Communications to the Editor

Synthesis of Amphiphilic Star Block Copolymers Using Ring-Opening Metathesis Polymerization

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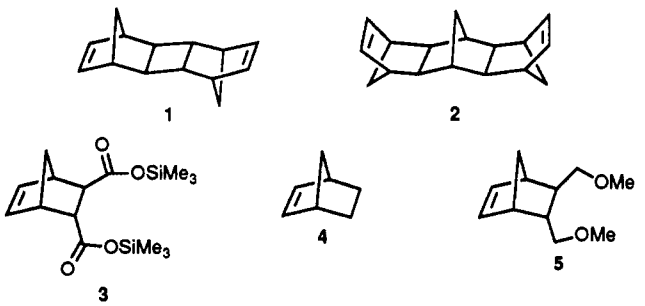
Received December 3, 1991
Revised Manuscript Received February 6, 1992

Introduction. The subject of star-shaped macromolecules has received much attention in recent years.[1] Bazan and Schrock[2] reported the synthesis of star polymers by ring-opening metathesis polymerization (ROMP) using a well-defined olefin metathesis initiator and a cross-linking agent. Other workers[3] have described the synthesis and properties of an amphiphilic star polymer that consists of a hydrophobic styrene–divinylbenzene microgel "core" and a poly(methacrylic acid) "shell"; free-radical polymerization methods were used to produce this novel star-shaped macromolecular amphiphile. A paper describing cationic amphiphilic star polymer synthesis has also recently appeared.[4] In this brief paper we report the synthesis of amphiphilic star block copolymers by ROMP methods, employing a new cross-linking agent and appropriately functionalized norbornene-type monomers.

Results and Discussion. *Exo-trans-exo*-pentacyclo-[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradeca-5,11-diene (1) was used[2] in



living ROMP as a cross-linking agent for star polymer synthesis, analogous to divinylbenzene in anionic polymerization.[5] Although 1 works well for ROMP-based star synthesis, the synthesis of 1 employs a catalyst that is not available commercially, and the yield of 1 is low.[6] In this work we employed *endo-cis-endo*-hexacyclo-[10.2.1.1^{3,10}.1^{5,8}.0^{2,11}.0^{4,9}]heptadeca-6,13-diene[7] (2) as the cross-linking agent. This compound is also obtained in a relatively low yield but requires no catalyst preparation and is easily purified.

The hydrophilic outer shell of our amphiphilic star polymers is prepared from a norbornene-type monomer containing two carboxylic acids protected by trimethylsilyl groups (TMSNBE) (3). Carboxylic acids must be protected because the ROMP initiator is sensitive to acid functionalities. The trimethylsilyl group was chosen because it hydrolyzes readily to the acid upon exposure to water. Homopolymers of this monomer were made and deprotected, and the resulting poly(carboxylic acid) polymers were indeed water soluble. The hydrophobic portion of our amphiphilic stars consists of norbornene (NBE) (4) or 5,6-bis(methoxymethyl)norbornene (DMNBE) (5).

Homopolymer star synthesis: Monomers 3–5 were all polymerized with the appropriate ROMP initiator[8] to give living homopolymers and cross-linked with 2 to form stars (stars 1–3, respectively, in Table I). GPC data show that for these homopolymer systems the elution peak is shifted significantly to higher molecular weight upon addition of 6 equiv of 2. Although the higher molecular weight peak evidently corresponds to the star polymer, it is not possible to determine the number of arms per star molecule[1,9] from GPC data. However, we may obtain a lower bound on the number of arms by dividing the apparent molecular weight of the star (vs polystyrene) by the apparent molecular weight of the corresponding linear branch before it is cross-linked to form the star. This gives a lower bound because a star polymer will have a smaller hydrodynamic volume than its linear analogue; the minimum values for the average number of arms per star in the NBE and DMNBE star molecules are 5.4 and 5.9, respectively (stars 2 and 3, respectively, in Table I).

Amphiphilic star polymer synthesis: To make amphiphilic star polymers, we first added 3 to the initiator, and after its consumption we added 4 or 5 in order to make the hydrophobic block. These living diblocks were then treated with 5–6 equiv of 2 to form the star polymer. This polymerization scheme is shown in Figure 1. In order to convert the TMS esters to carboxylic acids, we soaked the cast films of these polymers in water for 2–3 days. Four different amphiphilic star polymers were made, two that contain poly(4) as the hydrophobic block (stars 4 and 5 in Table I) and two that contain poly(5) as the hydrophobic block (stars 6 and 7 in Table I). The complete GPC data for star 4 at each step in the synthesis are shown in Figure 2a and for the final product of stars 5–7 in parts b–d of Figure 2, respectively.

The GPC data of Figure 2 show some linear and lightly branched chains present that are not coupled to the star, similar to observations for other systems.[4,10] This phenomenon is least prominent in star 4, which contains 43% of the hydrophobic portion; it is most prominent in stars 5–7, containing 14–17% of the hydrophobic portion. It can be shown that these chains were not prevented from coupling as a result of termination due to impurities; living chains are terminated by benzaldehyde addition at the end of the polymerization. Thus, all products which were living at the point of benzaldehyde addition are visible at 254 nm using the UV detector of our GPC. Chains terminated by impurities would not have this phenyl end cap and thus would not be picked up by the UV detector. Our UV–GPC data clearly show the uncoupled chains as well as the star polymer, and thus these chains were living at the time of termination with benzaldehyde. We also

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0024-9297/92/2225-2055$03.00/0

Table I
List of Star Polymers Made

star no.	M of poly(3)[a,d]	M of poly(4)[a]	M of poly(5)[a]	hydrophobic[b] core, %	polydispersity[c] of star
1	17 900			7	
2		10 000		100	1.06
3			29 000	100	1.21
4	10 000	7 000		43	1.41
5	23 000	2 000		17	2.63
6	23 000		2 000	17	1.76
7	25 000		2 000	14	1.86

[a] All molecular weights are in unts of grams per mole and are based on stoichiometry. [b] Including the tetrafunctional cross-linking agent as well as the hydrophobic block. [c] Polydispersities are based on GPC measurements in THF. The polydispersities of the linear chains for these systems fall in the range of 1.02–1.05. [d] This molecular weight is based on the diacid form after deprotection of the diester.

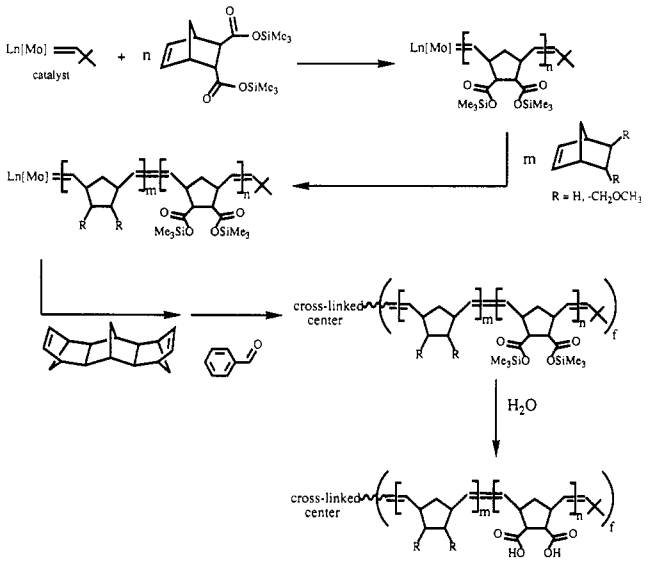

Figure 1. Synthesis of an amphiphilic star diblock copolymer with poly(4) or poly(5) as the hydrophobic block and poly(3) as the hydrophilic block.

observed for these systems that, up to 1 h after the addition of 2, the time allowed before termination made no difference to the appearance of the GPC trace; thus, the uncoupled chains do not arise as a result of premature termination of the star synthesis.

The existence of these uncoupled chains suggests a resistance to linking that may arise from two sources. The first could be a steric hindrance caused by the increased segment density at the core of the star, preventing the living ends of uncoupled chains from adding onto any remaining active sites. The other could be a diffusional barrier created by the outer hydrophilic shell of the already-formed stars. The living diblock chain ends, which in our polymerization are attached to the hydrophobic section of the molecules, might prefer to remain in solution rather than diffuse through the hydrophilic shell to find the core. Evidence suggests both of these phenomena are occurring. Star 2 contains a small amount of uncoupled chains. Since this star is made from homopolymer branches, there is no hydrophilic shell to create a diffusional barrier, and thus the relatively small resistance to coupling is most likely caused only by steric hindrance. Star 4 (Figure 2b) contains a significant amount of uncoupled chains. This star is made from branches of molecular weights similar to those of star 2 and should therefore encounter similar steric hindrance; however, this star contains diblock copolymer branches and therefore has a hydrophilic shell

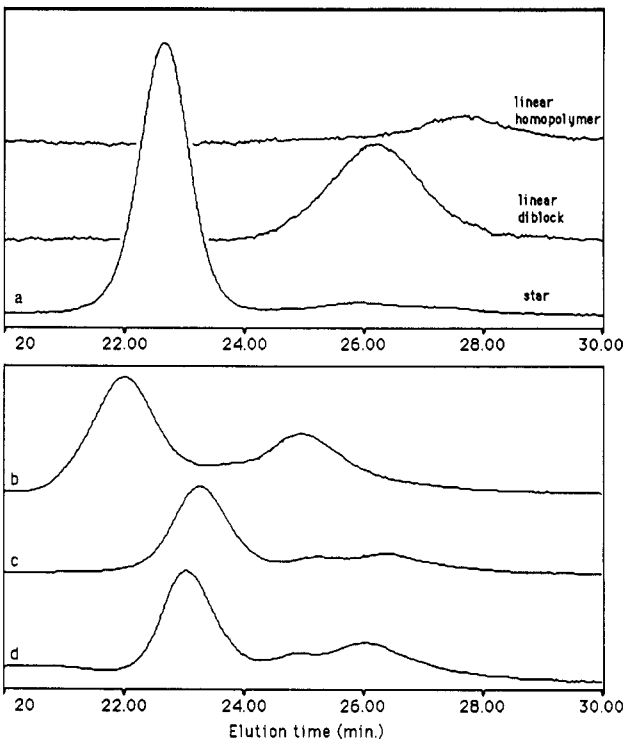

Figure 2. (a) GPC of star 4 of Table I, including all the steps of the synthesis. (b) Star 5 of Table I. (c) Star 6 of Table I. (d) Star 7 of Table I.

Table II
Solubility of Some Amphiphilic Stars in Different Solvents[a]

	water	methanol	THF	acetone	acetonitrile	50/50 water/THF
star 1	s	s	i	i	i	s
star 4	i[b]	i	s			i
star 6	i[c]	i[b]	p[c]	i	i	s

[a] i = insoluble, p = partially soluble, s = soluble. [b] Polymer swelled a small amount in this solvent. [c] Polymer swelled significantly in this solvent.

that can create a diffusional barrier and thus increase the resistance to coupling.

Stars 1, 4, and 6 were subjected to a variety of solvents to observe their solubility characteristics; the results are shown in Table II. Only star 1, containing just the cross-linking agent as its hydrophobic portion at 7 wt %, was completely water soluble. Star 6 was also subjected to a 1 M potassium hydroxide solution to determine if the potassium salt would be more water soluble. Under these conditions the polymer swelled more, to the point of breaking apart, but was still not completely solubilized. On the basis of the data in Table II, it can be concluded that for these systems it is necessary to maintain the hydrophobic portion of the amphiphilic stars to percentages below a value in the range of 7–17% in order to maintain water solubility. We are currently exploring other versions of monomer 3 which may lead to water-soluble amphiphiles with larger hydrophobic contents.

Summary. Amphiphilic star polymers can be made by facile ROMP techniques described here. Owing to the versatility of the ROMP initiator,[11] a variety of stars can be made with functional groups in the shell, in the core, or in both, to suit whatever application is desired. Uniform, low-polydispersity stars are obtained, provided that the right ratio of blocks and block lengths is targeted. Our motivation for making amphiphilic star polymers is to observe their behavior as model micelles in aqueous

solution. In view of this goal we have run into two competing factors; more uniform, monodisperse stars can be made by lowering the percentage of the hydrophilic portion, but water solubility requires increasing the hydrophilic portion. To obtain high molecular weight water-soluble stars free of uncoupled linear chains, the monomers or other aspects of the polymerization scheme need to be changed slightly, and these changes are the focus of ongoing research.

Acknowledgment. This work has been supported in large part by the National Science Foundation/MRL under Grant DMR-87-19217, through the CMSE at MIT. Special thanks go to Professor T. Alan Hatton at MIT for providing the initial concept for the application of these materials and thus the motivation for their synthesis. Partial support was supplied through the Charles E. Reed Initiatives Fund.

References and Notes

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