

Synthesis of Nanoparticles by Cross-linking Copolymerization

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ABSTRACT

Free radical cross-linking copolymerization of styrene with large amounts of ethylene glycol dimethacrylate (monomer feed: ST/EGDM = 5/5) has been investigated in toluene as a homogeneous solution. The conversion, the ratio of pendant vinyl groups and the size of the nanoparticles in the pregel state were measured at various reaction times until the onset of macrogelation.

It was found that the highest possible polymer yields were 65% at 0.556 mol/dm³ monomer concentration and nearly 100% at 0.278 mol/dm³ monomer concentration without gelation. The molecular weight distributions were monomodal at low conversions and multimodal at higher conversions. The multimodal molecular weight distributions were caused by branching reactions and cross-linking within the nanoparticles. The copolymers obtained were soluble in standard organic solvents such as toluene and chloroform. Transmission electron micrographs proved the formation of spherical particles (TEM).

Keywords: reactive polymeric nanoparticles, cross-linking polymerization

1 INTRODUCTION

Cross-linked polymers are formed by free radical polymerization in homogeneous solution or in emulsion and are used in many current and emerging applications, including dental materials [1,2], protective and decorative coatings [3], contact lenses [4], super absorbent materials and hydrogels for biomaterials [5].

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. The pendant vinyl groups can take part in cyclization [6], cross-linking or remain unreacted pendant groups. At higher conversion the addition of M_1 and M_2 to pendant double bonds may become significant, that leads to the formation of side chains. Also at higher conversion the addition of macroradicals to pendant double bonds may occur. When the polymer concentration becomes considerably higher, the formation of networks through cross-linkages is possible. It occurs in the gel state.

The focus of this work will be pointed how to be able to prepare reactive polymeric nanoparticles with free radical polymerization in homogeneous solution without macrogelation.

Although radical polymerization of multivinyl monomers usually proceeds with gelation that yields insoluble cross-linked polymers, except when the rate of cross-linker and/or reaction time (or to be more precise the conversion) was low [7,8]. Copolymerization with lower total amount of monomers results soluble polymers allowing much higher rate of divinyl monomer and the possible polymer yield is nearly 100%.

The presence of large amount of good solvent enhances the formation of soluble, partially cross-linked, nanosized polymers containing pendant vinyl groups. [9]

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

2 EXPERIMENTAL SECTION

2.1 Materials

A series of ST/EGDM copolymers were obtained by free radical copolymerization of monomers (ST and EGDM) in the presence of α,α' -Azobis(isobutyronitrile) (AIBN) as initiator. 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 Al₂O₃. AIBN obtained from Fluka was purified by recrystallization from methanol (MEOH).

2.2 Measurement

¹H NMR spectra were recorded on a Bruker 200 SY NMR spectrometer at 200 MHz. Deuterated chloroform

(CDCl₃) was used as a solvent. In the case of the spectra of the samples dissolved in CDCl₃ the integral value of the residual CHCl₃ 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) measurements were carried out using a Waters chromatograph equipped with four gel columns (7.8 mm x 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”.

Transmission Electron Microscopy (TEM). A Hitachi S-4300 transmission electron microscope was used to characterize the size and morphology of the dried ST-EGDM copolymer nanoparticles. The sample for TEM analysis was obtained by placing a drop of the colloid solution onto a carbon-coated copper grid. It was dried at room temperature and then examined by TEM without any further modification or coating. Mean diameter and the size distribution of diameters were obtained from measured particles visualized by TEM images.

2.3 Preparation of ST-EGDM copolymer

Like in a typical copolymerization reaction, ST, EGDM and AIBN were heated to 60°C in homogeneous solutions, in which the concentration of the total amount of monomers was 0.556 mol/dm³ and 0.278 mol/dm³. Samples were taken before the gelation process and then mixed with fourfold 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, then samples were again centrifuged. This purification process was then repeated twice and completed by drying at ambient temperature in vacuum.

3 RESULTS AND DISCUSSION

3.1 Conversion

Figure 1 shows the conversion values as a function of the polymerization time for all of the polymerization conditions studied (monomer ratio ST/EGDM = 5/5 in the feed, total amount of monomers 0.556 mol/dm³ and 0.278 mol/dm³, initiator concentration 5mol%, 10mol% and 20 mol%). The conversion was monitored up to the gelation point. At 0.556 mol/dm³ monomer concentration the gelation time decreased with the increasing concentration of the initiator, but no macrogelation was observed at 0.278 mol/dm³ monomer concentration. Comparison of these plots under the various reaction conditions mentioned above shows that different relative growth rates vary with the reaction environment. In all cases, the curves intersect

the y-axis at the zero conversion, which evidences that inhibition did not take place. The conversion at the lowest polymerization time increases linearly up to a critical reaction time, after which the growth rate declines and eventually cases. The results show that the system of 0.556 mol/dm³ reacts more rapidly than that of 0.278 mol/dm³. Furthermore, it was found that the more AIBN was applied, the faster the polymerization reaction was.

While the highest possible polymer yields were between 60 and 65% (based on the total weight of monomers) at 0.556 mol/dm³ monomer concentration without gelation, nearly 100% polymer yield was observed at 0.278 mol/dm³ monomer concentration at 20 mol% AIBN.

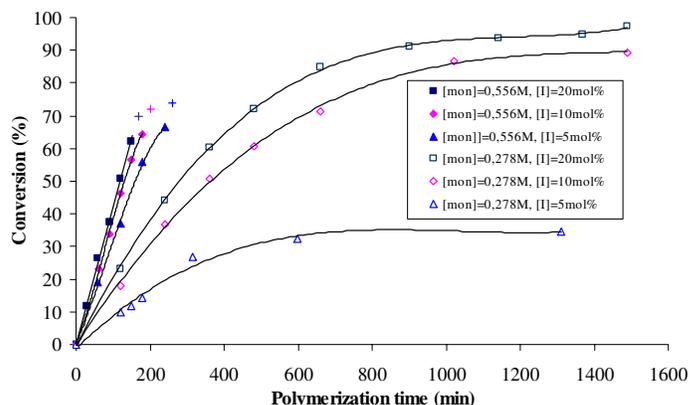


Figure 1: Conversion values of the copolymerization of styrene (ST) and ethylene glycol dimethacrylate (EGDM) using different reaction conditions (solvent: toluene; initiator (I): AIBN, concentration of the total monomers 0.278 mol/dm³ and 0.556 mol/dm³). Symbol + shows the gelation point.

3.2 Molecular weight and polydispersity

Figure 2 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. The initial total concentration of monomers was 0.556 mol/dm³ (ratio of monomers: ST/EGDM=5/5) and the amount of AIBN were 5, 10 and 20 mol% for series A, B and C, respectively. As the polymerization time for copolymerization increases, the polydispersity ratios grow and the distribution curves change from single peaks to wider, bimodal distributions. The shape of the GPC curves of the material prepared with reduced reaction time (max. 60 min) is essentially the same, irrespective of the amount of AIBN, while the GPC curves of copolymers prepared with longer reaction time are extended and shifted towards smaller elution volumes. It can be observed that the average molecular weight of copolymers synthesized with the same reaction time (120 min) increased significantly parallel to the growing amount of the initiator.

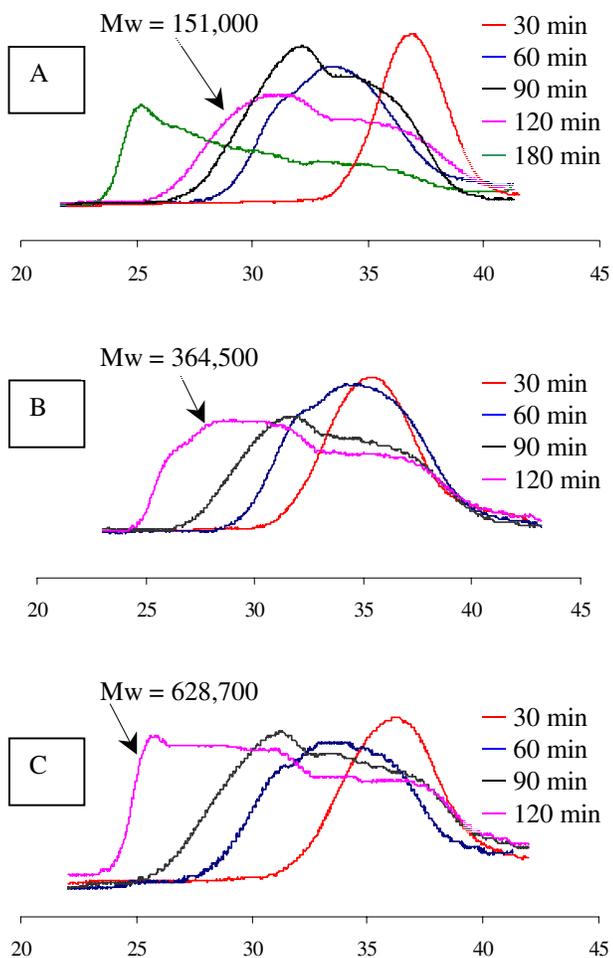


Figure 2: GPC chromatograms of pregel polymers isolated at different reaction times in ST-EGDM copolymerization. Total amount of monomers 0.556 mol/dm^3 . Initiator concentration = 5 mol% (A), 10 mol% (B) and 20 mol% (C). Numbers represent the reaction time and the average molecular weight (Mw).

Copolymerization with 0.278 mol/dm^3 monomer concentration yields nanoparticles with broader size distribution. Figure 3 shows GPC trace of polymer obtained at 22 hours reaction time and a yield 95-98%.

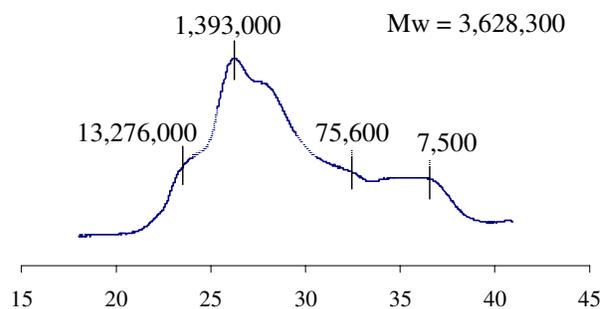


Figure 3: GPC curve for ST-EGDM copolymer (ST/EGDM = 5/5, [mon] = 0.278 M, AIBN = 20 mol%, reaction time = 22 hours).

3.3 Particle size by TEM

TEM micrographs provide visual evidence of the morphology and size as well as the size distribution of the dried copolymer nanoparticles. Figure 4 represents the TEM micrograph of ST-EGDM polymer prepared at 0.278 mol/dm^3 concentration of the total monomers with 20 mol% AIBN at 22 hours of reaction time. In order to obtain accurate images of separated polymer particles, the samples were diluted in chloroform then incorporated with a 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 was dried at room temperature. The TEM photographs of copolymer particles show that their size ranges from around 25 nm to 350 nm.

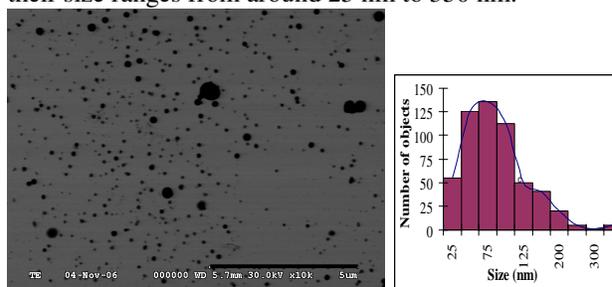


Figure 4: TEM image and size distribution of ST/EGDM copolymer nanoparticles. The bar in the Figure is $5 \mu\text{m}$. The size distribution of nanoparticles is given in the histogram to the right.

3.4 Pendant vinyl groups

In the present work, the pendant vinyl group content of ST/EGDM copolymers was measured by ^1H NMR. The integral values of the corresponding peaks in the ^1H NMR spectrum, namely that of the vinyl hydrogens between 5.4 - 5.7 ppm and 5.9 - 6.3 ppm and the $-(\text{CH}_2)_2-$ unit in EGDM between 3.6 and 4.6 ppm, were used to calculate the ratio of

the pendant. The percent of unreacted pendant vinyl group was calculated as follows:

$$P\% = \frac{I_{CH_2=}}{I_{-(CH_2)_2-}} \cdot \frac{2}{4} * 100$$

($I_{CH_2=}$) : Integral value of vinyl hydrogens

($I_{-(CH_2)_2-}$) : Integral value of methylene hydrogens of EGDM

The monomer concentrations [mon] were 0.556 mol/dm³ and 0.278 mol/dm³, and the monomer ratio in feed, n_{ST}/n_{EGDM}, was 5/5. The results are given in Figure 5.

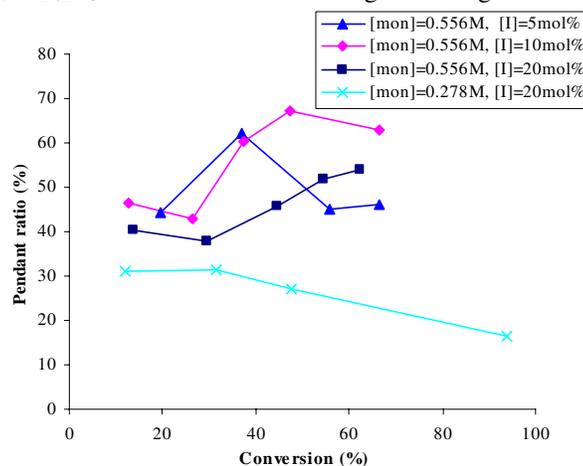


Figure 5: Dependence of the pendant vinyl ratio on the conversion.

The measurement of pendant double bonds showed an increased reactive group concentration at the start of the reaction, which then dropped with growing conversion. The decline of the content of pendant vinyl groups is due to the postpolymerization process. It is anticipated that at higher conversion the initiation of pendant double bonds results an intramolecular or intermolecular reaction of vinyl groups.

4 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, NMR and TEM instruments. Cross-linking reactions were generated up to high conversion rates and polymerization yielded soluble products. As a result of the copolymerization process, a conversion of up to 66% was obtained at 0.556 mol/dm³ total amount of monomers. The GPC results showed monomodal molecular weight distribution at low conversions and broad molecular weight distributions at higher conversions. Nearly 100% polymer yield was observed when the monomer concentration was 0.278

mol/dm³, the initiator concentration was 20 mol% and the reaction time was 22 hours. The GPC, and TEM results of prepared copolymers showed high polydispersity of molecular weight and size distribution of polymer particles. The measurement of pendant double bonds showed an increased reactive group concentration at the early stage 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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