*Pure Appl. Chem.*, Vol. 74, No. 11, pp. 2021–2030, 2002.


# Hierarchical transfer of stereochemical information in synthetic macromolecules*

Jeroen J. L. M. Cornelissen

*Department of Organic Chemistry, NSRIM Institute, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, Netherlands*

*Abstract*: In Nature, a wide variety of complex tasks (e.g., catalysis, transport, and information storage) is performed by biomacromolecules with precise composition, dimensions, and architecture. To achieve the precise organization required for efficient function, structural information is built into the smallest building blocks of biomacromolecules (i.e., amino and nucleic acids) and subsequently transferred in a hierarchical fashion to form larger quaternary structures. These construction principles have been an inspiration for synthetic and supramolecular chemists alike, and a number of synthetic biomimetic helical macromolecules have been reported in the recent literature. Here, some recent developments in the field of helical polyisocyanides will be reviewed in combination with new prospects on the self-organization of protein/polymer hybrid architectures.

## INTRODUCTION

Since van 't Hoff and Le Bel independently proposed the concept of the tetrahedral carbon atom [1], stereochemistry has been a key element in not only the chemical disciplines, but also the related areas of biology, physics, and materials science. On the molecular level, stereochemistry provides one of the main parameters by which we understand the properties of a substance and the way information is transferred in biomacromolecules and other biological systems essential in life [2].

In spite of its great importance, stereochemistry in synthetic polymeric materials remained an unexplored area until the development of the Ziegler catalysts and the pioneering work of Natta [3] and Pino [4] on stereoregularity and optical activity in polyolefins. These ground-breaking studies initiated the work on optically active helical polymers, resulting in a variety of examples (e.g., polyisocyanides [5,6], polyisocyanates [7], and bulky polymethacrylate esters [8,9]). More recently, this field has been extended with studies on (the folding of) well-defined oligomeric compounds, refered to as foldamers, designed to mimic the hierarchical structures of natural proteins [10]. In general, these investigations on synthetic helical polymers have shown the versatility of these kinds of systems and the analogy they display with (the formation of) structural motifs in proteins [6]. In synthetic macromolecules, however, examples of the hierarchical transfer of stereochemical or structural information from the monomer level to a defined polymeric architecture and subsequently to an ordered assembly of macromolecules, as seen in natural biopolymers, are very limited. A recent development is the formation of hierarchically organized structures by polymers and block copolymers from peptide-derived isocyanides. In addition, an intriguing new development is that of polymer/protein hybrid structures, which have the potential of forming highly organized architectures through processes of self-assembly and to combine this property with functions such as catalysis. An overview of both these areas will be presented here.**

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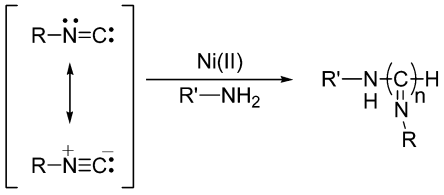
**Pure Appl. Chem.* **74**, 2021–2081 (2002). A collection of invited, peer-reviewed articles by the winners of the 2002 IUPAC Prize for Young Chemists.

**For extensive reviews on synthetic helical polymers and chiral architectures from macromolecular building blocks the reader is referred to refs. [6,9].

## POLYISOCYANIDES

Polyisocyanides have a rather well-defined $4_1$ helical conformation (i.e., 4 repeat units per helical turn) and are accessible in optically active form by a nickel-catalyzed polymerization reaction (Scheme 1). This polymerization is initiated by a nucleophile (e.g., an amine or alcohol), and during the reaction, the isocyanide monomers coordinate to the metal center and are incorporated into the growing chain by a series of consecutive insertion reactions. In this way, only a minor rearrangement of the chemical bonds is required to form the $4_1$ helical polymeric backbone.




**Scheme 1** Nickel(II)-catalyzed polymerization of isocyanides.

Previous research has shown that the $4_1$ polyisocyanide helix is only stable when sterically demanding side-chains are present [16,17]. For the majority of the polyisocyanides, the persistence length, which is a measure of the stiffness of the polymer chain, is limited (i.e., 3 nm) [18,19]. The occurrence of faults in the ideal helical backbone of these polymers not only reduces their persistence length, but also prevents the stereochemical information to be passed along the polymer chain. To guarantee the fidelity of hierarchical transfer of stereochemical information in these kinds of polymers, a new design of polyisocyanides with an increased rigidity in the polymer backbone was required.

### Polyisocyanopeptides

In the past, a number of peptide-derived isocyanides has been synthesized and polymerized (Chart 1) [11–14]. These polyisocyanopeptides have amide groups in their side-chains, which have the possibility to form intramolecular hydrogen bonds. As a result of the helical structure of polyisocyanides, side-chain *n* is more or less above side-chain (*n* + 4) with a distance suited for the formation of hydrogen bonds. Although it was already recognized by Visser and others [14] that the peptide-derived polyisocyanides had unprecedented properties, the presence of hydrogen bonds between the polymer side-chains was not recognized at that time. In more recent studies, polymers **1**, **2**, **6**, and **7** (Chart 1) have been synthesized to investigate whether hydrogen bonds between the side-chains are indeed formed and how these bonds affect the conformational properties of the polymers. Polyisocyanopeptide **10** has two amide groups per side-chain and is able to fold into a β-sheet-like architecture, mimicking the interactions present in naturally occuring β-helices [15].

Detailed infrared and $^1$H NMR spectroscopic investigations showed that virtually all amide groups present in these polymers participate in hydrogen bonding. The single-crystal X-ray structure of L-isocyanoalanyl-L-alanine methyl ester (the monomer for **1**) served as a reference in these investigations (Fig. 1). It appeared that in the dipeptide-derived polyisocyanides studied in this respect (see above), except in **7**, ordered arrays of hydrogen bonds along the polymeric backbone are present [11,15]. Analogous to the denaturation of proteins, the hydrogen bonds present in these polymers can be disrupted. This is, however, only possible with strong acids like trifluoroacetic acid and not with hydrogen-bonding solvents (e.g., methanol, DMSO), demonstrating the robust character of the hydrogen-bonding arrays. Powder X-ray diffraction experiments showed that in the solid state the rigid polyisocyanopeptides are organized in a pseudo-hexagonal arrangement. The acidified samples, which were studied for comparison, only gave broad signals pointing to a decrease in the level of organization of

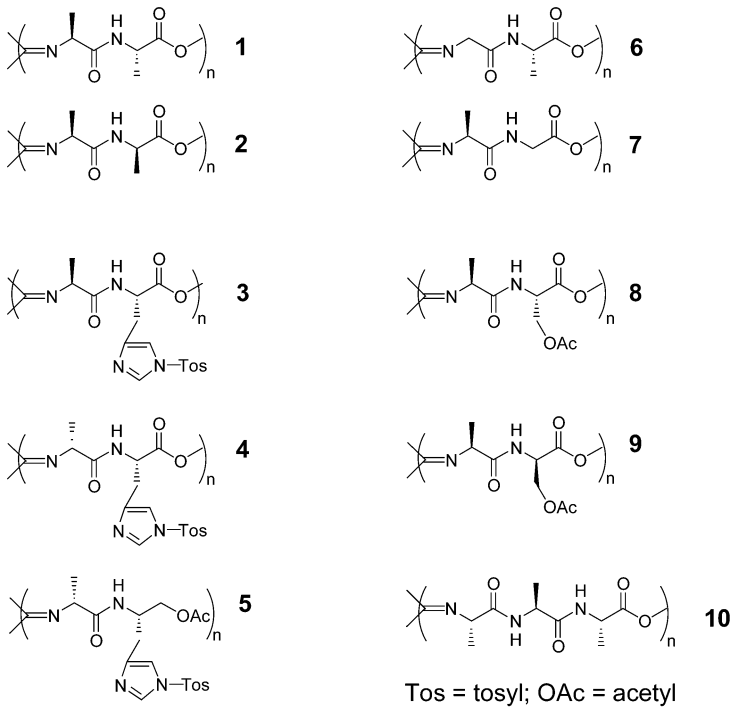



**Chart 1** Isocyanopeptide-based polymers. **1**: poly(L-isocyanoalanyl-L-alanine methyl ester) [11]; **2**: poly(L-isocyanoalanyl-D-alanine methyl ester) [11]; **3**: poly(L-isocyanoalanyl-*N*-tosyl-L-histidine methyl ester) [12]; **4**: poly(D-isocyanoalanyl-*N*-tosyl-L-histidine methyl ester) [12]; **5**: poly(L-isocyanoalanyl-*N*-tosyl-*O*-acetyl-L-histidinol) [13]; **6**: poly(isocyanoglycyl-L-alanine methyl ester) [11]; **7**: poly(L-isocyanoalanyl-glycine methyl ester) [11]; **8**: poly(L-isocyanoalanyl-*O*-acetyl-L-serine methyl ester) [14]; **9**: poly(L-isocyanoalanyl-*O*-acetyl-L-serine methyl ester); **10**: poly(L-isocyanoalanyl-L-alanyl-L-alanine methyl ester) [15].

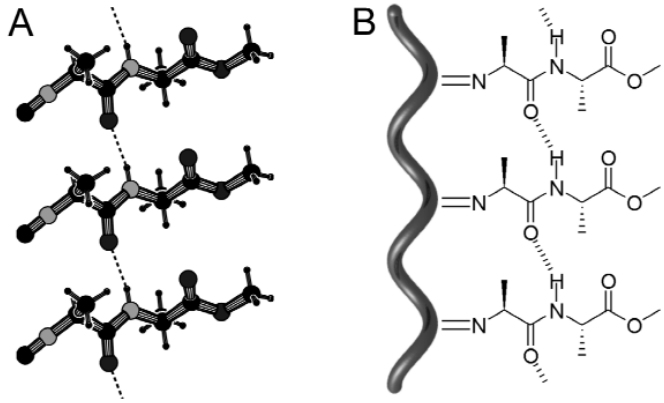



**Fig. 1** (A) Crystal structure of the monomer of **1**, showing the intermolecular hydrogen bonds between the stacked molecules. (B) Schematic representation of the hydrogen bonds between side-chains $n$ and ($n$ + 4) in polyisocyanopeptide **1**.

the polymeric molecules. The conformational properties in solution were studied by circular dichroism (CD) spectroscopy, which showed that polymers **1** and **2** are stable up to 40 °C and subsequently unfold

in a nonlinear (cooperative) process upon increasing the temperature. In the case of **6**, this process was significantly faster and started already at room temperature. The CD spectrum of polyisocyanide **7** did not display notable changes upon increasing the temperature or upon addition of acid, pointing to the absence of a secondary organization in this polymer. Based on the experimental data, it was concluded that the introduction of hydrogen-bonding units in the polyisocyanopeptide side-chains has a positive effect on the conformational properties of these macromolecules. Peptide-derived polyisocyanides in their protected form are stable in solution at room temperature, and as a result of the increased rigidity, it is possible to visualize the individual macromolecules by atomic force microscopy (AFM). Measuring the contour length of the macromolecules allowed the determination of the molecular weights and the polydispersities of the samples, which was not possible by more conventional techniques [11,20].

Relatively small changes in the side-chain configuration, as in **1** (L-Ala, L-Ala) and **2** (L-Ala, D-Ala), resulted in significant differences in the properties of the macromolecules. For **2**, a higher molecular weight and polydispersity was found than for **1** prepared under identical conditions. The former polymer also showed an increased tendency to form aggregates. A protein-like folding seems to take place during the polymerization reaction, since it has been found that polyisocyanopeptide **2** can also be prepared with the help of a small amount of acid as a catalyst, with the resulting polymers having an identical architecture to that formed using a nickel catalyst [15].

The assignment of the helix sense in peptide-derived polyisocyanides by CD spectroscopy is hampered by the overlap of signals arising from the backbone and the side-chains of the polymer. For an L-alanine-based polyisocyanide containing a spectator group (i.e., a diazo chromophore) in the side-chains, a right-handed (*P*) helical geometry was found. Since the helix sense in polyisocyanides is kinetically controlled, this handedness was tentatively assigned to all L-alanine-derived polyisocyanides [23]. Selected properties of polyisocyanodipeptides (**1**–**9**) are displayed in Table 1. When hydrogen

**Table 1** Selected properties of dipeptide-derived polyisocyanides.

| Compound | $[\alpha]^a$ | | $\Delta\varepsilon$ $(\lambda)^b$ | Screw sense | $[\eta]^c$ | $t_{pol}{}^d$ | H-bonds |
|---|---|---|---|---|---|---|---|
| | Monomer | Polymer | | | | | |
| **1**[e] | 33 | 338 | 5.6 (313) | *P* | 1.33 | <5 | Yes |
| **2**[e] | –5.6 | 487 | 5.8 (307) | *P* | 5.26 | <5 | Yes |
| **3**[f] | 164 | 580 | 6.5 (304) | *P* | 1.04 | ~240[k] | Yes |
| | | | –0.45 (345) | | | | |
| **4**[f] | 75 | –700 | 1.22 (270) | *M* | Insol.[j] | ~240[k] | No |
| **5**[f] | 14 | –610 | –5.5 (300) | *M* | 0.33 | ~240[k] | Yes/No[l] |
| **6**[e] | 19.2 | 196 | 5.1 (321) | *P* | n.d.[i] | <5 | Yes |
| **7**[e] | 5.7 | –32 | –1.5 (290) | *P* | n.d.[i] | >120 | No |
| **8**[g] | –58.1 | 205 | 8.6 (310) | *P* | 4.1 | <30 | Yes |
| | | | 0.17 (355) | | | | |
| **9**[g] | –12.0 | –33 | –1.3 (263) | *P* | 0.35 | 240 | No |
| **L-PIA**[h] | 16.7 | –280 | –0.5 (300) | *P* | 0.44 | 7200[k] | No |

[a]In °·dl/g·dm; for concentrations and solvent, see refs. cited.
[b]In l/mol·cm, maximal values at the indicated wavelength.
[c]In dl/g; for conditions, see refs. cited.
[d]In min., reaction time for complete consumption of the monomer.
[e]See ref. [11].
[f]See ref. [13].
[g]See ref. [14].
[h]Poly(L-isocyanoalanyl ethyl ester), see ref. [21].
[i]Not determined.
[j]Not measured due to low solubility.
[k]No exact reaction time was determined; after the indicated period the isocyanide was no longer detected.
[l]Hydrogen bonds are expected based on the CD data, which is, however, in contrast with the low viscosity.

bonds are proven to be present (e.g., **1**, **2**, and **6**) a positive optical rotation and a strong positive Cotton effect around $\lambda$ = 315 nm indicate the presence of a right-handed (*P*) helix. Taking the difference between polymers with and without hydrogen bonds into account, this assignment is consistent with other polyisocyanopeptides prepared in earlier studies (i.e., **3**–**5**, **8**, and **9**) in which high viscosities and short polymerization times suggest the presence of hydrogen bonds [12–14]. For the polyisocyanides where no hydrogen-bonding arrays are found, the optical rotations and the intensities in the CD spectra are significantly smaller (Table 1). All these polyisocyanides resemble the properties of poly(L-isocyanoalanyl ethyl ester) (**L-PIA**) [24]. As expected, opposite chiroptical properties are observed for the macromolecules for which a *M*-type helix is assumed, based on the use of D-alanine.

An interesting similarity is present between the mechanism by which chirality is transferred in polyisocyanopeptides and the way proteins are built up and subsequently fold in aqueous solution. To investigate whether the polyisocyanopeptides retain their structure in water, the methyl esters present in polymers **1**, **2**, and **10** were removed by base to yield water-soluble polyisocyanopeptides. Using IR and $^1$H NMR spectroscopy, it was shown that the hydrogen bonds remain intact in water for significant periods of time [22]. The conformational aspects in water were studied in detail with the help of CD spectroscopy. A helix geometry maintained by hydrogen bonds is expected to unfold in a cooperative process when the temperature is increased. For the three polymers investigated, cooperativity was indeed observed in the decrease of the intensities of the Cotton effects, both in the bands corresponding to the polymer backbone (260–400 nm) and in the amide transitions (200–260 nm). In the case of polymer **10**, the unfolding process appeared to be more complex than in the case of **1** and **2**. The two types of hydrogen-bonding arrays present in the former polymer appears to be disrupted at different temperatures [15].

## Self-organizing block copolymers

Block copolymers are known to form different types of self-assembled structures in pure form and in solution. To go up one level in the organizational hierarchy, (i.e., from the transfer of stereochemical information *within* the helical backbone of a polymer to the transfer between polymer chains), the self-organization of block copolymers containing a polyisocyanopeptide segment was studied. These types of block copolymers were synthesized by using macromolecular initiators in the Ni(II)-catalyzed polymerization reaction. Initiators consisted of amine-derived carbosilane dendrimers and amine-terminated polystyrene (Fig. 2). The block copolymers prepared from the polyisocyanopeptides and the carbosilane dendrimers were expected to display interesting properties because of the large differences in the two component blocks: the dendrimer has a convex architecture and is flexible, whereas the polyisocyanopeptide part is rod-like and rigid. These block copolymers appeared to selectively bind metal ions (**11** and **12** were specifically studied in that respect), like silver ions. These ions were complexed to the polyisocyanide segment and, as a result, aggregates were formed with dimensions ranging from hundreds of nanometers to over one micron (determined by light scattering). The formed aggregates were further investigated by electron microscopy, which showed a pattern of alternating dark and lighter stripes (Fig. 3A). It was shown that the dark stripes are rich in silver and that upon irradiation with the electron beam, nanowires of metallic silver are formed [25].

Removal of the methyl ester functionalities in block copolymers **13** and **14** resulted in chiral "superamphiphiles" consisting of a charged, helical polyisocyanopeptide head-group and a hydrophobic polystyrene tail. These superamphiphiles have properties comparable to traditional amphiphiles, but differ in size (about one order of magnitude larger). Under optimized conditions, the macromolecules of negatively charged **13b** self-assembled in aqueous solution to yield micellar rods having lengths up to several micrometers. Block copolymer **14b** displayed a similar behavior. Interestingly, in this case, it was possible to change the stiffness of the supramolecular rods by varying the type of counterion.

As with traditional surfactants, it was found that the ratio between the hydrophobic and hydrophilic segments in the macromolecules influences the aggregation behavior of the superamphiphiles.

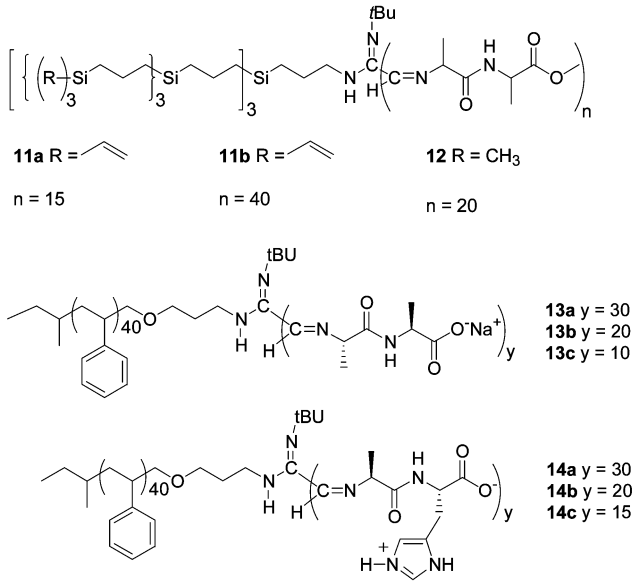



**Fig. 2** Block copolymers of isocyanopeptides and dendritic carbosilanes (**11** and **12**) and isocyanopeptides and styrene (**13** and **14**).

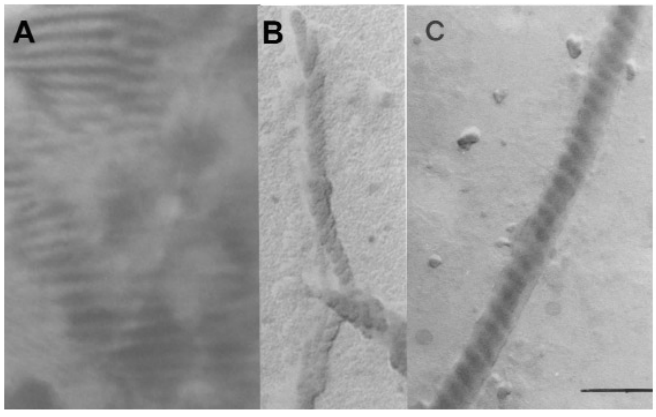



**Fig. 3** Striped pattern formed by **12** in the presence of $Ag^+$ ions (A). Right-handed helical architecture formed by **14c** in water (B). Left-handed superhelix formed by **13c** in water (C).

Compounds **13c** and **14c** formed in addition to bilayer-type assemblies like plates and vesicles, also helical assemblies (e.g., superhelices, Figs. 3B and 3C). The observed differences in the supramolecular structures generated by the negatively charged and zwitterionic copolymers suggest that the helices are formed by a complex assembly mechanism, involving the hierarchical transfer of chirality from the monomeric building blocks via the secondary helical structure of the polyisocyanide to the final chiral superstructures [26].

### Other peptide-like block copolymers

As shown in the previous section, polymer/peptide block copolymers constitute a promising class of compounds with respect to the hierarchical transfer of stereochemical information to larger assemblies of macromolecules [27]. The synthesis of a block copolymer having a truly polypeptide part and a purely synthetic segment (i.e., polystyrene or polybutadiene) was reported first by Gallot et al. [28]. Similar systems have been prepared and studied subsequently [29], but not with respect to their stereochemical properties. More recently, Klok, Lecommandoux, and coworkers investigated oligomers built from a polystyrene segment and an α-helical polypeptide in the solid state [30]. The same synthetic concept was used to prepare polybutadiene-*block*-poly(L-glutamatic acid), which formed vesicular aggregates in water [31]. In an independent study by Kukula et al., the same properties for these hybrid block copolymers were found [32]. Neither of these two studies revealed any transfer of the stereochemical information present in the polypeptide block to the assemblies formed. In the latter study, this was emphasized by the fact that no serious change of the vesicle morphology was observed during the pH-induced helix-coil transition of the poly(L-glutamate) block.

An interesting class of self-organizing macromolecules was prepared by Deming and coworkers. Using the transition metal-catalyzed ring-opening polymerization of *N*-carboxy anhydrides (NCAs) [33], block copolypeptides were synthesized, which displayed unprecedented properties with respect to the formation of ordered morphologies [34] and hydrogels [35]. In the latter case, it was found that the conformation (i.e., random coil, α-helix, or β-strand) significantly influenced the gelation process, which can be regarded as transfer of stereochemical information to the materials properties of the formed gels.

## POLYMER/PROTEIN HYBRID ARCHITECTURES

It appears to be a small step from the use of synthetic polypeptides, prepared by laboratory polymerization techniques, to the use of proteins (or enzymes) prepared by the biological machinery [36] as a constituent block of an amphiphilic copolymer. Examples of well-defined polymer/protein structures designed to allow control over their self-assembling properties, however, are limited. So-called giant amphiphiles (i.e., amphiphilic polymer/protein hybrids) have been constructed by the association of biotinylated polystyrene with streptavidin. The way these giant amphiphiles are synthesized leaves two streptavidin binding sites unoccupied. These can be used to create functionalized amphiphiles as was shown by the binding of the iron storage protein ferritin to the streptavidin part. Enzyme-containing hybrid macromolecules have been prepared by the complexation of biotinylated polystyrene to streptavidin, which contained covalently attached horse radish peroxidase (Fig. 4A). The resulting enzymatic conjugates were shown to form monolayers in which the enzyme molecules were still catalytically active [37].

A second example of a giant amphiphile (i.e., derived from a lipase and polystyrene) has recently been developed [38]. In a tetrahydrofuran/water mixture it was possible to specifically couple derivatized polystyrene to a reduced disulfide bridge present on the outer surface of the enzyme. The amphiphilic hybrid obtained in this way self-assembled in a tetrahydrofuran/water mixture and formed bundles of rods, presumably micellar in nature (Fig. 4B). The lipase present in these fibers still retained some of its catalytic activity, however, to a reduced extent. Despite the limited activity of this initial giant amphiphilic system, this approach holds great promise for the construction of biomimetic functional protein assemblies.

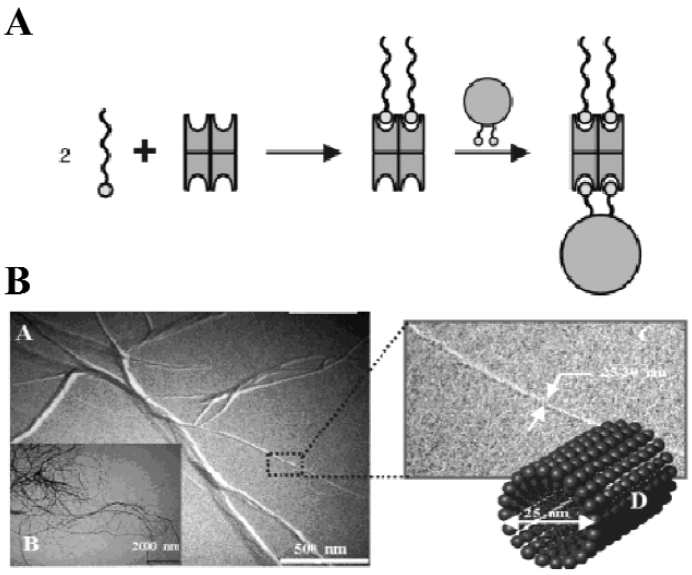



**Fig. 4** (A) Schematic representation of the giant amphiphiles formed by the association of biotinylated polystyrene and streptavidin and the modular construction of functional protein/polymer hybrids. (B) transmission electron microscopy (TEM) images of aggregates obtained after functionalizing lipase (CAL B) with polystyrene in tetrahydrofuran (THF)/water (9/1 v/v). The inset shows a single fiber, corresponding to a micellar rod. Reprinted with permission from Wiley Interscience (A) and the American Chemical Society (B).

## OUTLOOK

Stereochemistry is an important factor in the formation of precisely defined three-dimensional architectures formed by macromolecules. In recent years, researchers have accomplished the synthesis of an increased number of compounds that mimic the complex behavior of biomacromolecules. With respect to sophistication and function, however, Nature is still far ahead when compared to synthetic materials. Only recently, the first examples of transfer of stereochemical information (i.e., chirality) present in monomeric building blocks to different levels of organization in synthetic macromolecules have been reported [6]. This area is still expanding, and promising new classes of compounds with interesting conformational and self-assembling properties are to be designed by combining synthetic polymers with polypeptides and proteins. The control over the structure of these macromolecular amphiphiles enables the fine-tuning of their aggregation behavior. In the future, the combination of the self-assembling properties of well-defined block copolymers and the specific function of enzymes and proteins is expected to result in novel materials with interesting properties to be used in, for example, the fields of electron transfer, information storage, and (enantioselective) catalysis. Recently, the first examples of functional (electronic) materials formed by the self-organization of polymers have been reported [39]. In the emerging field of noncovalent (i.e., supramolecular) polymers [40], the concept of stereochemistry has also been successfully introduced, leading to helical architectures in both organic solvents and in water [41]. This gives chemists another approach to design and synthesize new macromolecular architectures, possibly in combination with covalent polymers or biomacromolecules. These design principles and the concepts discussed above will be applied to mimic the technologies used by Nature to transfer the stereochemical information present in small building blocks to a second level represented by the defined structure of a macromolecule. This information will subsequently be transferred to the assemblies formed by these macromolecules and/or eventually to the material itself.

## ACKNOWLEDGMENTS

The author would like to thank Prof. R. J. M. Nolte and Dr. N. A. J. M. Sommerdijk for their guidance and support. Dr. A. E. Rowan is acknowledged for critical comments and the Netherlands Organization for Scientific Research (NWO) for financial support.

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