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 $^1$H 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 trimethoxysilethyl or triethoxysilethyl pendent groups via hydrosilations to yield poly(dimethylsiloxane-b-[poly(methylvinyl)-co-(methyl-(2-trimethoxysilethyl)siloxane)] (PDMS-b-[PMVS-co-PMTMS]) or poly(dimethylsiloxane-b-[poly(methylvinyl)-co-(methyl-(2-triethoxysilethyl)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 methylvinylsiloxane units and methyl-(trialkoxy)silethyl)siloxane 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 Co\(_2\)(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 \(\approx 10\) to \(15\) nm. Specific saturation magnetizations of these cobalt-copolymer complexes ranged from 90-110 emu g\(^{-1}\) Co, comparable to literature values for this particle size.
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D₃  1,1,3,3,5,5-hexamethylcyclotrisiloxane
D₃ ¹  1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane
D₄  octamethylcyclotetrasiloxane
DMVS  dichlorovinylmethysilane
DMSO  dimethylsulfoxide
TEA  triethylamine
T₉  glass transition temperature
Tₘ  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
Mₙ  number average molecular weight
VSM  vibrating sample magnetometry
TEM  transmission electron microscopy
PDMS  polydimethysiloxane
PMVS  polymethylvinylsiloxane
PMTES  poly[methyl(triethoxysilylethylsiloxane)]
PMTMS  poly[methyl(trimethoxysilylethylsiloxane)]
THF  tetrahydrofuran
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