

**Complexation of Block Copolysiloxanes with Cobalt
Nanoparticles**

by

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Abstract

Poly(dimethylsiloxane-*b*-methylvinylsiloxane) (PDMS-*b*-PMVS) diblock copolymers were synthesized via anionic living polymerization with controlled molecular weights and narrow molecular weight distributions. Targeted molecular weights agreed well with experimental values determined by ^1H NMR, ^{29}Si NMR, and GPC. Morphologies were investigated by DSC to analyze glass transition temperatures. Only one T_g was observed for each PDMS-*b*-PMVS block copolymer suggesting that the blocks were miscible in bulk. T_g 's ranged from approximately -126 to -128 °C and were between the T_g 's of the PDMS (-123 °C) and PMVS (-137 °C) homopolymers. The PMVS blocks were functionalized with trimethoxysilyl or triethoxysilyl pendent groups via hydrosilations to yield poly(dimethylsiloxane-*b*-[poly(methylvinyl)-*co*-(methyl-(2-trimethoxysilyl)siloxane)]) (PDMS-*b*-[PMVS-*co*-PMTMS]) or poly(dimethylsiloxane-*b*-[poly(methylvinyl)-*co*-(methyl-(2-triethoxysilyl)siloxane)]) (PDMS-*b*-[PMVS-*co*-PMTES]) copolymers, respectively. The PMVS blocks were either derivatized with the functional groups or half of the repeat units were functionalized. The fully hydrosilated materials were diblock copolymers, and the materials that were 50% hydrosilated had a random sequence of methylvinylsiloxy units and methyl-(trialkoxysilyl)siloxy units. The PDMS-*b*-[PMVS-*co*-PMTES] block copolymers had T_g 's ranging from -124 to -126 °C and only one T_g was observed. Surface tension

measurements suggested that PDMS-*b*-[PMVS-*co*-PMTES] copolymers formed aggregates in toluene.

Stable suspensions of superparamagnetic cobalt nanoparticles were prepared in toluene in the presence of PDMS-*b*-[PMVS-*co*-PMTMS] or PDMS-*b*-[PMVS-*co*-PMTES] copolymers via thermolysis of $\text{Co}_2(\text{CO})_8$. It is hypothesized that the block copolymers functioned as micellar templates for the cobalt nanoparticles. TEM micrographs showed non-aggregated cobalt nanoparticles coated with copolymers that had mean particle diameters ranging from ≈ 10 -15 nm. Specific saturation magnetizations of these cobalt-copolymer complexes ranged from 90-110 $\text{emu g}^{-1} \text{Co}$, comparable to literature values for this particle size.

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Abbreviations

D ₃	1,1,3,3,5,5-hexamethylcyclotrisiloxane
D ₃ ^v	1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane
D ₄	octamethylcyclotetrasiloxane
DMVS	dichlorovinylmethylsilane
DMSO	dimethylsulfoxide
TEA	triethylamine
T _g	glass transition temperature
T _m	crystalline melting point
DSC	differential scanning calorimetry
NMR	nuclear magnetic resonance spectroscopy
FT-IR	fourier transform infrared spectroscopy
GPC	gel permeation chromatography
CMC	critical micelle concentration
M _n	number average molecular weight
VSM	vibrating sample magnetometry
TEM	transmission electron microscopy
PDMS	polydimethylsiloxane
PMVS	polymethylvinylsiloxane
PMTES	poly[methyl(triethoxysilylethylsiloxane)]
PMTMS	poly[methyl(trimethoxysilylethylsiloxane)]
THF	tetrahydrofuran

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