Helical Superstructures from Charged Poly(styrene)-Poly(isocyanodipeptide) Block Copolymers

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Amphiphilic block copolymers containing a poly(styrene) tail and a charged helical poly(isocyanide) headgroup derived from isocyano-L-alanine-L-alanine and isocyano-L-alanine-L-histidine were prepared. Analogous to low–molecular mass surfactants, these block copolymers self-assembled in aqueous systems to form micelles, vesicles, and bilayer aggregates. The morphology of these aggregates can be controlled by variation of the length of the poly(isocyanide) block, the pH, and the anion-headgroup interactions. The chirality of the macromolecules results in the formation of helical superstructures that have a helical sense opposite to that of the constituent block copolymers. The great variety of morphologies displayed by these block copolymers and the fact that they are easily accessible from poly(styrene) and different types of peptides open new opportunities for applications in the fields of life and materials sciences.

Chirality may be used as a tool to assemble molecules and macromolecules into larger structures with dissymmetric, for example, helical, shapes. Interesting applications for these chiral architectures can be foreseen in the fields of materials science and catalysis (*1*, *2*). It is well known that amphiphilic compounds with low molecular masses, such as phospholipids, amino acid and nucleic acid derivatives, and carbohydrate compounds (*3*), can form a variety of chiral superstructures in water. Amphiphilic diblock copolymers in an aqueous environment can also assemble into various nanosized morphologies, depending on the structure of the block copolymer (*4*, *5*) or the presence of inorganic salts (*6*). These types of block copolymers may be referred to as superamphiphiles, because they resemble the traditional surfactants in shape but differ in size. To the best of our knowledge, no amphiphilic block copolymers have yet been described that generate chiral nanosized architectures in water, in a similar way to the equivalent low–molecular mass surfactants. We present a chiral superamphiphile consisting of a block copolymer of styrene and an optically active isocyanodipeptide that forms such chiral architectures.

Polymers of isocyanides can adopt helical structures depending on their side chains, in particular when these are bulky. The helix sense of the poly(isocyanide) part can be controlled by the use of an optically active isocyanide monomer or a chiral Ni(II) catalyst (*7*–*10*). The charged block copolymers we discuss here have a helical poly(isocyanide) headgroup of one particular type, either left handed (M) or right handed (P) (Fig. 1) depending on the monomer used. Upon dispersal in water, they self-assemble to form different types of supramolecular structures, including superhelices. The sense of the superhelix is opposite to that of the constituent building blocks.

Isocyanides are polymerized by Ni(II) ions in the presence of a nucleophile (such as an amine) as the initiating species (*11*). In our study, we polymerized isocyanides derived from dipeptides [isocyano-L-alanine-L-alanine (IAA) and isocyano-L-alanine-L-histidine (IAH) (Scheme 1)], which resulted in the formation of helical peptide polymers. The monomers were prepared from the *N*-formyl–protected dipeptides according to standard procedures (*12*). The homopolymers were synthesized so that their chiroptical properties could be studied (*13*). A relatively strong Cotton effect, similar to that of other poly(isocyanide)s, was observed in the circular dichroism (CD) spectra of both homopolymers [poly(isocyano-L-alanine-L-alanine) (PIAA) and poly(isocyano-L-alanine-L-histidine) (PIAH)]. From the signs of the optical rotations and the shape of the Cotton effects (*7*), it was tentatively concluded that PIAA contains an excess of *P* helices and PIAH an excess of M helices (*14*). In both polymers, the helical structure is likely to be the result of steric interactions between the bulky side chains; additional stabilization of the helix probably originates from the amide functionalities in the dipeptides. Infrared (IR) spectroscopy showed the presence of intramolecular hydrogen bonds between these functionalities in side chains *n* and (*n* + 4) of the ~fourfold helical back-

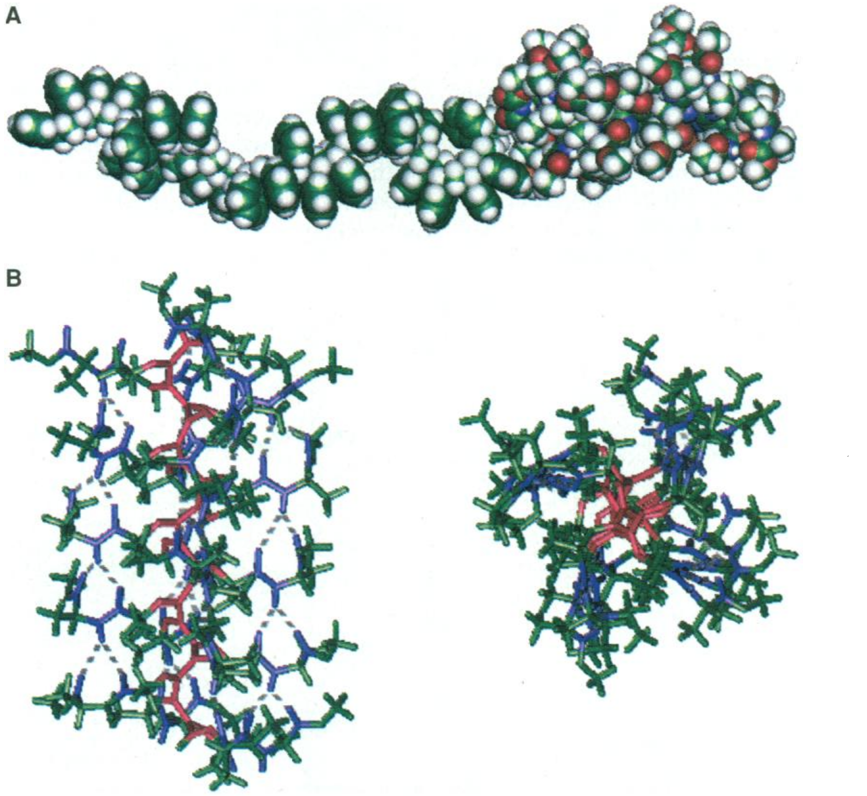

Fig. 1. (**A**) Computer-generated representation of PS-*b*-PIAA. (**B**) Right-handed helical backbone (shown in red) of PIAA. (Left) Side view; dashed lines depict hydrogen bonds. (Right) Top view.

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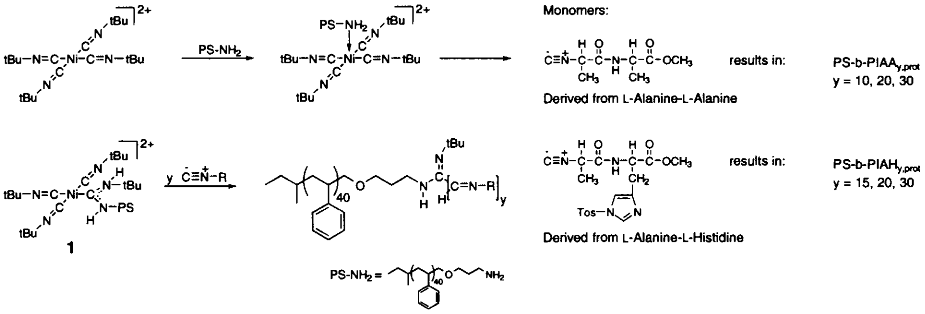
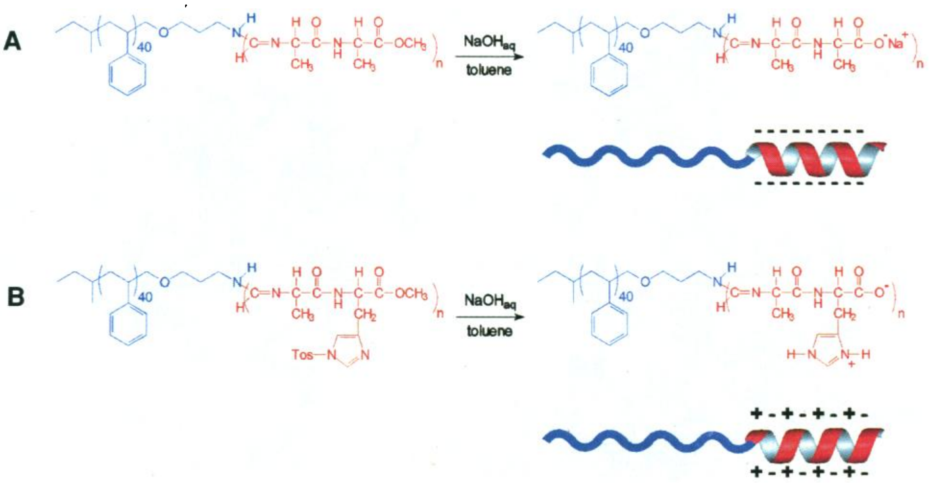
*To whom correspondence should be addressed. E-mail: tijdink@sci.kun.nl bone. Molecular modeling (*15*) provided further support for both the helical structure of the poly(isocyanide) backbone (Fig. 1B) and the presence of a hydrogen-bonding network. From the modeling studies, the dimensions of the poly(isocyanide) chain could be estimated: The 4/1 helical turn is about 4.16 Å long, corresponding to a contribution of 1.04 Å by each monomer (*16*). The diameters of the helices were estimated to be 21 Å for PIAA and 24 Å for PIAH.



Scheme 1. Synthesis of protected poly(styrene)-poly(isocyanide) block copolymers. Tos, *p*-toluenesulfonyl; tBu, *tert*-butyl.

A series of poly(styrene)-*block*-poly(isocyano-L-alanine-L-alanine) (PS$_x$-*b*-PIAA$_y$) and poly(styrene)-*block*-poly(isocyano-L-alanine-L-histidine) (PS$_x$-*b*-PIAH$_y$) block copolymers were prepared by the use of a poly(styrene) derivative of well-defined length, end-capped with an amino group, as the initiator of the Ni(II)-catalyzed polymerization reaction (Scheme 1). The macromolecular nickel complex **1** (*17*) in Scheme 1 was prepared by nucleophilic attack of the amine end-capped polystyrene (number-averaged molecular mass = 4.2×10^3 g/mol; polydispersity index = 1.05; $x = 40$) (*18*) on the stable complex Ni(II)(CN-*t*-Bu)$_4$(ClO$_4$)$_2$ (*t*-Bu, *tert*-butyl) (*19*). The polymerizations commenced when the dipeptide-based isocyanides were added, yielding the desired protected block copolymers as methyl esters (PS-*b*-PIAA$_{prot}$ and PS-*b*-PIAH$_{prot}$) in moderate to good amounts (60 to 85%). These macromolecules, in their protected form, were soluble in common organic solvents and could be characterized by nuclear magnetic resonance (NMR) spectroscopy (*20*), from which their molecular masses were determined. Using this approach, we obtained block copolymers with varying amounts of isocyanide (for PS$_x$-*b*-PIAA$_{y,prot}$, $x = 40$ and $y = 10$, 20, and 30; for PS$_x$-*b*- PIAH$_{y,prot}$, $x = 40$ and $y = 15$, 20, and 30). A predominantly helical conformation of the poly(isocyanide) backbone in the block copolymers was tentatively derived from CD spectroscopy and optical rotation data, which indicated a right-handed helix for PS-*b*-PIAA$_{prot}$ and a left-handed helix for PS-*b*-PIAH$_{prot}$ (*14*).

Removal of the ester functions of PS-*b*-PIAA$_{prot}$ by treatment with a 1 M aqueous NaOH-toluene (1:1, volume/volume) mixture resulted in a superamphiphile with a negatively charged helical headgroup (Scheme 2A); PS-*b*-PIAH$_{prot}$ gave a superamphiphile with a zwitterionic headgroup (Scheme 2B). The deprotected block copolymers were liberated from the excess of NaOH by ultrafiltration (Filtron; cutoff molecular mass, 10,000 daltons); lyophilization yielded spongy brown solids. These conversions could be conveniently monitored with IR spectroscopy, which demonstrated the disappearance of the ester vibrations at 1747 cm^{-1} and the concomitant appearance of new absorptions in the region of 1710 to 1730 cm^{-1}.



Scheme 2. Deprotection of the block copolymers (**A**) PS-*b*-PIAA to negatively charged superamphiphiles and (**B**) PS-*b*-PIAH to zwitterionic superamphiphiles. The >C=N-*t* -Bu unit has been omitted for reasons of clarity.

The CD spectra of dispersions of the block copolymers in water displayed substantial Cotton effects. However, scattering resulting from aggregation of the molecules prevented the recording of quantitatively reproducible spectra. Aggregate formation also hampered the potentiometric determination of the ionization state of the carboxylic acid and imidazole functions. It was assumed, therefore, that the ionization states of the amphiphilic block copolymers were similar to those of the respective homopolymers. The carboxylic acid groups in PIAA were measured to have a negative logarithm of the acid dissociation constant (pK_a) value of 5.6. The pK_a values of PIAH were determined previously (*21*); values of pK_a (COOH) = 3.1 and pK_a (Imidazole H) = 9.1 were observed, resulting in an isoelectric point of 5.4.

The aggregation behavior of the different poly(styrene)-poly(isocyanide) block copolymers was studied by transmission electron microscopy (TEM) and atomic force microscopy (AFM) (*22*). Aggregates were prepared by sonicating a 0.1 weight % dispersion in water of pH 7 for 1 hour at 70°C. At this pH, no clear morphologies were observed for PS$_{40}$-*b*-PIAA$_{20}$, whereas PS$_{40}$-*b*-PIAH$_{20}$ showed micellar aggregates (*23*). The dispersions were then buffered at a pH value of 5.6, to generate attractive interactions between the rodlike headgroups. At this value, about half of the available acid residues of PS-*b*-PIAA are expected to be protonated, thereby optimizing the possible formation of intermolecular hydrogen bonds. Rods with a diameter of 12 nm were observed (Fig. 2A) for this compound. In the case of PS$_{40}$-*b*-PIAH$_{20}$, the main part of the poly(isocyanide) block is expected to be zwitterionic at pH 5.6, minimizing the repulsive electrostatic interactions between the highly charged macromolecules. This minimization resulted in rodlike structures (not shown in Fig. 2) similar to those found for PS$_{40}$-*b*-PIAA$_{20}$. The rods are probably micellar aggregates consisting of a poly(styrene) core with a diameter of 8 nm and a corona of poly(isocyanide) blocks with a thickness of about 2 nm (Fig. 2B). On the basis of the dimensions of the block copolymers, one can calculate that a single rod of 1-μm length contains about 6000 macromolecules. TEM and AFM on polyvinyl formaldehyde plastic and mica showed that the rodlike aggregates had a zigzag structure (*24*) (Fig. 2, A and C).

It is known that the addition of ions can affect the self-assembly of both traditional surfactants and amphiphilic block copolymers. Changing the cation of the buffer (such as from sodium acetate to potassium acetate or ammonium acetate) at identical pH did not affect the morphology of the micellar rods formed by PS$_{40}$-*b*-PIAA$_{20}$ and PS$_{40}$-*b*-PIAH$_{20}$. However, when the anion of the buffer was changed from sodium acetate to sodium tartrate and then to sodium citrate (all pH 5.6), the micellar rods from PS$_{40}$-*b*-PIAH$_{20}$ became increasingly more flexible (Fig. 2D). PS$_{40}$-*b*-PIAA$_{20}$ did not respond to the change of anion in the buffer solution.

The effect of the poly(isocyanide) block length on the aggregation behavior of PS$_{40}$-*b*-PIAA$_y$ and PS$_{40}$-*b*-PIAH$_y$ was investigated in a sodium acetate buffer of pH 5.6. Rodlike micellar aggregates were observed for both systems when $y = 20$ (see above), whereas dispersions of block copolymers with $y = 30$ showed no clear morphologies. When PS$_{40}$-*b*-PIAA$_{10}$ was dispersed in the buffer solution, a variety of bilayer-type structures were observed. In addition to collapsed vesicles (with diameters ranging from tens to hundreds of nanometers and a bilayer thickness of 16 nm; Fig. 3A) and bilayer filaments (Fig. 3B), left-handed superhelices were also formed (Fig. 3C). These supercoils had diameters of 180 nm and a pitch of 110 nm (Fig. 3D). PS$_{40}$-*b*-PIAH$_{15}$ also formed helical superstructures when dispersed in the sodium acetate buffer of pH 5.6 (Fig. 3E). In contrast to the PS$_{40}$-*b*-PIAA$_{10}$ helix, this superhelix was right handed and had a diameter of 28 nm and a pitch of 19 nm. These dimensions are considerably smaller than those observed for the former block copolymer. In the case of PS$_{40}$-*b*-PIAH$_{15}$, one helix turn corresponds to the diameter of the micellar rods (12 nm, see above), and thus we propose that for this block copolymer the helical superstructure is composed of coiled rods. In the case of PS$_{40}$-*b*-PIAA$_{10}$, no clues as to the hierarchy of the assembly process can be given at this moment. The mechanism of formation of the helical superstructure is apparently different for PS$_{40}$-*b*-PIAA$_{10}$ and PS$_{40}$-*b*-PIAH$_{15}$. This difference may be attributed to dissimilarity in the poly(isocyanide) structure (anionic versus zwitterionic) and to the difference in the length of the poly(isocyanide) block (*5*).

The superhelix generated from PS$_{40}$-*b*-PIAA$_{10}$ has a left-handed twist, whereas the building blocks are right-handed helices. In the case of PS$_{40}$-*b*-PIAH$_{15}$, the reverse situation is found: Left-handed helical building blocks aggregate into a right-handed superhelix. These observations are of interest to compare with natural systems, for example, with helix bundle proteins, which contain α helices (right-handed) that can pack in a counterclockwise fashion to generate left-handed superstructures (*25*). The present copolymers, which are versatile and easily accessible from poly(styrene) and a large variety of dipeptides, may serve as experimental reference points for the theoretical study of the packing of helices (*26*). Also, in the field of materials science, the copolymers may be useful in investigating the connection between chiral molecular structure and the structure of supramolecular aggregates. This insight is important for the development of materials with liquid-crystalline (*27*) or nonlinear optical (*28*) properties.

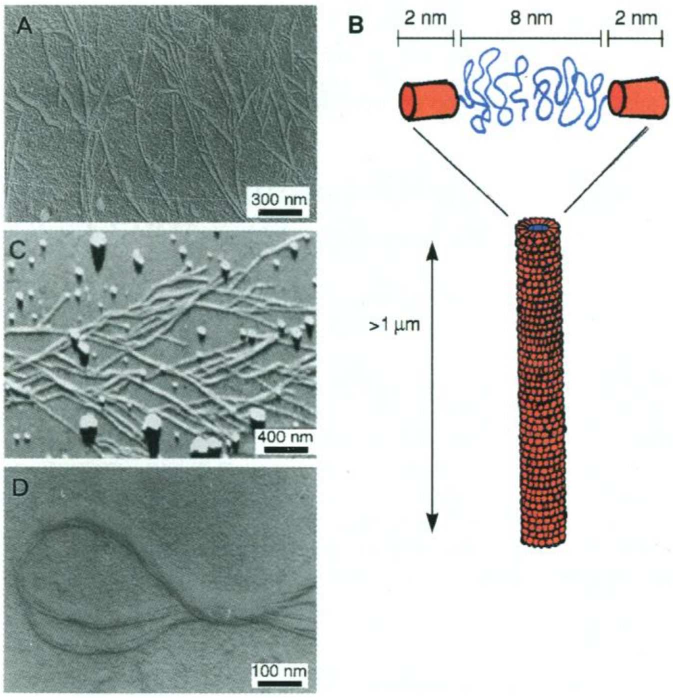


Fig. 2. Aggregates formed from poly(styrene)-poly(isocyanide) block copolymers at optimized pH. (**A**) TEM image of PS$_{40}$-*b*-PIAA$_{20}$ in a pH 5.6 sodium acetate buffer (0.2 mM). (**B**) Schematic model of the micellar rods, showing the relative positions of the poly(styrene) (blue) and poly(isocyanide) blocks (red) in the aggregates. (**C**) AFM image of PS$_{40}$-*b*-PIAA$_{20}$ in a pH 5.6 sodium acetate buffer (0.2 mM). (**D**) Aggregates visualized with TEM from PS$_{40}$-*b*-PIAH$_{20}$ in a sodium citrate buffer of pH 5.6 (0.2 mM).

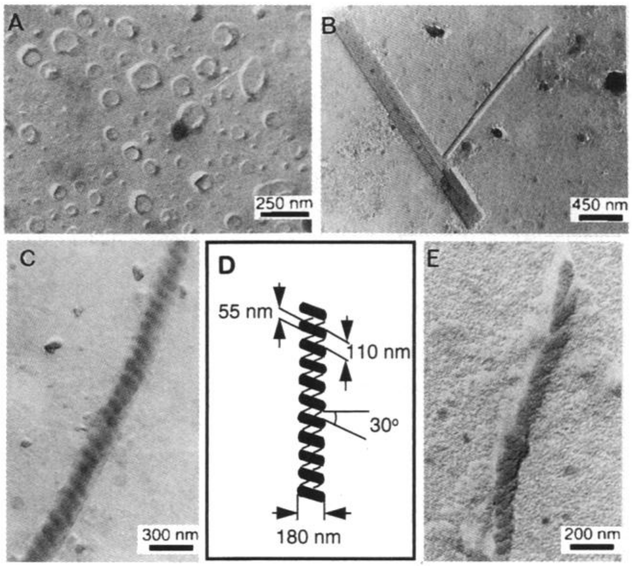


Fig. 3. TEM images of morphologies formed by PS$_{40}$-*b*-PIAA$_{10}$ in a sodium acetate buffer of pH 5.6 (0.2 mM). (**A**) Collapsed vesicles. (**B**) Bilayer filaments. (**C**) Left-handed superhelix. (**D**) Schematic representation of the helix in (C). (**E**) Right-handed helical aggregate formed by PS$_{40}$-*b*-PIAH$_{15}$ in a sodium acetate buffer of pH 5.6 (0.2 mM).

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12. The *N*-formyl–protected dipeptides were prepared according to standard protecting and coupling procedures and were converted into the isocyanides by a method developed by I. Ugi and R. Meyr [*Angew. Chem.* **70**, 702 (1958)]. The optical purity could easily be checked by proton NMR spectroscopy, because racemization results in diastereomers with different chemical shifts. Detailed syntheses and physical characterization will be published elsewhere.
13. The homopolymers were prepared by stirring the isocyanides with 4 mole percent of $Ni(ClO_4)_2(H_2O)_6$ in $CHCl_3$ for 6 to 8 hours, after which the polymer was precipitated by adding a tenfold excess of H_2O-MeOH (1/1, v/v).
14. PIAA displayed a negative couplet superimposed on a negative CD band in the region of 250 to 300 nm and a negative optical rotation $[\alpha]^{20}{}_D = -138°$ [$CHCl_3$, concentration (*c*) 0.1 g/dl]. PIAH showed a very strong positive CD band at about 300 nm and a positive optical rotation $[\alpha]^{20}{}_D = +541°$ ($CHCl_3$, *c* 0.35). These data indicate a *P* helix for PIAA and an *M* helix for PIAH. The physical and chiroptical properties of PIAH were reported previously [J. M. van der Eijk, R. J. M. Nolte, W. Drenth, A. M. F. Hezemans, *Macromolecules* **13**, 1391 (1980); A. J. M. van Beijnen *et al.*, *ibid.* **16**, 1679 (1983)]. The block copolymers had CD spectra very similar to those of the homopolymers. Optical rotation data: PS_{40}-*b*-$PIAA_{20}$, $[\alpha]^{20}{}_D = -88°$ ($CHCl_3$, *c* 0.06); PS_{40}-*b*-$PIAH_{20}$, $[\alpha]^{20}{}_D = +205°$ ($CHCl_3$, *c* 0.05).
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16. For a calculation of the structure of poly(isocyanide)s, see C. Kolmarr and R. Hoffman [*J. Am. Chem. Soc.* **112**, 8230 (1990)] and (*8*).
17. The spectroscopic data obtained for **1** perfectly matched the data of Ni(II) carbene complexes previously described (*11*).
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20. The block copolymers were characterized with proton (^1H) NMR, ^{13}C NMR, and IR spectroscopy. For example, PS_x-*b*-$PIAA_y$: ^1H NMR [in deuterochloroform ($CDCl_3$)]; chemical shift, δ (parts per million relative to internal tetramethylsilane) = 0.73 to 1.22 [*Bu*-(CH_2-CHPh)$_x$; Bu, butyl group; Ph, phenyl group], 1.22 to 1.75 [(C*H*$_2$-CHPh)$_x$ + (CN-CH(C*H*$_3$)-CONH-CH(C*H*$_3$)-CO_2CH_3)$_y$], 1.75 to 2.35 [(CH_2-C*H*Ph)$_x$], 3.42 to 3.90 [(CN-CH(CH_3)-CONH-CH(CH_3)-CO_2C*H*$_3$)$_y$], 3.90 to 4.88 [(CN-C*H*(CH_3)-CONH-C*H*(CH_3)-CO_2CH_3)$_y$], 6.28 to 7.25 [(CH_2-CH*Ph*)$_x$]. ^{13}C NMR ($CDCl_3$); δ = 14 [CH_3-CH_2-CH_2-CH_2-(CH_2-CHPh)$_x$], 15 to 19.5 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$], 20 to 24.5 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$], 22.5 [CH_3-CH_2-CH_2-CH_2-(CH_2-CHPh)$_x$], 27 [CH_3-CH_2-CH_2-CH_2-(CH_2-CHPh)$_x$], 32 [CH_3-CH_2-CH_2-CH_2-(CH_2-CHPh)$_x$], 33.5 to 39.5 (broad, CH_2-O-CH_2-CH_2-CH_2-NH_2), 40 to 46 [broad, (CH_2-CHPh)$_x$], 40.5 [broad, (CH_2-CHPh)$_x$], 46.5 to 48 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$], 49 to 51 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$], 61 to 64 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$], 68 (broad, CH_2-O-CH_2-CH_2-CH_2-NH_2 + CH_2-O-CH_2-CH_2-CH_2-NH_2), 124 to 127 [broad, (CH_2-CH*Ph*$_{para}$)$_x$], 127 to 129.5 [broad, (CH_2-CH*Ph*$_{ortho+meta}$)$_x$], 145 to 146.5 [broad, (CH_2-CH*Ph*$_{ipso}$)$_x$], 160 to 165 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$], 171 to 174 [broad, (CN-CH(CH_3)-CONH-CH(CH_3)-CO_2CH_3)$_y$]. IR (KBr pellet): 698, 1160, 1211, 1535, 1663, 1748, 2928, 3295 cm^{-1}.
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22. TEM was performed on a Philips EM210 microscope at an acceleration voltage of 60 kV. For AFM, a Nanoscope III instrument from Digital Instruments was used, operating in the tapping mode.
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29. We thank the Department of Macromolecular and Organic Chemistry (E. W. Meijer) of the Technical University Eindhoven for kindly providing some poly(styrene) samples, P. C. J. Kamer for useful suggestions, A. E. Rowan for the molecular modeling studies, M. M. Green for fruitful discussions, J. Gerritsen for the AFM measurements, and H. P. M. Geurts for help with the TEM. Supported by the Netherlands Foundation for Chemical Research with financial aid from the Netherlands Organization for Scientific Research.

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Identification of Water Ice on the Centaur 1997 CU26

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Spectra of the Centaur 1997 CU26 were obtained at the Keck Observatory on 27 October 1997 (universal time). The data show strong absorptions at 1.52 and 2.03 micrometers attributable to water ice on the surface of 1997 CU26. The reflectance spectrum of 1997 CU26 is matched by the spectrum of a mixture of low-temperature, particulate water ice and spectrally featureless but otherwise red-colored material. Water ice dominates the spectrum of 1997 CU26, whereas methane or methane-like hydrocarbons apparently dominate the spectrum of the Kuiper belt object 1993 SC, perhaps indicating different origins, thermal histories, or both for these two objects.

Studies of the physical properties and surface compositions of bodies in the outer solar system can give important clues to the conditions that existed in the early solar system. At the large heliocentric distances of bodies in the outer solar system, materials are expected to be much less modified by heating from the sun than those in the region of the terrestrial planets, thus preserving a less altered record of the chemical and physical properties of the original material from which the solar system formed.

An important suite of bodies in this regard is the small, irregular satellites of the Jovian planets, the Centaurs and the Kuiper belt objects (KBOs), which orbit beyond Neptune. The object designated 1997 CU26 (*1*) is one of the seven known Centaurs. The Centaurs are distinguished dynamically as a group of objects whose orbits cross those of the Jovian planets and whose perihelions lie outside the orbit of Jupiter. As a result, Centaur orbits are dynamically unstable on time scales of about 10^7 years (*2*). Thus, that they are observed at all implies a source of new bodies to replenish those that are lost from the Centaur region by collisions or catastrophic gravitational encounters with the Jovian planets (*2*, *3*). One possible source for these objects is the Kuiper belt (*4*). Therefore, determining the surface composition of objects in both regions is necessary to understand the dynamical and chemical evolution of bodies in the outer solar system.

Reported here are near-infrared spectroscopic observations of 1997 CU26 (*5*), conducted at the W. M. Keck Observatory on

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