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Research paper

# Functional organo-Mt/copolymer nanoarchitectures. Microwave-assisted rapid synthesis and characterisation of ODA–Mt/poly[NIPAm-*co*-(MA-*alt*-2,3-2H-DHP)] nanocomposites

Zakir M.O. Rzayev [a,*], Ayşe Uzgören-Baran [b], Ulviye Bunyatova [c]

[a] Division of Nanotechnology and Nanomedicine, Institute of Science and Engineering, Hacettepe University, Beytepe, 06800 Ankara, Turkey
[b] Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe, 06800 Ankara, Turkey
[c] Department of Biomedical Engineering, Faculty of Engineering, Baskent University, Baglica Campus, 06810 Ankara, Turkey

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ABSTRACT

In this work, novel octadecyl amine–montmorillonite (ODA–Mt) copolymer nanocomposites were synthesised by interlamellar microwave-assisted complex-radical copolymerisation. The microwave method is found to be a facile and highly effective means to clay polymer nanocomposites (CPNs) that provide a higher rate of interlamellar copolymerisation and conversion of micro- and nanoparticles. The chemical and physical structures, surface morphologies and thermal behaviours of the prepared CPN were investigated by FTIR and $^{1}H$ ($^{13}C$) NMR spectroscopy, XRD, SEM, TEM, thermal (DSC and TGA) and dynamic mechanical (DMA) analysis methods. That copolymerisation was accompanied by in situ complex formation (charge transfer complex and H-bonding similar with known copolymerisation without ODA–Mt) and the intercalative amidisation of anhydride units with the octadecyl amine groups of Mt was determined. These observed chemical and physical interfacial interactions as effective in situ processing play an important role in the formation of hybrid systems and micro- and nanocomposites with stimuli-responsive NIPAm polymer chains.



## 1. Introduction

The growing interest in dispersed polymer materials, especially in polymer layered silicate composites on micro- and nanosized scales, has yielded a significant increase in the synthetic pathways for the preparation of polymer nanosystems and nanomaterials containing stimuli-responsive fragments or blocks, including smart poly(isopropyl acrylamide) (PNIPAm) (Urban, 2011).

The microwave irradiation method has been developed into a highly useful technique and has become an effective alternative energy source for polymer synthesis and processing (Bogdal et al., 2003; Zong et al., 2003; Wiesbrock et al., 2004; Agarwal et al., 2005; Fischer et al., 2005; Iannelli and Ritter, 2005; Iannelli et al., 2005; Stange et al., 2006; Zhao et al., 2006; Zhu and Zhu, 2006; Hoogenboom and Schubert, 2007; Zhang et al., 2007). For CPN synthesis and processing, the microwave heating method shows unique advantages over other conventional methods (Aranda et al., 2003; Yoo et al., 2004; Uyanik et al., 2006; Liao et al., 2007). Pure and high crystalline hydrocalumites (Frieder's salt $[Ca_2Al(OH)_6]Cl–2H_2O$) were fast synthesised using autoclave under microwaves (Perez-Barrado et al., 2013). Korichi et al. (2009, 2012) reported the comparative analysis of the activation smectite employing heating and microwave irradiation, as well as structural properties (surface area, pore volume, pore size distribution and morphology) and physico-chemical characterisations (XRD and thermal behaviours) of the natural and purified clay in the homoionic Na form. According to the authors, small pores were created in the prepared materials using microwave-assisted method.

Liang et al. (2000) reported a temperature sensitive CPN with an enhanced temperature response based on organically modified clay–PNIPAm nanocomposites. The authors modified this CPN using a coupling agent to favour a more efficient thermal transition and studied the interfacial chemistry between the clay mineral and the polymer in the new CPN. Haraguchi (2007) reviewed the fundamental and recent developments related to nanocomposite gels, including PNIPAm based hydrogel nanosystems. The author described the nanocomposite gels prepared by in situ free-radical polymerisation, which had high yields under mild conditions (near ambient temperature, without stirring). Wang et al. (2010) synthesised a $SiO_2$–PNIPAm nanocomposite through a one-pot approach in supercritical carbon dioxide in the presence of vinyltriethoxysilane, tetraethoxysilane, a 2,2′-azobisisobutyronitrile initiator, a N,N′-methylenebisacrylamide cross-linker and the hydrolysis agent acetic acid. The authors found that well-dispersed particles with diameters less than 100 nm (TEM image) were formed, and the

* Corresponding author.
*E-mail address:* rzayevzmo@gmail.com (Z.M.O. Rzayev).

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CPN microgels exhibited higher low critical solution temperature (LCST) than PNIPAm microgels.

In the study of Zhang et al. (2014), the porous clay/PNIPAm hydrogels with pore sizes around 30–50 μm and the different mass ratios were prepared using a Li–Mg silicate hydrate as a clay mineral physical cross-linker to remove crystal violet (CV) from aqueous solution. According to the authors, CPN hydrogels as an efficient absorbent could absorb high concentrated CV solution.

NIPAm-based polymers with different structures for various bioengineering applications have been also reported (Hinrichs et al., 1999; Dincer et al., 2002; Turk et al., 2004; Rzaev et al., 2007; You et al., 2007; Zhang et al., 2008). Recently, the growing attention of researchers has been focused on nanocomposites and their applications in biology and medicine (Eeckman et al., 2004; Li et al., 2005; Zhang et al., 2005; Chen et al., 2008; Slowing et al., 2008; Meenach et al., 2009; Sousa et al., 2010; Tsao et al., 2010; Tian and Yang, 2011). Tian and Yang (2011) reported thermo-sensitive CPN based on mesoporous silica and PNIPAm by in situ radical polymerisation in mesopores. The authors used the resultant materials as carriers to construct temperature-responsive controlled drug delivery systems and reversible fast/slow transition switches or rate regulators, which were responsive to the environmental temperature, for other smart applications. Sousa et al. (2005) investigated the loading of a cationic drug, diltiazem hydrochloride into temperature sensitive NIPAm homo- and copolymer hydrogels and their release behaviour. The authors also reported a facile and direct synthetic method to obtain thermosensitive hybrid functional nanosystems based on silica-PNIPAm by using a neutral surfactant, and the assessment of its release rate of a model drug (Sousa et al., 2010). You et al. (2008) prepared thiol-functionalised micro-to-mesoporous silica nanoparticles with pyridyl disulphide-terminated PNIPAm. This silica/polymer nanocomposite shows a temperature-dependent uptake/release and storage of fluorescein, which are controlled by the polymer conformation (random coil vs globule). Zhou et al. (2007) synthesised a stimuli-response PNIPAm inside a mesostructured cellular foam by

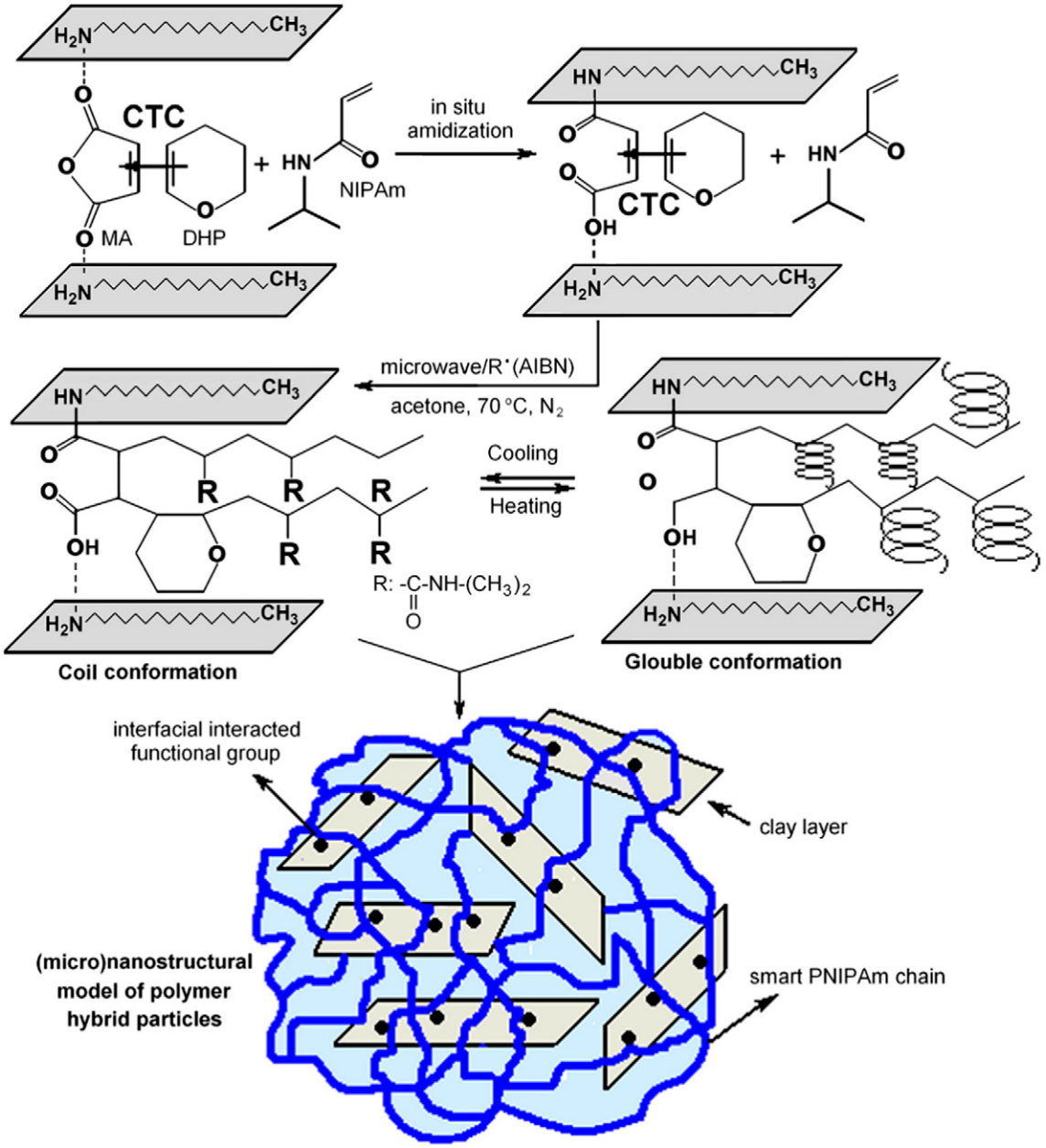


**Fig. 1.** Synthetic pathways of organoclay/copolymer hybrid nanocomposites via microwave-assisted interlamellar complex-radical copolymerisation and proposed mechanism of in situ processing.