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ORIGINAL CONTRIBUTION

Preparation of reactive polymeric nanoparticles (RPNPs)

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Abstract A series of reactive polymeric nanoparticles (RPNPs) was prepared by free radical nonlinear 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. It was found that the unswelled latex nanoparticles showed a narrower dispersity than in the organic solution of macromolecules. In latex, the size increased with the ratio of M_2 monomer due to its higher polarity in the aqueous medium. However, the swollen nanoparticles, dissolved or dispersed in organic solvent, showed a higher dispersity as a function of composition and the crosslinking density. 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 scanning electron microscopy (SEM). It was found that size of RPNPs is in the range of 50 to 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 nonlinear polymerization ·
Crosslinking polymerization ·
Reactive Polymeric Nanoparticles (RPNPs) ·
Miniemulsion · Number average vinyl functionality (NAVF)

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Introduction

There is intense interest in preparing polymeric nanoparticles in which the size, surface features and functionalities can be controlled [1–3]. Crosslinking polymerization methods have received considerable interest relating to the preparation of microgels [4–6], crosslinked nanoparticles [8], their composites [9], and to the study of gelation reactions [10–14]. Crosslinked systems have many commercial applications, which include restorative dentistry [15–18], paints, and powder coatings [19–21]. Cross-linked nanoparticles are formed in homogeneous solutions or in emulsion medium.

Formation of cross-linked structures was investigated to reveal the mechanisms of cyclization, crosslinking, and gelation. We found that the final mechanical properties were strongly influenced by the reactions mentioned above. Bowman described the mechanism of primary cyclization [22–24] and its effect on the conversion [25]. Shrinkage

[26, 27], flexure [28, 29], and water sorption [30] are additional properties that depend on the ratio of cyclization and crosslinking reactions. Matsumoto described the effect of polymer chain rigidity on intramolecular cyclization and crosslinking [31].

The pendant double bonds form so-called primary and secondary loops, followed by branching and crosslinking. Since pendant vinyl groups are less reactive, the final nanoparticles contain double bonds, which are susceptible to further thermal or photoinitiated postpolymerization [8, 21].

For dental filling materials, multivinyl monomers were recently crosslinked in situ by a photopolymerization process [17]. Contraction of dental composites is a significant problem in dentistry today. Volumetric shrinkage can compromise marginal seals and rupture of adhesive bonds created at the tooth restorative interface [26]. Additionally, allergic reactions generated by residual monomers may affect some patients [32]. The technology described in this paper addresses these problems, and offers a possible solution to them.

Polyreactions of water unsoluble or less soluble vinyl monomers in emulsion droplets lead to formation of nanosized latex macromolecules [33–36]. Recently, nanosized polymeric particles as polystyrene [37], and crosslinked particles with low crosslinking density [38–40] and particles with functional groups [41] have been synthesized. Polymerization of trimethylol propane trimethacrylate was also investigated [42] up to 20 mol% of crosslinker. In the literature [43, 44], microgels and nanogels have been described and their molecular weight was characterized. In this study we describe the formation of reactive polymeric nanoparticles (RPNPs) obtained by miniemulsion polymerization with low and high crosslinking density and, instead of their molecular weight, we determined their particle size. Dispersion of the droplets of mono and trivinyl monomers prevented gelation while allowing the growth of particles with defined volume. Nanoparticles with reactive vinyl groups have potential use as dental materials [47]. Because the major portion of polymerization is performed before the application by the dentist, limited volumetric shrinkage is expected during the final in situ photopolymerization step. Furthermore and importantly, sensitive patients will not be exposed to irritating monomers.

In this paper, the correlation of monomer feed, crosslinking density, particle size, reactivity, number average vinyl functionality (NAVF), and swelling behavior of RPNPs is described.

Results and discussions

Synthesis of nanoparticles

The free radical copolymerization of mono (M_1) and trivinyl (M_2) monomers was performed in emulsion in the presence of surfactant. The well-known nonlinear polymerization results linear growing radicals with pendant vinyl groups in the first step (Fig. 1).

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 groups further propagation

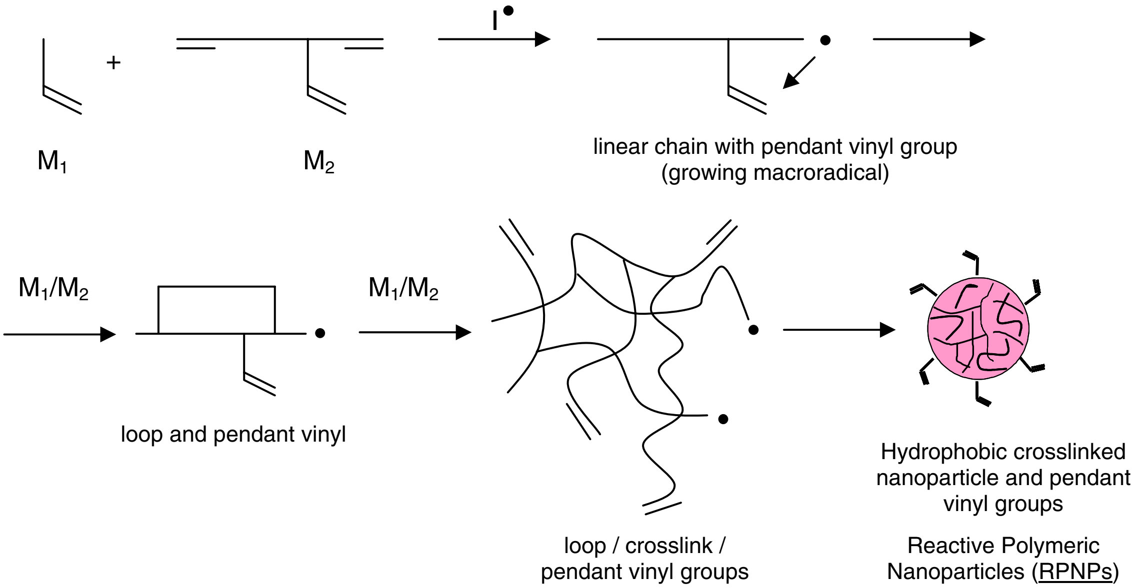


Fig. 1 Reaction scheme of the formation of reactive polymeric nanoparticles (RPNPs) by non-linear copolymerization

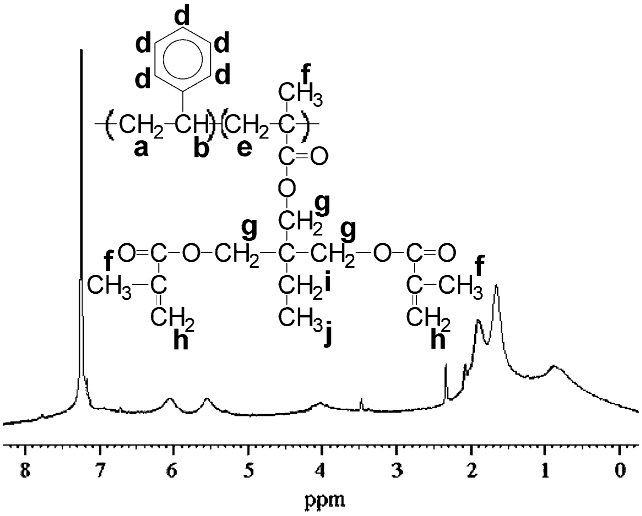


Fig. 2 ^{1}H NMR spectrum of a ST-TMPTMA copolymer sample in $CDCl_3$ (ST/TMPTMA=5/5, reaction time: 20 min) and schematic structure of a diad of the copolymer

and formation of crosslinks continue. In homogeneous solution, this process develops until the gel point when entire coherent system is obtained. However, the monomer droplet pay roles as a volumetric constrain avoiding gelation in the colloid system. Although there was a high ratio of crosslinker monomer (M_2), no gelation was observed for the studied experiments. The yield of copolymerization at 120 min reaction time was generally 85% or higher; thus, we anticipate that the composition of polymers is identical with the monomer feed. The resulting polymers were soluble or dispersible in organic solvent as toluene and chloroform.

NMR measurements

NMR spectroscopy is a powerful method to determine the structure of highly crosslinked RPNPs. Figure 2 shows the assigned ^{1}H NMR spectrum of the structure of a diad of the copolymer.

NMR chemical shift values are summarized in Table 1.

^{1}H NMR spectra of polymers taken at different reaction times and prepared with a constant M_1/M_2=5/5 monomer feed are shown in Fig. 3.

Table 1 ^{1}H NMR peak assignation of an ST-TMPTMA copolymer (ST/TMPTMA=5/5, reaction time 20 min)

Chemical shift (ppm)	Corresponding structural unit
6.7–7.8	d
5.2–6.4	h
3.5–4.5	g
1.1–2.5	a, b, e, i, j
0.1–1.1	f

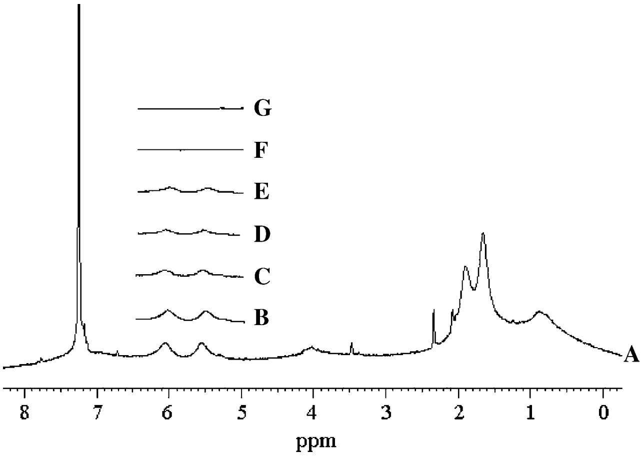


Fig. 3 ^{1}H NMR spectra of RPNP with M_1/M_2=5/5 monomer feed at extended reaction time, *A*, 20 min; *B*, 40 min; *C*, 60 min; *D*, 90 min; *E*, 120 min; *F*, 240 min, and *G* 480 min

In the early stage of polymerization process highly reactive particles were formed indicated by the intensive vinyl peaks in the range of 5.2–6.4 ppm (Fig. 3a and b). At 120 min reaction time with a yield of 80–95% reactive particles were still observed (Fig. 3e). However, at prolonged reaction times as 4 and 8 h, the vinyl signals declined to very low or near zero intensity (Fig. 3f and g).

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. (Fig. 4). At higher M_2 concentrations (M_1/

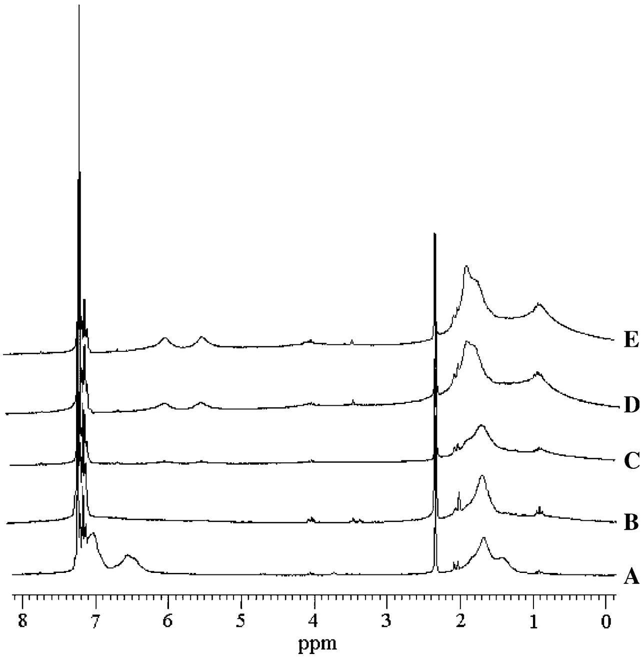


Fig. 4 ^{1}H NMR spectra of RPNPs samples. M_1/M_2 in the monomer feed: *A* 9/1; *B* 7/3; *C* 5/5; *D* 3/7 and *E* 1/9 (at 120 min reaction time). In *A* and *B* samples, the vinyl signals are very low. At higher M_2 content, an intensification of vinyl peaks was observed (*D* and *E*)

Table 2 Copolymer composition calculated by Kelen-Tudos method

Sampl.	p1	p2	Nm_1	Nm_2	F=2	brp	F=1	brp	F=0	brp
1	0.950	0.050	95	5	10	0	5	10	0	15
2	0.837	0.163	84	16	32	0	16	32	0	48
3	0.452	0.548	45	55	110	0	55	110	0	165
4	0.149	0.851	15	85	170	0	85	170	0	255
5	0.041	0.959	4	96	192	0	96	192	0	288

Number of different building blocks in a polymer chain containing 100 monomer chain length: styrene (ST), trimethylol propane trimethacrylate (TMPTMA), and theoretical values of vinyl groups and branching points at functionalities F=2, F=1 and F=0.
p1, Mole fraction of styrene (ST); *p2*, Mole fraction of trimethylol propane trimethacrylate (TMPTMA) in copolymer; Nm_1, number of ST and Nm_2, number of TMPTMA monomers in a polymer chain consisting 100 monomer units; *F*, vinyl functionality; *brp*, number of branching points

M_2=1/9 and 3/7) the pendant vinyl of RPNPs is significantly high (Fig. 4e and d). However, at lower M_1 ratios the vinyl content gradually decreases (Fig. 4a,b, and c).

Structure and composition

The copolymer composition and the number average vinyl functionality (NAVF) were determined by ^{1}H NMR spectra. The copolymer composition was calculated on the basis of the integral values of the aromatic protons (in Fig. 2 protons designated d) of styrene monomer I_{ST} and that of TMPTMA proton (I_{TMPTMA}) at 3.5 to 4.5 ppm (in Fig. 2 protons designated g). The copolymer compositions were calculated based on the integral ratio of I_{ST} and I_{TMPTMA}. On the bases of copolymer composition, the theoretical values of vinyl functionality (F) and the number of branching points (brp) were calculated. These values refer for polymer chain consisting of 100 monomer units. (Table 2).

On the basis of the monomer feed values and NMR intensities data, the Kelen-Tudos (KT) evaluation valid at higher conversion [48] has been performed. The relative reactivity ratios for styrene was r_1=1.44 and for TMPTMA monomer was r_2=1.41, respectively. The copolymerization diagram is shown in Fig. 5. The evaluation predicts a terminal model of the copolymerization.

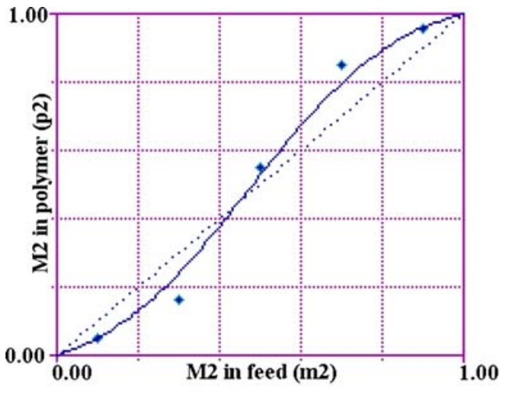


Fig. 5 Copolymer composition diagram for ST-TMPTMA copolymers

Fraction of unreacted pendant double bonds is a function of the monomer feed and the conversion as in a previous work was described [8]. In the propagation reaction of pendant double bonds both monomers take part.

The possible chemical structures of RPNPs with various number of pendant vinyl groups are shown in Fig. 6 (propagation with ST monomers is shown only).

The maximum residual functionality of vinyl groups is F=2, which means that the TMPTMA monomer incorporated into the polymer chain may hold two vinyl groups, which are subject of further reaction. Due to cyclization, propagation, crosslinking their number gradually declines to one (F=1) and finally to zero (F=0), thus unreactive nanoparticles with branching points are formed. In this case, the vinyl peaks disappear from the NMR spectrum (see Fig. 3g).

For the calculation of NAVF the NMR integral values of methyl groups I_{methyl} (in Fig. 2 protons designed f) and that of vinyl groups I_{vinyl} (protons h) of M_2 monomer were used. Data are summarized in Table 3.

Proposed structure for branching is shown in Fig. 6. At viny functionality F=2 the ratio of I_{vinyl} and I_{methyl} should be 1.33 and at functionality F=1 it has to be 0.33. Based on the experimental integral values at different mole ratio, the functionality and branching points per TMPTMA monomer units in the copolymer were calculated.

It was found that at the highest mole ratio of M_2 monomer (m2=0.9) the functionality is 0.935, and the number of branching points is 2.04 as it is shown in Fig. 6. At the lowest mole ratio of M_2 the intensity of vinyl signals declines, near zero. The experimental data show that the functionality (F) is in the range of 0.935 and 0 (estimated error±10%). It is caused by cyclization, propagation, and crosslinking, which decrease the number of pendant vinyl groups. Decreasing of mole fraction of M_2 monomer, the NAVF values decrease and the number of branching points per TMPTMA monomer increases. In other words, increasing the concentration of M_2 monomer, the reactivity of pendant vinyl groups decreases resulting highly reactive particles.

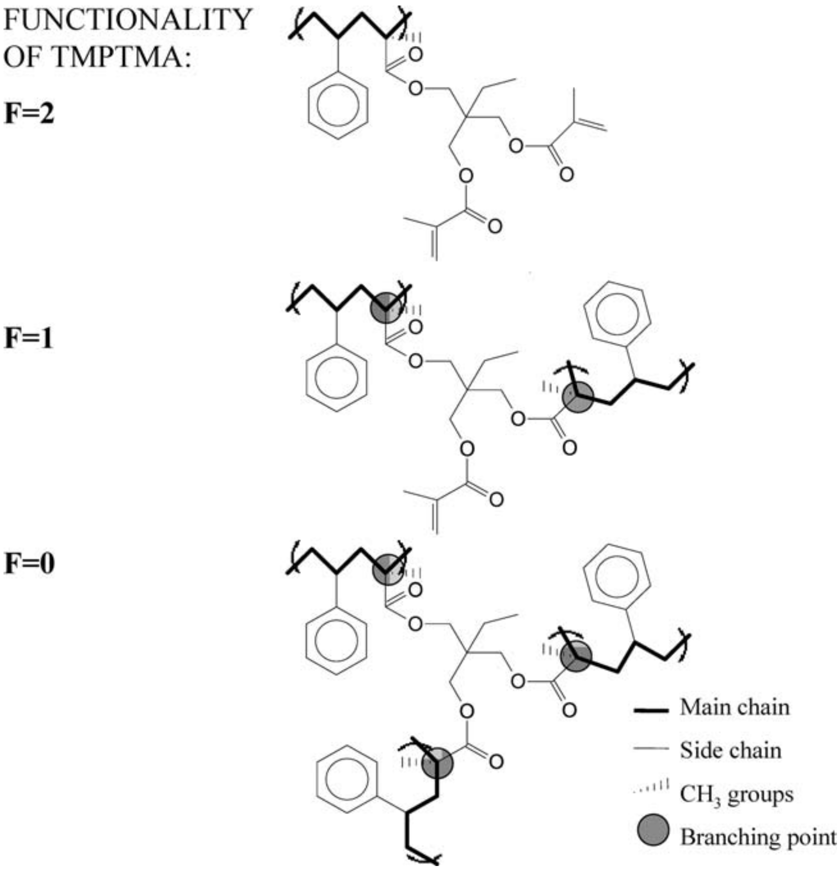


Fig. 6 Schematic structure of a diad of the copolymer showing the functionality, branching point, main and side chain. Propagation of pendant vinyl groups with styrene monomers. Branching points are formed

Determination of particle size. Latex particles

Miniemulsion mixtures of M_1 and M_2 were in 50 ml of deionized water and 0.6 g of SDS. The total weight of monomers was 2.5 g, and the monomer feed values were M_1/M_2=9/1; 7/3; 5/5; 3/7, and 1/9, respectively. As described in the literature [42], M_2 monomer has low solubility in water, and was also miscible in the organic phase. Figure 7 presents the liquid phases of monomers and water in the absence of surfactant.

In Fig. 7a, a heterogeneous mixture is shown. In samples 1 and 2, the organic layer is the upper layer, and for samples 3 and 4, the lower layer. In Fig. 7b, the organic layers (samples 2, 3, and 4) became opaque due to the miscibility with water. According to this experiment, it is anticipated that a water in oil-in-water (*w*/*o*/*w*) emulsion was formed, which influences the size of the latex particles developed during polymerization.

The size of the latex particles was examined in the aqueous continuous phase. Hydrodynamic diameter (H_D) of nanoparticles was determined by (dynamic laser light scattering) DLS measurements.

Figure 8 shows the particle size of latex using different monomer ratios obtained by oil-in-water miniemulsion copolymerization.

The latex prepared with the monomer ratio M_1/M_2=9/1 is stable at the reaction time of 20 to 120 min; the hydrodynamic

Table 3 Experimental data of pendant vinyl functionality (*F*) and the number of branching points (brp) per TMPTMA monomer units in the copolymer based on ^{1}H NMR integral values

Sample	$I\ H_{vinyl}$	$I\ H_{methyl}$	$\frac{I\ of\ H_{vinyl}}{I\ of\ H_{methyl}}$	F	brp
1	0.3	1.1	0.273	0.935	2.04
2	0.2	1.0	0.200	0.800	2.36
3	0.9	6.3	0.143	0.630	2.40
4	1.0	7.8	0.128	0.550	2.50
5	0.0	0.3	0.000	0.000	3.00

F, pendant vinyl functionality; *brp*, number of branching points

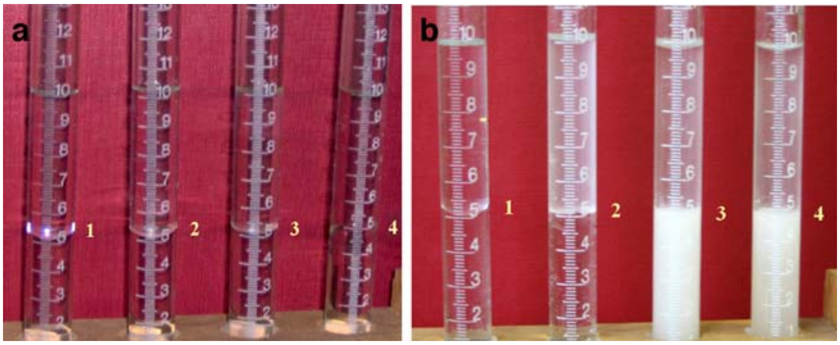


Fig. 7 Mixtures of water and monomers (**a** before sonication, **b** after sonication). Volume (ml) of components (water/M_1/M_2) *sample 1*: 5/5/0; *sample 2*: 5/4/1; *sample 3*: 5/1/4 and *sample 4*: 5/0/5. Density of components are: water 1 g/ml; M_1 0.87 g/ml and M_2 1.12 g/ml

diameter (H_D) measured by DLS was at a maximum of 25.4 nm. However, increasing the monomer ratio of M_2 in the feed resulted in larger latex particles. As it is shown in Fig. 9, the size of particles increased gradually to 497.0 nm.

This can be explained by the hydrophobic and hydrophilic nature of the monomers [46]; styrene monomer is highly hydrophobic, but the M_2 monomer, due to the ester linkage, is miscible with water. As shown in Fig. 7, the organic layer becomes opaque as the ratio of M_2 monomer increased.

We propose that a water in oil-in-water (*w*/*o*/*w*) emulsion has been formed when the ratio of M_2 monomer is increasing. In this case, during emulsion polymerization, the dispersed droplets contain the monomers and water, resulting in larger particles.

Particle size measurements of RPNPs by DLS

The latex polymer samples were precipitated and then dissolved or dispersed in toluene. The average size of particles was measured by DLS. As expected, crosslinked particles swell in suitable solvents. The swelling ratio depended on the density of crosslinking. As observed, the particle size of the unswelled latex increased steadily with increasing ratio of M_2 monomer in the feed; this was due to the reactive pendant vinyl groups. DLS measurements showed different size distribution of polymer nanoparticles (Fig. 10). However, the largest latex particles with highest crosslinking density displayed a reduced swell size. After swelling, the M_1/M_2=5/5 composed particles showed the largest particle size.

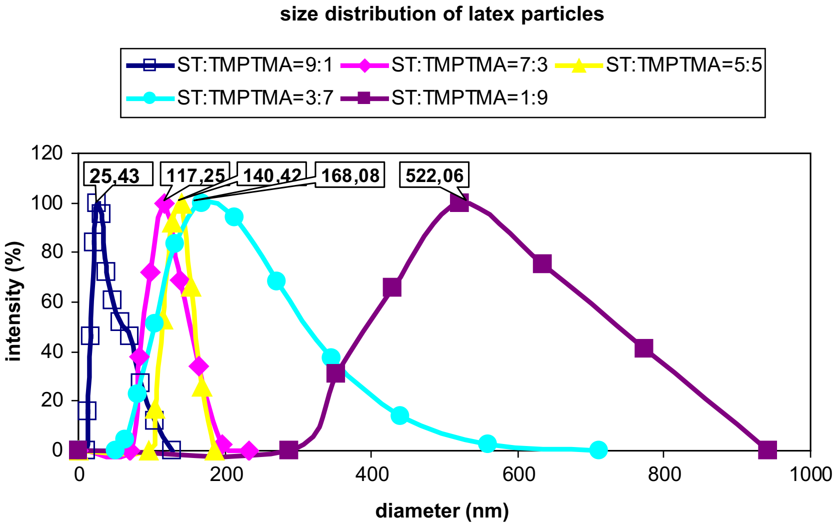


Fig. 8 Particle size of latex RPNP measured by DLS method. Samples were taken at reaction time 120 min. Ripening [40] of particle was not observed (e.g., for sample with monomer feed M_1/M_2=5/5 size of the latex particles was: at reaction time 20 min: 145.0 nm; 120 min: 144.4 nm; 240 min: 140.4 nm). When the yield of monomers exceeds 80%, these values remained constant, for as long as the maximum time it was observed (240 min)

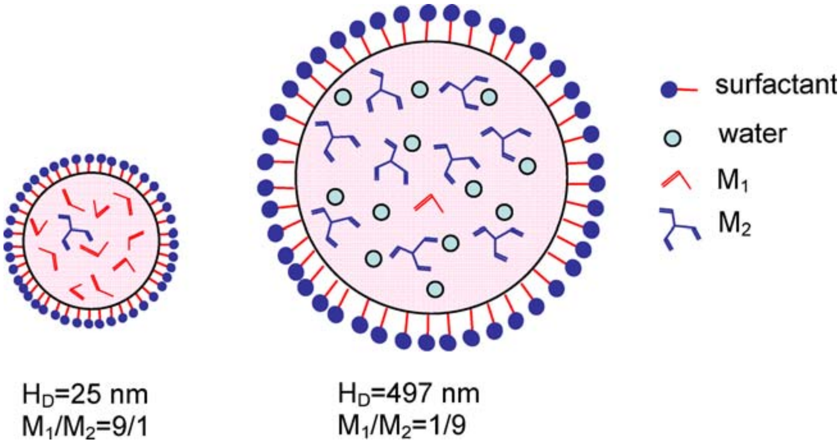


Fig. 9 Anticipated composition of nanodroplets before polymerization. After polymerization, the size of latex particles (H_D) was determined by DLS method

It was shown that the size of the particles depends on two parameters. At higher M_2 content, the size of particles increases. The higher crosslinking ratio of larger particles reduces their swelling behavior. Because of these two factors, the particles obtained with a monomer feed of $M_1/M_2=5/5$ presented the largest swelled particle size.

Transmittance studies

The isolated RPNP were dissolved or dispersed in suitable solvent. Nearly clear or opaque solutions or dispersions were obtained. Dispersion of RPNPs was prepared in toluene at a concentration of 1 mg/ml. The highest transmittance was observed for sample $M_1/M_2=9/1$ as smallest particles (H_D=66.8 nm) and for sample $M_1/M_2=1/9$ where the swelling ratio is minimal due to high crosslink density (Fig. 11).

The lowest transmittance value was observed for the sample with composition of $M_1/M_2=7/3$, which reflects their larger size and their large swelling capacity.

Particle size determination by scanning electron microscopy

Scanning electron microscopy (SEM) 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 SEM also increased. Selected SEM micrographs are shown in Fig. 12, demonstrating the individual spherical particles. 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 SEM 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.

Polydispersity of particles may be interpreted as a mixture of polymer generations. The particles born in the early stage of polymerization containing reactive vinyl groups may grow larger. Newly born particles at higher conversions

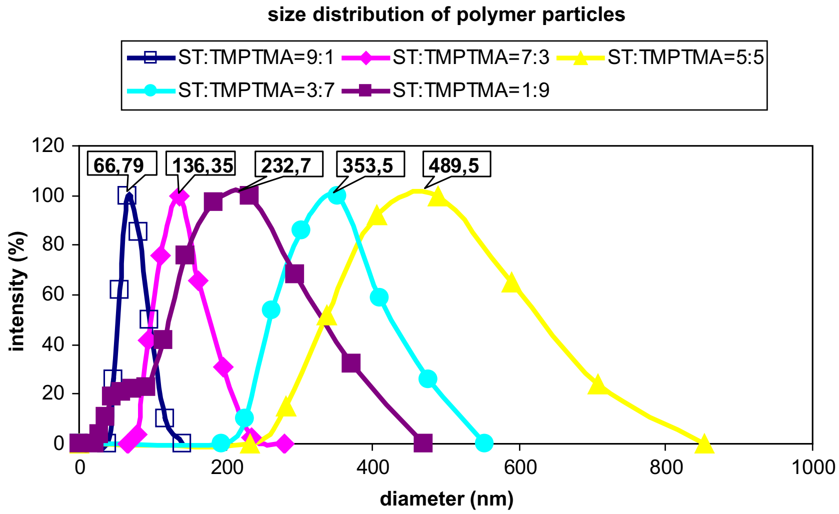


Fig. 10 Particle size of RPNP in toluene as measured by DLS method. The concentration of samples was 1 mg/ml in toluene

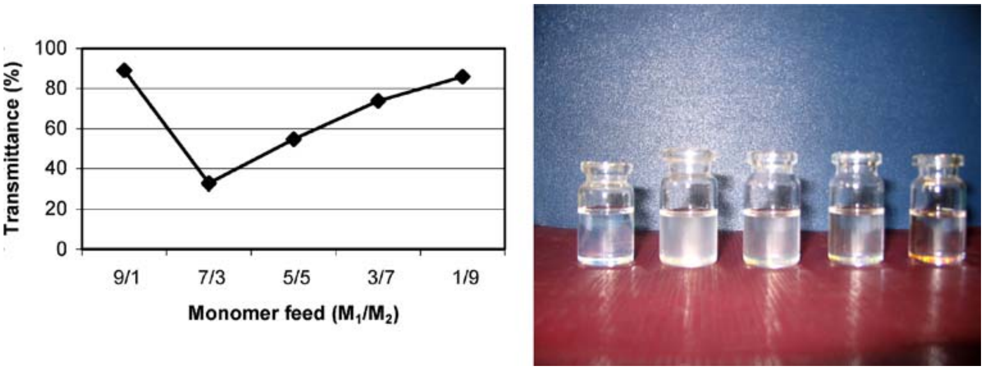


Fig. 11 Transmittance values and photograph of RPNP samples in toluene with concentration of 1 mg/ml

remain smaller. In the case of $M_1/M_2=1/9$ monomer feed, the highest particle size value was observed (300–450 nm).

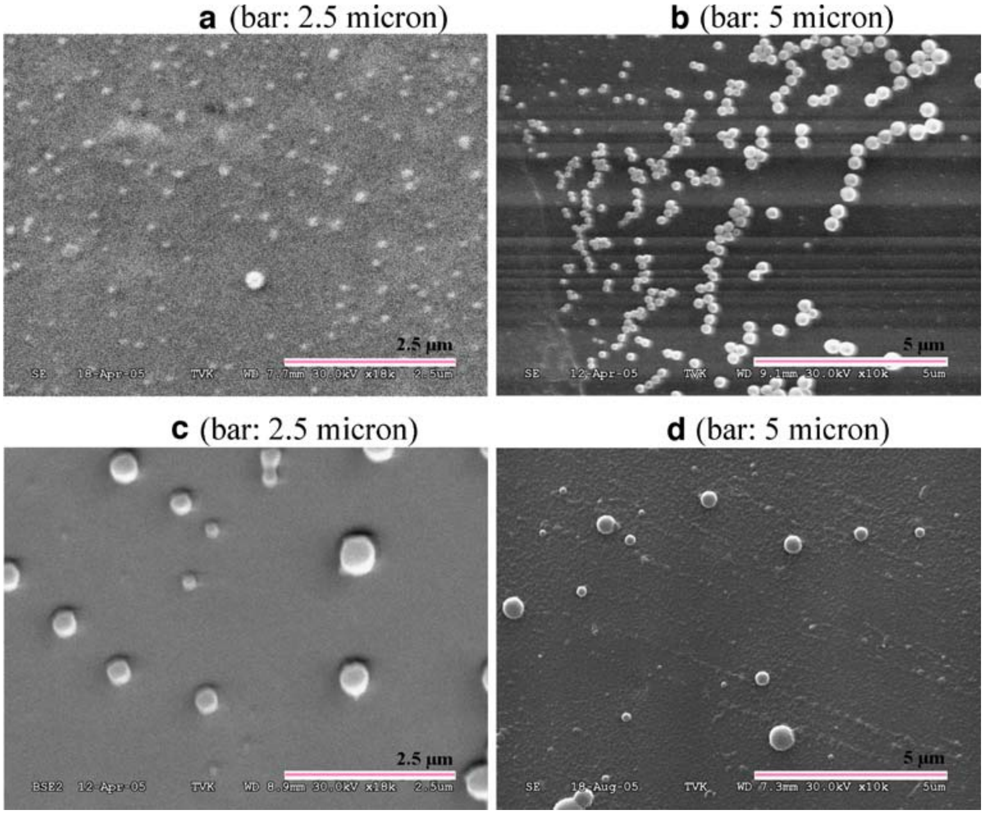
Histograms for demonstration of polydispersity were calculated on the basis of 100 objects or more for each SEM micrograph (Fig. 13).

Experimental

Materials Styrene (M_1, ST), trimethylol propane trimethacrylate (M_2, TMPTMA) monomers, and sodium dodecyl sulfate (SDS) surfactant were purchased from Sigma-Aldrich, Hungary, and were used as received without further purification.

Preparation of reactive polymeric nanoparticles Nanoparticles were prepared by miniemulsion copolymerization of styrene (M_1, ST) and trimethylol propane trimethacrylate (M_2, TMPTMA) 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, than sonicated for 10 min. The polymerization was performed

Fig. 12 SEM micrographs of RPNPs prepared with M_1/M_2 monomer feed **a** 9/1; **b** 5/5; **c** 3/7 and **d** 1/9



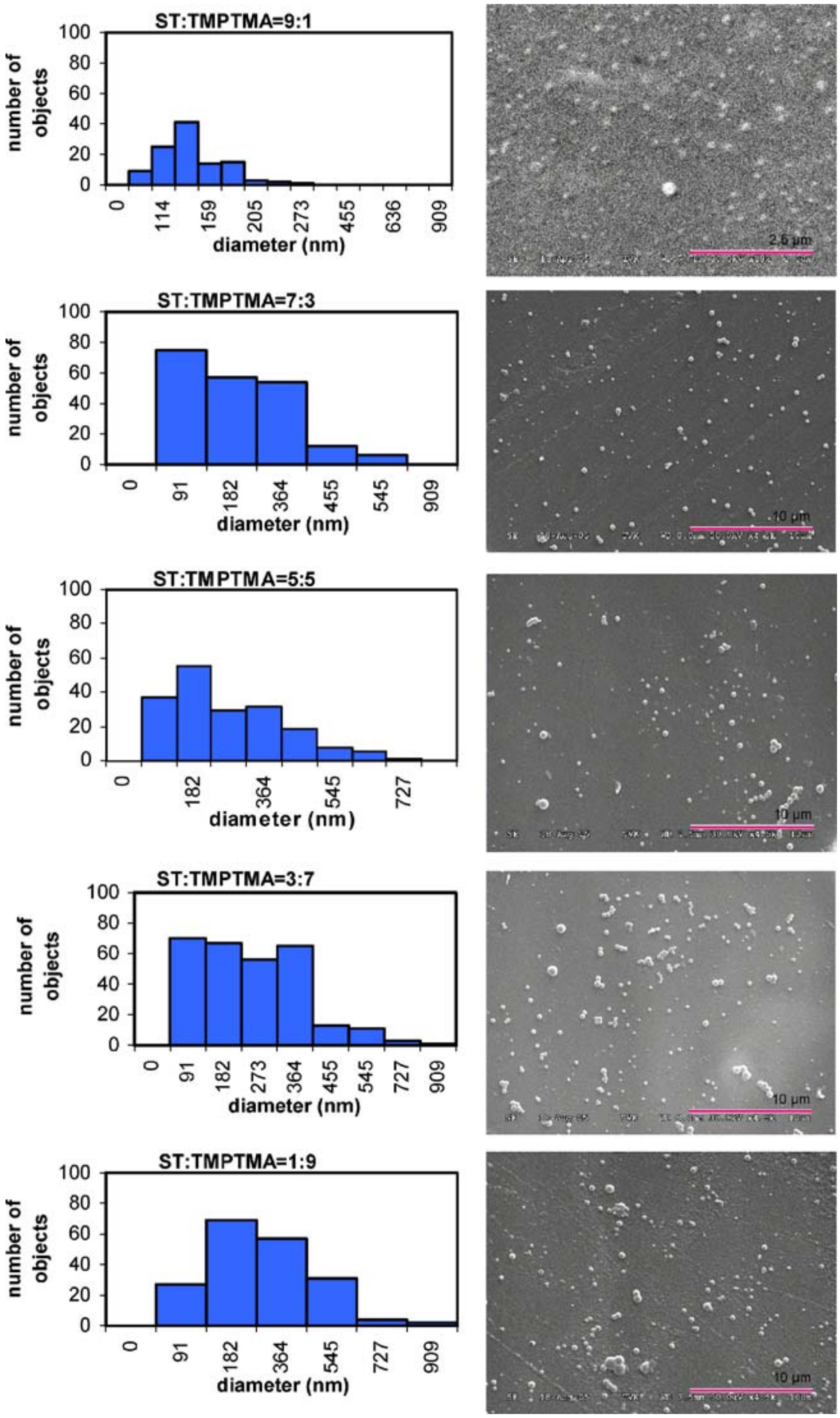


Fig. 13 SEM micrographs of RPNPs samples and histograms for size distribution (Bar: 2.5 and 10 micron)

under nitrogen atmosphere using potassium peroxide as initiator at 60°C. The RPNPs were precipitated from the aqueous latex by adding a threefold excess of methyl alcohol. The particles were purified by dissolving in toluene and precipitated three times with methyl alcohol. The yield increased gradually with the reaction time up to 120 min. The yield was in the range of 20 min (20–25%), 40 min (30–35%), 60 min (40–45%), 90 min (60–65%), 120 min (75–85%). The isolated nanoparticles were dissolved or dispersed in toluene for further experiments.

NMR measurements ^{1}H NMR experiments were performed on Bruker 200 WP instrument at 200 MHz operating frequency in $CDCl_3$ solution (at calculating of the copolymer composition 99.96 atm% $CDCl_3$ solvent was used; concentrations of RPNPs were of 18.75 mg/ml).

Dynamic laser light scattering Hydrodynamic diameter of the RPNPs nanoparticles 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 λ_o=532 nm. Measurements of the hydrodynamic diameters of RPNPs were performed at 25°C with an angle detection of 90° in optically homogeneous 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.

SEM measurements Experiments were performed on a Hitachi 3000N instrument to determine the particle size of RPNPs.

Transparency measurements were performed with a *Unicam* SP 1800 Ultraviolet Spectrophotometer at an operating wavelength λ_{max} (ε)=480 nm in optically homogeneous quartz cuvettes.

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. It was measured by NMR spectroscopy that the vinyl functionality declines as the M_2 content decreases in the monomer feed, and at the same time, the number of branching points increases. This observation quantitatively demonstrates that the reactivity of pendant vinyl groups decreases with the crosslinking density. Thus, the more dense network causes a sterical constrain, resulting reactive polymeric particles. In addition, 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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