Surface initiated ring-opening polymerization of lactones on iron oxide nanoparticles

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Abstract. In this work we report the synthesis of hybrid magnetic core-shell nanostructure with inorganic core consisting of magnetite surface-functionalized by glycolic acid or serine. For the attachment of the polymer chain on the preformed functionalized magnetite we applied the “grafting-from” strategy, where the polymerization is initiated directly from the particles surface to give a high number of end attached polymer chains. The surface initiated ROP of ε-caprolactone and lactic acid was initiated by the common catalysts, tin (II) 2-ethylhexanoate (Sn(oct)2) produced poly(ε-caprolactone), polylactic acid, respectively, containing one hydroxyl chain. Moreover we performed the surface initiated ROP of ε-caprolactone microwave assisted in the presence of Sn(oct)2. The morphology of magnetic core-shell nanostructure was determined by TEM. The chemical structure of the obtained polyesters coated magnetic nanoparticles was characterized by FT-IR.

1. Introduction

The functionalization of inorganic nanoscopic particles with a polymeric shell is a promising approach for the design of well-defined composite materials and dispersions [1-4]. The rapidly growing interest in biodegradable materials, polyesters as polycaprolactone (PLC) and polylactic acid (PLA) are one of the biodegradable industrial polyesters with excellent mechanical strength, biocompatibility and non-toxicity. PCL is suitable for controlled drug release because of its high permeability to many drugs and biocompatibility in physiological environments. Generally, polyesters are prepared by catalyzed ring-opening polymerization (ROP) of ε-caprolactone (CL) and lactic acid (LA) [5-8]. Tin compounds (including salts and complexes) have proven to be an extremely versatile and highly efficient group of catalysts or initiators. Among the numerous catalytically active tin compounds, tin(II) 2-ethylhexanoate (SnOct2) plays a predominant role, because it is the most widely used initiator for research purposes and for the technical production of polyesters and related copolyesters [9-22].

In this work, we report the classical ring opening polymerization of CL and lactic acid in the presence of the magnetic nanoparticle and the formation of PCL and PLA block copolymer on the iron oxide nanoparticles surface. We also describe about the solvent-free controlled microwave irradiation of CL in the presence of the magnetic nanoparticles. The cores are selected to possess
superparamagnetic behaviour, while the polymeric shell serves as a protective layer, which can be functionalized later on.

2. Experimental details

2.1. Synthesis and Modification of Magnetite Surface

The synthesis of magnetite and the adsorption of serine and glycolic acid on the magnetite surface were performed under inert (N₂) atmosphere (scheme 1). Magnetite nanoparticles were prepared by coprecipitation in basic conditions of a ferrous and ferric chloride (molar ratio 1:2) aqueous solution. The resulting magnetite particles were surface-stabilized in situ by the addition of L-serine or glycolic acid strongly stirred for 2 h at 80°C. The particles were then repeatedly washed with water and dried proving a brown dark powder (MP-OH).

2.2. Classical polymerization of CL and LA in the presence of magnetic nanoparticles

The surface-initiated ROP of ε-CL and LA onto magnetite was carried out according to the procedure shown in Scheme 2. The stabilized magnetic nanoparticles (MP-OH) were mixed with freshly distilled CL, lactic acid, respectively and strongly shaken at room temperature for 30 minutes at 1200 rotation/min. After this SnOct₂ was added as a catalyst and the reaction mixture was stirred in a shaker at 100°C for 5 h at 1200 rot./min. After reaction the particles (MP-PCL and MP-PLA) was repeatedly washed with chloroform and methanol for removing the catalyst and then dried.

2.3. Formation of block copolymer on the iron oxide nanoparticles

The surface-initiated ring-opening copolymerization of CL and LA (Scheme 3) in the presence of magnetic nanoparticles is a two step reaction and will direct us to obtain hybrid material containing a block copolymer and iron oxide (MP-PCL-b-PLA):
- First step is the ring opening polymerization of CL, the reaction condition was mentioned before
- Second step is polymerization of lactic acid in the same reaction condition as was mentioned before
2.4. Polymerization of CL onto magnetite nanoparticles by microwave irradiation
A mixture of magnetic nanoparticles, CL and Sn(oct)$_2$ was placed in a dried glass ampoule with a magnetic stirrer and was vacuum sealed. The reaction mixture was then subject to microwave irradiation and the temperature of reaction was recorded every second. After being irradiated for a period of time, the ampoule was cooled in an ice bath and the product (MP-MW-PCL) was dispersed in chloroform. The reaction was performed at the (200°C) at a microwave power of 200 W for 7 min while the pressure reached 8 bar. The energy uptake finished after 100 s.

3. Characterization of the hybrid material
The morphology of magnetic core-shell nanostructures based on PCL and PLA was determined by TEM using 1010 JEOL microscope and FT-IR spectra were carried out on a JASCO FTIR 610 spectrophotometer.

3.1. Morphologic characterization
The TEM images (figure 1) of magnetic nanoparticles modified with serine MP-OH (figure 1a) and the hybrid material MP-PCL presented in figure 1b, prove the core-shell structure. The shapes of the magnetic nanoparticles with the modified surface are nearly spherical with diameters between 11 nm - 16 nm. For the hybrid material the shape is approximately the same with diameters between 22-27 nm. These diameters of the magnetite cores are well below the critical domain size of magnetite and therefore a superparamagnetic behaviour was expected for the functionalized magnetic nanoparticles.

![Figure 1](image1.png)

(a) TEM image of MP-OH, (b) TEM image of MP-PCL (bar size 100 nm).

3.2. FTIR-investigation
FTIR spectra, shown in figure 2, exhibited characteristic adsorption bands of both component materials, namely the MP-OH and hybrid materials. The intense band located at 572 cm$^{-1}$ is characteristic of magnetite. The characteristic bands of PCL appear between 1157 cm$^{-1}$ and 2949 cm$^{-1}$. This characteristic vibration bands are significantly shifted to lower frequencies in the spectrum of all hybrid materials based on PCL. In the case of MP-PLA spectra, the characteristic –C=O band present in PLA spectra at 1746 cm$^{-1}$, is found at 1645 cm$^{-1}$. This shift of the –C=O band demonstrates the grafting of PLA on the iron oxide surface.
4. Conclusions
We obtained for the first time block copolymers based on PCL and PLA on the iron oxide nanoparticles surface. The Sn(oct)$_2$ catalyzed surface-initiated ROP of ε-CL in the presence of surface modified magnetite was successfully conducted by microwave irradiation for the first time. The effect of microwave irradiation on the polymerization involves the enhancement of chain propagation of PCL and the restraint of growing centre formation and allowed to finish the polymerisation in 10 min. In addition, solvents are not necessary in this process.

The FTIR spectra contain the characteristic absorption bands of both constituents, namely, hybrid materials and magnetite. TEM revealed the the size of the magnetite nanoparticles increased by the ROP from 13-16 nm to 22-27 nm.

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