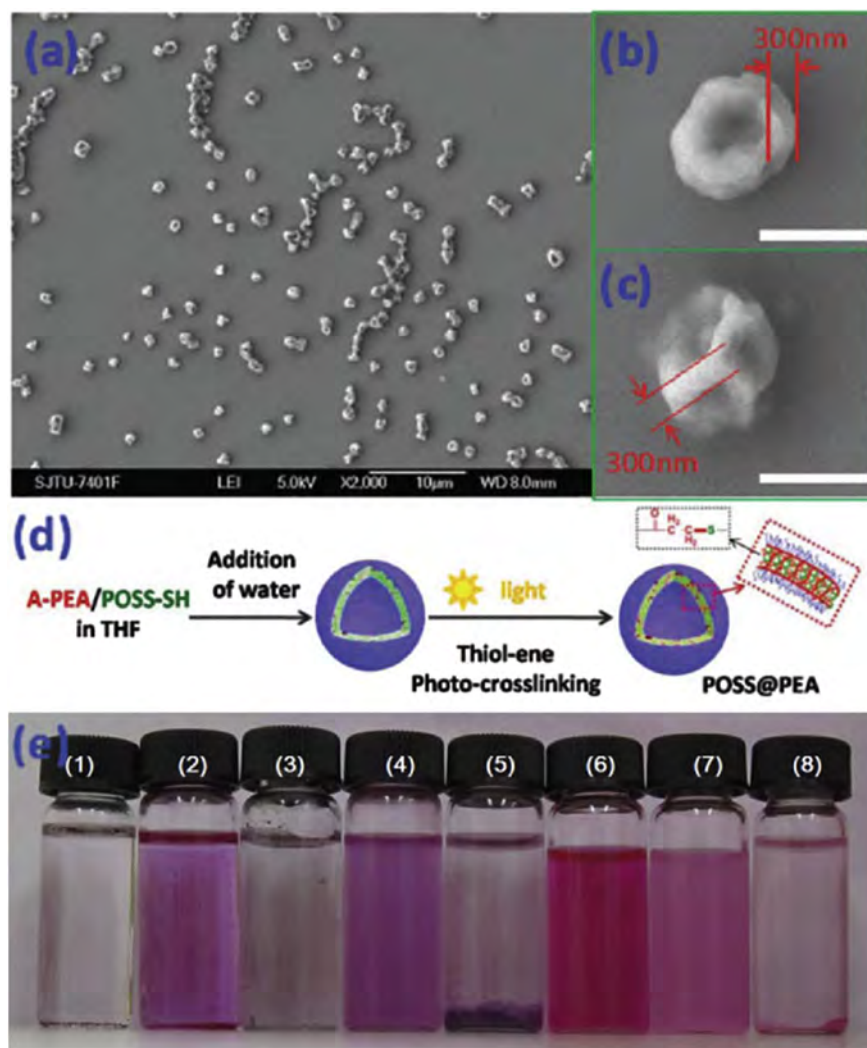


Fig. 16. (a)–(c) SEM image of the obtained vesicles; (d) scheme for the co-assembly of A-PEA and POSS-SH and its morphology; (e) photograph showing encapsulation of dyes: RB in toluene before (1), and after (2) addition of vesicles at room temperature; NR in water before (3), after (4) addition of vesicles at room temperature, and (5) heating to high temperature (75 °C); hydrophilic RB in water before (6), after (7) addition of vesicles at room temperature, and (8) heating to high temperature (75 °C). Reproduced from Ref. [130] with permission of The Royal Society of Chemistry.

3.3. 2-D smart assemblies

2D nanosheets are also of great interest for their excellent optical, electrical, and magnetic properties [136–138]. As a result, development of efficient and universal methods to prepare nanosheets with a large length-to-thickness ratio remains an urgent challenge. We introduced hydrophobic heptaisobutyl polyhedral oligomeric silsesquioxane (POSS) groups into the periphery of hydrophilic hPEA, and the resulting polymer can self-assemble into square-shaped hybrid nanosheets in water (Fig. 21) [102]. TEM and AFM images revealed that the average edge length and thickness of the hybrid nanosheets was $1.2 \pm 0.2 \mu\text{m}$ and $4.5 \pm 0.5 \text{ nm}$, respectively. The crystallization of POSS moieties plays an important role in the formation of the nanosheets, and crosslinking through dimerization of the anthracene moieties in the middle layer of the nanosheets makes the nanosheets more stable. The formation mechanism of the nanosheets is shown in Fig. 20. As water is added to a dioxane solution of HP1, the solvent becomes progressively poorer for the POSS and AN moieties. When the water content reaches a critical value, two HP1 molecules might assemble together by crystallization-driven aggregation of POSS as a result of

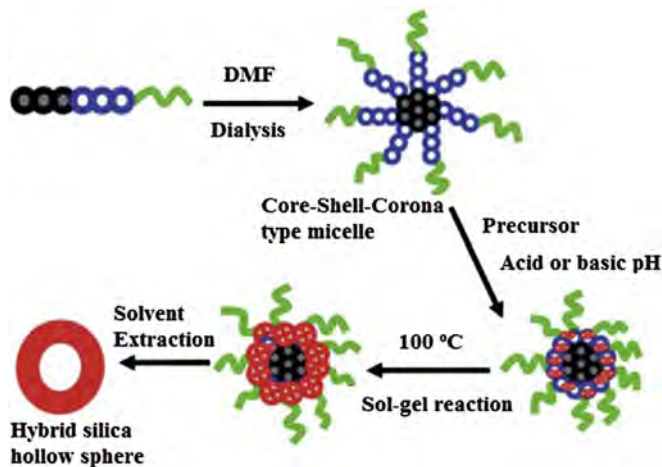


Fig. 17. Synthetic scheme for the preparation of inorganic hollow spheres using amine-containing polyethers. Reproduced from Ref. [131] with permission of The Royal Society of Chemistry.

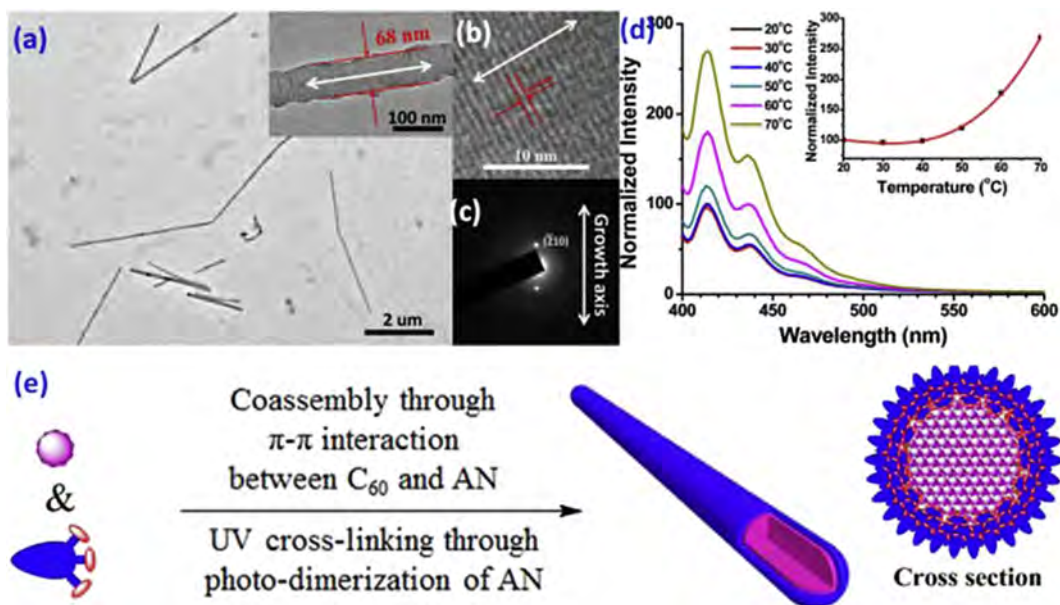


Fig. 18. (a)–(c) Typical morphology of obtained 1-D assemblies. (d) Fluorescence spectra of the abnormal temperature-enhanced fluorescence; (e) scheme for the co-assembly of hPEA-AN and C_{60} . Reprinted with permission from Ref. [135] Copyright 2013 American Chemical Society.

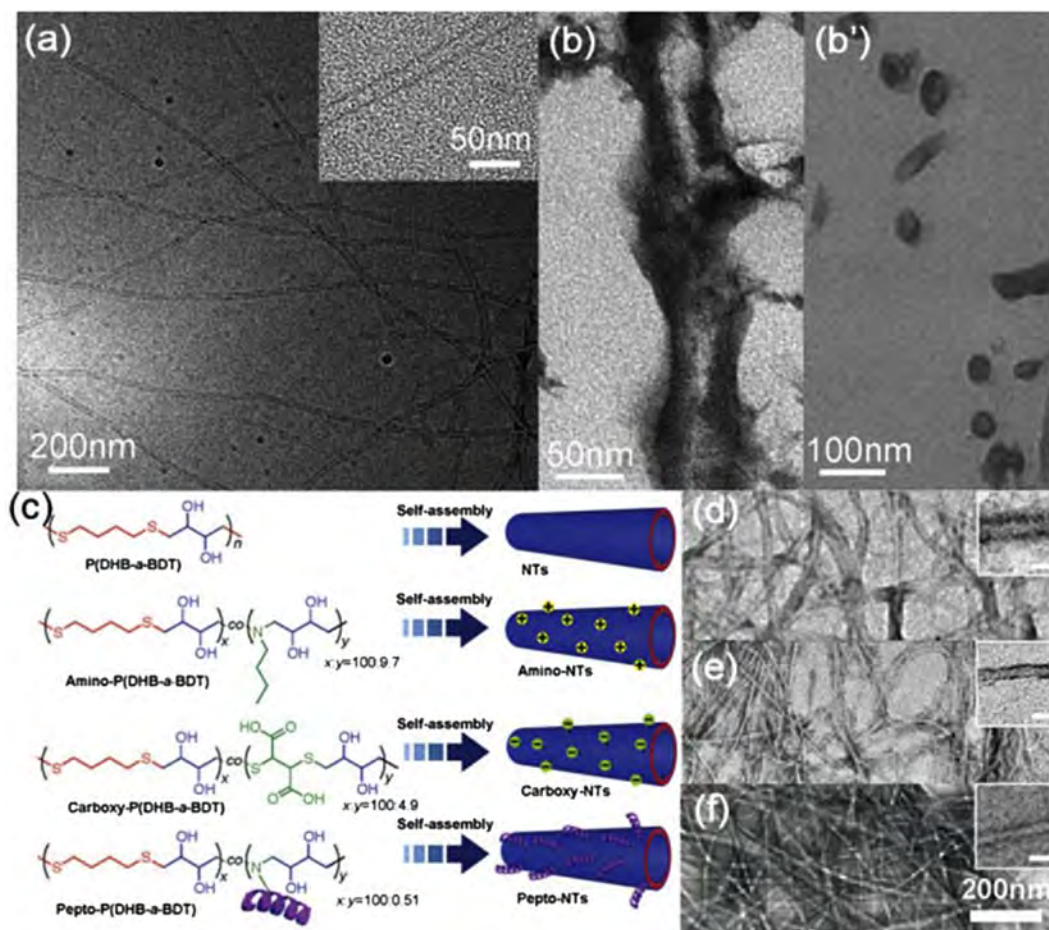


Fig. 19. (a) Typical morphology of P(DHB-a-BDT) nanotubes, (b) cross section of P(DHB-a-BDT) nanotubes, and (c) scheme for self-assembly of P(DHB-a-BDT) and its derivatives; (d),(e),(f), representative TEM imaging of amine-NTs, carboxyl-NTs, and pepto-NTs, respectively. Reproduce with permission from Ref. [46] Copyright 2015 John Wiley & Sons.

the lower solubility of the POSS moieties in water compared with the hydrophilic hPEA chains. Meanwhile, hPEA chains are extended

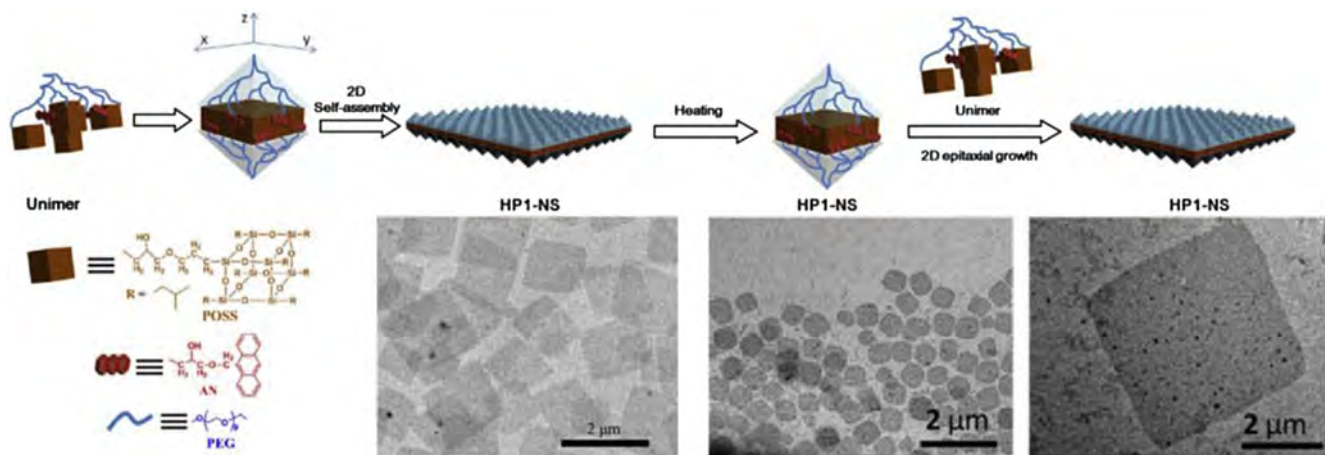


Fig. 20. Scheme for the preparation of polymeric nanosheets and its 2D epitaxial living growth behaviour. Adapted with permission from Ref. [102]. Copyright 2012 American Chemical Society. Adapted with permission from Ref. [139]. Copyright 2014 American Chemical Society.

to the opposite side in the *z*-axis direction, and “dual pyramid”-like structures could be formed. As the end of the hydrophilic hPEA in HP1 is fixed by the aggregation of POSS, the movement of the PEG chains is also restricted and cannot fully cover the hydrophobic POSS aggregations from all directions. Consequently, the hydrophobic area of POSS and AN exposed at the middle of the “dual pyramid”-like structure can lead to further aggregation along the *x*-axis and *y*-axis directions through the crystallization-driven aggregation of POSS and π - π stacking aggregation of AN, resulting in the formation of nanosheets. The nanosheets are composed of three layers like a sandwich; the hydrophobic POSS and AN moieties form the hydrophobic inner layer of the nanosheets, while the hydrophilic hPEA forms the outer layer that is in contact with the water. Several different functional groups such as anthracene, pyrene, naphthalene, and ferrocene can be introduced into the obtained nanosheets by self-assembly of the corresponding POSS-capped hPEA. The obtained hybrid nanosheets exhibited responses to multiple stimuli such as temperature and pH. The fluorescence of the hybrid nanosheets decreased with increasing temperature and pH. This work successfully incorporated functionality into the 2D structures. The ability to spatially isolate functionality in 2D is a very attractive target.

As hPEA nanosheets are formed through the crystallization of POSS moieties, we also prepared nanosheets using POSS-capped hPEA by adding water as a selective solvent to a unimer solution in 1,4-dioxane (Fig. 20). These nanosheets are formed by living crystallization-driven 2D self-assembly of the POSS capped hPEAs [139]. As a result, these nanosheets could be fragmented after melting of the POSS moieties upon heating, and regenerated after the recrystallization of the POSS moieties. Using fragments of the nanosheets as seeds for further growth, 2D nanosheets with a low polydispersity and a tunable edge length of 0.5–4.5 μm could be formed, with the size of the obtained nanosheets being dependent on the unimer-to-seed ratio. Also shown in Fig. 20, square nanosheets with tunable sizes were progressively formed by crystallization-driven aggregation of HP1 molecules from the *x*-axis and *y*-axis directions when the HP1 unimers in the solution attached to and epitaxially grew on the active POSS moieties in the middle-layer of the HP1 seeds. Meanwhile, mixed functionality nanosheets could also be prepared through the random co-crystallization of hPEA capped with POSS bearing different functional groups (e.g., anthracene and ferrocene). The 2D self-assembly of POSS-capped hPEA provides a new method to fabricate polymer nanosheets with tunable size and functionality.

Due to the presence of amine groups, hPEA nanosheets can act as a platform for metal nanoparticles [103,140]. These POSS-capped hPEA nanosheets decorated with metal nanoparticles are also responsive to temperature, pH, and ionic strength. Metal nanoparticles can be aggregated with the nanosheets at higher temperature, pH, or ionic strength. POSS-capped hPEA nanosheets also possess the ability to transfer reversibly between water and toluene when these parameters are altered. Gold nanoparticles can be reversibly transferred to the toluene phase with the POSS-capped hPEA nanosheets at higher temperature, pH, or ionic strength. The ultra-thin thickness of hPEA-NSs might decrease the attachment energy when they cross the oil–water interface, leading to the reversible phase transfer.

hPEA nanosheets can also be used as templates to prepare inorganic nanosheets (Fig. 21) [140]. The obtained nanosheets possess a large aspect ratio with an average edge length of 1–2 μm and thickness of ~ 40 nm. Various metal nanoparticles such as gold, silver, and platinum could further be embedded into these nanosheets using the hPEA nanosheets decorated with the corresponding nanoparticles as templates. These nanosheets possess a sandwich-like structure, which is comprised of amorphous SiO_2 as the inner layer, and anatase TiO_2 as the outer layer. The obtained nanosheets were mesoporous with a high surface area (~ 429 m^2 g^{-1}), and the SiO_2 inner layer could be removed by chemical etching with NaOH solution to obtain anatase TiO_2 nanosheet-like boxes embedded with gold nanoparticles (AuNPs). The photodegradation of Methyl Orange (MO) by the obtained nanosheets could be enhanced by embedding AuNPs, owing to the localized surface plasmon resonance (LSPR) effect of the AuNPs. The preparation of a silica/titania mesoporous nanosheets using hPEA-NS as the template should provide a convenient and general method to produce various square-shaped inorganic mesoporous nanosheets.

4. Conclusion and outlook

The combination of amines and polyethers endows the assemblies of amine-containing polyethers with the “smart” abilities of stealth properties, multi-responsiveness, and ease of functionalization. The PEG content endows the smart assemblies with excellent biocompatibility and temperature responsive behaviour, while the amine content provides the pH responsive behaviour. Furthermore, the amine groups can be further modified to obtain desired functionalities and properties.

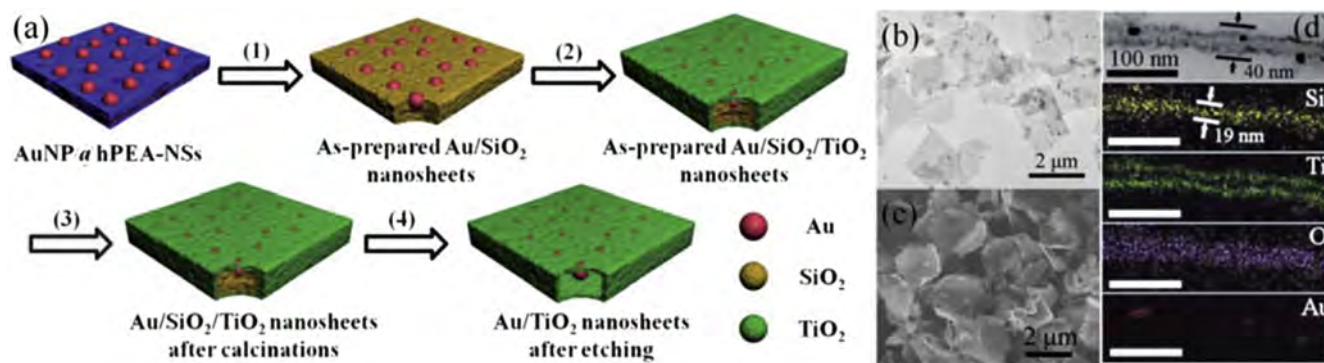


Fig. 21. (a) The strategy for preparing inorganic nanosheets using hPEA nanosheets as a template. (b) Typical morphology of Au/SiO₂ nanosheets; (c) Typical morphology of Au/SiO₂/TiO₂ nanosheets; (d) TEM images and EDS mapping of a section of a Au/SiO₂/TiO₂ nanosheet. Reproduced from Ref. [140] with permission of The Royal Society of Chemistry.

As one type of amine-containing polyether, the PEAs are synthesized via the robust click reactions of di-epoxy and amines. The structures and properties of PEAs can be tuned by using different di-epoxy and amines. The obtained PEAs can be further functionalized with epoxy-containing functional monomers or carboxyl-containing functional monomers, making these materials preferable for fabricating smart assemblies. Smart assemblies with 0-D, 1-D, and 2-D morphologies have already been prepared via the assembly of functionalized PEAs. The obtained assemblies are responsive to external stimuli such as temperature, pH, light, and more. The as-prepared PEA assemblies also exhibit intelligence in recognition and separation of guest molecules even with similar structures. It is also worth noting that 2-D polymeric nanosheets with living growth characteristics and tunable sizes, which are rarely reported, can be prepared using PEA-based polymers.

Smart assemblies hold promise for fabrication of functional materials with tailored structures and functionalities. However, the building blocks for fabricating smart assemblies remains an outstanding challenge. Amine-containing polyethers, which take advantage of the excellent biocompatibility and temperature responsive behaviour of PEG with the pH responsive behaviour and ease of functionality of amines, could pave way for the widespread application of smart assemblies.

Acknowledgements

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