

Preparation of Reactive Polymeric Nanoparticles (RPNPs)

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ABSTRACT

A series of reactive polymeric nanoparticles (RPNPs) was prepared by free radical non-linear copolymerization of mono (M_1) and trivinyl acrylic (M_2) monomers in miniemulsion. The crosslinking density was determined by the mole ratio of the trivinyl component. The unswelled latex nanoparticles showed a narrower dispersity than particles in organic solution. The residual vinyl groups adjacent to the nanoparticles were subjected to further crosslinking reactions. The reactive vinyl groups were detected by nuclear magnetic resonance spectroscopy (NMR). The size of particles in swollen state was determined by dynamic laser light scattering (DLS) method and the dried form by transmission electron microscopy (TEM). It was found that size of RPNPs is in the range of 50 and 500 nm. These particles possess properties that may allow their application in areas as disparate as dental filling material and as a component in industrial powder-based coatings.

Keywords: free radical non-linear polymerization, crosslinking polymerization, Reactive Polymeric Nanoparticles (RPNPs), miniemulsion

1 INTRODUCTION

Synthesis of polymeric nanoparticles attracts a great effort to obtain particles with desired size, surface and functionalities. [1, 2] Crosslinking polymerization methods have received considerable interest relation to the development of preparation of microgels [3, 4], crosslinked nanoparticles [5], their composites [6] and to study the gelation of reactions [7-11]. Crosslinked nanoparticles can be formed in homogenous solutions or under heterogenous medium in micellar or emulsion conditions [12]. Formation of polymers in emulsion also has an environmental aspect to reduce the volatile organic compounds (VOC).

Many application fields have related to bulk crosslinked system, e.g. in restorative dentistry [15-18], paint and powder coatings [19-21].

The present paper describes the formation of reactive polymeric nanoparticles (RPNPs). These were synthesized in miniemulsion by free radical non-linear crosslinked copolymerization of mono (M_1) and trivinyl acrylic (M_2)

monomers. The polymerization was performed by styrene (ST, M_1) and trimethylol propane trimetacrylate (TMPTMA, M_2) comonomers [22] which were used in different mole ratio.

Size of nanoparticles in dried and swelled was determined by transmission electron microscopy (TEM) and dynamic laser light scattering (DLS) method. Structure and reactivity of NPs were analyzed by nuclear magnetic resonance (1H NMR). The thermo-initiated polymerization of the isolated RPNPs was demonstrated by differential scanning calorimetry (DSC).

2 EXPERIMENTAL SECTION

2.1 Materials

Monomers were styrene (ST) and trimethylol propane trimetacrylate (TMPTMA); emulsifier was sodium dodecyl sulfate; initiator was potassium peroxide. These materials were purchased from Sigma-Aldrich Co., Hungary, and were used as received without further purification.

2.2 Characterization

Nuclear magnetic resonance (1H NMR) This experiments were performed on Bruker 200 WP instrument at 200 MHz operating frequency in $CDCl_3$ solution at an RPNPs concentration of 10 mg/ml.

Dynamic laser light scattering (DLS) Hydrodynamic diameter of the RPNPs were gauged by using a BI-200SM Brookhaven Research Laser Light Scattering photometer equipped with a NdYAg solid state laser at an operating wavelength of $\lambda_0 = 532$ nm. Measurements of the hydrodynamic diameters of NPs were performed at 25 °C with an angle detection of 90° in optically homogenous quartz cylinder cuvettes. The samples were taken from the latex and the RPNPs samples were dissolved in toluene at a concentration of 1 mg/ml. Each sample was measured three times and average serial data were calculated.

Transmission electron microscopy (TEM) Experiments were performed on a Hitachi S-4300 instrument to determine the dried particle size of RPNPs. The sample for TEM analysis was obtained by placing a drop of the colloid solution containing copolymer onto a carbon-coated copper

grid. It was dried at room temperature and then examined by TEM without any further modification or coating.

Differential scanning calorimetry (DSC) Thermal properties were studied with a Netzsch DSC 204 Phoenix differential scanning calorimeter with a scanning rate of $10^{\circ}\text{C}/\text{min}$.

2.3 Formation

Synthesis of RPNPs. Nanoparticles were prepared by miniemulsion copolymerization of styrene (ST, M_1) and trimethylol propane trimetacrylate (TMPTMA, M_2) using monomer feed of $M_1/M_2 = 9/1, 7/3, 5/5, 3/7$ and $1/9$ mol ratio. Monomers were emulsified by adding sodium dodecyl sulfate (SDS) as surfactant, then sonicated for 10 min. The polymerization was performed under nitrogen atmosphere using potassium peroxide as initiator at 60°C . The RPNPs were precipitated from the aqueous latex by adding a three-fold excess of methyl alcohol. The particles were purified by dissolving in toluene and precipitated three times with methyl alcohol.

3 RESULTS AND DISCUSSION

3.1 Preparation of reactive polymeric nanoparticles

Free radical copolymerization of mono (M_1) and trivinyl monomers (M_2) was performed in emulsion in the presence of surfactant. The well known non-linear polymerization results linear growing radicals with pendant vinyl groups in the first step. Propagation steps lead to the formation of side chains and loops. Loops are formed when the growing radical reacts with the pendant vinyl group sitting on the same polymer chain. Since the growing macromolecules permanently contain reactive pendant group further propagation and formation of crosslinks continues.

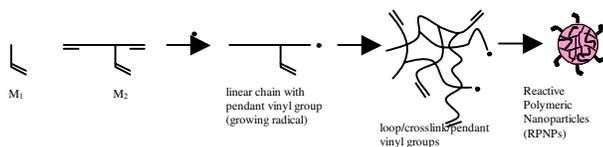


Figure 1: Reaction scheme of the formation of reactive polymeric nanoparticles (RPNPs) by non-linear copolymerization.

3.2 Structure determination. ^1H NMR measurements

NMR spectroscopy is a powerful method to determine the structure of highly crosslinked NPs. ^1H NMR spectra of polymers with a constant $M_1/M_2 = 5/5$ monomer composition were taken at different reaction time (Figure 2).

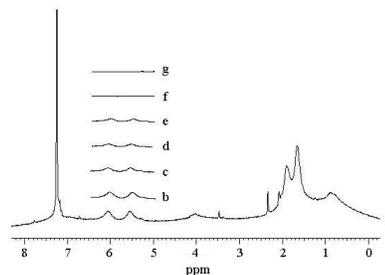


Figure 2: ^1H NMR spectra of RPNPs with $M_1/M_2 = 5/5$ monomer feed at extended reaction time, a: 20 min; b: 40 min; c: 60 min; d: 90 min; e: 120 min; f: 240 min and g: 480 min.

In the early stage of polymerization highly reactive particles were formed. At 120 min reaction time with a conversion of 95 % reactive particles were still observed. However, at prolonged reaction times the vinyl signals were decreased to near low intensity.

Various pendant vinyl concentrations have been observed for RPNPs obtained by copolymerization of monomer feed values as $M_1/M_2 = 9/1, 7/3, 5/5, 3/7$ and $1/9$ at a reaction time of 120 min (Figure 3). At higher M_2 concentrations ($M_1/M_2 = 1/9$ and $3/7$) the pendant vinyl of RPNPs is significantly high (Figure 3e and d). However, at lower M_1 ratios the vinyl content gradually decreases (Figure 3 a, b and c).

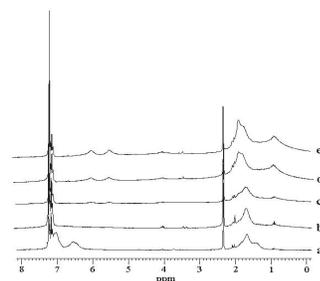


Figure 3: ^1H NMR spectra of RPNPs in the monomer feed: a: 9/1; b: 7/3; c: 5/5; d: 3/7 and e: 1/9 at 120 min reaction time.

3.3 Determination of particle size by dynamic laser light scattering (DLS)

The size of latex particles was examined in the aqueous continuous phase. Hydrodynamic diameter (H_D) of NPs was determined by DLS measurements (Figure 4). The particle size of latex obtained in different monomer ratios by miniemulsion copolymerization. Samples were taken at 120 min reaction time. The particle size increased with the mole ratio of TMPTMA. It was due to the more and more nanoparticles in the micelles are formed.

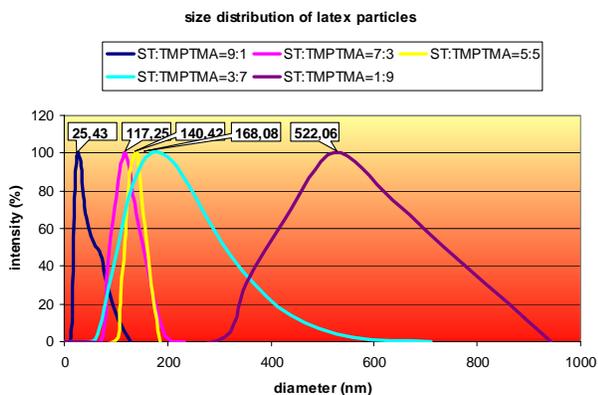


Figure 4: Particle size of latex RPNPs measured by DLS method.

The latex polymer particles were precipitated and then dissolved or dispersed in toluene. The average size of particles was measured by DLS (Figure 5). As expected, crosslinked particles swell in suitable solvents. The swelling ratio depended on the density of crosslinking. DLS measurements showed different size distribution of polymer nanoparticles. However, the largest latex particles with highest crosslinking density displayed reduced size. After swelling, the $M_1/M_2=5/5$ composed particles showed the largest particle size. It was shown that the size of the particles depended upon two parameters: (i) increasing the M_2 content resulted in an increased particle size, (ii) the crosslinking ratio of larger particles is higher resulting in the particles obtained with a monomer feed of $M_1/M_2=5/5$ presented the larger swelled particle size.

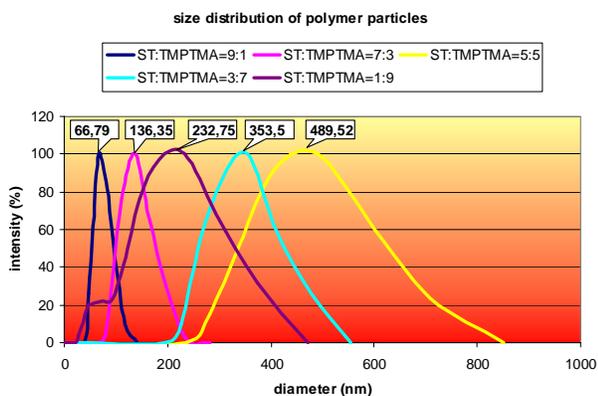


Figure 5: Particle size of RPNPs in toluene as measured by DLS method.

3.4 Particle size determination by transmission electron microscopy (TEM)

TEM measurements showed that the particle size increased with the ratio of M_2 in the monomer feed. In

accordance with the particle size measured for unswelled latex by DLS method, and it was found that the size of dried RPNPs measured by TEM also increased. Selected TEM micrographs are shown in Figure 6, demonstrating the individual spherical particles. The smallest particles were observed for $M_1/M_2=9/1$ monomer ratio (100-120 nm). In comparison with the DLS value ($H_D=66.8$ nm), it was observed that these particles on the TEM specimen grids were rather flat spheres. Because of low crosslinking density, the third dimension of these flattened particles was reduced and, therefore, appeared to have a larger diameter.

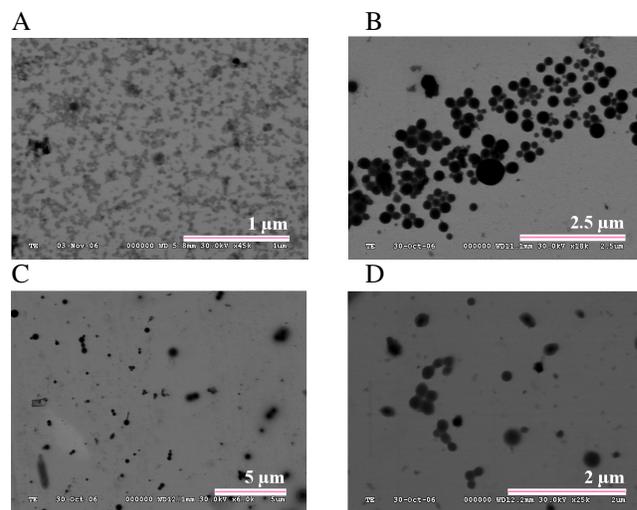
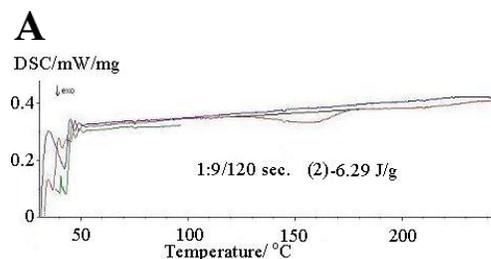


Figure 6: TEM micrographs of RPNPs prepared with M_1/M_2 monomer feed A: 9/1; B: 5/5; C: 3/7 and D: 1/9.

3.5 Thermoreactivity

NMR results showed that nanoparticles containing reactive vinyl groups were polymerized at elevated temperature due to thermal initiation. Thermograms showed an exotherm peak in the temperature range of 128-173 °C, indicating thermoinitiated crosslinking of particles. The RPNPs prepared by highest M_2 content showed a higher effect. Reactivity of particles is higher at higher M_2 content. Samples with lower M_2 content showed undetectable signals. NMR measurements detected a decrease of the pendant vinyl concentration which is in good agreement with the thermoreactivity of the particles.



B

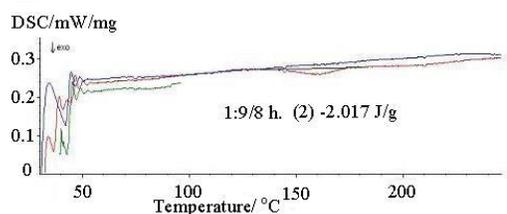


Figure 7: DSC thermograms of samples with monomer feed of $M_1/M_2=1/9$ at A: 120 min and B: 480 min reaction time. Green line: first run; red line: second run with exotherm peak in the temperature range of 128-173 °C and blue line: third run where no peak was observed, the exotherm polymerization was completed.

4 CONCLUSION

The preparation of RPNPs was performed by crosslinking polymerization. The size of the particles depended upon the monomer ratio and on the nature, hydrophilicity and hydrophobicity of the monomers applied. The reactivity of particles was due to the adjacent vinyl groups. The reactivity increased with the ratio of crosslinker. The swelling ratio decreased with the crosslink density. Nanoparticles produced by this method have a potential use as dental filling materials and as a component of industrial powder coatings.

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