Metal-Centered Star Block Copolymers: Amphiphilic Iron Tris(bipyridine)-Centered Polyoxazolines and Their Chemical Fragmentation to Bipyridine-Centered BAB Triblock Copolymers

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ABSTRACT: Amphiphilic metal-centered six-arm star block copolymers were prepared by the sequential addition of two different oxazoline monomers to the hexafunctional metalloinitiator, [Fe(4,4′-bis-(chloromethyl)-2,2′-bipyridine)]$(PF_6)_2$. Polymers of the form [Fe{bpy(PEOX−PUOX)$_2$}$_3$]X_2, [Fe{bpy(PUOX−PEOX)$_2$}$_3$]X_2, and [Fe{bpy(PEOX−PPOX)$_2$}$_3$]X_2 (PEOX = poly(2-ethyl-2-oxazoline); PUOX = poly(2-undecyl-2-oxazoline); PPOX = poly(2-phenyl-2-oxazoline); X = Cl, I, or PF_6) were generated by reaction of the appropriate 2-R-2-oxazolines (R = Et, Ph, undecyl). In some cases sodium iodide was added to activate the initiator, and dipropylamine was used for termination. Since the labile core polymers fragment during GPC analysis, the iron was removed by reaction with aqueous K_2CO_3 for MW characterization by multiangle laser light scattering in $CHCl_3$ solution. The resulting bpy-centered telechelic BAB triblock copolymers, bpy(PEOX−PUOX)$_2$, bpy(PUOX−PEOX)$_2$, and bpy(PEOX−PPOX)$_2$, exhibit narrow molecular weight distributions (PDIs < 1.1) and molecular weights close to targeted values. For polymers prepared from ethyl and undecyl monomers, differential scanning calorimetry (DSC) measurements were performed for Fe-centered star homopolymers and block copolymers as well as for the corresponding metal-free bpy-centered linear polymers. DSC runs of block copolymers show T_g and T_m values that correlate well with those observed for the respective ethyl- and undecyloxazoline homopolymers.

Introduction

The properties of block copolymer systems, both in the melt and in solutions, are of considerable current interest.[1] In the bulk, block copolymers microphase separate to form materials with discrete morphologies that are dependent upon the temperature, the degree of polymerization, the interaction parameter, χ, and the polymer structure.[1] Similar parameters affect the aggregation behavior of block copolymers in solution studies and at the air−solvent interface using Langmuir−Blodgett techniques.[2] As new functionalized materials become accessible and their phase behavior becomes better understood, numerous applications for these materials are being proposed and developed. Block copolymer assemblies are being explored as surface and electrode coatings, as templates for assembling metal particles into nanoscale arrays for electronic and electrooptic devices, as waveguides, as membrane filters with controllable pore sizes, and for lithography.[1a] To a large extent, these investigations are driven by the development of new living polymerization methodologies (e.g., anionic, cationic, radical, and transition metal mediated) that allow for the synthesis of well-defined block copolymers with a wide range of compositions and architectures. Though it is desirable to incorporate metals into nanopatterned materials both for their physical properties (magnetism, color, luminescence, and electron transfer) and for their reactivity, metal-containing block copolymers are far more rare than those made from main group reagents. One approach to metal incorporation involves the selective degradation and removal of one microdomain from a microphase separated polymer film followed by introduction of metals into these preformed channels.[3] By using metal-containing monomers, Schrock and co-workers have demonstrated that steps can be saved in nanofabrication if metals are already present in a polymeric material prior to film formation.[4]

Recently we introduced the metal core macromolecule (MCM) concept, which constitutes a convenient new approach to the synthesis of well-defined metal-containing materials.[5] By using functionalized metal complexes as polymerization initiators, metal-centered linear and star-shaped polymers may be readily prepared. MCM targets may also be accessed using chelation,[6] coupling,[7] or termination strategies. We have shown that metal complexes with 4,4′-bis(halomethyl)-2,2′-bipyridine ligands serve as efficient multifunctional initiators for the controlled polymerization of a variety of oxazoline monomers.[8] Schubert et al. have extended this methodology to tetrahedral Cu(I) complexes made from 6,6′-bis(bromomethyl)-2,2′-bipyridine.[9] The versatility of the MCM approach has recently been demonstrated with its extension to the bulk polymerization of styrene using Cu ATRP methodology[10] and inert Ru tris(bipyridine) initiators with two, four, and six functionalities.[11]

In this account we describe the preparation of metal-centered six-arm star block copolymers from the hexafunctional initiator, [Fe{bpy(CH_2Cl)$_2$}$_3$]$(PF_6)_2$ (**1**), and ethyl-, phenyl-, and undecyloxazoline monomers (**2**−**4**).[5,8] It is also possible to take advantage of the lability of $[Fe(bpy)_3]^{2+}$ and its sensitivity to base to fragment the star block copolymers at the core, thus generating metal-free bpy-centered telechelic BAB triblock copolymers. Homopolymers made from ethyloxazoline (**2**) are hydrophilic and soluble in polar solvents whereas those made from undecyloxazoline are hydrophobic and soluble in nonpolar media; hence, copolymers with poly(2-ethyl-

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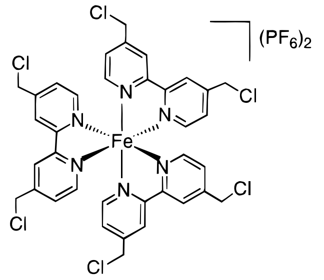
2-oxazoline) (PEOX) and poly(2-undecyl-2-oxazoline) (PUOX) blocks are amphiphilic.



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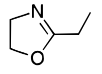

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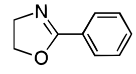

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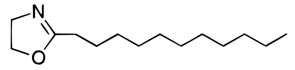

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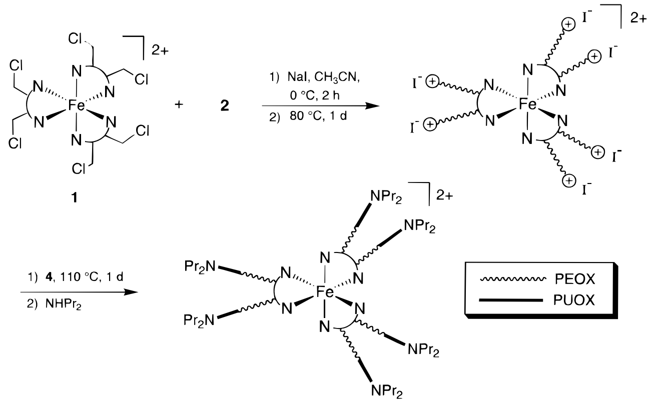
Results and Discussion

As part of our ongoing investigations of living polymerizations initiated by functionalized transition metal reagents and efforts to determine suitable reagents for preparing the targeted amphiphilic polymers, oxazoline monomers bearing different side chains were screened. To obtain well-defined block copolymers by a "one-pot two-stage" procedure,[12] it is necessary that the polymerization of the first block be living[13] and that it proceed smoothly to completion. The ethyl polymers met these criteria and were easiest to work up and to characterize. While the well-studied 2-methyl-2-oxazoline[14] system was also a serious candidate for a polar first block, the necessity of removing the Fe(II) cation and fragmenting the polymer for GPC analysis of the macroligand arms[5] proved to be problematic with poly(2-methyl-2-oxazoline). During the aqueous workup to remove salts, the methyl polymer formed an emulsion that was extremely difficult to resolve. While this bodes well for the preparation of amphiphilic materials, it complicates characterization of both the first and second blocks in copolymer synthesis. Since it was of interest to prepare materials with the hydrophilic block as the A block, near the cationic center, and others in which these polar blocks constituted the B blocks, separated from the metal core by a hydrophobic A block, the phenyl and undecyl monomers were also tested for their ability to serve as the first A block. Polymerizations of the undecyl-substituted oxazoline (**4**) also proceed to completion but with lower degrees of polymerization (DPs) and slightly higher polydispersities (PDIs) than are observed for the ethyl-substituted counterpart. Unfortunately, polymerizations with the phenyl monomer **3** do not consistently proceed to completion. High PDIs and low DPs are often obtained. Hence, the ethyl and undecyloxazoline monomers, **2** and **4**, proved more versatile for the first block in these investigations.

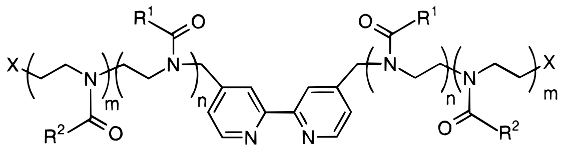
Iron tris(bipyridine)-centered star block copolymers were prepared by a one-pot two-stage procedure as is depicted for a PEOX−PUOX material in Scheme 1. In a typical reaction, the violet hexafunctional initiator, $[Fe\{bpy(CH_2Cl)_2\}_3](PF_6)_2$ (**1**), was combined with 2-ethyl-2-oxazoline (**2**) and NaI in acetonitrile solution. According to the procedure developed by Kobayashi et al. for conversion of benzylic chlorides to the corresponding iodides, the reaction was stirred at 0 °C for 2 h, and then it was heated to 80 °C for polymerization.[14b] After 1 day, an aliquot of living $[Fe(bpyPEOX_2)_3](PF_6)_2$ was removed for characterization of the first block, and the second monomer, either 2-phenyl-2-oxazoline (**3**) or 2-undecyl-2-oxazoline (**4**), was added. Reactions with the phenyl monomer were conducted at 100 °C for 2.5 days whereas the undecyl monomer was efficiently polymerized at 110 °C for 1 day. The undecyl monomer, **4**, is a solid at room temperature so it was necessary to warm it to >50 °C to ensure efficient delivery to the reaction by syringe. Since the PEOX−PUOX star block copolymers precipitate from the acetonitrile reaction medium as the length of the PUOX block increases, chlorobenzene was added with **4** to solubilize the polymer and to achieve higher DPs. Similarly, chlorobenzene was required for efficient polymerization of the inverse $[Fe\{bpy(PUOX-PEOX)_2\}_3]^{2+}$ star block copolymers. To generate the first block, the undecyl monomer, **4**, was reacted with **1** in a ~1:1 mixture of chlorobenzene and acetonitrile for 12 h at 110 °C. After removal of an aliquot for first block characterization, the second ethyl monomer was added, and the reaction was heated at 80 °C for 1 day. Upon completion, copolymerizations were typically terminated with dipropylamine and were concentrated in vacuo.

Scheme 1. Synthesis of Fe Tris(bipyridine)-Centered PEOX−PUOX Star Block Copolymers



Fe-centered homopolymer stars corresponding to the first block were purified by addition of methylene chloride or acetonitrile solutions to diethyl ether, thus precipitating red-violet solids. Like the Fe-centered star-shaped phenyl homopolymers, the ethyl−phenyl (PEOX−PPOX) star block copolymers readily precipitate as flocculant red-violet materials from CH_2Cl_2/Et_2O mixtures. Ethyl−undecyl and undecyl−ethyl star blocks, on the other hand, exhibit solubility features that are common for amphiphilic materials.[15] Whereas PEOX is soluble in chlorinated solvents and polar ones such as acetonitrile and alcohols, and may be precipitated from ether, PUOX exhibits opposite solubility properties. Namely, it is soluble in chlorinated solvents and may be precipitated from polar ones such as alcohols, DMF, and acetonitrile. Attempts to precipitate PEOX−PUOX and PUOX−PEOX copolymers by dissolution in a minimal amount of dichloromethane or chloroform followed by addition to either polar solvents such as methanol, ethanol, or acetonitrile or nonpolar ones such as diethyl ether or hexanes were all unsuccessful since the amphiphilic polymer remains in solution under these diverse conditions. These observations suggest that the amphiphilic PEOX−PUOX polymers are capable of exposing parts of the chain that are compatible with a given solvent environment and encapsulating segments which are not. Hence, ethyl−undecyl block copolymers were typically purified from any excess monomer and residual chlorobenzene by trituration with diethyl ether.

The UV/vis spectra of Fe-centered star block copolymers display absorptions typical for the red-violet



R^1 = Et, R^2 = Un; bpy(PEOX-PUOX)$_2$
R^1 = Un, R^2 = Et; bpy(PUOX-PEOX)$_2$
R^1 = Et, R^2 = Ph; bpy(PEOX-PPOX)$_2$
X = NPr_2 or OH

Figure 1. Telechelic bipyridine-centered BAB triblock copolymer macroligands.

[Fe(bpy)$_3$](PF$_6$)$_2$ chromophores [λ_{max} (ϵ) ~ 532–538 nm (9500)]. The ^1H NMR spectra are dominated by peaks attibutable to the polymer chains, PEOX, PUOX, or PPOX.[16] In both the Fe- and bipyridyl-centered PEOX derivatives, signals arising from core bipyridine (δ 8.2–8.7 br m, 7.1–7.5 br m) and "benzylic" bpy–CH_2– (δ 4.74, br s) protons are observable in CD_3CN solutions (DP = ~30 per halide initiator site). The fact that these signals are not evident in $CDCl_3$ solutions suggests that the polymer may possess a more compact structure.[15] The PUOX homopolymers are insoluble in acetonitrile. It is difficult to discern any peaks attributable to the bpy core protons in the ^1H NMR spectra of the undecyl polymers in $CDCl_3$ solution. For the higher molecular weight block copolymers in $CDCl_3$ solutions, no signals are observed in the ^1H NMR spectra for the benzylic or aromatic bipyridyl protons.

Since homopolymers and block copolymers with labile Fe cores fragment partially or entirely during molecular weight analysis by GPC,[5] they were routinely cleaved at the metal core using aqueous K_2CO_3 and were characterized as the metal-free macroligands. Interestingly, metal removal produces another functionalized polymer architecture, namely telechelic BAB triblock copolymer with a single bipyridine ligand in the middle of the A block (Figure 1). These are designated as bpy(P*A*OX–P*B*OX–X)$_2$ for sequential addition of A followed by B monomers where E = ethyl in PEOX, U = undecyl in PUOX, and P = phenyl in PPOX blocks of copolymer structures. Termination of the living polymers with $NHPr_2$ is expected to generate aminotelechelic materials (X = NPr_2) whereas reaction of the living Fe-centered star block copolymers with aqueous K_2CO_3 leads directly to the macroligands and is also an established protocol for introducing OH groups onto the chain ends.[17] Thus, hydroxytelechelic materials should result (X = OH). It should be noted that it is not possible to access these new bpy-centered macroligands directly from bpy(CH$_2$X)$_2$ (X = Cl, Br, I). Though these difunctional initiators generate narrow PDI polymers, their molecular weights are nearly twice the theoretical values. It has been demonstrated by Nuyken et al.[5a] that nucleophilic bpy nitrogens are capable of terminating oxazoline polymerizations, producing pyridinium chain ends,[18] which is a likely mechanism for polymer coupling reactions in these systems. Hence, the metal ion serves as a protecting group for the bipyridine moiety during cationic polymerization.

Molecular weight characterization of the metal-free polymers was conducted in chloroform solution using GPC equipped with refractive index (RI) and multiangle laser light scattering (MALLS) detectors. An overlay of GPC RI traces for a bpy(PEOX)$_2$ first block and the corresponding bpy(PEOX–PUOX–NPr$_2$)$_2$ triblock copolymer is provided in Figure 2.[19] Data obtained for a series of first block and BAB triblock copolymer macroligands made from ethyl and undecyl monomers **2** and **4** are given in Table 1. Entries 1–4 illustrate that it is possible to vary the lengths of the first and second blocks in PEOX–PUOX triblocks. The degree of polymerization per halide initiator site ranges from an average of ~55–90 for the first ethyl block and from 30 to 60 for the second undecyl block in these examples. Macroligand MWs of ~40 000 correspond to an Fe-centered star-shaped polymer of ~120 000. First block MWs are close to the targeted values, and for both the homopolymers and the triblocks, the PDIs are typically narrow. However, in most cases the second block reactions do not proceed to completion. The GPC data correlate well with block copolymer ethyl–undecyl ratios determined by integration of appropriate peaks in ^1H NMR spectra. A comparison of entries 4 and 5 (Table 1) shows that chloride and iodide initiators give rise to nearly identical results, indicating that the NaI additive is not necessary for the preparation of monodisperse Fe-centered star block copolymers. Overall, higher MWs are obtainable using the hexafunctional [Fe(bpy)$_3$] metal complex initiator **1** than are typically reported for monodisperse polyoxazoline systems.[14]

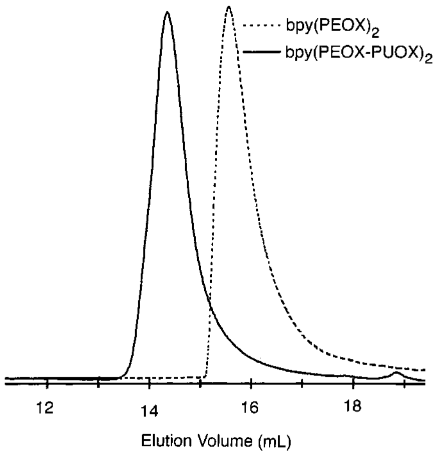


Figure 2. GPC traces for a first block bpy(PEOX)$_2$ homopolymer and the corresponding bpy(PEOX–PUOX)$_2$ triblock copolymer (RI detection, $CHCl_3$).

Preparation of metal-centered star block copolymers with hydrophobic inner cores were made by reacting with the chloride initiator **1** with 2-undecyl-2-oxazoline, **4**, first, followed by reaction with the ethyloxazoline, **2**. In general, this strategy was limited to lower DPs for the first block. Higher monomer loadings resulted in incomplete monomer consumption, broader PDIs, and, in some cases, slight low molecular weight shoulders on the GPC traces. Data in Table 1 indicate that reasonably well-defined star block copolymers were obtained from living PUOX with average degrees of polymerization ranging from 14 to 26 per halide initiator site (overall star DP = ~83–154). The bpy(PUOX)$_2$ first blocks typically exhibit slight shoulders on the low MW side of the GPC traces and broader PDIs than bpy(PEOX)$_2$ first block materials. However, the PDIs decrease, and the GPC curve becomes more symmetrical after polymerization of the second ethyl monomer, **2**. The bpy(PUOX–PEOX)$_2$ triblock copolymers reach an upper MW limit of ~22 000 regardless of monomer loading in the second block synthesis (entries 6–8). This type of upper MW ceiling has been observed previously in polymerizations of oxazoline monomers using inert

Table 1. Molecular Weight Data for Bipyridine-Centered Homopolymer and Block Copolymer Macroligands Obtained after Fragmention of the Respective [Fe(bpy)$_3$](PF$_6$)$_2$-Centered Six-Arm Star-Shaped Polyoxazolines[a]

entry no.	calcd MW ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PDI	calcd MW ($\times 10^{-3}$)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	PDI
		first block: bpy(PEOX)$_2$				triblock: bpy(PEOX−PUOX)$_2$		
1	20.2	18.4	20.8	1.13	42.0	32.6	34.7	1.07
2	15.2	15.7	16.8	1.07	38.7	29.9	31.1	1.04
3	10.3	11.2	11.8	1.05	35.7	28.6	31.0	1.08
4	10.3	10.8	11.4	1.06	35.3	29.6	31.7	1.07
5[b]	10.3	12.2	12.6	1.03	46.3	39.6	42.7	1.07
		first block: bpy(PUOX)$_2$				triblock: bpy(PUOX−PEOX)$_2$		
6	7.8	6.4	8.6	1.35	27.6	18.3	19.9	1.08
7	10.9	8.7	11.6	1.34	30.7	20.4	21.2	1.04
8	15.0	11.7	14.0	1.20	34.8	22.1	22.8	1.03

[a] Determined by GPC in CHCl$_3$ at 25 °C using MALLS and RI detection. PEOX = poly(2-ethyl-2-oxazoline); PUOX = poly(2-undecyl-2-oxazoline); bpy = bipyridine. [b] Chloride initiator **1**; no NaI added.

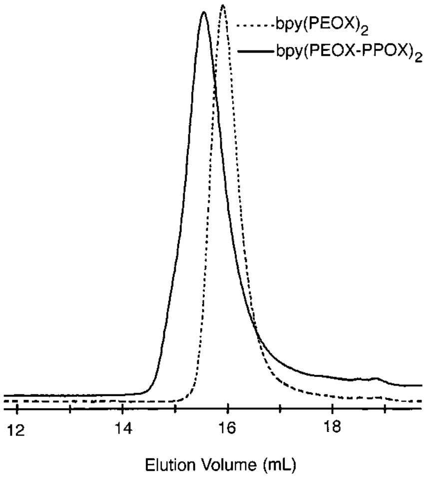


Figure 3. GPC traces for a first block bpy(PEOX)$_2$ homopolymer and the corresponding bpy(PEOX−PPOX)$_2$ triblock copolymer (RI detection, CHCl$_3$).

Ru tris(bipyridine) reagents with two, four, and six initiator sites.[20]

It was also possible to prepare Fe-centered star block copolymers by addition of ethyloxazoline, **2**, followed by the phenyl monomer, **3**. A GPC overlay of bpy(PEOX)$_2$ and the corresponding bpy(PEOX−PPOX)$_2$ triblock copolymer macroligand is given in Figure 3. The following molecular weight data were obtained: first block, M_n = 5500, M_w = 5800, and PDI = 1.05 for MW (calcd) = 6100; PEOX−PPOX triblock, M_n = 12 900, M_w = 14 500, and PDI = 1.12 for MW (calcd) = 14 900. Again, very narrow polydispersities were observed, and molecular weights were close to the theoretical values. This copolymer posseses an average of 25 ethyl and 25 phenyl repeat units per halide initiator site and an overall molecular weight of ~45 000 for the [Fe(bpy)$_3$]-centered star. In contrast to the bpy(PEOX−PUOX)$_2$ and bpy(PUOX−PEOX)$_2$ triblock copolymers, it must be noted that it was very difficult to obtain reproducible results with the PEOX−PPOX system. It is our experience that molecular weight data for phenyl-substituted polyoxazolines are dependent upon the solution and thermal histories, and it is not uncommon to obtain broad and multiple peaks in GPC traces. This has been observed previously by Litt et al., who have illustrated this variable GPC behavior for PPOX−PUOX copolymers.[21] These challenges that PPOX-containing systems present for routine GPC analysis make it extremely difficult to confirm whether PEOX−PPOX copolymers have been successfully prepared.

Table 2. DSC Data for Fe- and Bpy-Centered Polyoxazolines

sample	M_n (kg/mol)	PEOX T_g (°C)[a]	PUOX T_m (°C)[b]
[Fe{bpy(PEOX)$_2$}$_3$]$^{2+}$	55.2	55	
bpy(PEOX)$_2$	18.6	55	
[Fe{bpy(PUOX)$_2$}$_3$]$^{2+}$	27.2		131, 138
bpy(PUOX)$_2$	8.7		132, 142
[Fe{bpy(PEOX−PUOX)$_2$}$_3$]$^{2+}$	122.4	56[c]	112, 120
bpy(PEOX−PUOX)$_2$	39.6	56[c]	113, 123
[Fe{bpy(PUOX−PEOX)$_2$}$_3$]$^{2+}$	56.0	57	126, 135
bpy(PUOX−PEOX)$_2$	18.3	57	124, 136

[a] Middle of change of heat capacity. [b] Onset, peak. [c] T_g was obtained from the first heating cycle.

Thermal analysis of poly(oxazolines) is consistent with previous studies,[21,22] and Fe block copolymers also exhibit reversible thermochromism as was observed for Fe-centered homopolymers.[5a] Thermogravimetric analysis (TGA) revealed that the onset of thermal decomposition of the Fe and bpy-centered polymers was in the range 365−385 °C for samples heated under a nitrogen atmosphere. Less than 2% weight loss was observed prior to this temperature. Thermal data obtained by modulated differential scanning calorimetry (MDSC) are summarized in Table 2. All samples were subjected to the same heating regime. Polymers were heated to 160 °C to drive off residual solvent and for thermal conditioning. This end point (160 °C) is above the T_m of PUOX and below the temperature at which the red-violet Fe chromophores begin to bleach.[5a] Samples were then cooled to −10 °C before being reheated to 160 °C to record thermal events arising from PEOX and PUOX components. Finally, after cooling again to −10 °C, the samples were reheated to 210 °C in attempt to observe any thermal events attributable to changes at the Fe centers. The PUOX melting and PEOX glass transition temperatures reported in Table 2 were obtained from the heat capacity component (reversing heat flow) of the MDSC scans for the second heating cycles. DSC curves (reversing heat flow) corresponding to [Fe{bpy(PEOX)$_2$}$_3$] and [Fe{bpy(PUOX)$_2$}$_3$] star-shaped homopolymers and a [Fe{bpy(PUOX−PEOX)$_2$}$_3$] star block copolymer are shown in Figure 4. Glass transitions corresponding to amorphous PEOX are evident at ~56 °C in Fe-containing and metal-free bpy(PEOX)$_2$ homopolymers and bpy(PUOX−PEOX)$_2$ block copolymers. For bpy(PEOX−PUOX)$_2$ materials, glass transitions for the PEOX block are only evident in the first heating cycle. For Fe-centered and metal-free bpy(PUOX−PEOX)$_2$ samples, in contrast, the PEOX glass transition is evident even after several heating cycles to 160 °C. All homopolymer and block copolymer PUOX-containing materials exhibit

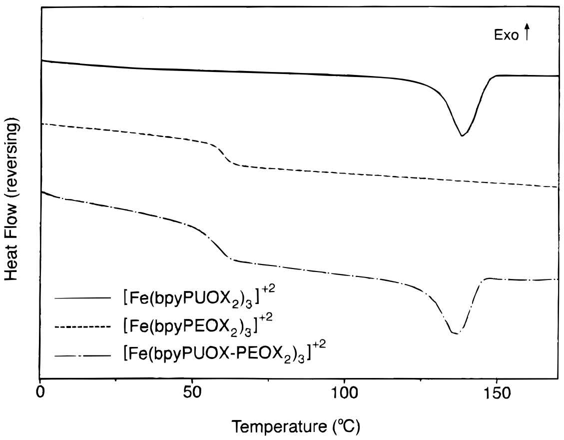


Figure 4. Comparison of DSC curves for $[Fe(bpy(PUOX)_2)_3]^{2+}$ and $[Fe(bpy(PEOX)_2)_3]^{2+}$ star-shaped polymers and a $[Fe(bpy(PUOX-PEOX)_2)_3]^{2+}$ star block copolymer.

a melt in the range ~120−142 °C (peak). When cooling cycles (5 °C/min) were monitored, crystallization of PUOX regions was observable in the 85−110 °C temperature range. Evidence of separate thermal events unique to each component of the block copolymer in $[Fe\{bpy(PUOX-PEOX)_2\}_3]$ is consistent with a microphase separated material. The Fe-centered PEOX−PPOX star block copolymer exhibited a T_g at 57 °C that remained over several heating cycles. Curiously, no thermal event is observable in the DSC scans between 180 and 210 °C, the temperature range over which red-violet samples of Fe-centered homopolymers and block copolymers begin to fade and eventually become colorless.[5a] More detailed spectroscopic analysis is underway to address the issue of reversible thermochromism in $Fe(bpy)_3$-containing star polymers and blends.

Conclusion

This investigation explored the possibilities for generating metal-centered star block copolymers using hexafunctional iron tris(bipyridine) initiators and a variety of different oxazoline monomers. Sequential addition of ethyloxazoline followed by either phenyl- or undecyloxazoline monomers generates red-violet Fe-centered PEOX−PPOX or PEOX−PUOX star block copolymer materials with molecular weights close to targeted values. These materials have charged metal complex cores surrounded by a hydrophilic PEOX region and hydrophobic PPOX or PUOX outer shells. Inverse amphiphilic PUOX−PEOX Fe-centered materials were formed by addition of the undecyl monomer first, followed by ethyloxazoline polymerization. These red-violet polymers also have charged Fe cores, but ones that are encapsulated by hydrophobic PUOX regions, with hydrophilic PEOX comprising the outer segments. In this study either dipropylamine or aqueous potassium carbonate was utilized to terminate these cationic polymerizations. These are known procedures for introducing amine and hydroxyl functionalities to the polymer chain ends. By varing the nucleophilic reagent used to terminate these cationic reactions, it should be possible to introduce new types of end groups into these fascinating new materials. The six-armed Fe-centered star-shaped block copolymers and their corresponding first block precursors may all be fragmented to generate metal-free telechelic bpy-centered macroligands using aqueous potassium carbonate for MW characterization. Star block copolymers yield telechelic bpy-centered BAB triblock copolymers. Moreover, the Fe(II) ion serves as a protecting group in macroligand synthesis since it is not possible to form these targets starting from the halomethyl bpy free ligand initiator. All polymers were analyzed by modulated DSC. For all PUOX materials a T_m was observed between 120 and 142 °C, whereas PEOXs prepared from Fe initiators exhibit glass transitions at ~57 °C. For certain polymers these are retained after repeated heating cycles; however, in the case of the polar core PEOX−PUOX Fe-centered stars, the PEOX T_g is no longer evident after the first heating. DSC scans of PUOX−PEOX polymers, in contrast, continue to exhibit isotherms arising from both PUOX and PEOX blocks after several heating cycles. This observation bodes well for obtaining microphase separated thin-film materials with $[Fe(bpy)_3]^{2+}$ chromophores embedded in the crystalline PUOX block that is segregated from the glassy PEOX regions. Moreover, these amphiphilic polymers could display interesting behavior in solutions and when combined with membrane lipids or surfactants. More detailed materials characterization is planned to further explore these issues.

Experimental Section

General Considerations. *Materials.* 2-Ethyl-2-oxazoline, 2-phenyl-2-oxazoline (Aldrich), and acetonitrile were purified by distillation from CaH_2. 2-Undecyl-2-oxazoline was prepared and purified by the method of Jung et al.[23] Anhydrous chlorobenzene (H_2O content <0.005%) and dipropylamine were used as received (Aldrich). The initiator, $[Fe\{bpy(CH_2Cl)_2\}_3](PF_6)_2$, was prepared by reaction of 4,4′-bis(chloromethyl)-2,2′-bipyridine[24] with $(NH_4)_2Fe(SO_4)_2$ as previously described.[5a]

Instrumentation. ^1H NMR spectra were recorded on a GE QE 300 spectrometer in $CDCl_3$, CD_2Cl_2, or CD_3CN. UV/vis spectra of polymers were obtained for $CHCl_3$ solutions using a Hewlett-Packard 8452A diode array spectrophotometer. IR spectra was obtained as KBr pellets with a Nicolet Impact 400D FTIR spectrometer. Molecular weight determination was performed by GPC in $CHCl_3$ solution using multiangle laser light scattering (MALLS), refractive index, and diode array UV/vis detection with Polymer Labs 5μ Mixed C columns and Wyatt Technologies Inc. and Hewlett-Packard instrumentation and software as previously described.[5a] Refractive index increments were obtained as previously described.[5a] Differential scanning calorimetry measurements were performed using a TA Instruments DSC 2920 modulated DSC. Analysis was performed in modulated mode (under N_2, amplitude = 1 °C; period = 60 s; heating rate = 5 °C/min; range = −10 to 160 °C (cycled twice) and a final ramp from −10 to 210 °C). Reported values of thermal events are from the second heating cycle and the reversing heat flow curve (T_g = the midpoint of the change in the heat capacity; T_m reported as onset and peak) unless otherwise indicated. Thermogravimetric analysis was conducted using a TA Instruments TGA 2020 thermogravimetric analyzer from 30 to 500 °C at a heating rate of 10 °C/min.

Representative Synthesis of $[Fe\{bpy(PEOX-PUOX)_2\}_3](PF_6)_2$ Star Block Copolymers. The Fe initiator **1** (0.0114 g, 1.03×10^{-5} mol) was combined with NaI (0.0185 g, 1.24×10^{-4} mol) in a dry Kontes tube under a nitrogen atmosphere. To this solid mixture was added 2-ethyl-2-oxazoline (0.306 g, 3.09×10^{-3} mol) and dry CH_3CN (2.4 mL). The red-violet reaction mixture was sealed and stirred at 80 °C for 1 day. For characterization of the first block, an aliquot of the ethyl homopolymer (1.4 mL) was transferred to a round-bottom flask, was cooled to room temperature (RT), and then was treated with dipropylamine (0.0221 g, 2.2×10^{-4} mol) to terminate. After stirring the aliquot for 1 day, the ethyl homopolymer was concentrated in vacuo to yield a dark red glassy polymer. To the remaining living Fe-centered PEOX was added chlorobenzene (0.4 mL) and 2-undecyl-2-oxazoline (0.383 g, 1.70×10^{-3} mol). The sealed mixture was stirred at 110 °C for 1 day before cooling to RT and terminating with dipropylamine (0.0221 mg, 2.2×10^{-4} mol). Concentration of the reaction mixture in vacuo followed by trituration with ether (30 mL) for 1 h afforded a dark red solid: 0.407 g (77%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.2−3.6 (br m, $-(\mathrm{N(C}H_2)_2)-$), 2.1−2.5 (br m, $-(\mathrm{C(O)C}H_2)-$), 1.5−1.7 (br m, $-(\mathrm{C(O)CH_2C}H_2\mathrm{(CH_2)_8})-$), 1.0−1.4 (br m, $-(\mathrm{C(O)CH_2C}H_3)$), $-(\mathrm{C(O)(CH_2)_2(C}H_2)_8)-$), 0.9 (t, $J = 7$ Hz, $(\mathrm{CH_2})_{10}\mathrm{C}H_3$)). IR (KBr): 2975 (CH aliphatic), 1644 (C=O), 1431 cm^{-1} (C−N). UV ($CHCl_3$) λ_{max}, 535 nm.

Representative Synthesis of [Fe{bpy(PUOX−PEOX)$_2$}$_3$](PF$_6$)$_2$ Star Block Copolymers. The Fe initiator **1** (0.0254 g, 2.30×10^{-5} mol) was delivered to a dry Kontes tube under a nitrogen atmosphere. To this mixture was added 2-undecyl-2-oxazoline (0.739 g, 3.28×10^{-3} mol), dry CH_3CN (2.5 mL), and dry chlorobenzene (2.8 mL). The red-violet reaction mixture was sealed and stirred at 110 °C for 12 h. For characterization of the first block, an aliquot of the undecyl homopolymer (2.0 mL) was transferred to a round-bottom flask, was cooled to RT, and was fragmented as described above for PEOX materials. To the remaining living Fe-centered PUOX was added 2-ethyl-2-oxazoline (910 mg, 9.27×10^{-3} mol). The sealed mixture was stirred at 80 °C for 1 day before cooling to RT and concentrated in vacuo. The product was triturated with ether (30 mL) for 1 h to afford a dark red solid: 1.010 g (72%) ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.2−3.6 (br m, $-(\mathrm{N(C}H_2)_2)-$), 2.1−2.5 (br m, $-(\mathrm{C(O)C}H_2)-$), 1.5−1.7 (br m, $-(\mathrm{C(O)CH_2C}H_2\mathrm{(CH_2)_8})-$), 1.0−1.4 (br m, $-(\mathrm{C(O)CH_2C}H_3)$, $-(\mathrm{C(O)(CH_2)_2(C}H_2)_8)-$), 0.9 (t, $J = 7$ Hz, $(\mathrm{CH_2})_{10}\mathrm{C}H_3$)). IR (KBr): 2930 (CH aliphatic), 1644 (C=O), 1426 cm^{-1} (C−N). UV ($CHCl_3$) λ_{max}, 535 nm.

Representative Synthesis of [Fe{bpy(PEOX−PPOX)$_2$}$_3$](PF$_6$)$_2$ Star Block Copolymers. The Fe initiator **1** (0.0280 g, 2.53×10^{-5} mol) was combined with NaI (0.0460 g, 3.07×10^{-4} mol) in a dry Kontes tube under a nitrogen atmosphere. To this mixture was added 2-ethyl-2-oxazoline (0.451 g, 4.55×10^{-3} mol) and dry CH_3CN (6.0 mL). The red-violet reaction mixture was sealed and stirred at 80 °C for 1 day. For characterization of the first block, an aliquot of the ethyl homopolymer (3.25 mL) was transferred to a round-bottom flask, was cooled to RT, and then was treated with dipropylamine (0.0221 g, 2.2×10^{-4} mol) to terminate. After stirring the aliquot for 1 day, the ethyl homopolymer was concentrated in vacuo to yield a dark red glassy polymer. To the remaining living Fe-centered PEOX was added 2-phenyl-2-oxazoline monomer, **3** (0.336 g, 2.28×10^{-3} mol). The sealed mixture stirred at 100 °C for 2.5 days before cooling to room temperature and terminating with dipropylamine (0.0221 g, 2.2×10^{-4} mol) as above. The reaction mixture was added to ether (30 mL) to precipitate a red flocculant solid. Collection by centrifugation and drying in vacuo afforded a dark red glassy solid: 0.450 g (80%). ^{1}H NMR (300 MHz, CD_2Cl_2, δ): 7.0−7.5, (br m, $-(\mathrm{C_6}H_5)$), 2.8−3.8 (br m, $-(\mathrm{N(C}H_2)_2)-$), 2.1−2.5 (br m, $-(\mathrm{C(O)C}H_2)-$), 1.0−1.2 (br m, $-(\mathrm{C(O)CH_2C}H_3)$). IR (KBr): 3057 (CH aromatic), 2936 (CH aliphatic), 1634 (C=O), 1420 cm^{-1} (C−N). UV ($CHCl_3$) λ_{max}, 538 nm.

Fe-Centered Star-Shaped Polymer Fragmentation. To the Fe-centered star-shaped polymer (PEOX homopolymers or PEOX−PPOX copolymers) (~0.200 g) was added K_2CO_3 (~0.200 g), H_2O (2 mL), and CH_3CN (6 mL). (Note: for the PUOX and PEOX−PUOX systems (~0.200 g), a H_2O (3 mL), CH_3CN (4 mL), CH_2Cl_2 (5 mL) solvent mixture was employed.) The mixture was stirred at 80 °C for 1 day in a sealed flask under air. After cooling to RT, H_2O (10 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (3×15 mL). Combined organic fractions were washed with H_2O (1×10 mL) and then were concentrated in vacuo to afford colorless powdery solids. (Note: the PEOX homopolymers form emulsions in this CH_2Cl_2/H_2O workup procedure. Typically these emulsions are not broken up with brine, but they clarify after standing for several hours. The amphiphilic PUOX−PEOX and PEOX−PUOX block copolymers also form emulsions, but typically these clarify more quickly.) Typical yields: bpy(PEOX)$_2$, 80−90%; bpy(PUOX)$_2$, essentially quantitative; bpy-centered block copolymers, 85−95%.^{1}H NMR spectra for the metal-free bpy-centered polymers are indistinguishable from the corresponding Fe-containing materials.

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References and Notes

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