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EPR Study of Spin Labeled Brush Polymers in Organic Solvents

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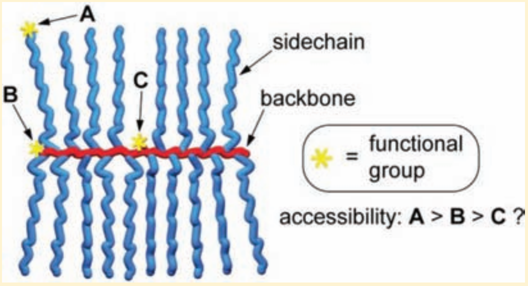
Supporting Information



ABSTRACT: Spin-labeled polylactide brush polymers were synthesized via ring-opening metathesis polymerization (ROMP), and nitroxide radicals were incorporated at three different locations of brush polymers: the end and the middle of the backbone, and the end of the side chains (periphery). Electron paramagnetic resonance (EPR) was used to quantitatively probe the macromolecular structure of brush polymers in dilute solutions. The peripheral spin-labels showed significantly higher mobility than the backbone labels, and in dimethylsulfoxide (DMSO), the backbone end labels were shown to be more mobile than the middle labels. Reduction of the nitroxide labels by a polymeric reductant revealed location-dependent reactivity of the nitroxide labels: peripheral nitroxides were much more reactive than the backbone nitroxides. In contrast, almost no difference was observed when a small molecule reductant was used. These results reveal that the dense side chains of brush polymers significantly reduce the interaction of the backbone region with external macromolecules, but allow free diffusion of small molecules.

INTRODUCTION

The combination of controlled polymerization techniques with selective, robust, postpolymerization chemistries has greatly improved our ability to control the size and functionality of macromolecular structures on length scales from tens to hundreds of nanometers.[1−5] Dendrimers, which have a globular shape, a uniform branched structure, and abundant surface functional groups, have been among the most widely studied macromolecular architectures[6−8] due to their potential in applications that range from nanomedicine to molecular electronics.[9−14] Despite this potential, the multistep, iterative synthesis of dendrimers limits their industrial application. Hyperbranched polymers represent an alternative to dendrimers with easier synthetic access; typically, their molecular weight (MW) is not easily controlled.[15−17] Bottle-brush polymers[18−20] and dendronized polymers,[21−23] which possess a very high density of polymer side chains or dendrons, uniformly grafted to the backbone of a linear polymer, are another highly branched polymer architecture. Their sterically crowded architecture leads to an extended backbone conformation and a corresponding cylindrical, wormlike nanostructure.[18−20] This cylindrical structure distinguishes the shape of bottle-brush polymers from the globular shapes of dendrimers and hyperbranched polymers; in applications like solution and bulk self-assembly, where polymer shape is a critical feature, brush polymers behave differently from spherical nanostructures.[24−33]

Recently, we and other groups have demonstrated that ring-opening metathesis polymerization (ROMP) of norbornene-terminated macromonomers (MMs) initiated by a Ru-based catalyst is a powerful, general approach for the synthesis of brush polymers via the "graft through" method.[31,33−39] Using this strategy, well-defined brush homopolymers and copolymers with high molecular weights (MWs) and low polydispersities (PDIs) can be easily prepared in high yields. Unlike spherical dendrimers, whose symmetric structures can be divided into two domains typically called the corona (periphery) and core, bottle-brush structures can generally be divided into three domains: periphery, backbone end, and backbone middle. We wondered if functional groups placed in these regions would display unique, location-dependent reactivities and interactions with the outside environment. In particular, we hypothesized that functional groups anywhere along the backbone would be less accessible to the outside medium than peripheral functional groups, and that functional groups located at the ends and in the middle of the backbone would have different mobilities and/or steric environments. Ultimately, these differences could be used for kinetic control of postpolymerization modification, or for controlled self-assembly and interaction with biological systems. Understanding the interactions of pendant functional

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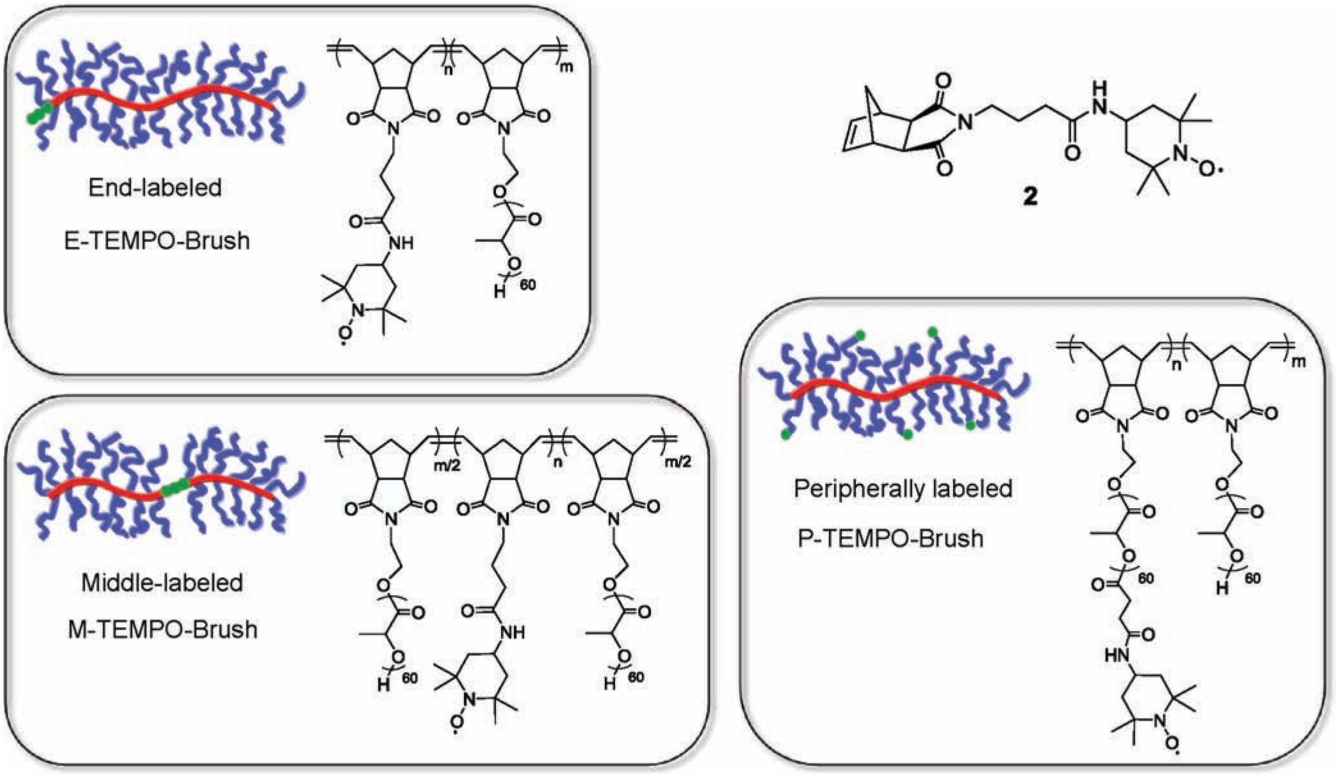
Chart 1. Structures of Norbornene-TEMPO Monomer 2 and TEMPO-Labeled Brush Polymers Used in This Study



groups with local side chains and their reactivity at different locations on a brush polymer is of fundamental importance for applications of brush polymers as well-defined, cylindrical molecular carriers in drug delivery, catalysis, and molecular recognition.

Electron paramagnetic resonance (EPR) spectroscopy is a powerful technique for the study of local structural and dynamic behavior of paramagnetic, spin-labeled polymer chains or molecular assemblies.[40−42] Common nitroxide free-radical spin-probes can be easily installed into macromolecules; their EPR spectra are very sensitive to local polarity, viscosity, and polymer segmental motion. As a result, EPR has been widely utilized to investigate polymer chain aggregation and segmental mobility as it pertains to phase transition behavior and/or heterogeneity in polymer blends,[43−45] block copolymers,[46−49] and polymer solutions[50,51] or gels,[52] as well as to obtain solution conformation and dynamic information about macromolecules.[53−56] Particularly, application of the EPR technique to study the dynamic structure of dendrimers has been actively pursued. For example, poly(amidoamine) (PAMAM) dendrimers have been spin-labeled either covalently at the periphery or noncovalently via encapsulation or diffusion of a spin label inside the dendrimer. EPR studies of these spin-labeled PAMAMs have provided useful information on the structure and dynamic behavior of the dendritic branches,[57−60] the interaction of dendrimers with surfactants,[61] biomolecules,[62−64] and surfaces,[65] and encapsulation of small molecules inside the "dendritic box".[66]

In this report, living ROMP of MMs has allowed us to easily incorporate spin-labels at desired positions along the backbone of narrowly dispersed brush polymers through sequential copolymerization of a small-molecule norbornene-nitroxide with norbornene-terminated polylactide MMs. EPR analysis of these brush polymers revealed different steric environments throughout the brush polymers and demonstrated position-dependent reactivity of nitroxide radicals toward a polymeric reactant. To the best of our knowledge, this report represents the first examples of chemically spin-labeled brush polymers and their subsequent study by EPR. These results provide quantitative information on the local environment of a brush polymer in solution.

■ RESULTS AND DISCUSSION

Synthesis of Spin-Labeled Brush Polymers. Using the fast initiating ruthenium catalyst (IMesH$_2$)-(PCy$_3$)(py)$_2$RuCl$_2$-(CHPh) **1**, ROMP of MMs with strained olefin end groups can proceed in a living fashion to produce brush block polymers if two types of MMs are polymerized sequentially.[31,39] We took advantage of this strategy to incorporate nitroxide radical spin-labels into different positions along the backbone. An *exo*-norbornenyl monomer **2** with a pendent 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) group was polymerized in CH$_2$Cl$_2$ using **1**. The resulting homopolymer had a very low PDI of 1.08 and a MW that matched the theoretical value as determined by the ratio of monomer to catalyst (Supporting Information Figure S2). This result indicates that the nitroxide radical does not interfere with living ROMP. Metathesis polymerization is particularly attractive, because unlike radical polymerization methods where TEMPO has to be formed by oxidation from tetramethyl-4-piperidinol or attached post polymerization, ROMP allows direct incorporation of TEMPO labels into polymers.

To prepare a brush polymer with TEMPO labels at the end of the backbone, a 5-fold excess of **2** was treated with **1** to form the first pseudo-block, followed by the addition of a MM to grow the brush polymer. Similarly, for the preparation of mid-backbone labeled brush polymer, 5 equiv of **2** was added after the first block of MM had completely reacted, followed by the addition of the third block of MM. Following this strategy, we prepared TEMPO-labeled polylactide (PLA) brush polymers (side chain MW = 4 kDa) with PDIs < 1.1 and high MWs close to the theoretical values (Chart 1, Table 1). A peripherally labeled sample was synthesized by coupling *N*-TEMPO-succinamic acid to ~5% of the hydroxyl end groups of PLA side chains of a PLA brush homopolymer. The same amide linkage to TEMPO was used for all the labeled brush polymers to ensure the same electronic environment of the nitroxide. The number of TEMPO labels per brush polymer chain was measured to be 6, 6, and 4 for the end, middle, and peripherally labeled brush polymers, respectively, against standard TEMPO solutions. The extent of TEMPO labeling in each case was consistent with the target stoichiometry of the labeling reaction.

Table 1. Characteristics of TEMPO-Labeled PLA Brush Polymers

sample name	$M_{w,\ GPC}$[a] (kDa)	$M_{w,\ theo}$[b] (kDa)	PDI[c]
E-TEMPO-Brush[d]	444	440	1.04
M-TEMPO-Brush[d]	410	440	1.03
P-TEMPO-Brush[d]	474	440	1.01

[a] Absolute MW determined by MALLS using $dn/dc = 0.05$, which was determined from the RI measurement. [b] Theoretical MW calculated using MW = 4400[MM/Ru]$_0$. [c] Determined by THF GPC using RI and MALLS detectors. [d] PLA brush polymers with TEMPO labels at the end of backbone (*E-TEMPO-Brush*), the middle of backbone (*M-TEMPO-Brush*), and the periphery (*P-TEMPO-Brush*).

EPR of Spin-Labeled Brush Polymers. EPR spectra of various labeled brush polymers were recorded in deoxygenated dichloromethane (DCM), dimethylformamide (DMF), and dimethylsulfoxide (DMSO) at 25 °C. The correlation time for the rotational diffusion motion, τ, was obtained by simulation of the experimental spectra.

In previous EPR studies of dendrimers (e.g., PAMAM), nitroxide radicals were covalently attached at the periphery. Strong spin−spin exchange interactions between spin-labels usually led to significantly broadened peaks in the EPR spectra, and eventually to collapse of the lines into a single exchange-narrowed line, especially for dendrimers with a large number of spin-labels.[57,58] In contrast, each of the brush polymers studied here displayed characteristic nitroxide 1:1:1 triplet signals in the EPR spectrum regardless of the location of the nitroxide label (Figure 1). This observation suggests that the labels in these brush polymers are well separated; the electron exchange integral J is much less than the ^{14}N hyperfine coupling constant ($J \ll a_N$). Indeed, even for the polynorbornene-TEMPO homopolymer, triplet signals were observed when DCM, DMF, or DMSO was used as the solvent. When THF was used as the solvent for poly(**2**), we observed a broad, single EPR peak, which suggests a collapsed chain conformation and close proximity of the spin labels in THF (Supporting Information Figure S3A). Therefore, only DCM, DMF, and DMSO were used for our EPR study.

In the range of nitroxide concentration from 0.1 to 0.001 mM, no concentration-dependent EPR line-broadening was observed for spin-labeled brush polymers (Supporting Information Figure S4), which indicates that the polymers are segregated and that nitroxides on different polymers do not interact. Therefore, we used a nitroxide concentration of 0.05 mM for all the brush polymers in the EPR experiments. τ is an important EPR parameter that is sensitive to the change of environment surrounding

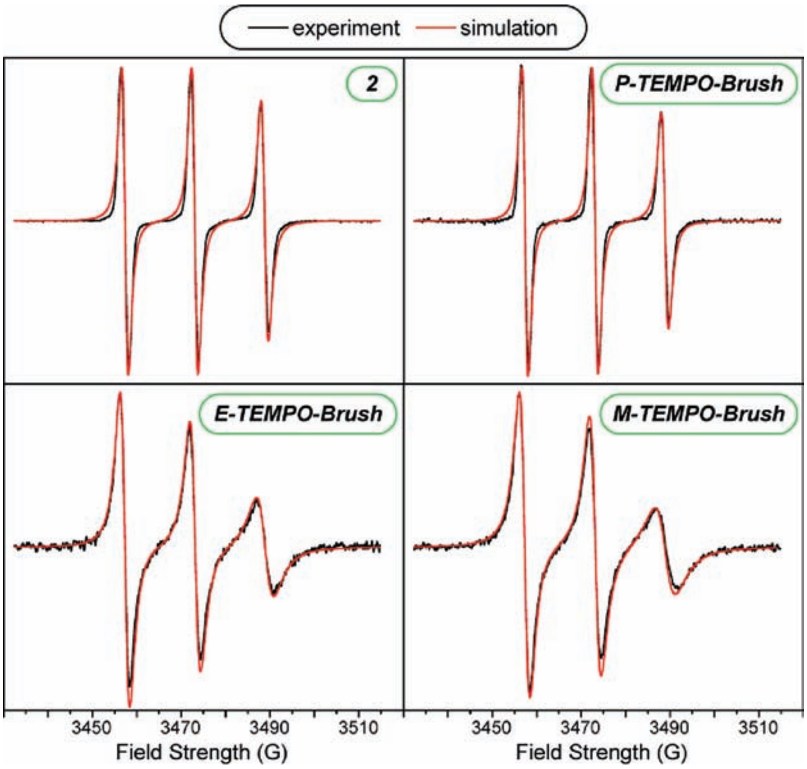


Figure 1. EPR spectra of TEMPO-labeled PLA brush polymers in DMSO ([nitroxide] = 0.05 mM).

Table 2. EPR Characteristics of Monomer 2 and Brush Polymers with Spin-Labels at Different Chain Locations in Deoxygenated DCM, DMF, and DMSO at [nitroxide] = 0.05 mM

	solvent	τ/ns	% broad	anisotropy
Monomer **2**	DCM	0.005	0	No
	DMF	0.037	0	No
	DMSO	0.095	0	No
E-TEMPO-Brush	DCM	0.235	21	No
	DMF	0.36	25	Yes
	DMSO	0.59	0	Yes
M-TEMPO-Brush	DCM	0.235	19	No
	DMF	0.36	15	Yes
	DMSO	0.81	8	Yes
P-TEMPO-Brush	DCM	0.005	0	No
	DMF	0.033	0	No
	DMSO	0.13	0	No

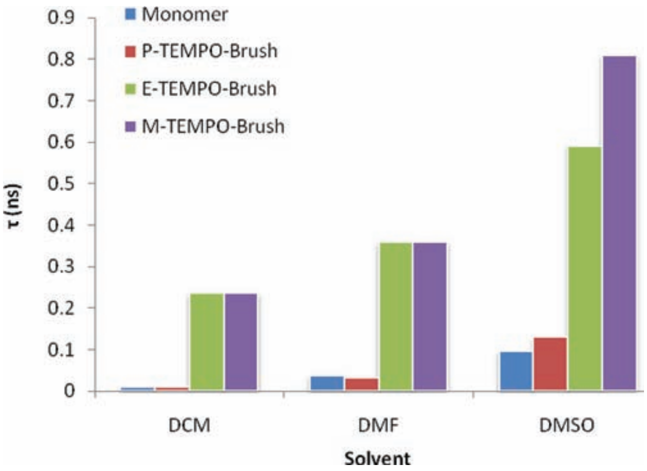


Figure 2. Rotational correlation times (τ) of TEMPO monomer and brush polymers with spin-labels at different chain locations in deoxygenated DCM, DMF, and DMSO at [nitroxide] = 0.05 mM.

the radical, such as solvent viscosity and steric hindrance. Computation of the EPR spectra by a well-known procedure reported by Budil et al.[67] accurately provided the τ values. Brownian rotational diffusion was assumed in the calculation. The τ values increased in the order $\tau_{DCM} < \tau_{DMF} < \tau_{DMSO}$ for the monomer and for each of the spin-labeled brush polymers at the same concentration (Table 2), consistent with the increase of solvent viscosity. As we compared τ for each type of spin-labeled brush polymer in all three solvents, the same trend was observed: peripherally labeled brush polymer (P-TEMPO-Brush) gave the smallest τ, almost the same as that of the monomeric TEMPO, but when the labels were tethered on the backbone, either at the end (E-TEMPO-Brush) or in the middle (M-TEMPO-Brush), considerably larger values of τ were observed (Figure 2 and exemplary spectra in DMSO shown in Figure 1). In DCM and DMF, the τ values for both the end and middle-labeled brush polymers were the same, but accurate simulation of the spectra for these samples required addition of another component, which was termed "broad" (Table 2). This component arises from interaction of adjacent nitroxides, which results in line broadening in the EPR spectrum. In DMF and DCM, the percentage of this broad component is higher for the E-TEMPO-Brush than for the M-TEMPO-Brush, which may be due to the lower steric hindrance and greater flexibility of nitroxides to interact with each other at the end versus the middle of the backbone. In DMSO, there was almost no broad signal contribution, indicating that the EPR signal in DMSO originates only from individual spin-labels. Therefore, DMSO is identified as the best EPR solvent to differentiate steric environments among the different brush polymer regions. In DMSO, the M-TEMPO-Brush had a larger τ than the E-TEMPO-Brush, and labels in both backbone regions had much larger values of τ than labels on the periphery. Since τ is inversely related to the mobility of the spin-label, this result clearly indicates a difference in the mobility of spin-labels at different locations of the brush polymers in DMSO. Considering all the labeled brush polymers had almost the same MW and composition, the difference is attributed to the steric crowding created by dense side chains and the chain mobility of different regions of a brush polymer.

The EPR spectra of M-TEMPO-Brush and E-TEMPO-Brush also exhibited anisotropy in DMF and DMSO, while anisotropy was not observed for the monomeric TEMPO and P-TEMPO-Brush. Anisotropy in the orientation of the rotational main axis of spin labels confirms that steric interactions lead to hindered rotation for the spin labels on the backbone in DMF and DMSO.[68] In contrast, peripherally labeled samples exhibited no anisotropy, which suggests that the peripheral spin labels freely rotate and are not constrained.

Quenching Experiment. Since dense side chains provide steric shielding to the backbone functional groups, the more shielded areas should be less accessible to external reactants. This effect may be most manifested for a polymeric reactant since the reaction may become diffusion limited in the most hindered sites. Encouraged by the different τ values of labeled brush polymers, we designed a quenching experiment to test our hypotheses on the site dependent reaction accessibility on brush polymer for both small molecules and polymeric reactants. It is well-known that nitroxide radicals can be efficiently reduced to hydroxylamine by phenylhydrazine ($PhNHNH_2$), leading to quenching of the EPR signal.[69] Here we used a small molecule quencher, $PhNHNH_2$, and a polymer-tagged quencher, hydrazine-functionalized polystyrene ($PS-NHNH_2$), to study the rate of quenching as a function of nitroxide location. The polymeric quencher was prepared by atom-transfer radical polymerization (ATRP) of styrene along with a small amount of *para*-chlorostyrene. The aryl chloride moieties in the copolymer were converted to aryl hydrazines via a recently reported palladium cross-coupling strategy.[70] The MALDI spectrum of $PS-NHNH_2$ clearly showed the hydrazine functionality on the polymer (Supporting Information Figure S5).

We compared the quenching of P-TEMPO-Brush, E-TEMPO-Brush, and M-TEMPO-Brush at the same nitroxide concentration and used the same loading for quenchers. The quenching rate was monitored by the intensity of the low-field peak of the EPR spectra as a function of time. When $PhNHNH_2$ was used, regardless of the position of the TEMPO labels on the brush polymer, the EPR signal was rapidly quenched at almost the same rate; the reaction was almost complete in ~30 min (Figure 3A). In contrast, when the polymeric quencher was used, significantly different quenching rates between spin-labels at different brush locations were observed: more than 90% of P-TEMPO-Brush was quenched after ~3 h, but quenching of the backbone-labeled

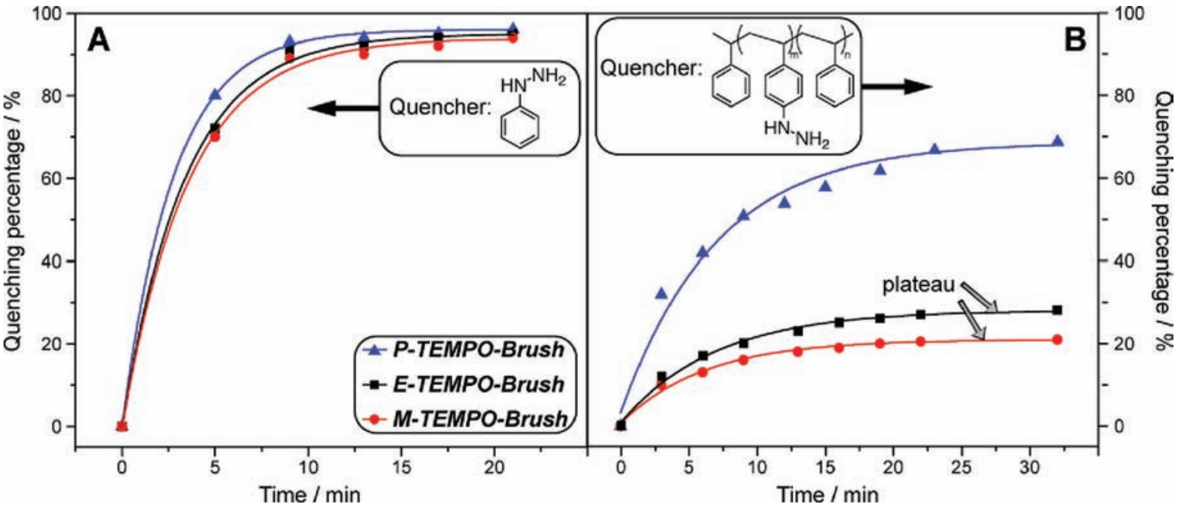


Figure 3. Quenching of the EPR signal for brush polymers with TEMPO labels at different positions: (A) quenched by $PhNHNH_2$; (B) quenched by PS-$NHNH_2$ (MW = 2400 Da). $[\text{nitroxide}]_0 = 5 \times 10^{-5}$ M in air-saturated DMF at room temperature.

samples reached a quasi-plateau after 20 min with ~30% quenching for E-TEMPO-Brush and ~20% quenching for M-TEMPO-Brush (Figure 3B), and prolonged time did not result in increased quenching. This striking difference is attributed to the limited access of polymeric quencher to the core of the brush polymer because it has to penetrate through the dense side chains in order to react with spin-labels at the backbone. A similar quasi-plateau has been reported for quenching of nitroxides by excess ascobate.[71] This was attributed to the reoxidation of the reduced product of nitroxide, hydroxylamine, by O_2 to regenerate the EPR-active nitroxide.[71] Therefore, an equilibrium exists between the reduction reaction and reoxidation. To keep the same oxygen level in the sample solutions, we used air-saturated solvent for quenching experiments. For peripherally labeled polymer, the reduction rate is much faster than the reverse oxidation rate, leading to almost complete quenching at the end. However, for the middle- and end-labeled polymers, the initial reduction rates were only about 20% of that of the peripheral polymer after addition of PS-$NHNH_2$. On the other hand, reoxidation involves a small molecule reactant (O_2); because its diffusion should not be substantially affected by the side chains, oxidation becomes competitive with reduction and a dynamic equilibrium characterized by partial quenching is reached. To test this hypothesis, we measured quenching of M-TEMPO-Brush in carefully degassed DMF; 92% quenching was indeed observed after 26 h (Supporting Information Figure S6).

These quenching studies suggest that the brush architecture provides a unimolecular system with distinct core and shell regions. The dense side chains of brush polymers significantly reduce the interaction of the core (backbone) region with external macromolecules (i.e., PS-$NHNH_2$), but allow free diffusion of small molecules (i.e., phenylhydrazine and O_2).

CONCLUSIONS

We report the EPR study of spin labeled brush polymers, which were efficiently synthesized using ROMP. Living ROMP allowed accurate and convenient incorporation of finite numbers of functionalities (e.g., spin labels) at different positions of brush polymers. The EPR analysis suggests that brush polymers can possess either two or three distinct domains depending on the solvent: periphery and core, or periphery, backbone end, and backbone middle. Reactions between large external reductants and nitroxide spin-labels bound to brush polymers exhibit location-dependent rates. Peripheral nitroxides react rapidly with both small-molecule and polymeric reductants. Core-bound nitroxides react rapidly with a small reductant, but steric hindrance to the backbone limits their reactivity with a polymeric reductant. Ultimately these differences in reactivity could be exploited for kinetically controlled, orthogonal functionalization of brush polymers. The efficiency of ROMP for the synthesis of multifunctional, narrowly dispersed brush polymers makes it a convenient alternative to widely studied dendritic and hyperbranched polymer structures. The ease of synthesis and the unique properties of brush polymers make them appealing macromolecular structures in a range of applications where nanoscopic structures have great impact. Our future research is focused on the development of brush polymer based drug delivery systems[36,37,72,73] that take advantage of their unique structural features and modular synthesis. Toward this end, we will report on the EPR study of water-soluble poly(ethylene glycol)-based brush polymers in a subsequent paper.

ASSOCIATED CONTENT

S **Supporting Information.** Experimental section, ^{1}H and ^{13}C NMR spectra, GPC traces, and additional EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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