Synthesized of Phosphonic Acid Based Amphiphilic Polymer Encapsulated Magnetite Nanoparticle via Atom Transfer Radical Polymerization

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Polystyrene brush is grown from the surface of magnetite nanoparticles (MNs) by atom transfer radical polymerization (ATRP), after immobilizing a phosphonic acid based tertiary bromide initiator [1] on to the MNs surface, at 100 ^{o}C. The ATRP was carried out in the presence of CuBr/PMDETA complex [2], without a sacrificial initiator [3]. The grafting density, which is defined as the amount of polymer grafted on the surface of the particle is calculated after ascertaining the molecular weight of the polymer from gel permeation chromatography (GPC) as well as from thermogravimetric analysis (TGA) and its average value is found to be nearly 0.74 chain/nm^2 using grafting density formula as reported by Bartholome *et al.,* [4]. For is purpose, MNs is synthesized by massart's method [5] and the surface area of MNs is measured by BET method, which is found to be 115 m^2/g. On the other hand, the polydispersion index (PDI) of the degrafted polystrene from the MNs is considerably broader due to lack of control, which in turn due to the low concentration of Cu(II) [6] and control is brought about with increase in polymerization time due to persistent radical effect, this is evident from Table 1 data. Thus, this increase in grafting density with increase in polymerization time is due to formation of Cu(II) and indicates that Cu(II) is necessary for better control. An amphiphilic diblock polymer based on 2-hydroxylethyl methacrylate is synthesized from the polystyrene monolayer grafted on MNs surface, as the end-groups remain active at the end of polymerization which is one of the advantage of ATRP [7]. The polymer grafted MNs shows dispersion in particular solvent as shown in Figure 1.

Table 1: ATRP of styrene from MNs surface at 100 ^{o}C

Time (h)	$M_n \times 10^3$ (g/mol) from GPC	PDI	% weight loss from TGA	Grafting density in chain/nm^2
2	18	2.96	64	0.48
4	32	2.37	73	0.41
6	41	2.54	82	0.55
8	52	2.47	91	1.01
10	64	1.84	94	1.26

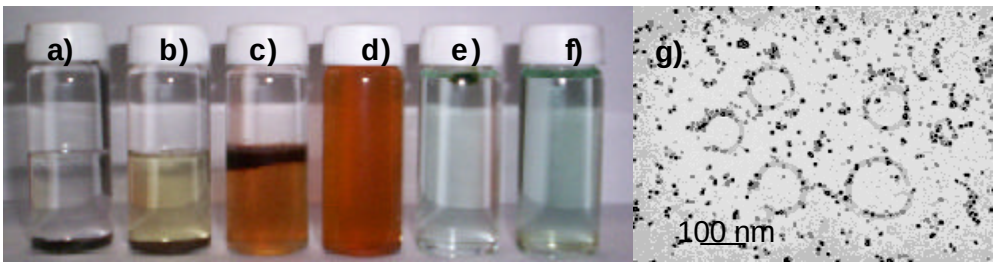

Figure 1. Photoimages of "as synthesized" MNs in $CHCl_3$/water solvent shows insoluble (a), initiator anchored MNs in $CHCl_3$/water solvent also shows insoluble (b), polystyrene grafted MNs in $CHCl_3$/water solvent shows some insoluble (c), polystyrene grafted MNs in complete $CHCl_3$ solvent shows complete soluble (d), poly(styrene-*b*-2-hydroxyethyl methacrylate) grafted MNs in $CHCl_3$ solvent shows insoluble (e), poly(styrene-*b*-2-hydroxyethyl methacrylate) grafted MNs in DMF solvent shows complete soluble (f) and, transmission electron microscopy image of polystyrene grafted MNs in THF solvent shows complete dispersion (g).

Reference:

1. K. Babu, and R. Dhamodharan, Nanoscale Research Letter 3 (2008) 109.
2. A. Ramakrishnan, R. Dhamodharan, and J. Rühe, Macromol. Rapid Commun. 23 (2002) 612.
3. G. D. Fu, Z. Shang, L. Hong, E. T. Kang, and K. G. Neoh, Macromolecules 38 (2005) 7867.
4. C. Bartholome, E. Beyou, L. E. Bourgeat, P. Chaumont, and N. Zydowicz, Macromolecules 36 (2003) 7946.
5. A. Miguel, C. Duarte, M. Giersig, N. A. Kotov, and L. M. Liz-Marzán, Langmuir 14 (1998) 6430.
6. B. Wade, and K. Matyjaszewski, Prog. Polym. Sci. 32 (2007) 93.
7. K. Matyjaszewski, and J. Xia, Chemical Reviews 101 (2001) 2921.