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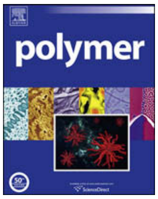

Synthesis and characterization of new UV absorbing microspheres of narrow size distribution by dispersion polymerization of 2-(2′-hydroxy-5′-methacryloxyethylphenyl)-2*H*-benzotriazole

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ABSTRACT

New UV absorbing microspheres of sizes ranging between 0.2 ± 0.03 and 3.0 ± 0.2 μm were formed by dispersion polymerization of the monomer 2-(2′-hydroxy-5′-methacryloxyethylphenyl)-2*H*-benzotriazole (trade name: NORBLOC) in methyl ethyl ketone as a continuous phase. The effect of various polymerization parameters, such as monomer concentration, initiator type and concentration, stabilizer concentration and crosslinker monomer concentration, on the size and size distribution, and on the polymerization yield of the produced PNORBLOC microspheres has been elucidated. Polyethylene/PNORBLOC resins and films of 150 ± 25 μm thickness were prepared by melt blending of low density polyethylene with 2% (w/w) PNORBLOC microspheres of 0.25 ± 0.03 μm diameters, followed by a tubular blown process at 170–190 °C. The UV irradiation (200–390 nm) cut-off efficiency of these films has been demonstrated.

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1. Introduction

Exposure to ultraviolet (UV) radiation may cause significant degradation of many materials. The UV radiation damage is responsible for the discoloration of dyes and pigments, weathering, yellowing of plastics, loss of gloss and mechanical properties (cracking), sun-burn skin, skin cancer and other problems associated with UV light [1–5]. Paints, plastics, contact lenses and cosmetics manufactures have great interest in offering products that remain unaltered for long periods of time under exposure to UV light.

Chemical materials known as UV absorbers are used to protect materials from the damaging effects of UV radiation. Materials as *o*-hydroxybenzophenones, 2-(2′-hydroxyaryl)-2*H*-benzotriazoles and 2-(2′-hydroxyaryl)-1,3,5-triazines are commonly used for protection against photodegradation, owing to their exceptional photostability and low quantum yield of photodecomposition. Also, these molecules are required for their ability to transform the absorbed radiation energy into less damaging thermal energy via a photo-physical process through intramolecular hydrogen bonds [6,7].

Coatings containing benzotriazole ultraviolet stabilizers are well-known as effective UV stabilizers for plastics materials, contact lenses and automotive coatings [8]. The main disadvantage of these UV absorbers is that they leak from the polymeric coating matrix with time, due to their relatively small molecular weight. To solve this problem, or to decrease the diffusion rate, efforts to incorporate polymeric UV absorbing particles within desired matrices have been accomplished. These particles were prepared by heterogeneous homo or co-polymerization of monomeric UV absorbing molecules in the absence, or presence, of an additional vinylic monomer [9–11].

The present manuscript describes a method to prepare new UV absorbing polymeric microspheres of narrow size distribution of sizes ranging between 0.2 ± 0.03 and 3.0 ± 0.2 μm. These particles were formed by dispersion polymerization of the benzotriazolic UV absorbing monomer: 2-(2′-hydroxy-5′-methacryloxyethylphenyl)-2*H*-benzotriazole (Fig. 1) under variation of several parameters [12,13]. This UV absorbing monomer is commercially known as TINUVIN® 796 or NORBLOC® 7966 [14]. For simplicity this monomer will be named in this manuscript as NORBLOC. Polyethylene/PolyNORBLOC (PE/PNORBLOC) composite resins and films of 150 ± 25 μm thickness were prepared by melt blending of low density PE (LDPE) with 2% (w/w) PNORBLOC microspheres of 0.25 ± 0.03 μm, followed by a tubular blown process at 170–190 °C [15,16]. The UV irradiation (200–390 nm) cut-off efficiency of these films has been demonstrated.

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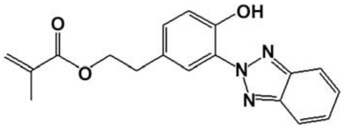

Fig. 1. Chemical structure of the monomer NORBLOC [2-(2′-hydroxy-5′-methacryloxyethylphenyl)-2*H*-benzotriazole].

2. Experimental

2.1. Chemicals

The following analytical-grade chemicals were used without further purification: divinyl benzene (DVB, 80%), benzoyl peroxide (BP; 98%), 2-methoxyethanol, ethyl acetate and methyl ethyl ketone from Aldrich, 2-(2′-hydroxyl-5′-methacryloxyethylphenyl)-2*H*-benzotriazole (NORBLOC) from Ciba® Specialty Chemicals Inc., Pluronic F127 from BASF, LDPE (IPETHENE 320 of 0.92 g/cm^2 density) from Carmel Olefins Ltd, Israel. 2,2′-Azobisisobutyronitrile (AIBN; Aldrich) was recrystallized from ethanol. Water was purified by passing deionized water through an Elgastat Spectrum reverse osmosis system, Elga Ltd, High Wycombe, UK.

2.2. Methods

2.2.1. Synthesis of PNORBLOC microspheres

PNORBLOC microspheres of sizes ranging from 0.2 ± 0.03 to 3.0 ± 0.2 μm were formed by dispersion polymerization of the monomer NORBLOC in methyl ethyl ketone, as a continuous phase. Briefly, PNORBLOC microspheres of 0.25 ± 0.03 μm dry diameter were formed by dissolution of 0.5 g NORBLOC (5% w/v), 0.5 g Pluronic F127 and 20 mg BP in 10 mL methyl ethyl ketone. The 20 mL vial containing this solution was then shaken at 65 °C for 24 h. The formed PNORBLOC microspheres were then washed from excess reagents by intensive centrifugation cycles with methyl ethyl ketone and ethanol, and then dried by ethanol evaporation. The effect of various polymerization parameters, such as monomer concentration, initiator type and concentration and stabilizer concentration, on the size and size distribution and the polymerization yield of the particles was elucidated.

The % conversion (polymerization yield) of the NORBLOC to PNORBLOC microspheres was calculated from the following expression:

$$\text{Polymerization yield (weight\%)} = (W_{\text{PNORBLOC}}/W_{\text{NORBLOC}}) \times 100$$

where W_{PNORBLOC} is the weight of the dried PNORBLOC microspheres and W_{NORBLOC} is the initial weight of the monomer NORBLOC.

The number of the PNORBLOC microspheres was calculated according to the following expression:

$$N = \frac{W_{\text{PNORBLOC}}}{V \times d}$$

where N is the number of the PNORBLOC microspheres, W_{PNORBLOC} is the weight of the dried PNORBLOC microspheres, V is the volume of the PNORBLOC microspheres ($V = 4/3(\pi \times r^3)$), and d is the density of the PNORBLOC microspheres (1.2 g/cm^3).

2.2.2. Preparation of PE/PNORBLOC resins and films

PE/PNORBLOC resins and films were prepared according to the literature, by melt blending of LDPE with the PNORBLOC microspheres of 0.25 ± 0.03 μm dry diameter, followed by a tubular blown process [15,16]. Briefly, PE/PNORBLOC composite resins for films formation were prepared by melt blending of LDPE and PNORBLOC microspheres of 0.25 ± 0.03 μm dry diameter (2% final weight microspheres concentration) in Prism (England) twin screw extruder, with a length/diameter ratio of 16 and diameter of 25 mm, operating with a temperature profile from 170 to 190 °C and 65 rpm in corotating mode. Then, the mixtures were cooled in a water bath and pelletized. The films of the PE/PNORBLOC pellets were then prepared with a tubular blown LDPE film equipment at a 2.0 blownup ratio. The equipment had a screw with a 40 mm diameter, a length/diameter ratio of 24 and spiral die with a die gap of 2.5 mm. The temperature profile of the extrusion was between 170 and 190 °C. The films thickness was controlled to be between 125 and 175 μm.

PE/NORBLOC films were prepared similarly as PE/PNORBLOC films substituting the PNORBLOC microspheres for the monomer NORBLOC.

2.3. Characterization

2.3.1. FTIR

Fourier transform infrared (FTIR) analysis was performed with a Bomem FTIR model MB100 spectrophotometer (Hartman & Braun). The analysis was performed with 13 mm KBr pellets that contained 2 mg of the detected material and 198 mg of KBr. The pellets were scanned over 100 scans at a 4 cm^{-1} resolution.

2.3.2. Mass spectra

Mass spectra (MS) were obtained with Auto spec Premier (Waters UK) – Magnetic Sector, by chemical ionization in methane (CI/CH$_4$) using solid probe with a thermal gradient under CI/CH$_4$ conditions. Briefly, 1 mg dried sample was heated from 50 to 600 °C under high vacuum at a heating rate of 10 °C/min.

2.3.3. Measurements of hydrodynamic size

Hydrodynamic particles size and size distribution were measured in the continuous phase methyl ethyl ketone with a model N4MD submicrometer particle analyzer (Coulter Electronics).

2.3.4. Measurements of dry size

Dried particle size and size distribution were measured with a Scanning Electron Microscope (SEM). SEM pictures were obtained with an FEI SEM model Inspect S. For this purpose, a drop of dilute microspheres dispersion in ethanol was spread on a glass surface, and then dried at room temperature. The dried sample was coated with gold in vacuum before viewing under SEM. The average particles' size and distribution were determined by the measurement of the diameters of more than 100 particles with image analysis software (Analysis Auto, Soft Imaging System GmbH, Germany).

2.3.5. XRD

Powder X-ray diffraction (XRD) patterns were recorded using an X-ray diffractometer (Model D8 Advance, Bruker AXS) with Cu Kα radiation.

2.3.6. TGA and DSC

Thermal behavior of the particles was measured with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The analysis was performed with a TC15 system equipped with TGA (model TG-50) and DSC (model DSC-30, Mettler–Toledo), using approximately 6 mg of dried samples under nitrogen atmosphere (200 mL/min) at a heating rate of 10 °C/min.

2.3.7. BET

Surface area of the microspheres was measured by the Brunauer–Emmett–Teller (BET) method with a Gemini III model 2375 (Micrometrics) [17].

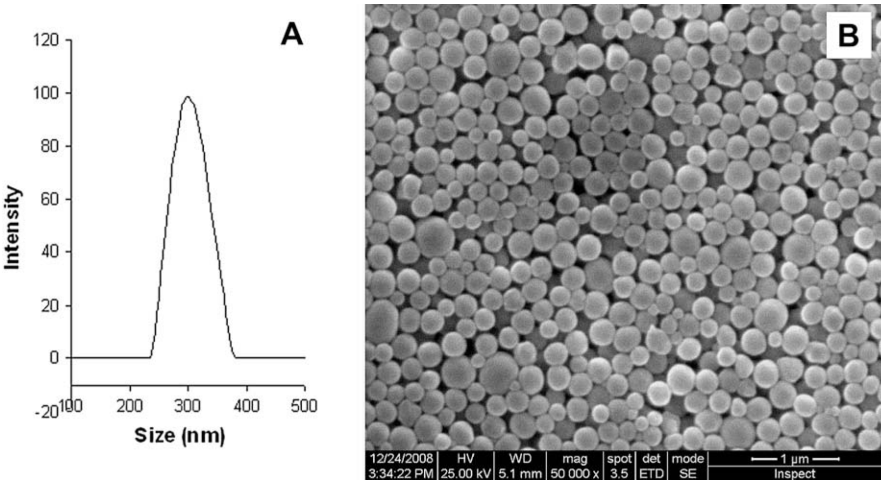

Fig. 2. Hydrodynamic size histogram (A) and an SEM image (B) of the PNORBLOC microspheres. The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section.

2.3.8. *UV analysis*

UV–vis spectra (%transmittance, absorption) were measured with UV–vis Spectrophotometer Carry-1E (Varian, Australia) for the liquid samples, and Lambda 6 Spectrophotometer, Perkin–Elmer for the PE films.

2.3.9. *Light microscope*

Optical microscope pictures were obtained with an Olympus microscope, model BX51.

3. Results and discussion

3.1. *Characterization of the PNORBLOC microspheres*

Fig. 2 presents a typical hydrodynamic size histogram (A) and an SEM image (B) of the PNORBLOC microspheres prepared in the presence of 5% (w/v) NORBLOC, according to the Experimental section. A careful examination of these figures shows that the hydrodynamic diameter and size distribution of these PNORBLOC microspheres dispersed in the continuous phase are 310 ± 35 nm while those illustrated in the SEM image are 250 ± 30 nm. The slightly larger hydrodynamic diameter is due to the fact that the hydrodynamic diameter also includes the adsorbed and swollen solvent molecules while the SEM image shows the dry diameter [18].

Fig. 3 presents FTIR spectra between 1500 and 1800 cm^{-1} of the monomer NORBLOC (A) and the PNORBLOC microspheres (B). The FTIR spectrum of the monomer shows absorption peaks at 1520 cm^{-1} corresponding to the tertiary amine stretching band, at 1570 cm^{-1} corresponding to the C=C conjugated double bond stretching band, at 1600 cm^{-1} corresponding to the C=N conjugated double bond stretching band, at 1625 cm^{-1} corresponding to the vinylic double bond stretching band and at 1730 cm^{-1} corresponding to the carbonyl stretching band [19]. The FTIR spectrum of the PNORBLOC microspheres is similar to that of the monomer NORBLOC except for the disappearance of the vinylic double bond peak at 1625 cm^{-1} and the broadening and shifting of the carbonyl peak at 1730 cm^{-1} to 1750 cm^{-1}. The disappearance of the NORBLOC double bond is probably due to the efficient NORBLOC polymerization. The difference in the carbonyl stretching band peak location of the NORBLOC and the PNORBLOC is due to the different chemical character of these carbonyls: the carbonyl of NORBLOC is conjugated to the vinylic double bond while that of the polymer is not. The broadening of the polymeric carbonyl peak as opposed to the monomeric one is due to the inhomogeneous chemical environment of the polymeric carbonyl group compared to that of the monomer.

The BET measurements demonstrate that the microspheres prepared in the presence of 5% NORBLOC according to the experimental section possess a specific surface area of 17.9 m^2/g. Pycnometric measurements indicate a density of 1.2 g/cm^3 for these

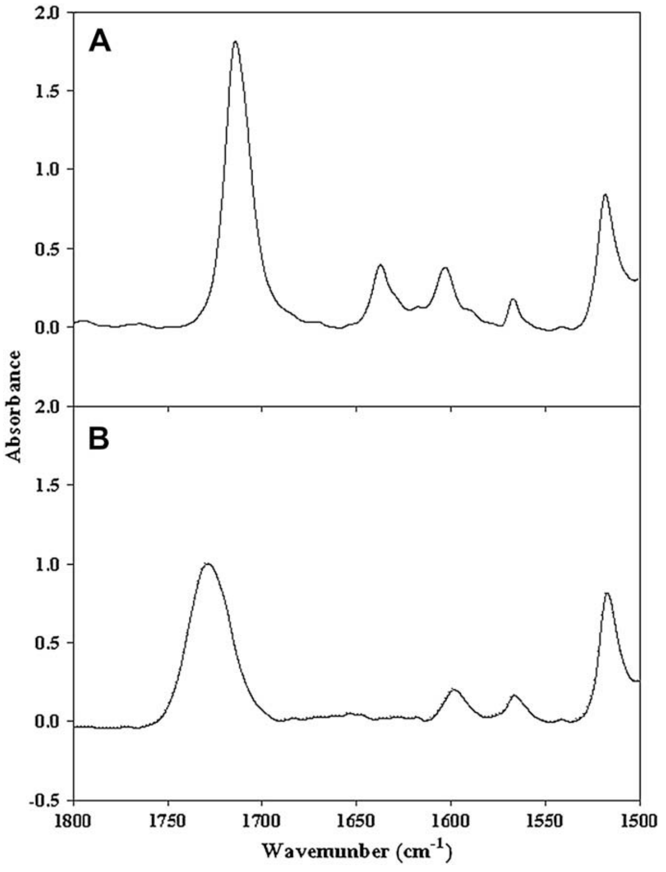

Fig. 3. FTIR spectra of the NORBLOC (A) and the PNORBLOC microspheres (B). The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section.

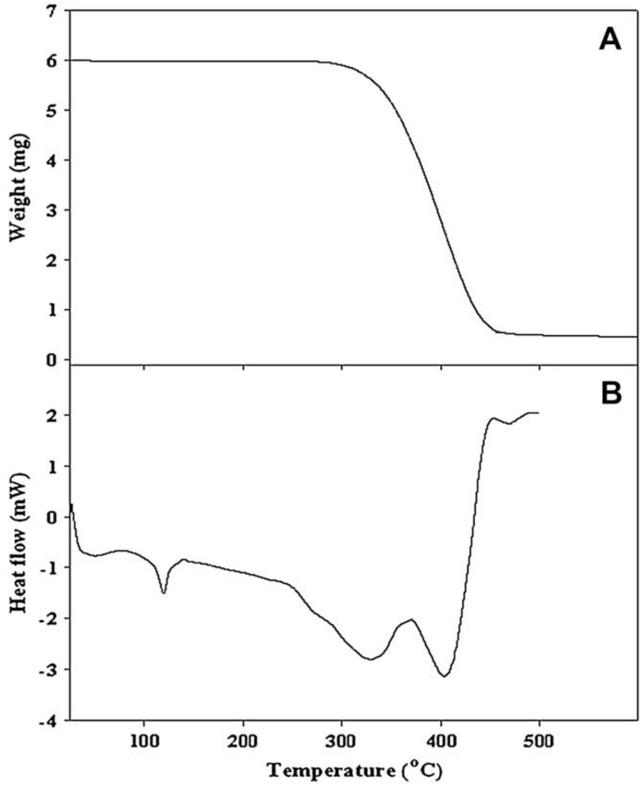

Fig. 4. TGA (A) and DSC (B) thermograms of the PNORBLOC microspheres. The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section.

microspheres. The BET measured surface area indicates that these particles are nonporous, since their specific surface area is similar to the calculated theoretical surface area of nonporous particles of 0.25 μm diameter and density of 1.2 g/cm^3: $S = 6/(D \times d) = 20.0$ m^2/g, where S is the specific particle surface area (m^2/g), D is the particle diameter (μm), and d is the particle density (g/cm^3) [20].

Fig. 4 presents TGA (A) and DSC (B) thermograms of the PNORBLOC microspheres prepared in the presence of 5% NORBLOC, according to the Experimental section. The TGA thermogram of the PNORBLOC microspheres indicates almost 100% weight loss at temperatures between 315 and 430 °C. This weight loss is due to the decomposition of the polymer, as indicated by the two endothermic DSC peaks at 330 and 415 °C. These two endothermic peaks may be interpreted by MS (Fig. 5) as covalent bonds cleavage. MS analysis shows two fragmentation peaks (255 and 237) which observed around 400 °C. The fragmentations are probably due to C–O bonds cleavage: one C–O bond cleavage of ester group leads to the 255 peak and the other is adjacent to this bond and leads to the 237 peak, as shown schematically in Fig. 5. The DSC thermogram (Fig. 4B) also shows an endothermic peak at approximately 120 °C. In order to interpret this peak we scanned the working temperature from 25 to 200 °C, then quenched back to the initial temperature, and then scanned again up to 200 °C. During the re-scan the endothermic peak disappeared. These results may indicate that this peak may due to the melting of a locally crystalline region. It should also be noted that the TGA and DSC behavior of the monomer NORBLOC are similar to that shown for the polymer except that the decomposition of the monomer decreased from the temperatures range 315–430 °C to that between 280 and 410 °C.

Fig. 6 illustrates the X-ray diffraction patterns of the NORBLOC (A) and the PNORBLOC microspheres (B) prepared in the presence of 5% NORBLOC, according to the Experimental section. The X-ray diffraction measurements on the NORBLOC monomer crystals (Fig. 6A) display clear sharp and narrow diffraction peaks typical for crystalline materials. A total of 16 diffraction peaks are observed between $2\theta = 20$ and 60 with four main intense peaks at 2θ (Cu-Ka) = 23.45, 24.04, 25.8 and 27.85°. Those X-ray powder diffraction patterns indicate the crystalline nature of the NORBLOC. The X-ray powder diffraction data of the PNORBLOC microspheres (Fig. 6B), on the other hand, reveal very poor diffraction patterns with one very broad peak in the region between $2\theta = 41°$ and 47° indicating the existence of a fully amorphous phase of the microspheres.

Fig. 7 demonstrates the kinetics of the polymerization of 5% NORBLOC to form the PNORBLOC microspheres according to the

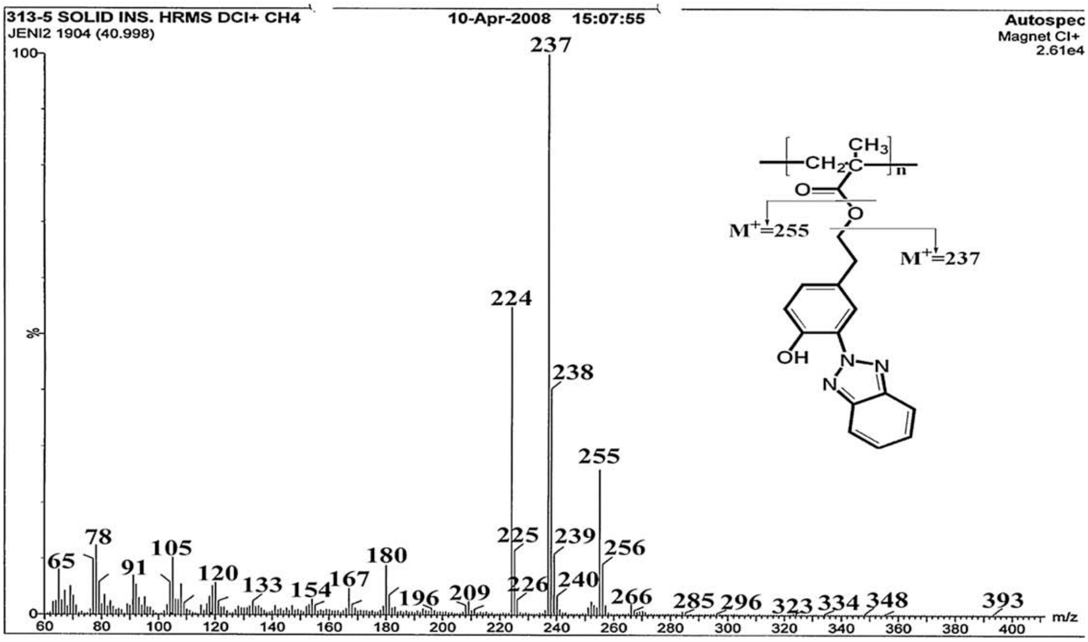

Fig. 5. Mass spectra of the PNORBLOC microspheres. The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section [255: (2-(2′-hydroxy-5′-ethanolphenyl)-2*H*-benzotriazole + H$^+$) and 237: (2-(2′-hydroxy-5′-ethylphenyl)-2*H*-benzotriazole cation)].

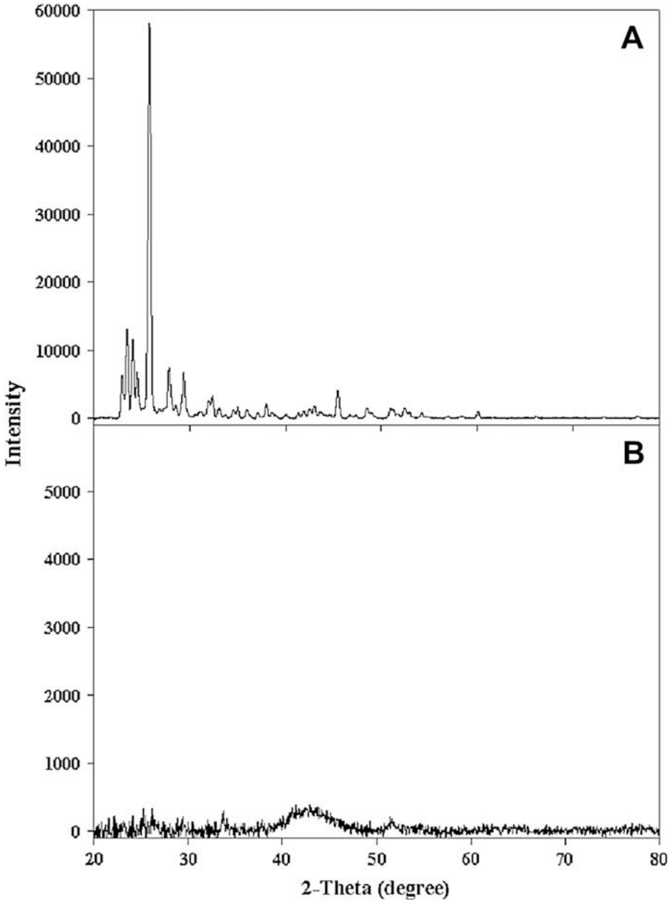

Fig. 6. XRD diffraction patterns of the NORBLOC (A) and the PNORBLOC microspheres (B). The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section.

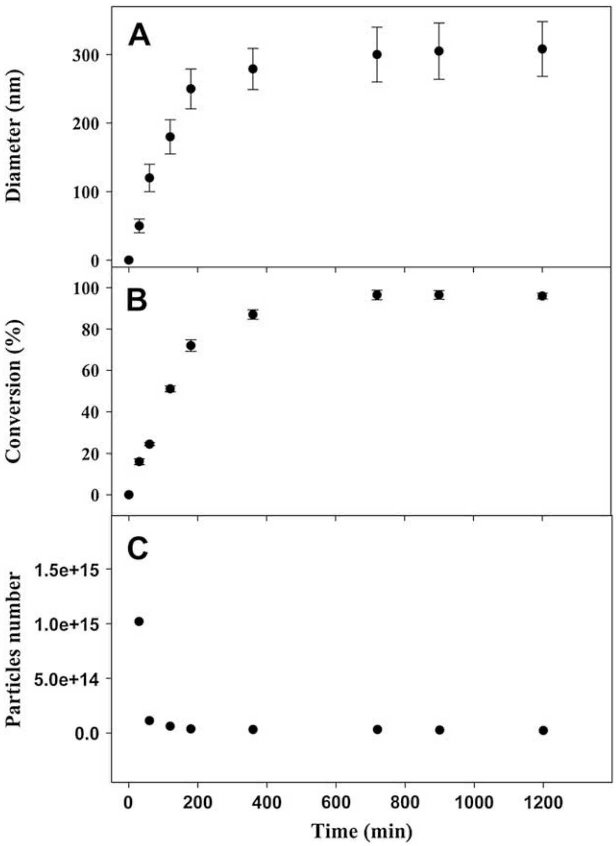

Fig. 7. Polymerization kinetics of the NORBLOC, by following the diameter of the produced PNORBLOC microspheres (A), the conversion of the NORBLOC to PNORBLOC microspheres (B) and the number of the PNORBLOC microspheres (C). The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section.

experimental section, by following the hydrodynamic diameter of the produced microspheres (A), the % conversion of the NORBLOC to PNORBLOC microspheres (B) and the number of the PNORBLOC microspheres (C). The % conversion (polymerization yield) and the number of the NORBLOC to PNORBLOC microspheres were calculated according to the description in the Experimental part. Fig. 7 shows a marked increase in size, size distribution and polymerization yield of the produced PNORBLOC microspheres in the first 4–5 h, followed by a much milder increase in the size and the polymerization yield during the next 6–8 h. For example, 0.5, 1.0, 2.0, 3.0, 6.0 and 8.0 h following the initiation of the polymerization, the hydrodynamic size and size distribution increased from 50 ± 10 nm to 120 ± 20, 180 ± 25, 250 ± 29, 279 ± 30 and 289 ± 35 nm, respectively. Similarly, during that period of time the weight % polymerization yield increased from 16 ± 2% to 24 ± 1, 51 ± 2, 72 ± 3, 87 ± 2 and 90 ± 3%, respectively. Fig. 7C illustrates that the number of the formed PNORBLOC particles 30 min. after the initiation of the NORBLOC polymerization process is 10^{15}, 30 min later, the calculated number of particles decreased by approximately one order of magnitude (1.1×10^{14}). The number of particles remained similar for the remainder of the process. The significant drop in the number of particles 60 min after the initiation of the polymerization relative to that measured after 30 min is probably due to particle agglomeration via a collision mechanism. The, more or less, constant number of particles during the continuation of the polymerization indicates that new particles are not nucleated and that the growing process of the existing particles is at the same rate. These results are consistent with the fact that the formed PNORBLOC microspheres possess quite a narrow particle size distribution.

3.2. Effect of the monomer concentration

Fig. 8A shows the effect of the NORBLOC concentration on the hydrodynamic size and size distribution of the formed PNORBLOC microspheres. This figure demonstrates that increasing the monomer concentration leads to increase in the size and size distribution of the produced PNORBLOC microspheres, e.g., when the concentration of the NORBLOC increased from 0.1 to 5.0 and 15% (w/v), the size and size distribution of the formed PNORBLOC microspheres increased from 100 ± 10 nm to 310 ± 53 and 1200 ± 200 nm, respectively. The increase in the average diameter of the PNORBLOC microspheres as a function of the monomer concentration agrees with the works of Paine et al., Tseng et al. and Lok et al., which describe dispersion polymerization processes of hydrophobic monomers (styrene and butylmethacrylate) in polar solvents (alcoholic solvents such as ethanol) [21–23]. On the other hand, Horak et al. have reported the opposite behavior for dispersion polymerization of polar monomers (2-hydroxyethyl methacrylate and *N*,*O*-dimethacryloylamine) in a mixture of toluene and 2-methylpropan-1-ol; that is, an increase in the monomer concentration results in decreasing average diameter [24]. This contradictory result for the effect of the monomer concentration on the average diameter of the produced particles can be explained by the effect of the monomer concentration on the dispersion polymerization mechanism. Increasing the monomer concentration can

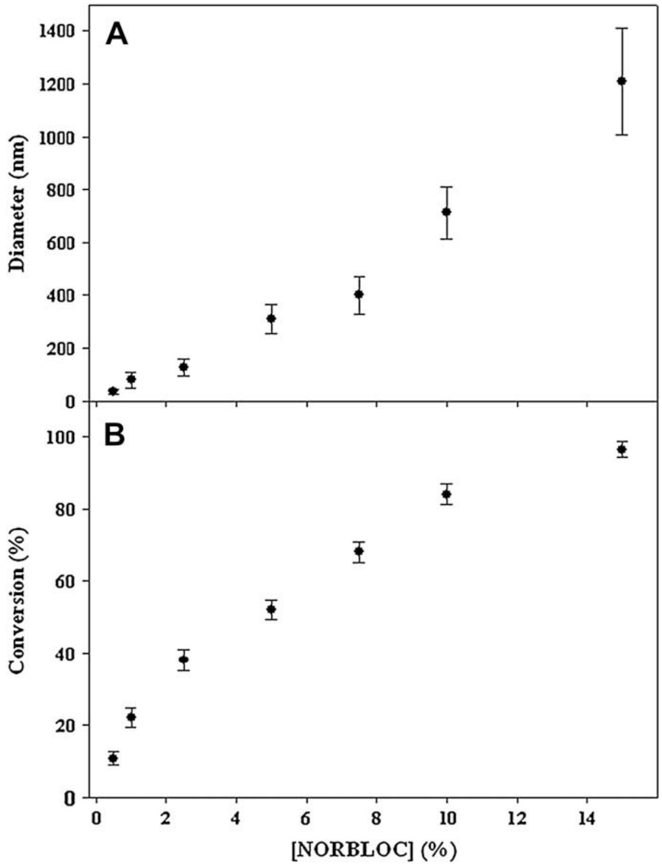

Fig. 8. Influence of the NORBLOC concentration on the diameter of the PNORBLOC microspheres (A) and on the conversion of the NORBLOC to PNORBLOC microspheres (B). The PNORBLOC microspheres were prepared in the presence of different concentrations of NORBLOC, according to the Experimental section.

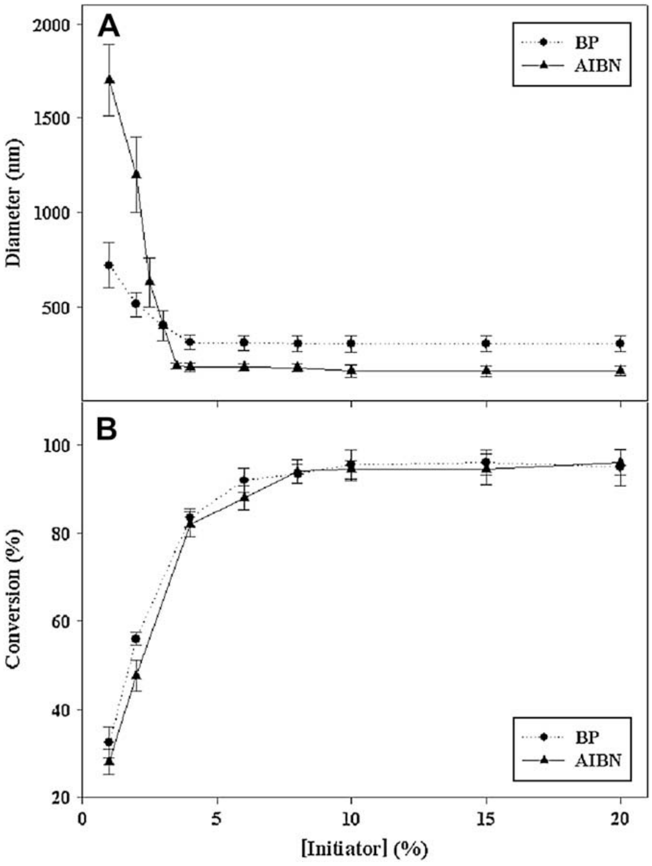

Fig. 9. Influence of the initiator type and concentration on the diameter of the PNORBLOC microspheres (A) and on the conversion of the NORBLOC to PNORBLOC microspheres (B). The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC and different concentrations of BP or AIBN, according to the Experimental section.

affect the initial solvency of the reaction medium by decreasing or increasing (depending on the monomer type and the continuous phase) the solubility of the forming oligomers, so they can have shorter or longer chain lengths before precipitating. In addition, increasing the monomer concentration may decrease or increase the solubility of the stabilizer, thus increasing or decreasing its adsorption on the growing particle. Both effects contribute to the decrease or increase in the particle size. In the present system, increasing the hydrophobic NORBLOC concentration should raise the solubility of both the forming PNORBLOC oligomers and the Pluronic stabilizer, resulting thereby in increasing average diameter.

Fig. 8B illustrates the effect of the monomer concentration on the polymerization yield of the NORBLOC to form the PNORBLOC microspheres. This figure shows that increasing the monomer concentration leads to increase in the polymerization yield. For example, increasing the monomer concentration from 1 to 5 and 15% leads to increase in the polymerization yield from 11% to 50 and 98%, respectively. As can be expected, increasing the NORBLOC concentration may increase the polymerization rate, and thus increase the precipitation rate of the oligomeric chains. Therefore, larger and more numerous nuclei would be expected.

3.3. Effect of the initiator type and concentration

The effect of the initiator type (BP and AIBN) and concentration on the hydrodynamic size and size distribution of the formed PNORBLOC microspheres is illustrated in Fig. 9A. The two curves, that belonging to the BP and that belonging to the AIBN, intersect in the presence of 3% initiator, namely, at this concentration of BP or AIBN the diameter of the formed PNORBLOC microspheres is the same: 400 ± 80 nm. Below this concentration, the diameter and diameter distribution of the particles produced in the presence of AIBN as initiator are significantly larger than those of the particles formed in the presence of similar weight % of BP. Also, below 3% initiator, the lower the initiator concentration the higher the difference between the diameters of the particles produced in the presence of AIBN or BP. For example, in the presence of 2% initiator the diameters of the particles formed in the presence of AIBN or BP are 1200 ± 200 and 514 ± 64 nm, respectively, while in the presence of 1% initiator the diameters are 1700 ± 190 and 721 ± 120 nm, respectively. On the other hand, above 3% initiator the reverse behavior is observed, namely, the diameters of the particles formed in the presence of AIBN are smaller than those formed in the presence of similar weight % of BP. Also, the difference in the diameters is similar for all measured concentrations of the initiators. For example, in the presence of 6 or 15% initiator, the diameters of the particles formed in the presence of AIBN are 179 ± 20 and 160 ± 30 nm, respectively; while in the presence of BP the diameters for both concentrations are 308 ± 39 nm. It should be noted that the influence of the initiator concentration on the size of particles formed by a dispersion polymerization process is controversial. Horak [25] and Margel et al. [10,12,26] reported that increasing the initiator concentration led to a decrease in the diameter of the formed microspheres. On the other hand, the opposite effect was reported by Tseng [22], El-Aasser [27] and others [21,28–31]. The decrease in the average diameter of the

PNORBLOC microspheres as the initiator concentration increasing can be explained according to Horak [25], i.e. increasing the initiator concentration causes an increase in the oligomeric radicals' concentration and thus produce more numerous, but smaller, particles. The concentration and decomposition rate of the initiator and temperature are expected to affect the rate of production of free radicals in the continuous phase. The decomposition rate of AIBN is significantly higher than that of BP at the same polymerization temperature (half-lives at 70 °C of 289 and 1049 min, respectively) [22]. Peroxy radicals (belonging to BP decomposition) are known to be more effective than cyanoalkyl radicals (belonging to AIBN decomposition) in the hydrogen abstraction processes that lead to grafting of the steric stabilizer (Pluronic) to the polymeric particles, thus resulting in smaller particles [32]. This indeed may explain the smaller size particles formed in the presence of BP compared to AIBN at concentrations below 3%, as shown in Fig. 9A. On the other hand, the opposite behavior at initiators concentrations above 3% is still not clear for us.

Fig. 9B shows the influence of the initiator concentration on the polymerization yield of NORBLOC to form the PNORBLOC particles. This figure demonstrates similar behavior for both types of initiators, i.e. increasing the initiator concentrations from 1 to 6% leads to a marked increase in the polymerization yield from about 20 to 90%. An additional increase in the initiator concentrations from 6 to 20% does not influence the polymerization yield significantly.

3.4. Effect of the stabilizer concentration

The effect of the Pluronic F127 concentration on the size and size distribution of the formed PNORBLOC microspheres is illustrated in Fig. 10. This figure shows that increasing the stabilizer concentration leads to the formation of smaller particles with a narrower size distribution. For example, increasing the Pluronic F127 concentration from 0.1 to 1 and 5% leads to a decrease in the average size and size distribution of the PNORBLOC particles: from 1472 ± 200 nm to 728 ± 90 and 350 ± 40 nm, respectively. Inverse proportionality between the stabilizer concentration and the average size of particles formed by the dispersion polymerization of monomers such as MMA, HEMA, and styrene was also previously reported [12,24,33]. A higher stabilizer concentration results in increasing amounts of stabilizer adsorbed onto the nuclei leading to better protection against growing processes.

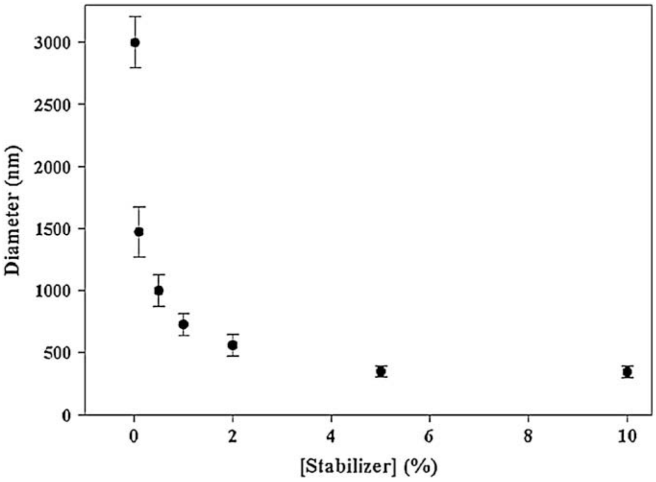

Fig. 10. Influence of the stabilizer concentration on the size and size distribution of the PNORBLOC microspheres. The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC and different concentrations of Pluronic F127, according to the Experimental section.

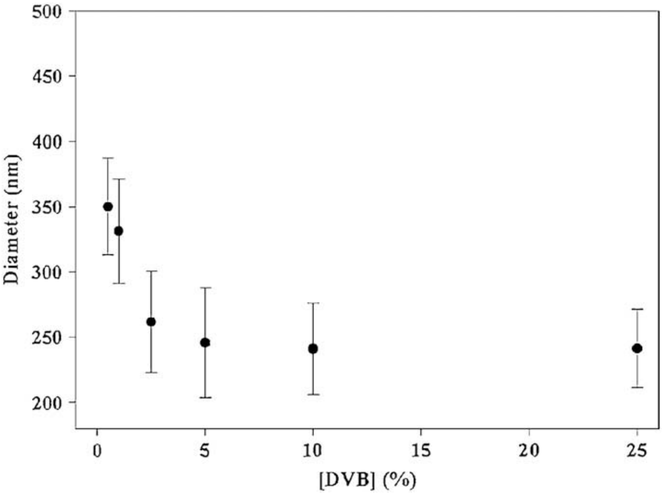

Fig. 11. Influence of the DVB concentration on the size and size distribution of the PNORBLOC microspheres. The PNORBLOC microspheres were prepared in the presence of 5% by weight of total monomers (NORBLOC + DVB) and different concentrations of DVB, according to the Experimental section.

3.5. Effect of the crosslinker monomer concentration

To avoid partial or complete dissolution of the PNORBLOC, crosslinked microspheres were produced by dispersion polymerization of the NORBLOC with the crosslinker monomer DVB. This was accomplished by keeping the total monomer (NORBLOC and DVB) weight % constant (5%) while the weight % ratio between the two monomers was altered. The effect of the DVB weight % on the size and size distribution of the formed PNORBLOC microspheres is illustrated in Fig. 11. This figure shows that the diameter decreases

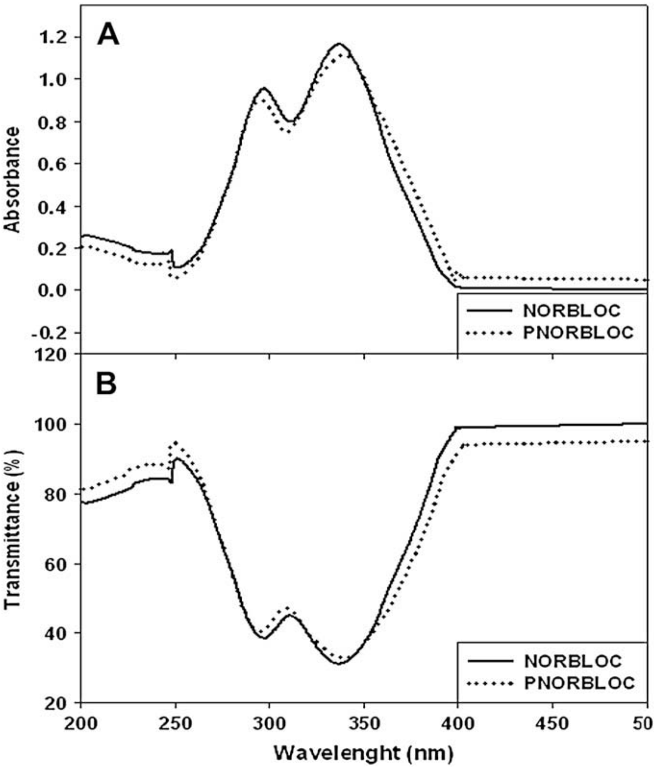

Fig. 12. Absorbance (A) and transmittance (B) spectra of the NORBLOC and the PNORBLOC microspheres (20 mg/L, ethyl acetate). The PNORBLOC microspheres were prepared in the presence of 5% NORBLOC, according to the Experimental section.

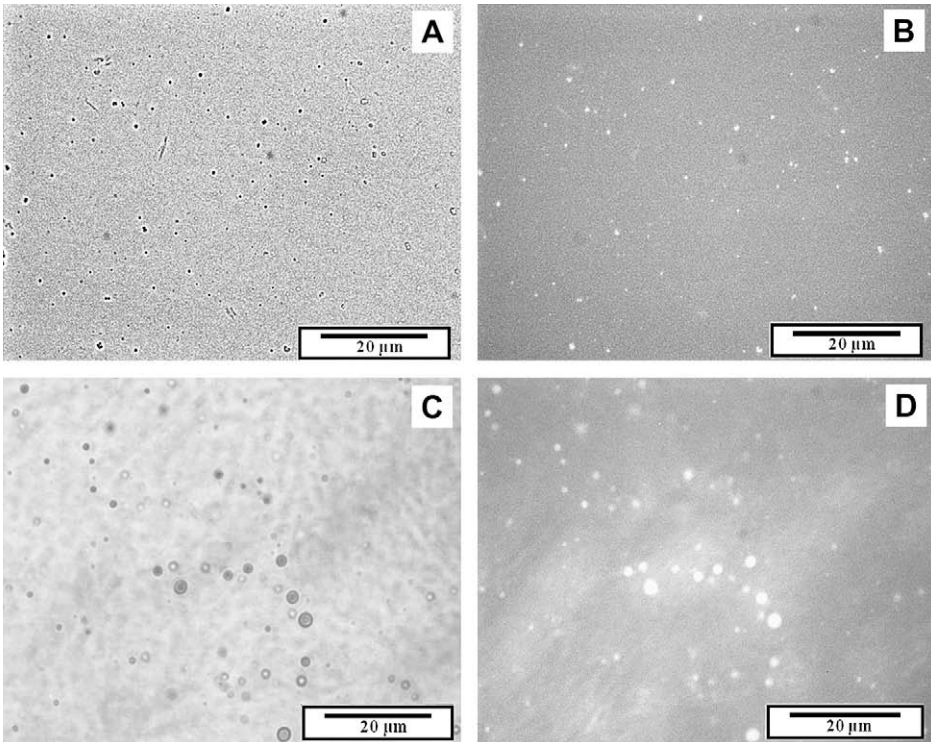

Fig. 13. Light (A, C) and fluorescence (B, D) microscope images of the PNORBLOC microspheres (A, B) and the PE/PNORBLOC films (C, D). The PNORBLOC microspheres and the PE/PNORBLOC films were prepared according to the Experimental section.

and the size distribution are not affected as long as the weight % of DVB increases. For example, when the DVB weight % increases from 0.5 to 2.5 and 10.0%, the average particle size decreases from 350 ± 37 nm to 262 ± 39 and 241 ± 35 nm, respectively. A similar effect of a crosslinker monomer on the average diameter of the polyacrylate particles has been reported by Margel [9,12]. This behavior may be explained by the formation of more crosslinked nuclei, which are therefore more difficult to grow by monomer swelling than the relatively non-crosslinked nuclei.

3.6. *UV absorbance of the NORBLOC and the PNORBLOC microspheres*

Fig. 12 shows UV–vis absorbance/transmittance spectra of the NORBLOC and the PNORBLOC microspheres. The absorption curves of the NORBLOC and the PNORBLOC microspheres (A) exhibit similar behavior, e.g., strong absorption in the UV range between 250 and 390 nm and negligible absorption in the visible region, above ca. 390 nm. Fig. 12 also shows three peaks at ca. 238, 300 and 335 nm in the absorption spectrum of the NORBLOC and the PNORBLOC microspheres in ethyl acetate. The transmittance spectra shown in Fig. 12B demonstrate the cut-off wavelength effect of the NORBLOC and the PNORBLOC microspheres with low transmittance in the 250–390 nm range and a sharp rise in the transmittance (up to approximately 95%) beyond ca. 390 nm.

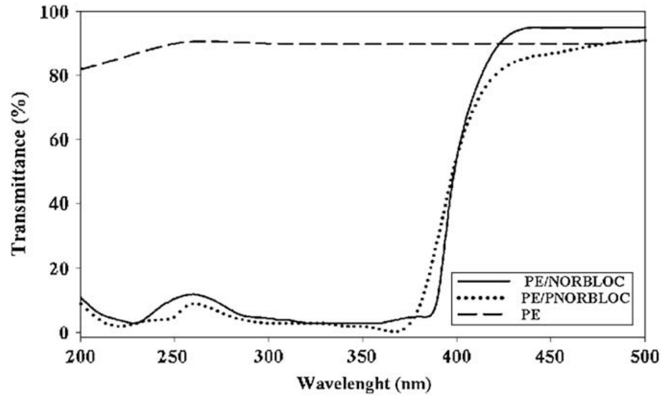

Fig. 14. Transmittance UV–vis spectra of the PE/NORBLOC and the PE/PNORBLOC films. The PNORBLOC microspheres and the PE/NORBLOC and PE/PNORBLOC films were prepared according to the Experimental section.

3.7. *Dispersion of the PNORBLOC microspheres in PE films*

Fig. 13 shows light microscope images of the PNORBLOC microspheres of 250 ± 30 nm dry diameter (A) and the PE/PNORBLOC films prepared with the same microspheres (B). Fluorescence images [34], as shown in pictures C (PNORBLOC microspheres) and D (PE/PNORBLOC films), improve the contrast between the microspheres and the surroundings; thereby better demonstrating the homogeneous dispersion of the PNORBLOC microspheres within the PE film. A careful look at images B and D shows that the PNORBLOC microspheres encapsulated within the PE film are slightly aggregated and possess a diameter of 1640 ± 630 nm instead of the original diameter of 250 ± 30 nm. This aggregation may be explained by the fact that the chemical structure of the PNORBLOC microspheres is not completely compatible with that of the PE.

Fig. 14 shows the transmittance spectra of the PE, PE/PNORBLOC and PE/NORBLOC films. The composite films contain either 0.8 weight % NORBLOC or 2 weight % PNORBLOC microspheres of 250 ± 30 nm original diameter, prepared according to the Experimental section. This figure demonstrates that the UV transmittance of the PE film is almost 90%. On the other hand, Fig. 14 illustrates that the cut-off wavelength effect in 200–390 nm of the PE films containing 0.8% NORBLOC is similar to that containing 2% of the PNORBLOC microspheres.

4. Summary and future work

The present paper describes the synthesis and characterization of new UV absorbing microspheres of a relatively narrow size distribution, formed by the dispersion polymerization of NORBLOC. The effect of various polymerization parameters on the size and size distribution and on the polymerization yield of the produced PNORBLOC microspheres has been elucidated. The PNORBLOC microspheres of 250 ± 30 nm were entrapped within PE films by melt blending of the PE with 2% of the microspheres, followed by a tubular blown process at 170–190 °C. The UV irradiation (200–390 nm) cut-off efficiency of these films has been demonstrated. Efforts to improve the UV cut-off efficiency of these films, by substituting the present entrapped PNORBLOC microspheres by crosslinked PNORBLOC particles of significantly smaller diameter than 250 ± 30 nm are planned for future work.

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References

[1] Soane DS, Fan S, Hino T. Application: US patent 2003-004277; 2003.
[2] Bret WL, Eian GL. Application: US patent 2001-6,312,807 B1; 2001.
[3] Vincent KD, Ganapathiappan S. Application: US patent 2004-0197531; 2004.
[4] Bojinov VB, Grabchev IK. J Photochem Photobiol A Chem 2005;172(3):308–15.
[5] Gugumus F. In: Gächter R, Müller H, editors. Plastic additives handbook. 3rd ed. Munich, Vienna, New York: Hanser; 1990. p. 129–271 [chapter 3].
[6] Parejo PG, Zayat M, Levy D. J Mater Chem 2006;16(22):2165–9.
[7] So YH. Polym Int 2006;55(2):127–38.
[8] Crawford JC. Prog Polym Sci 1999;24(1):7–43.
[9] Galperin A, Margel D, Margel S. J Biomed Mater Res A 2006;79A(3):544–51.
[10] Galperin A, Margel S. J Polym Sci Part A Polym Chem 2006;44(12):3859–68.
[11] Galperin A, Margel S. Biomacromolecules 2006;7(9):2650–60.
[12] Bamnolker H, Margel S. J Polym Sci Part A Polym Chem 1996;34(10):1857–71.
[13] Kawaguchi S, Ito K. Adv Polym Sci 2005;175(Polymer particles):299–328.
[14] http://www.ciba.com/tinuvin_r_796.htm.
[15] Basfar AA, Idriss Ali KM. Polym Degrad Stab 2006;91(3):437–43.
[16] Wang KH, Koo CM, Chung IJ. J Appl Polym Sci 2003;89(8):2131–6.
[17] Hunter RJ. Introduction to modern colloid science. Oxford: Oxford University Press; 1993. p. 170–4.
[18] Horak D, Krystufek M, Spevacek J. J Polym Sci Part A Polym Chem 2000; 38(3):653–63.
[19] Van der Mass JH. Basic spectroscopy. 2nd ed. London: Heyden & Son Ltd., Spectrum House Press; 1972. p. 99–103.
[20] Boguslavsky L, Margel S. J Polym Sci Part A Polym Chem 2004;42(19):4847–61.
[21] Paine AJ, Luymes W, McNulty J. Macromolecules 1990;23(12):3104–9.
[22] Tseng CM, Lu YY, Elaasser MS, Vanderhoff JW. J Polym Sci Part A Polym Chem 1986;24(11):2995–3007.
[23] Lok KP, Ober CK. Can J Chem 1985;63(1):209–16.
[24] Horak D, Chaykivskyy O. J Polym Sci Part A Polym Chem 2002;40(10): 1625–32.
[25] Horak D. J Polym Sci Part A Polym Chem 1999;37(20):3785–92.
[26] Boguslavsky L, Baruch S, Margel S. J Colloid Interface Sci 2005;289(1):71–85.
[27] Shen S, Sudol ED, El-Aasser MS. J Polym Sci Part A Polym Chem 1993;31(6): 1393–402.
[28] Candau F, Ottewill RH. An introduction to polymer colloids. Dordrecht: Kluwer; 1990. p. 35–72.
[29] Christian P, Giles MR, Griffiths RMT, Irvine DJ, Major RC, Howdle SM. Macromolecules 2000;33(25):9222–7.
[30] Kedem M, Margel S. J Polym Sci Part A Polym Chem 2002;40(9):1342–52.
[31] Saenz JM, Asua JM. Macromolecules 1998;31(16):5215–22.
[32] Barrett KEJ. Br Polym J 1973;5(4):259–71.
[33] Bulmus V, Tuncel A, Piskin E. J Appl Polym Sci 1996;60(5):697–704.
[34] Jiang YC, Wu SK, Sustic A, Xi F, Vogl O. Polym Bull 1988;20(2):169–76.