Activators generated by electron transfer for atom transfer radical polymerization of styrene in the presence of mesoporous silica nanoparticles

Khezrollah Khezri [a],*, Hossein Roghani-Mamaqani [b]

[a] School of Chemistry, University College of Science, University of Tehran, PO Box 14155-6455, Tehran, Iran
[b] Department of Polymer Engineering, Sahand University of Technology, PO Box 51335-1996, Tabriz, Iran

ARTICLE INFO

ABSTRACT

Activator generated by electron transfer for atom transfer radical polymerization was employed to synthesize well-defined mesoporous silica nanoparticles/polystyrene composites. Inherent features of spherical mesoporous silica nanoparticles were evaluated by nitrogen adsorption/desorption isotherm, X-ray diffraction and scanning electron microscopy analysis techniques. Conversion and molecular weight evaluations were carried out using gas and size exclusion chromatography respectively. By the addition of only 3 wt% mesoporous silica nanoparticles, conversion decreases from 81 to 58%. Similarly, number average molecular weight decreases from 17,116 to 12,798 g mol^{-1}. However, polydispersity index (PDI) values increases from 1.24 to 1.58. A peak around 4.1–4.2 ppm at proton nuclear magnetic resonance spectroscopy results clearly confirms the living nature of the polymerization. Thermogravimetric analysis shows that thermal stability of the nanocomposites increases by adding nanoparticles content. Decrease of glass transition temperature is also demonstrated by the addition of 3 wt% of silica nanoparticles according to the differential scanning calorimetry results.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Combination of nanoparticles with polymer matrices results in a new class of materials which is commonly known as polymer nanocomposites [1,2]. These materials combine the different properties of the constituents such as rigidity and thermal stability from inorganic parts and flexibility and ductility from the organic polymers [3,4]. Therefore, addition of nanofillers results in considerable enhancement in several properties of nanocomposites in comparison with the conventionally filled composites [5,6]. Titanium dioxide, magnetic iron oxide, montmorillonite, silica, and mesoporous silica are some of the most important nanofillers in polymer nanocomposites [7–10]. Although polymer matrix and nanofiller characteristics dictate the nanocomposites properties, processing condition is an effective parameter. Physical mixing and polymerization in the presence of nanofillers are the two general procedures for nanocomposite production [11,12].

After the discovery announcement of novel class of mesoporous M41S molecular sieves by the scientist from the Mobil Oil Company in 1992, a great attention is shown to apply this family

of materials in various applications [13–15]. By using templating method and also phase transformation approach, various morphologies of mesoporous silica can be obtained. Therefore, controlling morphology of mesoporous materials for different purposes is an important factor which needs to be considered. Tubules-within-tubule (TWT), pillar-within sphere (PWS), spherical, rod-like, and top-like morphologies are reported for MCM-41 nanoparticles [16–18]. The M41S family has been classified into four main groups: disordered rods and three well-defined structures of MCM-41, MCM-48 with a three-dimensional cubic pore, and MCM-50 with an unstable lamellar structure [19]. Narrow pore size distribution with size controllable pores, large pore openings, high surface area, and ownership of hexagonal arrangement of uniformly sized parallel channel pores are some unique characteristics of MCM-41 nanoparticles. According to the unique features of MCM-41 nanoparticles, it can be used in many different applications such as separation of proteins, selective adsorption of large molecules, and heterogeneous catalysis [16,20–22].

Weakness of free radical polymerization (FRP) to synthesize pure block copolymers, low PDI polymers, and precise control over the molecular weight of polymers is a driving force to explore and developing new polymerization methods. Controlled radical polymerization (CRP) is a robust route to synthesize polymers

Table 1
Designation of the samples.

Sample	Preparation method	Content of MCM-41 nanoparticles (wt%)	Time of MCM-41 nanoparticles dispersion in monomer (h)
NPS	AGET ATRP	0	–
PSN 1	*In situ* AGET ATRP	1	15
PSN 2	*In situ* AGET ATRP	2	15
PSN 3	*In situ* AGET ATRP	3	15

Fig. 1. General mechanism of AGET initiation process in ATRP.

with well-defined structures and low PDI values. CRP methods are generally based on establishing a rapid dynamic equilibrium between the growing free radicals and dormant species. Atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), and reversible addition–fragmentation chain transfer (RAFT) are three main categories of CRP. Among these methods, ATRP has attracted more attention because it provides some unique benefits such as its application for a large range of monomers, various polymerization media, and commercial availability of its reagents [23–27].

Application of CRP techniques for the preparation of mesoporous silica nanoparticles/polymer composites has been reported rarely. Hong et al prepared core–shell nanostructure with mesoporous silica nanoparticle core and polymer shell around the exterior surface of mesoporous silica nanoparticles synthesized by surface RAFT polymerization [28,29]. Bals et al employed surface initiated NMP for grafting polystyrene chains in both the inner and outer surface of mesoporous silica nanoparticles. They used various types of mesoporous silica nanoparticles with different morphologies and pore sizes [30]. Pasetto et al synthesized hybrid materials by grafting polymer chains on the surface of mesoporous silica nanoparticles via surface-initiated ATRP (SI-ATRP) [31]. They used various shapes of mesoporous silica nanoparticles as substrates such as micrometric particles, submicrometric polydisperes spherical particles, and monodisperse core–shell particles They compared the macromolecular features of the free and attached polymer chains and therefore their study has highlighted the effect of mesoporous confined space and channel length on the results of the polymerization. Also, core–shell nanostructure with mesoporous silica nanoparticles core and hyperbranched polymer shell has been prepared by Li et al via surface-initiated self condensing atom transfer radical polymerization. Their results indicate that hybrid nanoparticles showed appropriate dispersibility in organic solvents [32]. Meer et al investigated the effect of mesoporosity on thermal and mechanical properties of silica/polystyrene composites [11]. They incorporated mesoporous and colloidal silica particles into polymer matrices via
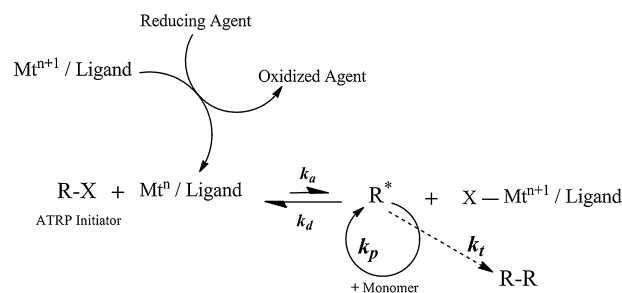
two different methods of melt blending and SI-ATRP. Their results indicate that both the composites have similar grafted polymer characteristics. In addition, Liu et al synthesized MCM-41/poly (acrylic acid) composites by using FRP. They introduced acrylic acid and initiator into the channels of MCM-41 nanoparticles by using supercritical carbon dioxide as solvent at low temperature followed by polymerization at a higher temperature [33].

In this study, benefits of ATRP were employed to synthesize predetermined molecular weight polystyrene chains in the presence of MCM-41 nanoparticles. Among different initiation techniques of ATRP, normal ATRP involves lower oxidation state metal complexes in which special handling procedures will be required. Reverse ATRP (RATRP), applies more stable metal species and therefore its process is generally more convenient. Disability to produce pure block copolymers and independently reduction of complex concentration are two main drawbacks of RATRP. Overcoming to drawbacks of normal ATRP and RATRP can be achieved by AGET initiation technique. Therefore, in this research, AGET ATRP as an interesting initiation process was selected since it applies less oxygen sensitive component at the start of reaction (general mechanism of AGET ATRP is illustrated in Fig. 1). In addition, by AGET ATRP, polymerization rate can be directly controlled by the amount of added reducing agent. Participation of mesoporous silica nanoparticles in the polymer matrix was performed by using in situ polymerization technique. Synthesis and characterization of mesoporous silica nanoparticles, nanocomposites preparation method, effect of mesoporous silica nanoparticles on the AGET ATRP, and thermal properties of the products are discussed in detail.

2. Experimental

2.1. Materials

Styrene (Aldrich, 99%) was passed through an alumina-filled column to remove inhibitors. The compounds copper(II) bromide
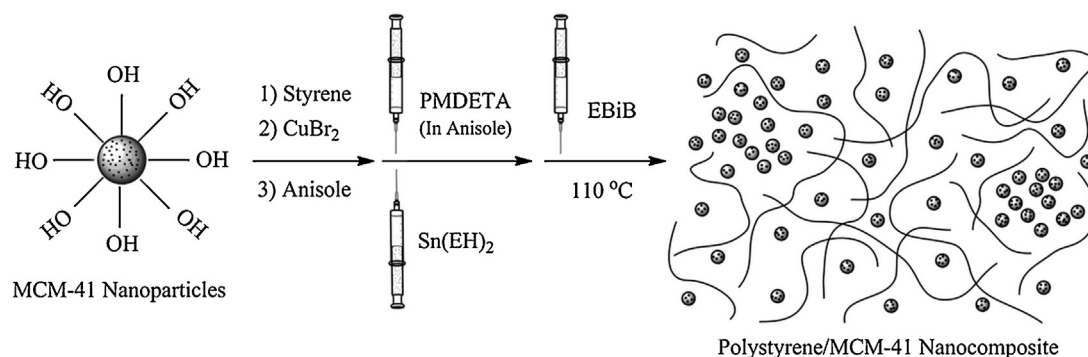
Fig. 2. General procedure for preparation of polystyrene/MCM-41 nanocomposites via in situ AGET ATRP.