



# DEVELOPMENT OF ANTIOXIDANT POLY(THIOETHER-ESTER) NANOPARTICLES

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**Abstract** - Poly(Thioether-Ester) nanoparticles synthesized via thiol-ene polymerization from a renewable castor oil monomer are produced by miniemulsion polymerization and emulsification/evaporation of pre-formed polymer. Its antioxidant activity, probably due to the oxidation of sulfide groups, is confirmed by 2,2-diphenyl-1-picryl hydrazyl (DPPH) free radical-scavenging and  $\beta$ -carotene/linoleic acid assays, with an amount of polymer required to reduce the initial concentration of DPPH $\cdot$  radicals by 50% of  $\sim 195 \mu\text{g}\cdot\text{ml}^{-1}$  promoting hydrogen or electron exchange and the capability to prevent lipid peroxidation of  $\sim 55\%$ . The results show a promising application in food packing.

**Keywords:** Polymer nanoparticles; antioxidant activity; thiol-ene polymerization; poly (thioether-ester).

## INTRODUCTION

Some conductive polymers, such as polypyrrole (PPy), poly (3,4-ethylenedioxythiophene) (PEDOT) and polyaniline have been reported to have radical scavenging properties and the antioxidant activity of these polymers have been studied (Hsu et al., 2008; Gizdavic-Nikolaidis et al., 2004). Also polysaccharides chemically modified to obtain sulfated derivatives have been studied for their antioxidant activities recently (Xie et al., 2016). However, the antioxidant activity of poly(thioether-ester)s synthesized by thiol-ene reactions has never been reported.

Thiol-ene addition reactions have been known for more than a century and studied throughout the years (Türünç and Meier, 2010). The reaction is simply the thiol and ene group combination, with or

without photo- or thermo-initiators, which proceeds via a radical addition mechanism, followed by chain transfer to a thiol end group, thus reinitiating the cycle (Hoyle and Bowman, 2010). Thiol-ene polymerization presents some advantages such as rapid polymerization rates, high overall functional group conversion, and little sensitivity to oxygen inhibition (Cramer et al., 2010).

A wide range of enes with activated and non-activated species and multiply-substituted olefinic bonds can be used as suitable substrates (Lowe, 2010). However, some attention has been given to renewable feedstocks, like plant oils (Cardoso et al., 2014; Türünç and Meier, 2010), due to the minimization of hazards, and the generation of substances with as little toxicity as possible, plus the biodegradable nature of the products (Salimon et al., 2012).

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Thiol-ene polymers have been successfully synthesized from different kinds of multifunctional enes and thiols, finding application in the biomedical field as polymeric nanoparticles and hydrogels for drug-delivery systems, biomimetic hydrogels, and dental restorative resins (Machado et al., 2016). For polymeric nanoparticle production, some researchers have been producing nanoparticles with pre-formed polymers from “click” thiol-ene reactions using emulsification/evaporation techniques (Durham et al., 2015.; Poetz et al. 2015). Moreover, as a fresh field, thiol-ene polymers have also shown potential to be synthesized in dispersed media, like miniemulsion polymerization, and some works are reported in the literature using different enes and thiols in photopolymerization (Amato et al., 2015; Durham et al., 2017; Jasinski et al., 2014). In this way, polymeric nanoparticles can be synthesized by different techniques, which depend of the origin of the polymeric material used as matrix material, which can be synthesized *in situ* or by preformed polymers.

The objective of this work was to synthesize poly(thioether-ester) (PTEE) nanoparticles from a renewable  $\alpha,\omega$ -diene diester monomer, derived from castor oil and isosorbide. Dianhydro-D-glucityl diundec-10-enoate (DGU) was copolymerized with 1,4-butanedithiol ( $\text{Bu}(\text{SH})_2$ ) via thiol-ene polymerization in bulk and miniemulsion, resulting in poly-co-dianhydro-D-glucityl-diundec-10-enoate-co-1,4-butanedithiol. The obtained nanoparticles were individually assessed for their possible antioxidative capacities by employing DPPH free radical-scavenging and  $\beta$ -carotene/linoleic acid assays.

## MATERIALS AND METHODS

### Materials

10-Undecenoic acid (Sigma-Aldrich, 98%), dianhydro-D-glucitol (Aldrich, 98%), p-toluenesulfonic acid monohydrate (Sigma-Aldrich, 98.5%), 1,4-butanedithiol ( $\text{Bu}(\text{SH})_2$ ), Sigma Aldrich), azobisisobutyronitrile (AIBN, Vetec, 98%), Crodamol GTCC (Crodamol, Alpha Química), a saturated triglyceride from coconut oil, Lutensol AT 80 (Lut. AT80, BASF), dichloromethane (DCM, MARCA), Poly Vinyl Alcohol (PVA, MARCA), and distilled water were used for all formulations.

### Synthesis of the renewable monomer

Dianhydro-D-glucityl diundec-10-enoate (DGU) synthesis was conducted by esterification of

10-undecenoic acid (318.9 mmol), dianhydro-D-glucitol (107.8 mmol) and (15.7 mmol) p-toluenesulfonic acid. For that, 200 mL of toluene were added to the mixture and heated to 135 °C under magnetic stirring; the resultant mixture was cooled down and toluene was evaporated. Purification was realized by filtration in a short pad of aluminum oxide and silica gel (using hexane as eluent). After hexane evaporation the final product was dissolved in diethyl ether and washed twice with 1N  $\text{NaHCO}_3$  solution and once with distilled water. Finally, the organic fraction was dried with anhydrous  $\text{MgSO}_4$  and the solvent was removed under reduced pressure.

### Nanoparticles production

For the production of the PTEE nanoparticles, two techniques were employed: Miniemulsion polymerization (i) and Emulsification/ evaporation (ii).

(i) Miniemulsion polymerization was conducted by stirring in an adequate flask the organic phase, composed of 1000 mg of DGU as monomer, 123 mg of Crodamol as coestabilizer and 3.4 mg of AIBN as initiator, with an aqueous phase containing the surfactant Lutensol AT 80 at 3% (w/v) and 5.5 mL of water, during 15 min, followed by the addition of the second monomer dithiol ( $\text{Bu}(\text{SH})_2$ ) in quantities of 240 mg and stirred again for 5 min. The final emulsion was submitted to ultrasonication using a Fischer Scientific Sonic Dismembrator (Model 500) in an ice bath during 2 min (10 s on, 5 s off) at 70% of amplitude. Finally, the solution was transferred to an ampoule and immersed in a thermal bath at 80 °C for 4 h producing NP 1.

(ii) For the emulsification/evaporation technique, PTEE was synthesized by bulk polymerization immersing an ampoule containing DGU,  $\text{Bu}(\text{SH})_2$  and AIBN (at the same concentration cited previously for the miniemulsion polymerization technique) in a thermal bath at 80 °C for 4 h. A quantity of 100 mg of the resulting polymer was solubilized in 4 mL of dichloromethane and, after complete dissolution of PTEE, the organic phase was dripped into 20 mL of aqueous phase composed of a poly(vinyl alcohol) (PVA) solution at 0.3 wt.%, and stirred at room temperature for 15 min, followed by application of ultrasonication in an ice bath at an amplitude of 70% during 2 min (15 s on, 10 s off) to reduce the droplets to submicrometric range. After obtaining the dispersion, the solvent was evaporated under magnetic stirring at room temperature and atmospheric pressure for 12 h, producing NP 2.

## Particle size measurements

Particle size distribution measurements of intensity average particle size (Dp) and polydispersity index (Pdl) were realized by dynamic light scattering (DLS) using a Zeta Sizer Nano S equipment from Malvern Instruments. Analyses were performed after dispersion in water to 0.5% of total solids and measured at 25 °C in a glass cuvette.

## Chemical analysis

The absorption spectra of dried samples were determined using Fourier Transform Infrared Spectroscopy with a Shimadzu spectrophotometer (IRPrestige-21) using a conventional KBr pellet method; samples were ground and compressed with anhydrous KBr to form pellets. The scanning range was 400-4000 cm<sup>-1</sup> and the resolution was 4 cm<sup>-1</sup>.

<sup>1</sup>H NMR analyses were recorded in deuterated chloroform (CDCl<sub>3</sub>), using a Bruker Ascend 600 spectrophotometer at 600 MHz. Chemical shifts (δ) are reported in part per million (ppm) relative to the internal standard tetramethylsilane (TMS, δ = 0 ppm) used to calibrate the chemical shift.

## Molar mass measurements

The molecular weight distribution measurements of the PTEE nanoparticles were carried out by gel permeation chromatography (GPC) using a High Performance Liquid Chromatography equipment (HPLC, model LC 20-A) and Shim Pack GPC800 Series Columns (GPC 801, GPC 804 and GPC 807) both from Shimadzu. After complete dissolution of 0.02 g of each dried sample in 4 mL of tetrahydrofuran (THF), the solutions were filtered through a nylon syringe filter with 0.45 μm pore size and 33 mm diameter. THF was used as eluent with a volumetric flow rate of 1 mL.min<sup>-1</sup> at 40 °C. The GPC system was calibrated using polystyrene standards with molecular weight ranging from 580 to 9.225x10<sup>6</sup> g.mol<sup>-1</sup>.

## Particles Morphology

Transmission Electron Microscopic analyses using a JEM-1011 TEM (100 kV) were conducted to provide information about particle morphology. Samples NP 1 and 2 were diluted in distilled water up to 0.1% of solids; one drop of each sample was placed on a carbon-coated grid and dried under room conditions overnight.

## Antioxidant activity

The DPPH free radical scavenging measurements were used to determine the scavenging capacity of NP 1 and 2. With minor modification, the method previously described (Blois, 1958; Brand-Williams et al., 1995) was employed. Briefly, 500 μL of NP samples were mixed with 1000 μL of ethanolic DPPH solution (0.125 mM) and incubated in a dark room for 1 h at room temperature. Then, the tubes were centrifuged at 10.000 rpm for 30 min and the supernatant was taken for measurement at 517 nm using a Hitachi (U-1900) UV-vis spectrophotometer. Blank samples were prepared by mixing 500 μL of distilled water with 1000 μL of DPPH ethanolic solution. The percentage of DPPH scavenging activity (SA%) of NP samples was calculated following Equation 1.

$$SA\% = \left(1 - \frac{A_s}{A_0}\right) \times 100 \quad (1)$$

where,  $A_s$  and  $A_0$  are the absorbance of sample and absorbance of blank, respectively.

The β-carotene/ linoleic acid assay was conducted by evaluation of the inhibition of the peroxidation effects of NP 1 and NP 2, using a linoleic acid system determined by the β-carotene bleaching test (Matthäus, 2002; Kang et al., 2006), quantifying the difference between the initial and final (after 120 min) amount of β-carotene discolored by spectrophotometric measurements at 470 nm. First, an emulsion with 3.4 mg of β-carotene and 44 μL of linoleic acid was prepared using 364 μL of Tween 20 and 1 mL of chloroform for better solubilization; the solution was shaken and the chloroform was evaporated in a rotaevaporator at 40 °C. After that, 100 mL of water was added and homogenized. A blank emulsion was also done containing just 44 μL of linoleic acid, 364 μL of Tween 20 and 100 mL of distilled water. Samples were prepared at a concentration of 1.6 mg.mL<sup>-1</sup> of polymer nanoparticles. Tests were performed by adding 200 μL of sample (NP 1 and NP 2) and 5 mL of β-carotene emulsion in test tubes, and 200 μL of sample with blank emulsion. The tubes were then placed in a thermal bath at 50 °C and the absorbance measured at 470 nm in 0, 15, 30, 60 and 120 min. Control samples were prepared with 200 μL of ethanol and 5 mL of β-carotene emulsion and 200 μL of ethanol with 5 mL of blank emulsion. The antioxidant activity of samples was determined using Equation 2.

$$AA\% = \left[1 - \frac{As_{t120} - As_{t0}}{Ac_{t120} - Ac_{t0}}\right] \times 100 \quad (2)$$

where,  $Ac_{120}$  and  $Ac_{t0}$  are the absorbance of the control after 120 and 0 min, respectively, and  $As_{120}$  and  $As_{t0}$  are the absorbance of the sample after 120 and 0 min, respectively.

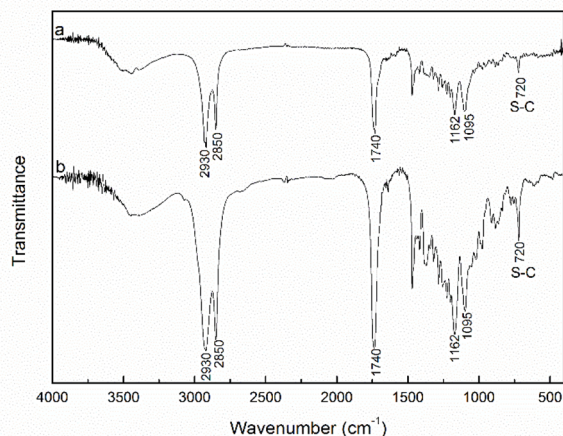
## RESULTS AND DISCUSSION

Particle size was evaluated by both techniques used, as seen in Table 1. NP 1 and NP 2 presented Dp between 206 and 261 nm, with a PDI below 0.2. Both samples analyzed remained stable after the storage time of 30 days, with a slight change in Dp and PDI for NP1, from  $207.1 \pm 1.1$  to  $238.8 \pm 1.2$ , and from  $0.150 \pm 0.030$  to  $0.190 \pm 0.010$ , respectively.

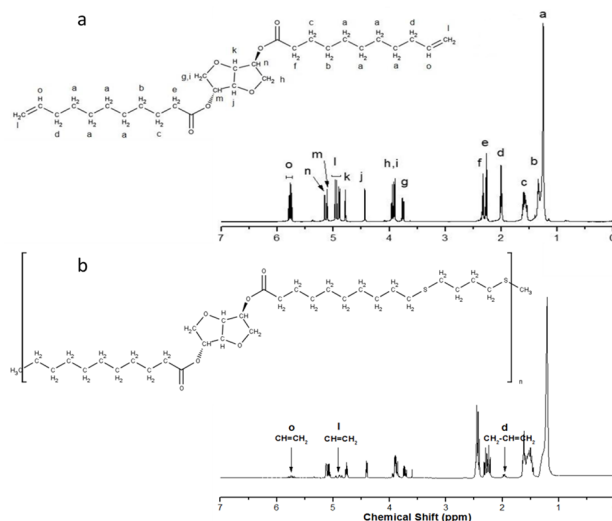
Molar mass results expressed in terms of Mn and Mw are exposed in Table 1. The formation of the polymer by both techniques employed, miniemulsion and bulk, achieved polymers of low molecular weights with Mw of 7.48 and 13.99 kDa, respectively.

Chemical analyses were realized to prove PTEE formation. Fourier Transform Infrared (FT-IR) spectra of the dried samples of NP 1 and NP 2 are presented in Figure 1. Results for both samples show characteristic peaks of DGU at  $2930 \text{ cm}^{-1}$  corresponding to CH antisymmetric and symmetric stretching of  $-\text{CH}_3$  and  $\text{CH}_2$ , at  $2850 \text{ cm}^{-1}$  to the presence of CH stretching modes from  $-\text{CH}_3$  attached to oxygen, and at  $1740 \text{ cm}^{-1}$  to C=O stretch of esters, as well as peaks at 1162 and  $1095 \text{ cm}^{-1}$  corresponding respectively to C-O-C antisymmetric stretch in esters and C-O-C symmetric stretch in ethers. A specific peak at  $720 \text{ cm}^{-1}$  indicates the presence of sulfide bonds (S-C) formed during the thiol-ene polymerization reaction, which were formed by the consumption of double bonds of vinyl compounds ( $\text{CH}=\text{CH}_2$ ) in the region of  $910 \text{ cm}^{-1}$  and also the double bonds of DGU at  $1640 \text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretch), resulting in the addition of the thiyl radicals across the ene group. The similar results for FT-IR suggest that both polymerization methods, miniemulsion and bulk, were able to produce PTEE with similar characteristics.

To complement these results and prove PTEE formation,  $^1\text{H}$  NMR analyses were also used. Figure 2a shows the chemical structure and  $^1\text{H}$  NMR spectrum of DGU monomer before polymerization with



**Figure 1.** FT-IR spectra of nanoparticles obtained by: (a) Miniemulsion polymerization (NP 1); and (b) Emulsification/evaporation (NP 2).



**Figure 2.**  $^1\text{H}$  NMR spectra for (a) monomer DGU and (b) Poly(thioether-ester), indicating the composition and consumption of the double bonds after polymerization for the miniemulsion sample. (a)  $^1\text{H}$ -NMR (600 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 5.81-5.74 (m, 2H,  $2x\text{-CH}=\text{CH}_2$ ), 5.16 (d, 1H,  $-\text{COO}-\text{CH}-$ ), 5.11 (q, 1H,  $-\text{COO}-\text{CH}-$ ), 4.98-4.89 (m, 4H,  $2x\text{-CH}=\text{CH}_2$ ), 4.79 (t, 1H,  $-\text{CH}_2-\text{O}-\text{CH}-$ ), 4.43 (d, 1H,  $-\text{CH}_2-\text{O}-\text{CH}-$ ), 3.97-3.94 (dd, 1H,  $-\text{CH}_2-\text{O}-\text{CH}-$ ), 3.93-3.89 (m, 2H,  $-\text{CH}_2-\text{O}-\text{CH}-$ ), 3.76 (dd, 1H,  $-\text{CH}_2-\text{O}-\text{CH}-$ ), 2.33 (t, 2H,  $\text{CH}_2\text{COO}-$ ), 2.27 (t, 2H,  $\text{CH}_2\text{COO}-$ ), 2.00 (q, 4H,  $2x\text{CH}_2-\text{CH}=\text{CH}_2$ ), 1.63-1.53 (m, 4H,  $2x\text{CH}_2\text{CH}_2\text{COO}-$ ), 1.36-1.31 (m, 4H,  $2x\text{CH}_2$ ) 1.29-1.23 (br.s, 16H,  $2x[4\text{CH}_2]$ ) ppm. (b) Peaks equal to those of a of lower intensity at 5.81-5.74 (o), 4.98-4.89 (l) and 2.00 (d), with additional peaks at 3.60, 2.50-2.40 and 1.55-1.45, which can be attributed to the presence of surfactant and water in the miniemulsion sample.

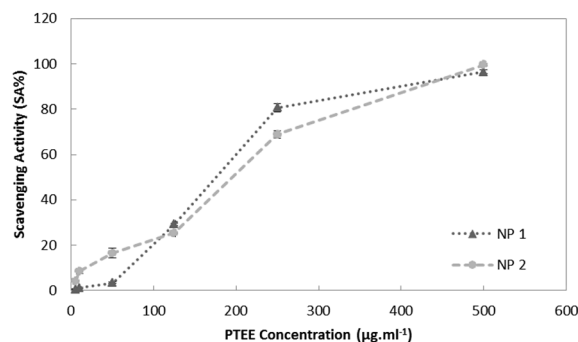
**Table 1.** Particle size (Dp), Polydispersity index (PDI), stability evaluation of the formed NPs by DLS on day 1 and day 30 and Molar mass (Weight average molecular-Mw, Mean average-Mn) of the formed polymers.

Sample	Stability Day 1		Stability Day 30		Molar mass	
	Dp $\pm$ S.D. (nm)	PDI $\pm$ S.D.	Dp $\pm$ S.D. (nm)	PDI $\pm$ S.D.	Mn (kDa)	Mw (kDa)
NP 1	$207.1 \pm 1.1$	$0.150 \pm 0.030$	$238.8 \pm 1.2$	$0.190 \pm 0.010$	3.26	7.48
NP 2	$258.2 \pm 3.4$	$0.193 \pm 0.015$	$253.5 \pm 2.4$	$0.193 \pm 0.013$	6.68	13.99

characteristic peaks in the region 5.81-5.74 , 4.98-4.89 and 2.00 corresponding to the  $\text{CH}=\text{CH}_2$  bonds. In contrast, Figure 2b shows the  $^1\text{H}$  NMR spectrum of the polymer formed, showing a reduction of the relative intensities of the three peaks attributed to  $\text{CH}=\text{CH}_2$ , which indicates the consumption of double bonds of diene monomer during thiol-ene reaction of polymerization and suggesting the formation of PTEE.

Transmission Electron Microscopy (TEM) was conducted to provide information about nanoparticle morphology and shape. TEM images show that particles obtained by miniemulsion polymerization (NP 1) presented spherical shape with particle diameters around 200-400 nm (Figure 3a), whereas particles produced by emulsification/evaporation (NP 2) also presented spherical shape, but with some imperfections on the surface and particles diameters around 80-150 nm (Figure 3b). The imperfections observed on the particle surface in NP 2 could be attributed to coalescence of smaller particles during the evaporation step. The results of FTIR and TEM showed that the different techniques affected the particle size but did not change polymer properties.

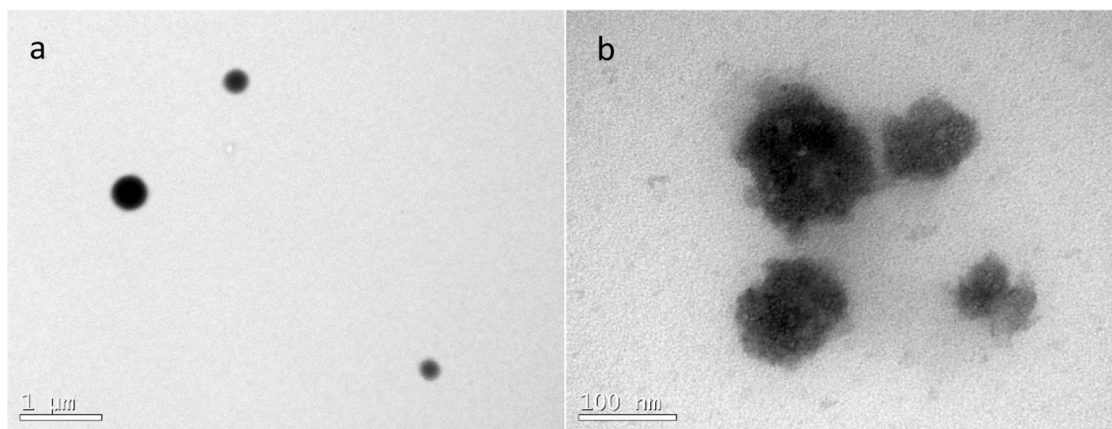
The antioxidant activity of PTEE nanoparticles was evaluated by its capability as a hydroxyl radical scavenger through the use of 2,2-diphenyl-1-picrylhydrazyl (DPPH), via a spectrophotometric assay. When a hydrogen atom or electron is transferred to the odd electron in  $\text{DPPH}^\cdot$ , the absorbance decreases due the  $\text{DPPHH}$  non-radical formation, which can be detected at 517 nm. Figure 4 shows the scavenging activity of PTEE nanoparticles, with PTEE concentrations varying from 5 to 500  $\mu\text{g}\cdot\text{mL}^{-1}$ . It is possible to note that increasing PTEE concentration led to an increase of the antioxidant activity for both samples (NP 1 and NP 2). The  $\text{EC}_{50}$  was also determined, denoting the amount of



**Figure 4.** DPPH scavenging activity after 30 min of exposure at different PTEE concentrations. Results for PTEE nanoparticles obtained by: Miniemulsion polymerization (NP 1); and Emulsification/evaporation (NP 2).

polymer required to reduce the initial concentration of  $\text{DPPH}^\cdot$  radicals by 50%. As shown in Table 2,  $\text{EC}_{50}$  for NP 1 and NP 2 was respectively  $177.97 \pm 3.29 \mu\text{g}\cdot\text{mL}^{-1}$  and  $212.28 \pm 2.36 \mu\text{g}\cdot\text{mL}^{-1}$  after 30 min of exposure. Similar results were found by Gizdavic-Nikolaidis et al. (2004) for polyaniline grafted with lignin at 20 wt% in an antioxidant test with methanolic DPPH $^\cdot$  assay. As a result, a concentration of 200  $\mu\text{g}\cdot\text{mL}^{-1}$  was enough to reduce the level of 72  $\mu\text{M}$  of  $\text{DPPH}^\cdot$  radicals by close to 50%. These results indicated that PTEE has potential as a scavenger of the DPPH free radical. Its activity is probably due to an inevitable polymer oxidation during the process, and the oxidation product may involve positively charged centers, with consequent donation of one or more protons from the polymer to form  $\text{DPPHH}$  (Gizdavic-Nikolaidis et al., 2004).

Inhibiting peroxidation effects of nanoparticles was also determined on a linoleic acid system determined with the  $\beta$ -carotene bleaching test. The free radical is formed from linoleic acid and a hydrogen atom removed from a methyl group of the  $\beta$ -carotene



**Figure 3.** TEM images of nanoparticles obtained by: (a) Miniemulsion polymerization (NP 1); and (b) Emulsification/evaporation (NP 2).

**Table 2.** Antioxidant Activity of Poly (thioether-ester) nanoparticles by DPPH free radical scavenging activity and  $\beta$ -carotene/linoleic acid assay.

Sample	DPPH $E_{c_{50}}$ ( $\mu\text{g}\cdot\text{ml}^{-1}$ )	$\beta$ -carotene-linoleic acid Antioxidant Activity (%)
NP 1	177.97 $\pm$ 3.29	53.41 $\pm$ 0.62
NP 2	212.38 $\pm$ 2.36	57.45 $\pm$ 2.25

molecule followed by a discoloration of  $\beta$ -carotene. The effect of the presence of PTEE nanoparticles in the  $\beta$ -carotene/linoleic acid assay was evaluated and the results are displayed in Table 2. The antioxidant activities in percentage for NP 1 and NP 2 were found to be 53.41 $\pm$ 0.62 and 57.45 $\pm$ 2.25, respectively. These results show that the polymer at the concentration of 1.6  $\text{mg}\cdot\text{ml}^{-1}$  was able to prevent the  $\beta$ -carotene discoloration by almost 60%. This result showed that the polymer had the capability of inhibiting the free-radical induction, Preventing the hydrogen atom exchange, lipid molecules cannot be converted into lipid hydroperoxide and, consequently, the lipid peroxidation is interrupted. However, the present antioxidant activity can be due to electron transfer, where a compound can deactivate a free radical by first forming a radical cation followed by rapid and reversible deprotonation in solution (Wright et al., 2001).

## CONCLUSION

Results show that the poly (thioether-ester) nanoparticles obtained by miniemulsion polymerization or emulsification/ evaporation presented antioxidant activity, confirmed by DPPH free radical scavenging activity and  $\beta$ -carotene/linoleic acid assay, probably due to polymer oxidation during the process, which is able to donate hydrogen or an electron to the free radical. This property of PTEE polymers indicates their potential as a functional barrier material in the packing industry to avoid food or lipid degradation by oxidation, besides acting as a physical barrier in the composition of the polymer film.

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