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ORIGINAL PAPER

Synthesis of a new oxazoline macromonomer for dispersion polymerization

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Abstract We synthesized new macromonomers containing vinylsilane moiety by cationic ring-opening polymerization of 2-ethyl-2-oxazoline. Kinetic studies proved that initiation with vinylsilane derivative, bearing chloride counterion, is a fast process followed by a slow propagation and absence of termination. We used the dispersion polymerization of styrene as test for the stabilizing efficiency of the newly synthesized macromonomer. The dispersion polymerization tests allowed the investigation of the effect of the macromonomer concentration on the number average diameter of the prepared polystyrene microspheres and its polydispersity index. In addition, we compared the stabilizing efficiency of commercial poly (*N*-vinylpyrollidone) with that of our macromonomer. Copolymerization of styrene with 10 wt% oxazoline macromonomer yielded stable and monodisperse microspheres, having the number average diameter of 1.8 μm and a good size polydispersity index of 1.05.

Keywords Macromonomer · Dispersion polymerization · Oxazoline · Microspheres · Styrene

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Introduction

Micron-size monodisperse polymeric microspheres are used in a wide variety of applications, such as instrument calibration standards, column packing materials for chromatography, spacers for liquid crystal displays, or for biomedical and biochemical analyses [1–3].

Due to commercial and scientific interest in these particles, research into their design has been active for the past two decades. Micron-size monodisperse particles are usually difficult to be obtained, as the desired size is in-between the diameter range of particles produced by conventional emulsion polymerization (0.06–0.7 μm) in a batch process or suspension polymerization (50–1,000 μm). The solution consists in dispersion polymerization, a technique allowing the manufacture of such monodisperse particles. However, this type of polymerization implies the use of stabilizing agents. They promote particle nucleation (as a precursor) and subsequently, provide stability for particles formed in organic media. Literature reports the use of various stabilizing agents, such as homopolymers, copolymers, and macromonomers [4–8]. In the mid-1970s, Imperial Chemical Industries (ICI) introduced the macromolecular monomers, so-called macromonomers, as reactive stabilizers in dispersion polymerization [9]. Macromonomers are polymers or oligomers with polymerizable end groups, widely investigated for the preparation of functional polymers and/or polymer microspheres by dispersion polymerization [10–12].

For microspheres, the macromonomers should be designed so that to copolymerize with the main monomers in such a way as to produce graft chains that perform as efficient stabilizers; in other words, their main chain should be covalently bound to the particle surface and the graft chains should extend into the polymerization medium. In such polymerizations, the macromonomers possess both hydrophobic and hydrophilic parts, which can form micelles in aqueous or non-aqueous media. The hydrophobic parts of the macromonomers react with the hydrophobic monomers, while the hydrophilic macromonomer parts act as steric stabilizers against coagulation. Thus, the presence of macromonomers on the particle surface improves the stability of the polymer through sterical stabilization.

Among all classes of macromonomers, the one provided by the cyclic iminoethers is probably, the most interesting one. Their versatility is due both to their chemistry and their areas of application. They can undergo facile ring-opening polymerization with various initiators. The polymerization of 2-oxazoline exhibits a living character under appropriate reaction conditions due to the stability of onium or covalent propagating species. Based on this living character, precisely controlled polymers such as block and graft copolymers, macromonomers, and/or telechelics have been synthesized [13, 14]. Recently, we have reported a new method of synthesis of a macromonomer based on 2-ethyl-2-oxazoline with a styryl polymerizable group [15].

In this article, we present the synthesis and characterization of a novel vinyl oxazolinic macromonomer obtained by cationic ring-opening polymerization. Subsequently, we assess the stabilization properties of this macromonomer in dispersion polymerization of a hydrophobic monomer, namely, the styrene.

Experimental

Materials

2-Ethyl-2-oxazoline (EtOZO, Merck) and *o*-dichlorobenzene (DCB, Merck) have been purified by cryogenic distillation over sodium hydride then stored under argon. Styrene (St, Merck) was purified by low-pressure distillation. Azoisobutyronitrile (AIBN, Aldrich) was recrystallized from ethanol prior to use. Methylvinyldichlorosilane (MeVyDCl, Merck), diethyl ether (EtEt, Merck), ethanol (EtOH, S.C. Chemical Company), and Poly (*N*-vinyl-pyrrolidone) (PVP, $M_w = 40{,}000$, Aldrich) were used as such.

Synthesis of macromonomers

Vinyl silane oxazoline macromonomers were synthesized by initiating the cationic polymerization of 2-ethyl-2-oxazoline with methylvinyldichlorosilane (also known as the "initiator method") [16]. EtOZO was dissolved in DCB under argon cushion and cooled at −10 °C; afterward, MeVyDCl was added. The mixture was kept under vigorous stirring and allowed to react up to 90 h at 100 °C. The macromonomer was subsequently isolated by precipitation into diethyl ether and dried at 60 °C under vacuum.

Three initial compositions have been used; the molar ratios EtOZO/MeVyDCl = 15; 20 and 30 correspond to the tests M_1, M_2, and M_3. In all experiments, we have used EtOZO at a constant concentration (3 mol/L).

Dispersion polymerization

In a typical run, the macromonomer and the monomer were dissolved in an ethanol/water mixture (90:10 vol). Subsequent to initiator (AIBN) addition (1% w/w to monomers), the final solution was degassed in an ultrasonic bath and sealed under argon cushion. The polymerization was carried out at 70 °C for 24 h. The resulting stable dispersion was separated by centrifugation and the particles were washed twice with distilled water.

Characterization

FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer fitted with a Harrick MVP2 diamond ATR device. ^{1}H-NMR spectra were recorded on a Varian Unity INOVA 400 spectrometer in $CDCl_3$, at room temperature and in deuterated *o*-dichlorobenzene at 100 °C. The thermal analysis (simultaneous TGA–DSC), MS hyphenated, was performed on a NETZSCH STA 449C Jupiter/Aëolos 403C Mass Spectrometer. TGA–DSC for all the samples were typically carried out from ambient temperature up to 700 °C at a heating rate of 5 °C/min under helium gas flow. Low temperature DSC was performed on a Setaram DSC 131 instrument at a heating rate of 5 °C/min under helium gas flow. A Hitachi Scanning Electron Microscope (SEM) was used to investigate the morphologies of the synthesized PS particles. The average number diameter was obtained by counting 100 particles in SEM photographs as usual [4], using Scion Image Analyzer. Polydispersity (PDI) index of the particle size was obtained as follows:

$$D_n = \frac{\sum_{i=1}^{n} d_i}{N} \tag{1}$$

$$D_\mathrm{w} = \frac{\sum_{i=1}^{n} d_i^4}{\sum_{i=1}^{n} d_i^3} \tag{2}$$

$$\mathrm{PDI} = \frac{D_\mathrm{w}}{D_n}, \tag{3}$$

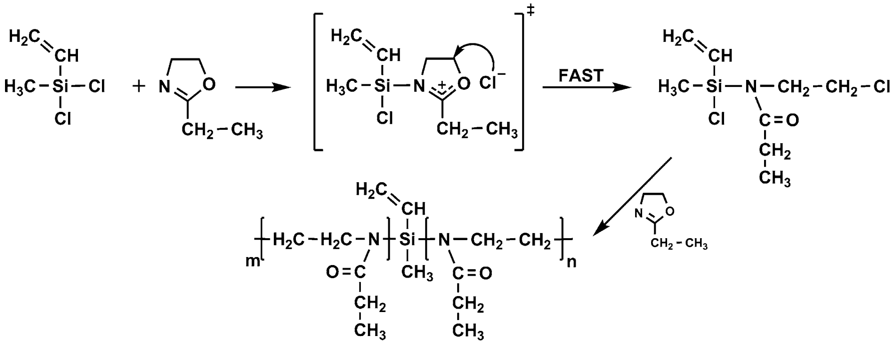
where D_n is the number average diameter, D_w is the weight average diameter, N is the total number counted, and d_i is the diameter of particle "i" [17].

The weight average molecular weights (M_w) of the macromonomers were evaluated by SEC with Agilent 1200 Series Refractive Index Detector, (G1310A)-ISO HPLC Pump, PL gel MixC 300 × 7.5 column; using dimethylformamide as eluent (flow rate 1 mL/min), at 23 °C, against polystyrene (PS) standards (six points from 10^2 to 10^6 Da). The elemental analysis was carried out on a Costech ECS 4010 CHNS analyzer.

Results and discussion

The polymerizations involve the use of an initiator which posses a vinyl bond and also a group able to initiate the cationic ring-opening polymerization of oxazoline giving rise to a poly(EtOZO) macromonomer (see Scheme 1). Chloride counter ion is known to produce the polymerization of 2-oxazoline via covalent active centers characterized by low reaction rates, therefore, in order to accelerate the polymerization rate, this reaction should take place at higher temperatures (i.e., 100 °C).

We have considered the ^{1}H-NMR spectroscopy as the most appropriate experimental method for kinetic measurements; accordingly, we polymerized 2-ethyl-2-oxazoline in NMR tubes at 100 °C, in deuterated *o*-dichlorobenzene.



Scheme 1 Polymerization mechanism of 2-ethyl-2-oxazoline initiated by MeVyDCl

MeVyDCl spectra (see Fig. 1a) showed two signals: a multiplet at 6 ppm (due to the double bond protons) and at 0.9 ppm (characteristic for methyl protons bound to the silicium atom). Upon addition of the initiator (MeVyDCl) to the oxazoline solution, instant initiation took place. The methyl protons (MeVyDCl) from 0.9 ppm shifted to 0.15 ppm (see Fig. 1c), most certainly due to the nitrogen–silicium new formed

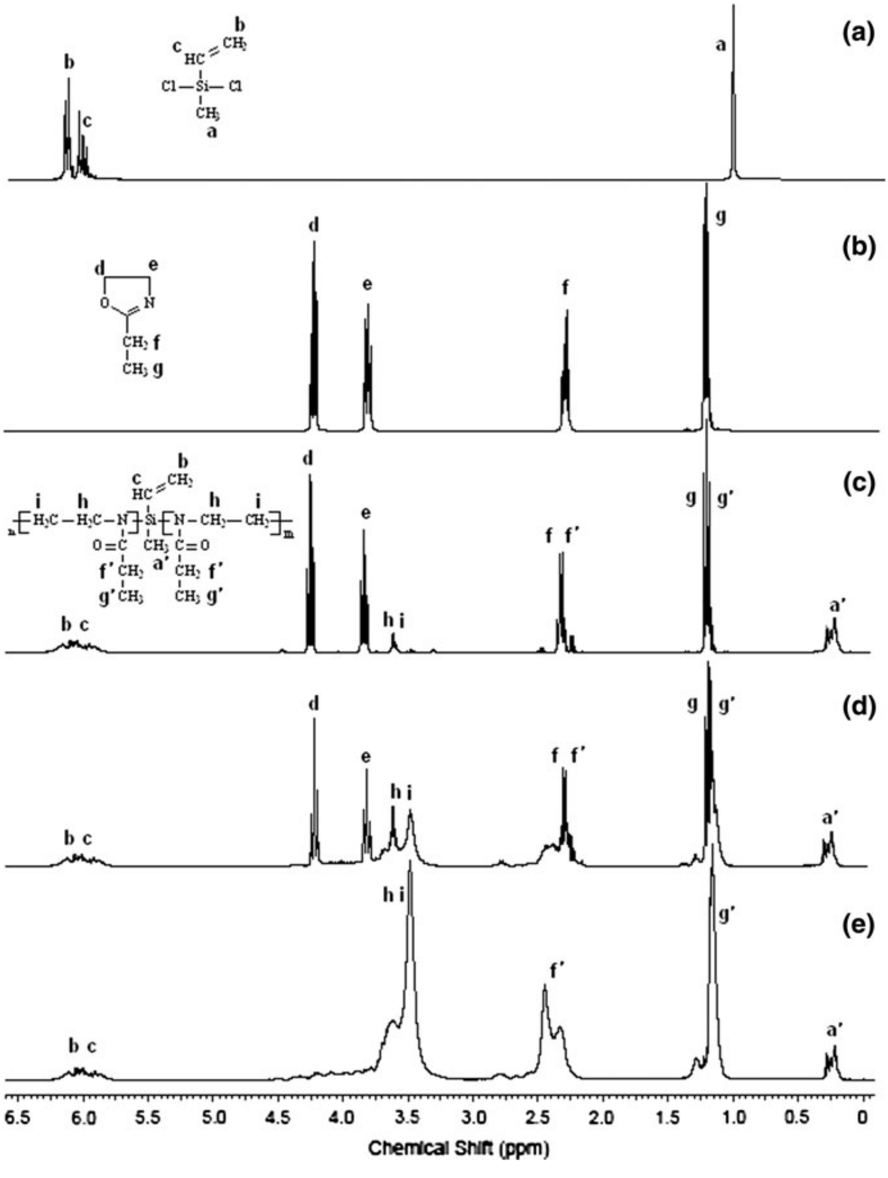


Fig. 1 ^{1}H-NMR spectra for the M_1 polymerization at different reaction times. **a** MeVyDCl spectra, **b** EtOZO spectra before adding the initiator; **c**–**e** reaction mixture spectra after adding the initiator at 0 min, 42 h and 90 h, respectively

bond. Simultaneously a novel peak appeared at 3.5 ppm, thus certifying that ring opening of 2-ethyl-2-oxazoline took place. The decrease in intensities of the characteristic peaks from the oxazolinic ring, with respect to all methyl protons peaks, afforded conversion–time plots.

The integrals of unreacted monomer signals at 4.2 ppm (2H; d peaks) and of reacted and unreacted integrals of methyl protons signals at 1.1 ppm (3H; g,g′ peaks) allowed us to make—see Eq. 4—conversion calculations.

$$c = \frac{\frac{\text{area under g,g}' \text{ peaks}}{3} - \frac{\text{area under d peaks}}{2}}{\frac{\text{area under g,g}' \text{ peaks}}{3}} \times 100 \tag{4}$$

In order to evaluate correctly the final conversion we used gravimetric measurements. At over 90% conversion, the errors of integration of the NMR signals of unreacted monomer increase.

The initial molar feed ratio between EtOZO and MeVyDCl was relatively high, allowing us to establish the macromonomer composition with accurate precision from ^{1}H-NMR based on the methyl protons bond to the silicium atom and the reacted oxazoline (see formula 5).

This fact is equivalent with measuring the number average molar weight at any time, during the reaction. We considered the kinetic investigations as reliable for the M_1 macromonomer only. The measurements on the other substrates could be affected by integration errors, due to the higher monomer-to-initiator ratio.

$$n_{\text{PEtOZO}} : n_{\text{Si}} = \left[\frac{\text{area under g, g}' \text{ peaks}}{3} - \frac{\text{area under d peaks}}{2}\right] : \frac{\text{area under a}' \text{ protons}}{3} \tag{5}$$

The time–conversion plots of the polymerization course (Fig. 2a) established that in the first reaction step an amount of the oxazoline, equimolar with the amount of added initiator was almost instantaneously consumed. Only later on, the slow

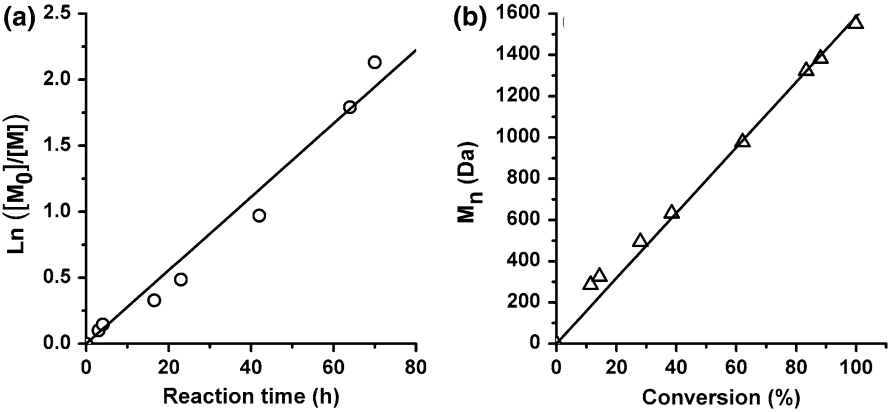


Fig. 2 **a** First order kinetic plot for the M_1 cationic ring-opening polymerization; **b** M_n plotted versus monomer conversion, for the M_1 cationic ring-opening polymerization

polymerization proceeded. This proves that the first step of the reaction consists in a fast initiation process.

The average number molecular weights, calculated from ^{1}H-NMR using formula (5), plotted against monomer conversion (see Fig. 2b) showed an increase in the M_n of the polymers with increasing conversion. The final polydispersity index, from SEC, was found to be 1.18. This fact was in good agreement with the proposed fast initiation stage, followed by a slow polymerization rate and absence of chain termination.

The final macromonomers were characterized by FT-IR spectroscopy. All three compounds exhibited the same characteristic peaks. Typical vibrations for the carbonyl amide peak were observed at 1620 cm^{-1} accounting for the cationic ring-opening polymerization of EtOZO. The silane fragment generated peaks at 1421 cm^{-1} due to the deformation vibration of CH_2 group (from the double bond), at 1010 cm^{-1}, the wagging vibration of *trans* CH and at 1240 cm^{-1}, the symmetric deformation vibration of the CH_3 group, respectively. The attempt of evaluating the ratio of acylated amine units to silane units from the IR spectra, following our previously described method [18], failed because the carbonyl amide vibration at 1620 cm^{-1} exhibited a hyperchromic effect when the molecular weight of the polyoxazoline increased.

The final molecular weights were measured using three methods ^{1}H-NMR (as previously explained), elemental analysis and SEC (see Table 1).

The obtained M_n values from ^{1}H-NMR and elemental analysis were similar to each other. The systematically lower values given by SEC analysis might be a consequence of using PS standards. The low polydispersity index (PDI) underlines once again that this process can be considered a genuine living polymerization.

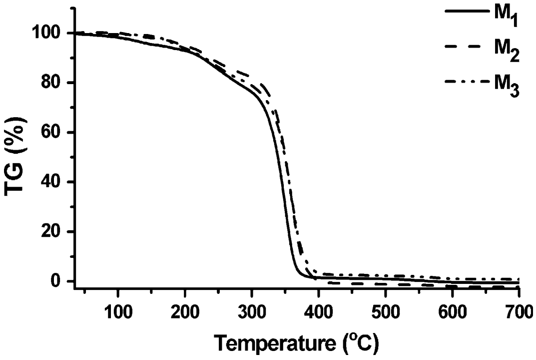
The thermal stability of the macromonomers was investigated, in order to determine their range of application using DSC–TGA–MS analysis. All three macromonomers exhibited a similar thermal behavior (see Fig. 3). TGA–DSC analysis reveals three decomposition steps and the absence of a clear-cut T_g above 40 °C. The chain length did not affect the thermal stability of the macromonomers, furthermore, the weight losses and enthalpies were found to be similar in every case. Since no major differences between the thermal behavior of macromonomers were noticed, as a typical example, the TGA–MS analysis for M_3 only is further discussed.

The mass spectrometry offers valuable information from point of view of thermal degradation mechanism. The first degradation step was related to the water loss (5.81% weight loss)—see Fig. 4. The thermal decomposition actually begun at

Table 1 Characterization of the synthesized macromonomers

Code	M_n (Da)				PDI	T_g (°C)
	Theoretical	^{1}H-NMR	Elemental analysis	SEC	SEC	DSC
M_1	1,559	1,550	1,510	1,280	1.18	9.5
M_2	2,054	2,042	2,050	1,900	1.17	15.2
M_3	3,044	3,030	3,020	2,800	1.18	32.9

Fig. 3 TGA–DSC analysis for macromonomers



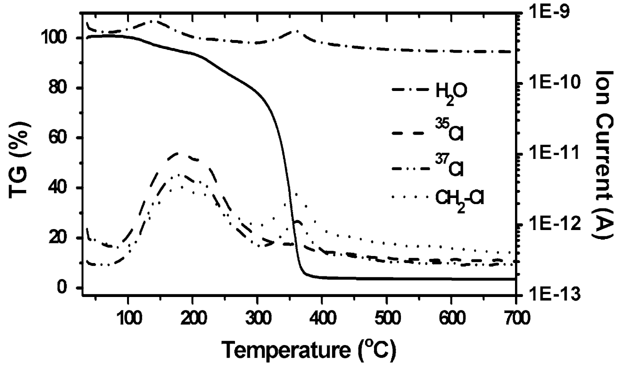


Fig. 4 TGA–MS spectra of M_3 for the first and second degradation steps

180 °C (12.7% weight loss). The mass spectra pointed out three fragments correlated with the chlorine elimination (^{35}Cl and ^{37}Cl) and with CH_2–Cl groups from the polymeric chain.

The third degradation step was a very complex one, and the weight loss was 78.24% (see Fig. 5). In this stage, deacylation of the polymeric chain accompanied by releasing of carbon monoxide took place simultaneously with breaking off the structural oxazolinic units. The presence of water at this temperature was due to elimination reactions. The TG analyses proved that the macromonomer can be safely used either as stabilizer in dispersion polymerization or as compatibilization agent in melting processes.

The absence of a glass transition in the TGA–DSC temperature range led to the idea of a DSC analysis at low temperature. The glass transition temperatures for the three macromonomers are shown in Table 1. The T_g values were strongly influenced by the molar mass. With the increase of the molecular weights, the T_g values raised.

The synthesized macromonomers were used for the preparation of micron-size PS particles with narrow size distribution. We were interested in establishing the effect of the molecular weight of macromonomers on the particle size and size distribution. Relatively monodisperse microspheres were successfully prepared by

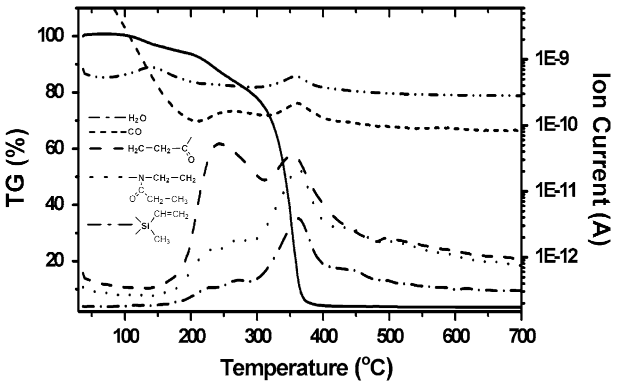


Fig. 5 TGA–MS spectrum of M_3 for the third degradation step

varying the macromonomer concentration from 1 to 10 wt% relative to styrene. SEM micrographs of the synthesized particles with M_1, M_2, and M_3 (5 wt% macromonomer content) are shown in Fig. 6. PS particles were spherical in the micron range and their surface was smooth, implying that macromonomer acted as a stabilizer. The average particle size decreased when molecular mass of the stabilizers increased.

The stabilizer concentration was a primary factor that influenced the final particle diameter and size distribution. In Fig. 7 is underlined the effect of the macromonomers concentration on the size and polydispersity index of the PS particles. Regardless of molar mass, increasing the macromonomer concentration, the particle diameter decreased. At the same concentration of macromonomers the particles diameter obtained with M_3 was smaller than that of M_2 and M_1, indicating that a higher molecular weight macromonomer stabilizes the polymer particles more efficiently. Below 10 wt% stabilizer the polydispersity indices of the particles were strongly affected no matter what type of macromonomer was used.

The relatively high amount of macromonomer needed to obtain a low diameter and monodisperse particles was due to both the low reactivity of vinyl silane double bond and the hindered access to it by the two oxazolinic arms.

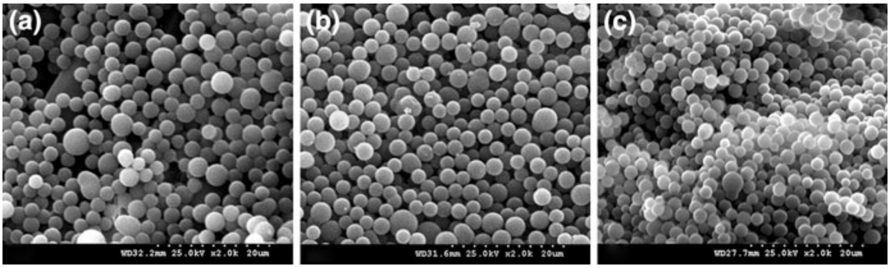


Fig. 6 SEM micrographs of polystyrene particles **a** M_1, **b** M_2, and **c** M_3; macromonomer content was 5 wt% in all runs

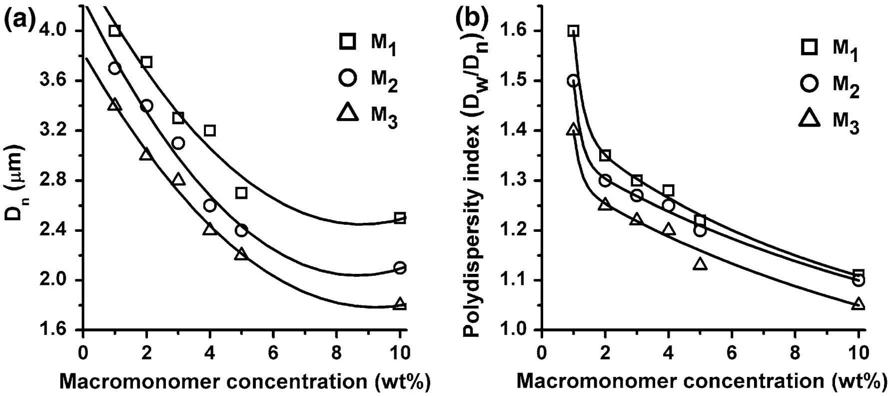


Fig. 7 **a** Relationship between the macromonomers (M_1, M_2, and M_3) concentration and the PS number average particles diameter. **b** Relationship between the macromonomers (M_1, M_2, and M_3) concentration and polydispersity index of the PS particles

Since M_3 possesses the highest stabilization ability, we found useful to compare it with a conventional dispersion polymerization stabilizer PVP (M_w = 400,000 Da), with respect to the dispersion polymerization of styrene in the aqueous/ethanol solution (Fig. 8).

As the concentration of the stabilizing agent (M_3 or PVP) increased from 1 to 10 wt%, the number average particle diameter decreased from 3.4 to 1.8 μm and from 3.7 to 2.65 μm, respectively (Fig. 8a). This phenomenon proved that the macromonomer effectively stabilizes a higher surface area of the PS particles.

Figure 8b represents the polydispersity index of the microspheres versus the concentration of M_3 and PVP. As showed in this figure, the change in the polydispersity indices of the particles synthesized with M_3 was more pronounced that in the presence of PVP and monodisperse particles were obtained at 10 wt%

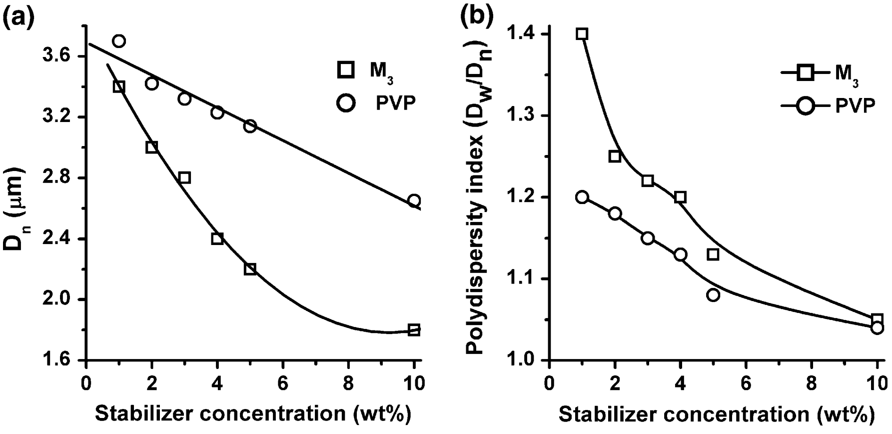


Fig. 8 **a** Relationship between stabilizer concentration and the PS number average particles diameter. **b** Relationship between stabilizer concentration and polydispersity index of the PS particles

concentration. This fact is probably due to the different number of reacting sites. For PVP, labile hydrogen atoms bearing pyrrolidone group served as the grafting sites [19]. Therefore, the number of reactive sites for PVP theoretically equals the degree of polymerization. However, the macromonomer had only one active site, which was the vinyl group and the low concentration of macromonomer was not enough to bring monodisperse particle distribution.

Conclusions

Three new oxazolinic macromonomers have been synthesized from methylvinyldichlorosilane and 2-ethyl-2-oxazoline. Using ^{1}H-NMR spectroscopy kinetic investigations were carried out. The time–conversion plots revealed that the system was characterized by fast initiation and slow propagation. Although the polymerization proceeded via covalent species, it exhibited a living character so that the molar mass of the macromonomers could be adjusted from the monomer-to-initiator feed ratio.

TGA–DSC–MS analyses proved that the chain length has no influence on the thermal stability, but the glass transition was affected. The higher the molecular weight, the superior value of T_g was registered.

The macromonomers were used to stabilize PS particles in dispersion polymerization. The ability of the macromonomer to stabilize the system proved to be dependent upon the molecular weight. The characteristic of the particles prepared using the new macromonomers were compared with those of a conventional stabilizer, namely, PVP. We synthesized monodisperse PS particles at 10 wt% of macromonomer with respect to styrene; the polydispersity index of the particles being the same as for the particles obtained with PVP at that concentration. The number average diameter of the PS particles obtained with our macromonomer was significantly lower than that obtained with PVP.

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