Dispersion Polymerization of Styrene in the Presence of 2-ethyl-2-oxazoline Macromonomer

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Mechanism and kinetics of dispersion polymerization of styrene in the presence of a new macromer based on 2-ethyl-2-oxazoline have been investigated. Partial conversion-time curves have been obtained by continuous NMR measurements. Final conversion of styrene was 88% in contrast to 35% for oxazoline macromonomer. The kinetic data proved that particles become sterical stable at 15% conversion. The weight average molecular weight and polydispersity index are in the range of typical dispersion polymerization. The thermal stability and glass transition temperature are increased when a higher amount of stabilizer is used. The presence of the macromer on the surface of the final beads and the fraction of grafted stabilizer were evaluated by XPS.

Keywords: dispersion polymerization, macromonomers, 2-ethyl-2-oxazoline, X-ray photoelectron spectroscopy

Micrometer-sized monodisperse polymer particles have a variety of applications, the calibration of various measuring instruments and techniques, model systems in aerosol research, medical diagnostics tests, and model systems in colloidal studies. Generally, monodisperse polymer particles were prepared by polymerization in heterogeneous systems, which contain in addition to the monomer and initiator, water as the continuous phase (for aqueous systems) or organic solvent (ethanol) and a surfactant. The polymerization can take place in monomer droplets, in the continuous phase, or in monomer swollen polymer particles. Polymeric particles with 10 nm and greater diameters have been prepared by suspension polymerization (also referred to as pearl polymerization), seeded emulsion polymerization, dispersion polymerization, and by the swelling method [1-4a-d].

In spite of disadvantage of using hydrocarbons or alcohols instead of water as the polymerization media, dispersion polymerization has a unique merit for producing monodisperse 1–10 μm sized microspheres which had been obtained by time-consuming successive seeding method or multi-stage swelling process.

The mechanism of dispersion polymerization is complex. Dispersion polymerization processes are composed of two major stages: (a) nuclei formation and then (b) nuclei growth [5]. At the start of the process, the monomer, stabilizer (surfactant), and initiator are dissolved and form a homogeneous solution in the continuous phase. Upon polymerization, the initiator radicals react with solute monomer molecules to form oligomeric radicals which at a critical chain length precipitate as small nuclei. These nuclei may then grow to the final size by a variety of mechanisms, agglomeration of small nuclei, polymerization of monomer in the swelled nuclei, and seeded polymerization of the monomer on the nuclei surfaces. The stabilizer in the dispersion polymerization is adsorbed on the particle surfaces and thereby stabilizes the particles by a process which is only qualitatively understood. The particles stop growing when all of the monomer is consumed and/or when the stabilizer is adsorbed and forms a relatively packed coating on the particle surfaces. The stabilizer adsorption on the particle surfaces, depending on its packing, may prevent, or significantly decrease, some, or all, of the processes previously described through which the nuclei grow to their final size.

Polymeric steric stabilizers are anchored to the colloidal particle in one of two ways. They are chemically grafted directly to the surface of the particle, or are physically adsorbed to the particle surface. As adsorbed stabilizers, amphiphilic copolymers (copolymers containing both lyophilic and lyophobic groups) are most effective and are used extensively [6]. The lyophobic portions of the molecule adsorb to the particle surface, and the lyophilic portions extend into the solvent, creating a steric barrier to flocculation. Certain types of copolymers function well in this capacity, including AB block, ABA block, BAB block, and graft copolymers. Graft copolymers allow the lyophobic backbone to be strongly anchored to the particle, while each solvated side chain extends into the dispersion medium.

Chemical grafting, however, is a more effective method of stabilization than physical adsorption, due to the irreversibility of the particle/stabilizer bond and it can be realized by using macromonomers. Amphiphilic macromonomers usually consist of hydrophilic polymer chains and hydrophobic (co)polymerizable end groups as tails and heads. So far numerous macromonomers or surfmers have been reported for design of various kinds of polymer microspheres [7-8].

Because of their strong hydrophilicity, poly(oxazoline) (PEtOZO) macromonomers have been investigated for use as stabilizers in aqueous solutions [9-11]. The anchoring backbone is often either poly(methyl methacrylate) or a styrenic compound. Some of the stabilizers parameters that have been found to influence the subsequent dispersion stabilization properties are: the backbone

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molecular weight, the side chain graft density, and the side chain length.

In the current work we present the polymerization kinetic investigations of polystyrene microspheres obtained by dispersion polymerization of styrene in a mixture of ethanol and water in the presence of vinyl silane oxazoline macromonomer using ^{1}H-NMR investigation technique. Also, the influence of stabilizer concentration on the molecular weight and thermal properties of the formed polystyrene microspheres were investigated. Chemical composition of the particle surface analysis was determinated using X-ray photoelectron spectroscopy (XPS).

Experimental part

Materials

The VySiEtOZO macromonomer (M_n = 2000 Da, see its chemical structure in fig. 1), synthesis and characterization have been reported in our previous paper [10]. The macromonomer was purified according to procedure described elswere [12-13]. Styrene (St, Merck) was purified by low pressure distillation. Lauroyl peroxide (LP, Aldrich) was recrystallized from ethanol prior to use. Ethanol (EtOH, S.C. Chemical Company), deuterated water (Aldrich, 99.96%) and deuterated ethanol (Aldrich, 99.8%) were used as such. 2,3-Pyridine-dicarboxilic acid (PCA, Aldrich) was used as internal standard for ^{1}H-NMR measurements.

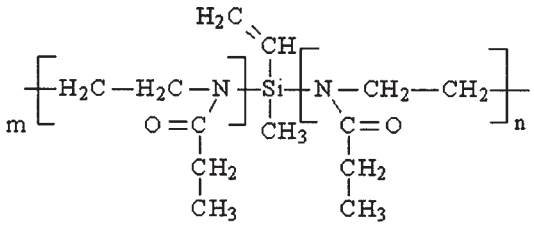

Fig. 1 Chemical structure of VySiEtOZO macromonomer

Dispersion Polymerization

In a typical run, the macromonomer and the vinyl monomer were dissolved in an ethanol/water mixture (90:10 vol). Subsequently to initiator addition, the final solution was degassed in an ultrasonic bath and sealed off under argon cushion. The polymerization was carried out at 70°C for 30h. The resulted stable dispersion was separated by centrifugation, while the particles were washed twice with distilled water. The mixtures used for dispersion polymerization are listed in table 1.

Characterization

^{1}H-NMR spectra were recorded on a Varian Unity 400 spectrometer in $CDCl_3$ and in a mixture of deuterated ethanol/deuterated water, at room temperature and also at 70°C, respectively. The thermal analysis (simultaneous TGA-DSC), MS hyphenated was performed on a NETZSCH STA 449C Jupiter /MS 403C Aeolos Mass Spectrometer, samples conditioned as previously described [14]. SEC (GPC) analyses were carried out using an Agilent 1200 Series Refractive Index Detector, (G1310A)-ISO HPLC Pump, using dimethylformamide as eluent (flow rate 1mL/min), against polystyrene standards.

XPS tests have been performed using a K-Alpha apparatus (Thermo Scientific); the monochromatic source was Al Kα (1486.6 eV). The measurements have been recorded at a residual pressure of 2 * 10^{-9} mbar and the pass energy has been 200 eV. Electrical charges have been compensated applying an Ar-ion cannon.

Results and discussion

The influence of the vinyl silane oxazoline macromonomer (VySiEtOZO) stabilizer amount on the particle diameter and uniformity was discussed in a previous paper [10], but no investigation regarding the copolymerization kinetics and the surface composition were made. In order to elucidate the polymerization mechanism we followed the reaction kinetics using the ^{1}H-NMR technique.

Nuclear magnetic resonance (NMR) spectroscopy is one of the most widely and frequently used methods for structure analysis in chemical research. NMR is also an invaluable tool for the qualitative and quantitative analyses of polymers [15], enabling description of subtle molecular details [16-17]. This method was first used to investigate the dispersion poly-merization of n-butyl methacrylate in the presence of poly-(ethylene) oxide macromonomer [18].

Kinetic investigations were carried out only for the substrate with 10 wt% macromonomer, due to the higher macromonomer to styrene ratio, so that the measurements would not be affected by integration errors. In order to determine the precise conversion the monomer must be dissolved in solution through-out the polymerization reaction time. The monomer present in the swollen particles can not be detected by ^{1}H-NMR analysis. Nevertheless, the method is sufficiently precise because the concentration of monomer in swollen particles is very low as it can be seen by the diffusive control in the stages 2 and 3 from fig. 5a).

The characteristic spectra for dispersion polymerization of styrene in the presence of poly-ethyl-oxazoline (PEtOZO) macromonomer at different reaction times are depicted in figure 2.

As previously mentioned, 2, 3 – pyridine-dicarboxilic acid was used as internal standard for ^{1}H-NMR measurements. The ratio of the peak area of PCA protons which appear at 7.5 – 9.0 ppm, to that of solvent protons (at 4.8 ppm) remains constant throughout the polymerization reaction. This pointed out that PCA was stable under the reaction conditions, being present only in the continuous phase and it was not incorporated into particles. There are two noteworthy features of the system noticed in these spectra: (1) the reaction implying the double bonds from styrene and macromonomer; (2) the disappearance of styrene NMR peaks which is related to the polymer particle formation.

It can easily be noticed that NMR peak intensities assigned to the double bonds of styrene and the macromonomer decreased with the polymerization time, as compared to the peaks of PCA standard. After 30 h of polymerization the polystyrene conversion was found to be as high as 88%.

Table 1
RECIPES FOR DISPERSION COPOLYMERIZATION

System	Styrene [g]	PEtOZO macromonomer [%wt][a)]						Water [ml]	Ethanol [ml]	LP [%wt][b)]
		M1	M2	M3	M4	M5	M10			
Experimental variations	0.906	1	2	3	4	5	10	1	9	2

[a)] %wt relatively to styrene; [b)] %wt with respect to the total amount of monomers

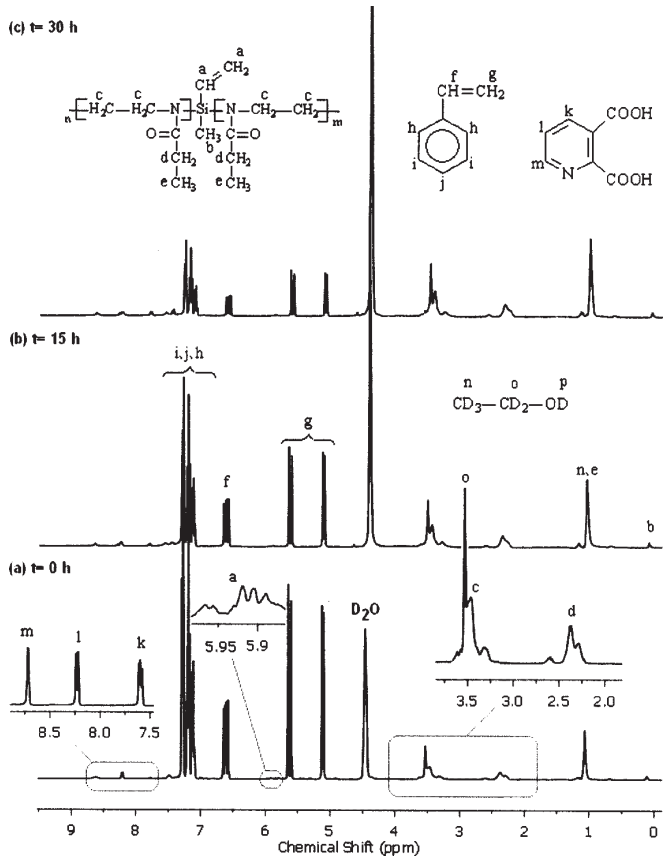

Fig. 2 ^{1}H-NMR spectra of reaction mixtures taken before (a), and also during dispersion polymerization (b), and (c)

Polystyrene precipitated from the continuous phase to form latex particles, however stabilized at their surface by oxazoline chains. After 30 h of polymerization a sample of the dispersion was centrifuged, washed twice with ethanol and dried. The ^{1}H-NMR spectrum for the polystyrene particles was taken in deuterated chloroform and illustrated in figure 3. The disappearance of double bond signals typical for macromonomer, untraceable in the baseline noise, pointed out that the macromonomer acted as a stabilizer through a radical mechanism. Therefore, the particles were chemically stabilized, not due to the macromonomer adsorption on the particles surface, but due to the radical copolymerization of the macromonomer with the main monomer (styrene). This proves that the stabilizing process occurs accordingly with the mechanism proposed for the polymerization of styrene with poly ethylene oxide macromonomers [5].

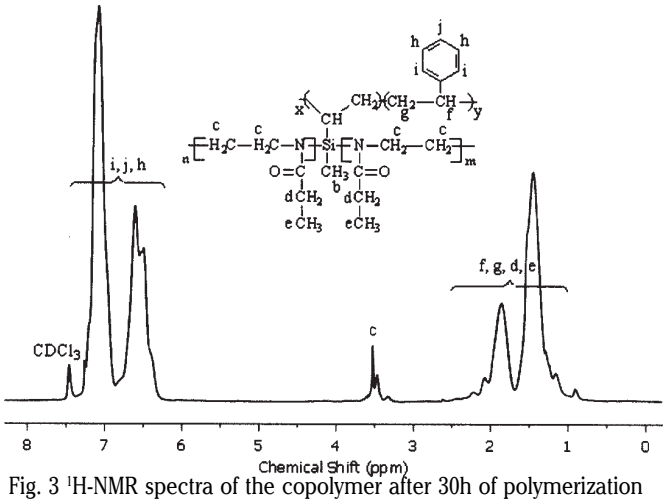

Fig. 3 ^{1}H-NMR spectra of the copolymer after 30h of polymerization

From the areas of the vinyl protons, relative to those of the PCA standard, we could determine the extent of conversion of styrene (C_S) and the macromonomer (C_M). These were calculated using the equation (1)

$$c_i(\%) = \left[1 - \frac{(a_i / f)_t}{(a_i / f)_{t=0}}\right] \cdot 100 \qquad (1)$$

where $(a_i/f)_t$ is the ratio of the peak area of the double bond protons of species *i* to that of PCA protons at a given time (t) and $(a_i/f)_{t=0}$ is the corresponding ratio at t=0. The time-conversion curves are shown in figure 4. At early times, the polymerization rate of macromonomer is close to that of pure styrene. However, above 15% styrene conversion, the polymerization occurs faster than that of the macromonomer; this may be related to the locus of the monomer polymerization in the system.

It is to be noted that the shape of styrene curve is matching that of emulsion polymerization, whereas the macromonomers conversion curves are more likely similar to the one for solution polymerization. After 30 h of polymerization, the styrene conversion was 88% in contrast to 35% for oxazoline macromonomer. This fact proved that the macromonomer did not form micellar structures, but mainly randomly copolymerized with styrene in the continuous phase.

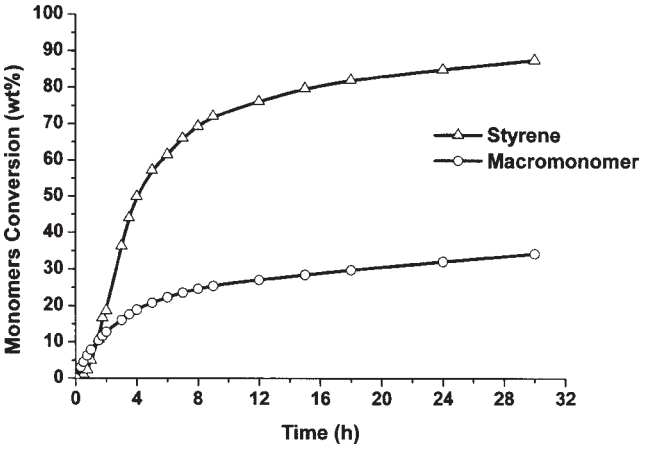

Fig. 4 Time-conversion curves (Δ) styrene; (o) VySiEtOZO

In figure 5 we have plotted the derivatives of curves presented in figure 4, the disappearance rates of styrene and macromonomer at their respective conversions.

The polymerization rate of styrene rapidly increased until 15% conversion, levelling off from 15 to 55% conversion; then decreased sharply on further increasing conversion. These three intervals presented in fig. 5 a) are very similar with those observed in a typical emulsion polymerization. As for the macromonomer's disappearance rate, it was noticed a continuously decrease with its conversion (fig. 5 b).

The kinetic data suggested that dispersion polymerization began in the homogenous solution; subsequently, the growing oligomers were formed, and at a certain chain length they precipitated from the system as they start to coagulate, due to the insufficient oxazoline group attached on their surface. The coagulation continued until "sterical"-particles were formed. For this particular system the particles became "sterical" stable at 15% conversion. This value is somehow higher than those reported in literature (5-10% conversion) [19]. This behaviour may be caused by the low molecular weight of the macromonomer (short chain) compared to poly (N-vinyl-pyrrolidone), or hydroxy propyl cellulose.

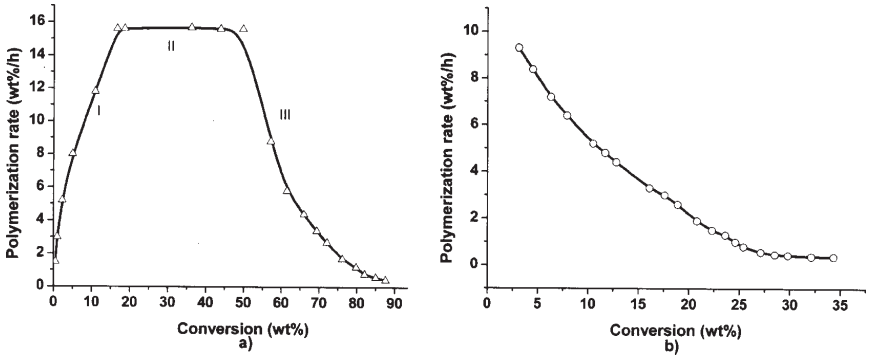

Fig. 5 a) Polymerization rate of styrene versus conversion; b) Polymerization rate of VySiEtOZO versus conversion

After this point, no other nuclei, or particles were formed. The particles might grow either by the diffusive capture of oligomers, followed by coagulation of very small unstable particles (nuclei, precursors) produced in the continuous phase, or by the polymerization of the monomer trapped within the particles until all of the monomers are consumed. The total number of such sterically-stabilized particles remained constant so that their size was dependent upon the amount of polymer produced. In the second period, the polymerization rate was determined based on the monomer concentration both in the continuous phase and in particles. During this interval, polymerization proceeded in the polymer particles as the monomer concentration in the particles was maintained at an equilibrium (saturation) level by diffusion of monomer from solution. After reaching a 50% conversion, the rate of polymerization continuously decreased due to the reduction of styrene concentration both in the particles and in the continuous phase. The particle number remained unchanged in the second and third interval.

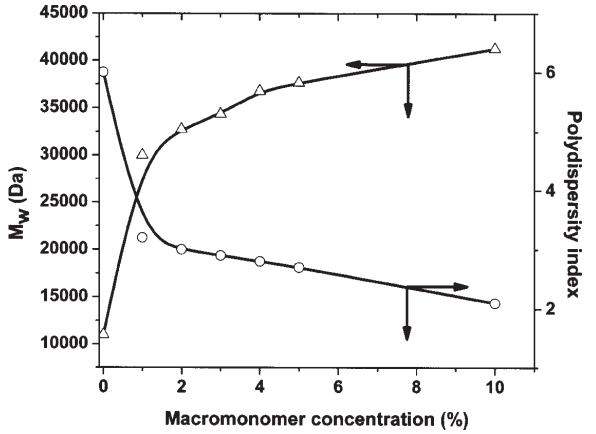

Fig. 6. Weight average molecular weight (Mw) and polydispersity index of the obtained polymer

The final physical properties (molecular weight and thermal degradation) of the particles were discussed in comparison with a sample synthesized without stabilizer in the exact same conditions.

The evolution of final weight average molecular weight and polydispersity index (PDI) of polystyrene with respect to the amount of macromonomer are represented in figure 6. The molecular weights and PDI values are in range of typical dispersion polymerization; thus, the molecular weight increases from 30.000 to 41.250 Da with the increase of the macromonomer concentration from 1 to 10 wt%. In the absence of the macromonomer, transfer reactions with the medium are favoured and led to a lower molar weight of polystyrene, namely 11.000 Da, as compared to stabilized polymer particles.

Presumably, this increased molecular weight originates from the decrease in the size of PS microspheres. This is a typical phenomenon usually noticed in the dispersion polymerization and it may be related to the suppressed termination reactions in particle phase; which are more likely to occur in the small ones, due to the higher viscosity of the monomer/polymer particle medium. Furthermore, the oligomer capture also happens in the case of small particles due to their higher speciffic area, which leads to a superior molecular weight [19].

Figure 7 shows the glass transition temperatures of the polystyrene particles prepared in the presence of different amounts of macromonomer and without it. The glass transition temperatures lies in the range 98.4–104.6°C, regardless of macromonomer concentrations. When a high amount of macromonomer content was used , the glass transition temperatures were only slightly increased; a 4°C jump of the T_g occured in the range of 2-4% macromonomer content, followed by a slow steady increase.

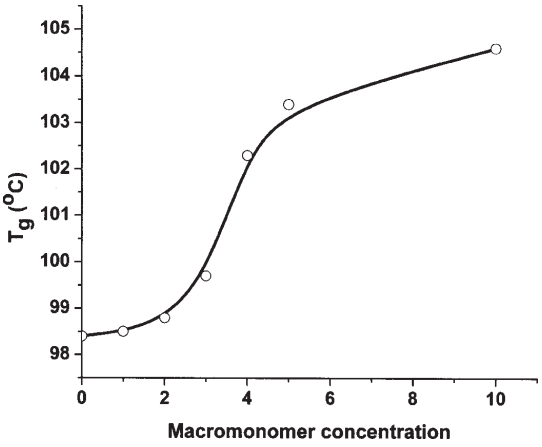

Fig. 7. Glass transition temperatures versus concentration of macromonomer

Figure 8 shows the onset temperature of the thermal degradation of the PS micro-spheres prepared with macromonomer and without it. It has been noticed that the degradation temperature for the PS polymerized in the absence of any stabilizer is 381.3°C. The degradation temperature marginally increases from 382.9 to 385.8°C with the macromonomer concentration, showing the same small irregularity in the range of 2-4% macromonomer content. This fact may be due to the polyamine chains generated from the de-acylation of oxazoline pendant units, which led to an enhanced thermal stability.

X-ray photoelectron spectroscopy is often used as a convenient method for determination of the chemical composition on particles surface. XPS measurements consist in irradiation of the investigated sample with X-rays with a known energy and subsequently measuring the kinetic energy of the primary (not scattered) electrons ejected from particular orbitals of atoms in the sample [20]. The layer from which electrons may escape not scattered is about 3-5 nm thick [20].

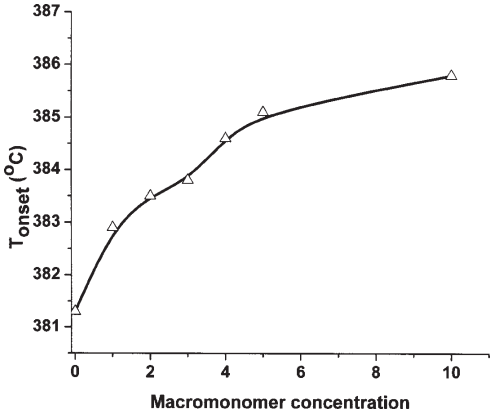

Fig. 8 Decomposition temperatures against macromonomer concentration

The XPS spectrum of PS microspheres showed an intense carbon peak (C_{1s}) at 284 eV, along with peaks corresponding to the nitrogen (N_{1s}) at 400 eV and oxygen (O_{1s}) at 531 eV. The percentage of stabilizer at surface was calculated using the nitrogen peak. The oxygen determination might be affected by errors due to the fact that we have used lauroyl peroxide as initiator.

The percentage of macromonomer at the surface was determined using Margel and Bamnolker equation (see equation 2) [21].

$$\%\,\text{Surface stabilizer fraction} = \frac{\%\,\text{Surface N}}{\%\,\text{N of the stabilizer}} \cdot 100 \quad (2)$$

The surface percentage of polystyrene was calculated by subtracting from 100% the surface percentage of stabilizer fraction. The results are listed in table 2.

Table 2
SUMMARY OF THE XPS CHARACTERIZATION DATA FOR PS MICROSPHERES

Sample	XPS weight (%)		% Surface Stabilizer	% Surface Polystyrene	Particle Diameter [μm]*
	N	C			
M1	1.48	94.48	10.46	89.54	3.7
M2	1.58	79.34	11.17	88.83	3.4
M3	2.72	91.11	19.23	80.77	3.1
M5	3.58	89.21	25.3	74.7	2.4
M10	3.81	90.00	26.9	73.1	2.1

*see reference [10]

XPS analysis testified that the graft oxazoline copolymer was present mainly at the surface and played the role of the stabilizer. Table 2 illustrates that content of oxazoline chains at surface increased with increasing the concentration in the feed.

In dispersion polymerization the particles size decreases with increasing coverage of the macromonomer on the particle size. XPS proves that when using under 5%wt macromonomer in the feed the surface covered by the stabilizer is small and this fact leads to an increased diameter of the particles. The small difference between M5 and M10 percentage surface stabilizer demonstrates that an efficient stabilization has been achieved.

Conclusions

We report a 1H-NMR study of dispersion polymerization of styrene in the presence of a vinyl silane oxazoline macromonomer in deuterated aqueous ethanol. The time-conversion of both styrene and macromonomer were put into evidence. The shape of styrene conversion curve is similar to that for emulsion polymerization, whereas the macromonomers conversion curves is similar to the one for solution polymerization.

The molecular weight of the polymeric micro-spheres has been found to be in the range of typical dispersion polymerization. Thermal degradation was enhanced when using a high amount of macromonomer due to the formation of polyamine structures. The T_g values were slightly influenced by the macromonomer feed ratio, only in the 2-5% range, recording Tg-s as high as 104.6 °C.

XPS analysis proved that the surface of the particles is enriched in oxazoline units and that chemically stabilized particles are obtained only when the macromonomer content in the feed is above 5%.wt.

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