Synthesis of Polymeric Nanoparticles by Cross-Linking Copolymerization

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ABSTRACT: Soluble cross-linked nanoparticles were prepared by free radical copolymerization of styrene (ST, M_1) and ethylene glycol dimethacrylate (EGDM, M_2) monomers in homogeneous solution. Spherical nanoparticles were obtained in the early stage of polymerization, and no gelation occurred up to 66% of yield. The isolated particles are decorated with pendant vinyl groups that are target for further polymerization. The molar feed ratio was ST/EGDM = 5/5, the monomer concentration 0.556 mol/dm^3 and the initiator concentration 5 mol %. It was found that as the conversion increased, the ratio of pendant vinyl groups reached a maximum value; however, the size of nanoparticles continued to increase with the reaction time. The molecular weight distributions were monomodal at short reaction times (30 and 60 min), however, at longer reaction times (90, 120, and 180 min) these became multimodal. This was caused by intraparticle reactions (branching and cross-linking) and possibly also by interparticle reactions (coupling). The reactive vinyl groups were detected by nuclear magnetic resonance spectroscopy (NMR). The size of nanoparticles in swollen state was determined by dynamic laser light scattering (DLS) method and in dried form by scanning electron microscopy (SEM). Molecular weight and distributions were measured by gel permeation chromatography (GPC).

Introduction

The synthesis and application of nanoparticles have attracted significant attention in recent years because of their potential use as building blocks for a variety of nanotechnology applications.[1,2] Although there is a large number of techniques available for the synthesis of nanoparticles, the preparation of more complex, structured nanoparticles is significantly more challenging (homogeneous or inhomogeneous, inorganic or organic, functionalized core−shell,[3,4] cross-linked,[5] multilayer nanoparticles,[6−8] etc.)

Cross-linked polymers formed by free radical polymerization in homogeneous solution or in emulsion medium are used in many current and emerging applications, including dental materials,[9−12] protective and decorative coatings,[13,14] contact lenses,[15] superabsorbent materials and hydrogels for biomaterials.[16,17] Soluble microgels isolated from vinyl−divinyl reacting systems and their NMR characterizations were first reported by Dusek and Spevacek.[18,19] In solution at low conversion the main process is the addition of monovinyl (M_1) and divinyl (M_2) monomers to linear radicals when the macroradicals formed contain reactive pendant double bonds (Figure 1, notice I). The pendant vinyl groups can take part in cyclization[20−22] (Figure 1, notice a), cross-linking (Figure 1, notice b), or remain unreacted pendant groups (Figure 1, notice c). Two types of cyclization are defined, primary and secondary. With primary intramolecular cyclization, the cycle is formed when the macroradical attacks the pendant vinyl groups in the same kinetic chain (Figure 1, notice II/1). During the secondary intramolecular cyclization reaction, the radical attacks double bonds pendant on a side chain already chemically connected to the same molecule (Figure 1, notice II/2). The structures formed in the intramolecular cyclization reactions are called microgels.[21,23] At higher conversion, the addition of M_1 and M_2 monomers and macroradicals to pendant double bonds may become significant as it leads to the formation of side chains (Figure 1, notice III). When the polymer concentration becomes considerably higher, cross-linking is possible. Interparticular reaction can result in macromolecules with larger size and molecular weight or an entire gel. (Figure 1, notice IV). The possible reactions are the primary and secondary cyclization, addition of M_1, M_2 monomers and macroradicals to pendant double bounds, and partly interparticular reaction that results in cross-linked nanoparticles with pendant vinyl groups (Figure 1, notice V).

When designing a cross-linked polymer for a specific application, it is important to understand the network formation and the synthesized material properties. Bowman described the mechanism of primary cyclization,[24−27] its effect on the conversion,[28] and measured the differences between divinyl and trivinyl cross-linking agents.[29] Shrinkage,[30,31] flexure,[32,33] and water sorption[34] are additional properties that depend on the ratio of cyclization and cross-linking reactions. Matsumoto described the effect of polymer chain rigidity on intramolecular cyclization and cross-linking.[35]

Sherrington et al. reported soluble branched copolymers which were synthesized by free radical copolymerization using a monovinyl and divinyl monomer, typically methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDM), and a thiol as chain transfer agent. In the presence of the chain transfer agent, the molecular weight of the primary chains is substantially reduced and gelation can be suppressed, even at high conversion.[40−42] Sato et al. have performed the polymer-

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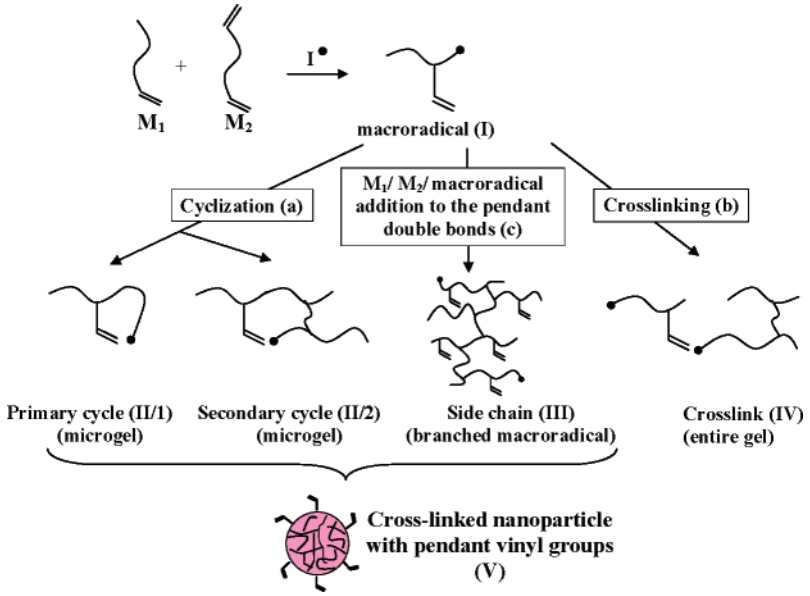

Figure 1. Reaction pathway of free radical copolymerization for formation of cross-linking nanoparticles. M_1, monovinyl monomer; M_2, divinyl monomer; and I•, initiator. Symbol —• represents local radicals, while the double bond with the vertical line represents pendant double bonds.

ization of divinyl adipate (DVA) as an effective cross-linker with azobis(isobutyrate) (MAIB) as the initiator in a homogeneous solution using a large amount of initiator as a strategy for avoiding cross-linking.[43]

The focus of this work is how to prepare reactive polymeric nanoparticles with free radical polymerization in a homogeneous solution without macrogelation. Although radical polymerization of multivinyl monomers usually proceeds with gelation to yield insoluble cross-linked polymers except when the ratio of cross-linkers and/or the length of reaction time (or to be more precise, the rate of conversion) are low,[34,35] the use of a much lower total concentration of monomers causes the resulting polymer to be soluble even if there is a much higher ratio of divinyl and the possible polymer yield is nearly 100%. The presence of a large amount of good solvent enhances the formation of soluble, partially cross-linked, nanosized polymers containing pendant vinyl groups.[23] The objective of this work is to provide a basis on how to influence the size, the size distribution and the ratio of the pendant vinyl groups of the polymer nanoparticles by the concentration of monomers and the initiator, the ratio of divinyl monomers, and the reaction time.

In this study the polymerization of the monofunctional styrene (ST) and the bifunctional ethylene glycol dimethacrylate (EGDM) in a homogeneous solution is investigated at a comonomer feed of 5/5. The reaction conditions of the preparation of soluble, reactive polymeric nanoparticles are described. The main properties were investigated as molecular weight, polydispersity, the size of particles in the dissolved state and the dried form, and pendant content of the copolymeric nanoparticles.

Materials and Methods

Materials. A series of ST/EGDM copolymers were obtained by free radical copolymerization of monomers in the presence of azoisobutyronitrile (AIBN). The stabilizers of the monomers, namely, 4-*tert*-butylcatechol for ST and hydroquinone monomethyl ether for EGDM were removed by extraction with 10% NaOH solution followed by extraction with distilled water. Then the styrene was distilled at low pressure, and ethylene glycol dimethacrylate was purified via column chromatography over Al_2O_3. AIBN obtained from Fluka was purified by recrystallization from methanol (MeOH). Solvent, toluene was used after distillation.

Preparation of ST−EGDM Copolymer. In a typical copolymerization reaction of ST, EGDM monomers, and AIBN initiator the reaction mixture was heated to 60 °C in homogeneous solutions under nitrogen. The concentration of the total amount of monomers was 0.556 mol/dm^3, and the initiator concentration was 5 mol %. A typical value of initiator concentration (mol %) would be 1%, but the polymerization process is very slow at 1 mol % initiator concentration in this system; thus, a higher initiator concentration was used (5 mol %). Samples were taken before the gelation process and then mixed with 4-fold excess of methyl alcohol, and the copolymer precipitate was removed using an ultracentrifuge. The copolymers were then purified by dissolution in toluene followed by repeated precipitation with quadruple excess of methyl alcohol and then samples were again centrifuged. This purification process was then reproduced and completed by drying at ambient temperature in vacuum.

Methods. Nuclear Magnetic Resonance Spectroscopy (NMR) ^{1}H NMR spectra were recorded on a Bruker 200 SY NMR spectrometer at 200 MHz. Deuterated chloroform ($CDCl_3$) was used as a solvent. In the case of the spectra of the samples dissolved in $CDCl_3$, the integral value of the residual $CHCl_3$ peak at 7.26 ppm had to be subtracted from that of the wide peak of the styrene unit of the copolymer.

Gel Permeation Chromatography (GPC). These analyses were carried out using a Waters chromatograph equipped at 35 °C with four gel columns (7.8 mm × 300 mm, Styragel HR3, HR4, HR5, and HR6), a Waters 600 HPLC pump, and with Waters 490E UV and Waters 410 refractive index detectors. Calibration was achieved using polystyrene standards with peak molecular weights (M_p) in the range 581−7 520 000 g/mol in solution of THF (tetrahydrofuran; $c = 0.5\%$ *m*/*m*). The determined molecular weights are not absolute values but "polystyrene equivalents". At the measuring of the average molecular weight of styrene cross-linked with ethylene glycol dimethacrylate, there is a limitation due to the branched and intramolecular cross-linked structure of the copolymer. At low molecular weight, the deviations are not significant because mainly linear polymers are formed at low conversion.

Dynamic Laser Light Scattering (DLS). Determination of size and distribution of nanoparticles was carried out by a BI-200SM Brookhaven Research laser light scattering photometer equipped with a NdyAg solid-state laser at an operating wavelength of $\lambda =$ 532 nm. In the application of DLS for particle sizing and size distribution, the autocorrelation functions were at 90° angle and at 25 °C. The macromolecular concentration in a toluene solution was 0.01−0.4 mg/cm^3.

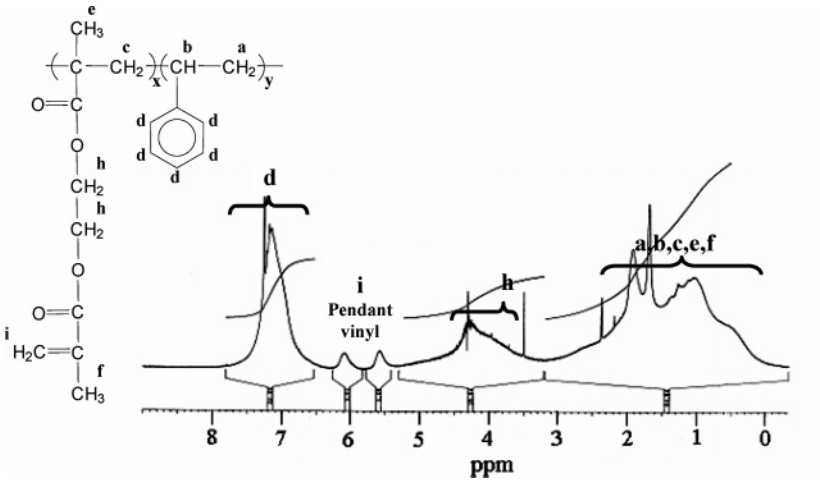

Figure 2. ^{1}H NMR spectrum together with the structural assignments of a ST/EGDM copolymer sample in $CDCl_3$ (monomer feed 5/5, [monomer] = 0.556 mol/dm^3, reaction time 120 min, [I] = 5 mol %).

Table 1. ^{1}H NMR Shift Values and Assignments

chemical shift values (ppm)	assignment
6.6−7.4	d: aromatic protons of ST monomer
5.3−5.7 and 5.8−6.2	i: magnetically nonequivalent protons of pendent vinyl groups
3.2−5.2	h: CH_2 of EGDM monomer
−0.3−3.2	a, b, c, e, and f aliphatic protons of ST and EGDM monomers

Scanning Electron Microscopy (SEM). The morphological characterization of the copolymer particles was carried out with a Hitachi 3000N scanning electron microscope. Drops of copolymer solution (10:1 mixture of chloroform and methanol) were placed on a carbon film coated on a copper grid and then were dried at room temperature. Observation was done at an accelerating voltage of 30 kV.

Results and Discussion

Copolymerization. The conversion of monomers and the formation of nanoparticles were strongly influenced by the concentration of monomers and the initiator. At higher comonomer concentration at a low conversion, the entire reaction mixture turns to gelation. It was found that the optimum monomer concentration to avoid the gelation and to get reasonable high yield was 0.556 mol/dm^3. In these experiments the yield related to different reaction times was in the range of 30 min, 10%; 60 min, 19.5%; 90 min, 27.1%; 120 min, 37%; 180 min, 56%; 240 min, 66.4% (based on the total weight of monomers) at [mon] = 0.556 mol/dm^3 and [I] = 5 mol % without gelation. The isolated nanoparticles were soluble in toluene or chloroform for further experiments.

Structure Determination by NMR Spectroscopy. The ^{1}H NMR spectrum of polymeric nanoparticles and the structural assignments are shown in Figure 2. The samples were dissolved in chloroform-*d*, and the chemical shift values and the assignment are summarized in Table 1. On the basis of the spectrum, the ratio of pendant groups was determined.

Landin and Macosco[36] attempted to measure the pendant double bonds in methyl-methacrylate/EGDM copolymers by the ^{1}H NMR technique. They obtained linear pendant conversion versus monomer conversion relations in a series of experiments with varying amounts of EGDM and monomer concentration. Later, Dotson et al.[37] reported that ^{1}H NMR measurements result in negative pendant conversion values for a number of highly branched copolymers. They explained these anomalies with the decreased mobility of protons of highly intramolecularly cross-linked structures.

The percent of pendant vinyl groups was calculated according to eq 1. The pendant ratio (P%) is the pendant content of nanoparticles related to the total vinyl content of EGDM in the feed. The ratio was calculated on the basis of NMR integral values of pendant vinyl group (2 protons) and methylene groups of EGDM side chain (4 protons). Because of the broad signals from polymers, the pendant ratio was measured and calculated on the basis of the integral values of pendant vinyl groups. With assessment of the typical error, the spectra of the copolymer were integrated three times. The typical error was within 5%. The probability of the cross-linking reactions increases with the conversion and reaction time and it is reflected into the pendant vinyl content, at 60 min (19.50% conversion), 44.4%; at 120 min (36.94% conversion), 62.2%; at 180 min (55.99% conversion), 45.0%; and at 240 min (66.35% conversion), 39.0%.

$$P\% = \frac{\dfrac{I_{CH_2=}}{2}}{\dfrac{I_{-(CH_2)_2-}}{4}} \times 100 \qquad (1)$$

The change of the pendant ratio related to conversion is shown in Figure 3. It was observed that at low conversion, the ratio of pendant vinyl groups increases and the maximum value at 37% conversion is 62%. The reason is that in the growing nanoparticles the sterical hindrance of pendants increases. However, at prolonged reaction times, further reaction occurs causing a decline of the ratio of pendant double bonds.

Determination of Particle Size. GPC and DLS Analysis. The molecular weight of copolymeric nanoparticles was determined by the GPC method using polystyrene standards. Figure 4 shows a representative set of gel-permeation chromatograms (GPC) for reaction products isolated at different reaction times up to the vicinity of the gelation point. According to GPC measurements, the molecular weight (M_w) showed an increase with reaction time. As the polymerization time for copolymerization increases, the polydispersity (PDI) ratios grow and the distribution curves change from single peaks to wider, bimodal distributions and are extended, shifted toward smaller elution time. It can be observed that M_w and PDI increase with reaction time.

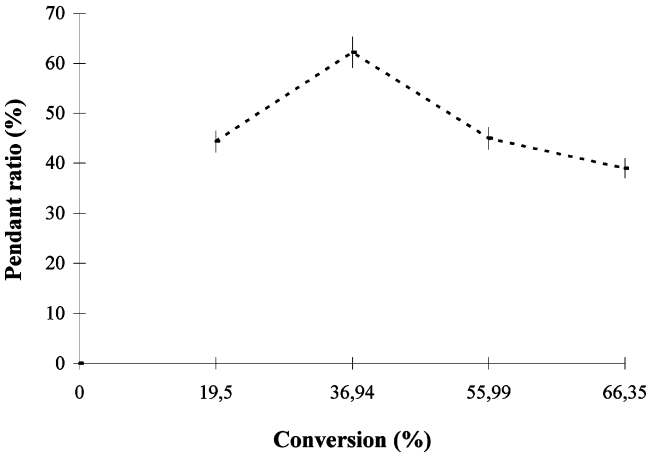

Figure 3. Relation of conversion on the relative content of pendant vinyl groups for ST/EGDM copolymers ([monomer] = 0.556 mol/dm^3, [I] = 5 mol %).

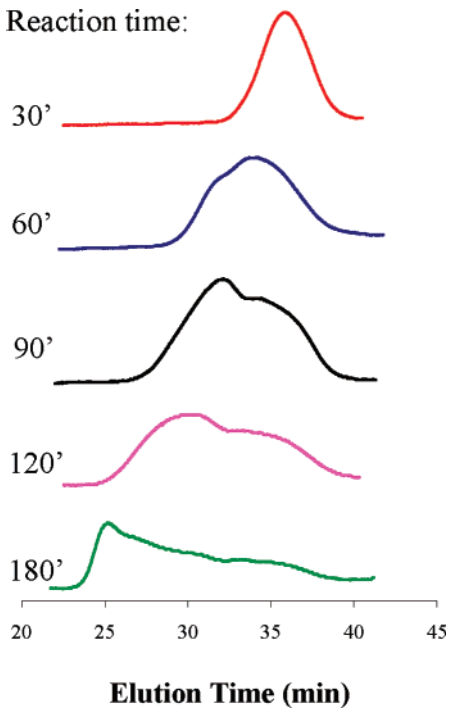

Figure 4. GPC tracess of pregel polymers isolated at different reaction times of ST/EGDM copolymerization ([monomer] = 0.556 mol/dm^3, [I] = 5 mol %).

At 30 min reaction time, the peak refers to 17 000 Da and it is a symmetrical, monomodal polymer. However, at 90 and 120 min reaction time, the GPC trace shows a bimodal form with a new maximum at 147 000 Da. It means that small particles are still present, and new larger particles are formed, respectively. At 180 min reaction time, very large polymers were detected with a peak at 3 120 000 Da molecular weight. Data are summarized in Table 2.

Hydrodynamic diameters of RPNPs isolated at 30, 60, and 120 min reaction time were measured by DLS. At 30 min reaction time, the average hydrodynamic diameter of swollen nanoparticles is in a range of 9−11 nm, at 60 min reaction time ranges from 17 to 60 nm, and at 120 min reaction time, the size of the distribution is broad (see Figure 5).

The results show that the size of nanoparticles increases and the distribution curves shift toward the large particle size region. As it is expected, the cross-linked nanoparticles swell in toluene.

Table 2. Changes of Molecular Weight and Polydispersity with Reaction Time for ST/EGDM Copolymers (ST/EGDM = 5/5, 5 mol % AIBN)

reaction time (min)	M_w by GPC[a] (Da)	$M_{w,p}$ by GPC[a] (Da)	PDI by GPC	GPC curve shape[b]
30	21 600	17 000	1.5	mo
60	74 100	61 000	1.6	as
90	134 900	94 400	2.9	sh
120	151 000	147 000	3.2	sh
180	1 243 000	3 120 000	11.0	mu

[a] $M_{w,p}$ was determined using polystyrene calibration; results are not absolute values, but "polystyrene equivalents" (p = peak). [b] Explanation: mo = monomodal, symmetric; as = monomodal, asymmetric; sh = shoulder; mu = multimodal.

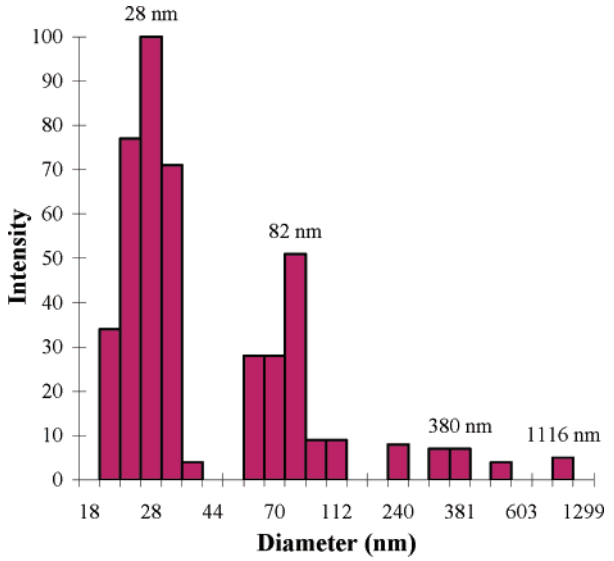

Figure 5. Intensity-size distributions obtained by DLS at $\Theta = 90°$, λ_0 = 532 nm at 25 °C, calculated by NNLS ([monomer] = 0.556 mol/dm^3, [I] = 5 mol %, reaction time = 120 min).

The swelling ratio depended on the density of cross-linking which was influenced by the reaction time at a constant monomer ratio and initiator and monomer concentrations. At longer reaction and high monomer concentration, a large number of individual macroradicals starts to grow in the solution.

SEM Micrographs. For demonstration of particle size distribution, one sample was analyzed and Figure 6 (parts A−C) represents the SEM micrographs and histograms of the ST/EGDM copolymer sample prepared at 120 min reaction time with [mon] = 0.556 mol/dm^3 and [I] = 5 mol % AIBN. In order to obtain accurate images of separated polymer particles, the sample was dissolved and diluted in chloroform then mixed with 10 v/v% amount of MeOH until the solution turned opalescent. Subsequent to this, a 0.08 mol/dm^3 SDS solution was added to the polymer solution, and after drying it was coated with a thin gold film. The images were obtained at 25 and 30 kV voltage and at different magnification factors.

In order to observe larger particles in the range of 300−1600 nm and smaller ones in the range of 36−300 nm, images were taken at different magnifications of the same sample (Figure 6A,B). It was found that a high number of small particles were aggregated in other areas of the image taken of the same sample.

Large spherical particles were disclosed, which show an individual form on the carbon layer of the copper grid (Figure 6A). Necessarily the smaller particles can also be found on the picture (not contrast points). However, size and quantity of these

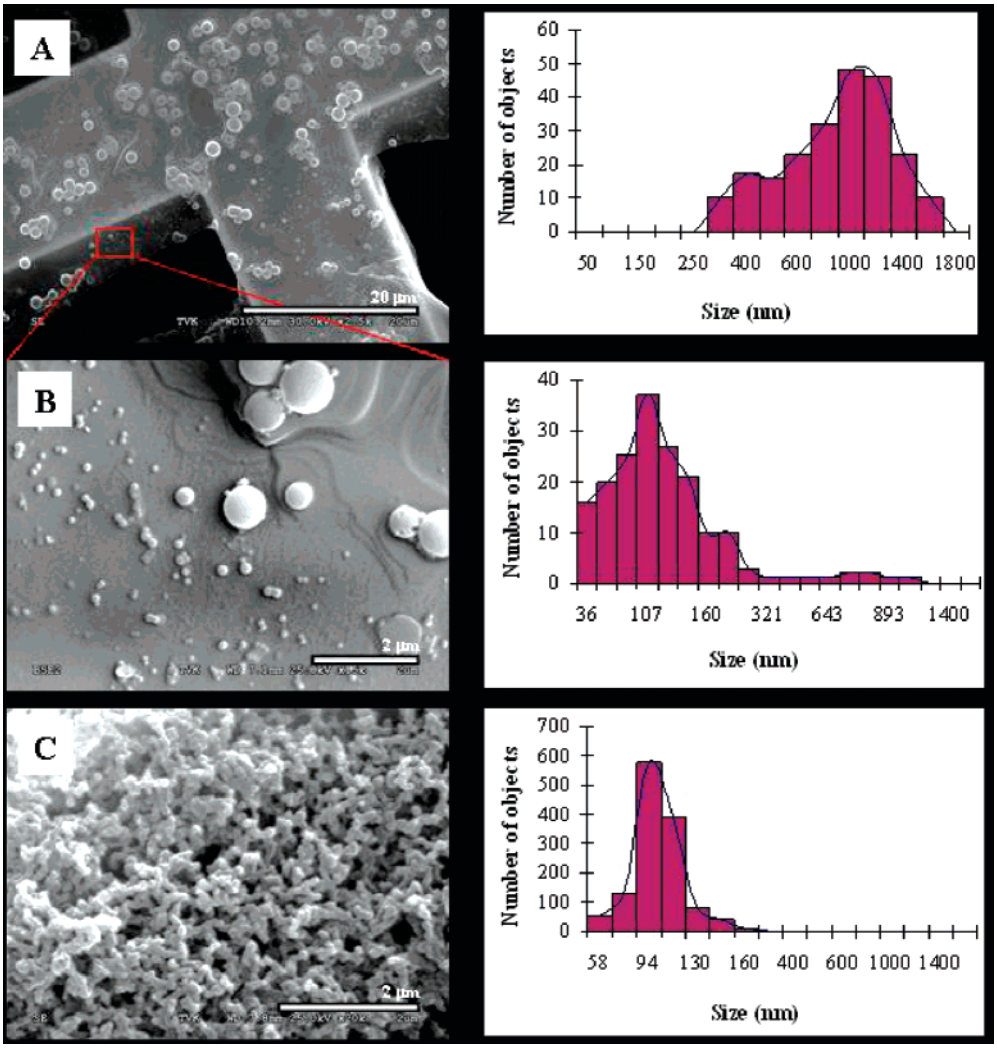

Figure 6. (A−C) SEM micrographs and size distributions of ST/EGDM copolymer ([monomer] = 0.556 mol/dm^3, [I] = 5 mol %, reaction time = 120 min).

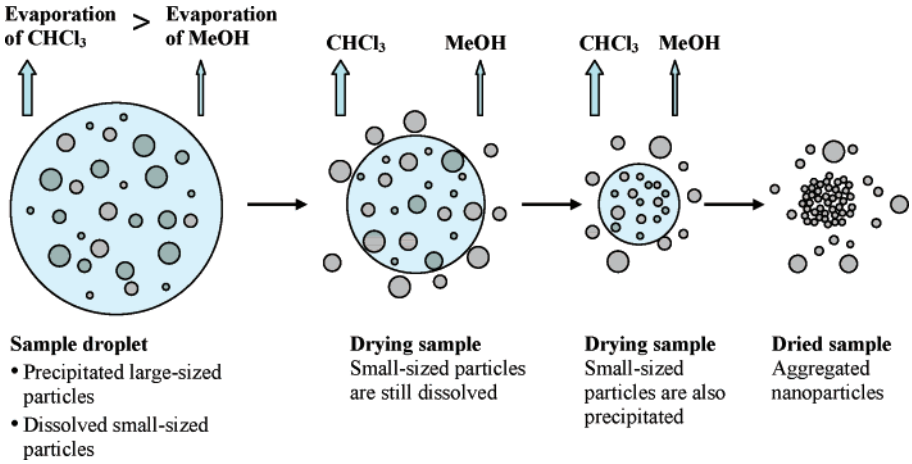

Figure 7. Schematic representation of the "fractional precipitation and aggregation" copolymer sample during preparation of the SEM sample.

particles cannot be determined at this magnification; thus, it was not presented on this histogram.

The small particles (36−300 nm) are also in individual forms on the carbon layer of the copper grid at higher magnification of Figure 6A (see Figure 6B).

However, in the same sample in the hole of the grid, the particles are stacked to the carbon layer which shows a completely different picture from that above (Figure 6C). These agglomerates are very similar in conformation and typically consist of polymer particles in the range of 50 to 150 nm. Formation of agglomerates is presented in Figure 7, which shows a fractional precipitation and it was caused by a different speed of evaporation of solvents (mixtures of chloroform and methyl alcohol).

The SEM images also support the results of GPC and DLS, according to which copolymers produced at 120 min or longer reaction times show a great extent of polydispersity.

Conclusion

Styrene was copolymerized with a large amount of ethylene glycol dimethacrylate (monomer feed: ST/EGDM = 5/5) by free radical copolymerization in homogeneous solution. The samples were analyzed with GPC, DLS, NMR, and SEM methods. Cross-linking reactions were generated up to high conversion rates, and polymerization yielded soluble nanoparticulate products. As a result of the copolymerization process, a conversion of up to 66% was obtained at 0.556 mol/dm^3 total amounts of monomers and the GPC and DLS results showed monomodal molecular weight and monomodal size distribution of polymer particles at low conversions and multimodal molecular weight distributions at higher conversions. The polydispersity of the particle size confirmed by SEM micrographs represented that individual spherical nanoparticles were formed. At a longer reaction time, the size of particles increased and submicrometer sized particles were obtained. The measurement of pendant double bonds showed an increased reactive group concentration at the start of the reaction, which then dropped with growing conversion.

We found that there are very promising methods of the application of examined reactive copolymer nanoparticles in the production of coatings or restoration materials.

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Note Added in Proof. In Figure 1, the label macroradical (I) was missing and has been added. This manuscript was published ASAP January 19, 2008; the corrected version was published ASAP January 25, 2008.

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