Synthesis and Dispersion Copolymerization of Poly(2-methyl-2-oxazoline) Macromers with Cinnamoyl End Groups

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ABSTRACT: Poly(2-methyl-2-oxazoline) (PMOZO) macromers bearing cinnamoyl functional groups were synthesized either by utilizing the end-capping method of growing PMOZO living chains with cinnamic acid or by coupling glycolic PMOZO telomers with cinnamoyl chloride. The first approach was proved to be more efficient and convenient, giving rise easier to a quantitative functionalization. Dispersion copolymerization of styrene with the resulted macromers in an ethanol–water system has been studied in order to obtain monodisperse micrometer size beads. The effect of some variables, such as macromer dimension and concentration, initiator type, alcohol/water ratio, on conversion, particle size and size distribution was investigated. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 2191–2199, 2001

Key words: poly(2-alkyl-2-oxazoline); macromonomers; amphiphilic graft copolymers; dispersion polymerization; monodisperse particles; polystyrene

INTRODUCTION

Control in polymer synthesis is a topical requirement in macromolecular chemistry. Most of the approaches developed have been based on the peculiarities of living polymerization. Block copolymerization by sequential monomer addition and end-capping of living growing chains with suitable electrophiles (in anionic polymerization) or nucleophiles (in cationic polymerization) represent two powerful tools for obtaining end-functionalized polymers with controlled architecture.

Taking advantage of the living nature of the cationic ring-opening polymerization of cyclic im-ino ethers for appropriate reaction conditions, a large number of PROZO—poly(2-alkyl-2-oxazoline)—macromers and telechelics have been synthesized in recent years.[1–3] Macromonomers containing methacrylate,[4] styryl,[5] vinylbenzyl,[6] vinyl ester,[7] or butadiene[8] end groups have been described. Some have been copolymerized with monomers of a similar reactivity (styrene, methyl methacrylate, vinyl acetate), giving rise to monodisperse small particles[9,10] or amphiphilic copolymers.[1,2]

In its essentials, obtaining monodisperse polymeric microspheres requires emulsion copolymerization or dispersion copolymerization of hydrophobic monomers with hydrophilic macromonomers in polar solvent without any emulsifier. Molecules of poly(2-alkyl-2-oxazoline) (R: methyl, ethyl), characterized by hydrophilicity, biocom-

Table I   Synthesis of PMOZO Macromers with Cinnamoyl End Groups

| Sample Code | Polymerization[a] | | | Functionalization | | | |
| | Initiator Type | [MOZO] | | Procedure | T (°C) | t (h) | Yield (%) |
		[I]	DP_{PNAI}[b]				
Cin 1	MI	8	8	AII	30	1	97
Cin 2	BB	30	31	AI	40	2	50
Cin 3	BB	15	16	AII	40	2	90
Cin 4	DBB	40	42	AII	40	2	90
Cin 5	DBB	30	31	AII	40	3	85
Cin 6	BB	40	42	AII	40	4	85
Cin 7	BB	15	16	B	0	1	70
					Tc	18	
Cin 8	DBB	15	16	B	0	1	65
					Tc	18	

[a] Polymerization conditions: [MOZO] = 3 m, 54°C, Ar, 20 h.
[b] From ^{1}H-NMR spectra.

patibility, or low toxicity and an ability to help enzyme immobilization, are between the polymeric materials recommended for its hoped-ford applications, primarily in the biomedical field.

This article reports on the preparation of poly(2-methyl-2-oxazoline) macromers bearing cinnamoyl end groups and their use in dispersion copolymerization with styrene. The cinnamoyl polymerizable group was chosen because polymeric materials based on cinnamic acid or its derivatives have already been tested as ingredients in the medical and cosmetics areas.[11] The current study compared the synthetic approaches of quenching with cinnamic acid and the coupling of hydroxyl end-capped PNAI prepolymers with cinnamoyl chloride.

EXPERIMENTAL

Materials

2-Methyl-2-oxazoline (MOZO, Aldrich Chem. Co., Milwaukee, WI) and styrene, a commercial reagent, were freshly distilled under reduced pressure. The MOZO was stored on molecular sieves, and the styrene was kept at 0°C until was used. The other reagents, such as benzyl bromide (BB, Aldrich), methyl iodide (MI, Aldrich), 1,4-dibromo-2-butene (DBB, Aldrich), cinnamic acid (CinA, Aldrich), cinnamoyl chloride (CCin, Aldrich), triethylamine (TEA,

Merck AG, Darmstadt, Germany), and the initiators—1,1′-azobisisobutyronitrile (AIBN, Merck), 4,4′-azobis-4-cianopentanoic acid (ACV, Aldrich), and benzoyl peroxide (POB, Aldrich)—were used as received. Chloroform was purified by distillation over P_2O_5. Diethyl ether was distilled over sodium wire. Absolute ethanol, a commercial reagent, was used without further purification. Deionized water was used throughout the work. As described in the literature,[12] suspension polymerization was used to obtain copolymer PyDVB beads [poly(4-vinylpyridine-co-divinylbenzene)], which have a diameter of about 4 mm. PyDVB beads have a content of 10.4% N and were used as macromolecular proton scavengers.

Synthesis of Macromonomers

Two synthetic approaches were used:

1. For the direct termination of living propagating species with cinnamic acid: The procedure for a typical run is as follows (Table I, sample Cin 2): A mixture of benzyl bromide (0.24 mL, 2 mmol) and MOZO (5 mL, 60 mmol) in chloroform (10 mL) was maintained under argon for 20 h at 54°C. The reaction was carried out in a glass sealed ampoule equipped with a magnetic stirrer and a rubber septum. After cooling to room

temperature, TEA (0.3 mL, 2.15 mmol) and CinA (0.32 g, 2.16 mmol) dissolved in chloroform (1 mL) were added with a syringe (procedure AI). The temperature was raised to 40°C for 2 h. After passing over alumina chromatographic columns to remove the bromohydrate, the mixture was poured into a large amount of dried diethyl ether, and the polymeric product was collected and dried to produce 2.7 g of polymer (yield 50%). When TEA was replaced by the macromolecular proton scavenger (Table I, samples Cin 1 and Cin 3–Cin 6—procedure AII), the reaction mixture was filtered after the end-capping, and the filtrate was poured into excess dried diethyl ether in order to obtain the precipitate. The polymeric product was then weighed and analyzed.

2. The coupling of mono- or dihydroxy-PMOZO with cinnamoyl chloride: PMOZO-bearing cinnamoyl end groups at one or both ends also was prepared by using hydroxyl end-capped prepolymers as intermediates (Table I, samples Cin 7 and Cin 8). The synthesis of mono- or α,ω-dihydroxy-PMOZO was performed by hydrolysis of the alkyl bromide end groups of PMOZO synthesized in the presence of BB or DBB, as described in the literature.[13] The coupling of the hydroxyl end-capped prepolymers with cinnamoyl chloride was carried out under an argon atmosphere in dried chloroform in a 100-mL four-necked round-bottomed flask dotted with reflux condenser and containing a $CaCl_2$ tube, a stopcock gas inlet, a dropping funnel, a thermometer, and a magnetic stirrer. The reaction mixture, consisting of the required amounts of hydroxylated prepolymer (1 g, 0.7 mmol of mono- or bifunctionalized prepolymer) and proton scavenger (0.12 mL, 0.86 mmol or 0.22 mL, 1.6 mmol TEA, respectively) and 15 mL of chloroform, was cooled to 0°C. The appropriate amounts of cinnamoyl chloride (0.14 g or 0.26 g, depending on the prepolymer functionality) dissolved in chloroform (4 mL) were added dropwise to the stirred solutions over 40 min. Then the reaction was continued at room temperature for 18 h. The purification of the resulting macromonomers from the unreacted terminating agent and sec-

ondary products was performed by passing the reaction mixture on alumina columns followed by precipitation in diethyl ether.

Dispersion Copolymerization of Styrene with PMOZO Macromonomers

Depending on the reaction conditions, the dispersion copolymerizations were carried out under inert atmosphere (argon) in (a) a 100-mL two-necked round-bottomed flask equipped with a stopcock gas inlet, immersed in a thermostated bath or in (b) a thermostated sealed quartz ampoule situated at 16 cm from a 500-W high-pressure mercury lamp. Both were equipped with a magnetic stirrer. Concentrated solutions of ACV in the chosen polar solvent mixtures and of POB in styrene were prepared. The appropriate weight of these was added to the weighted comonomers (macromers) and finally enough solvent to make a 50-mL mixture. The reaction mixtures were purged with argon for 15 min and then thermostated at the chosen temperature for 6 h. Depending on the ratio of the comonomers in the polymerization systems, the conversions (x) were determined gravimetrically by precipitating the dispersion in methanol and weighing the dried polymer or by lyophilization of the polymer particles followed by weighing.

Macromer Characterization

^{1}H-NMR spectra were registered on a Jeol-C-60HL instrument using $CDCl_3$ or DMSO-d_6 as solvents. IR (KBr pellets) spectra were obtained with the aid of a Specord M-80 spectrophotometer.
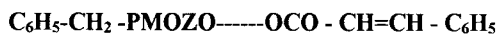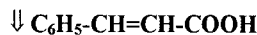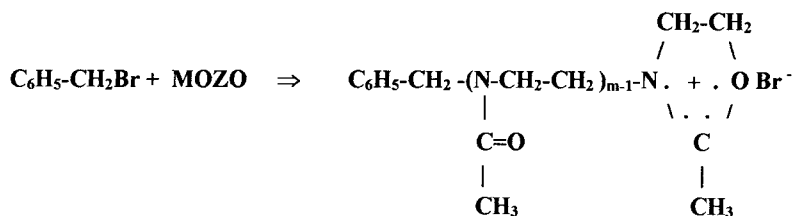
Particle-Size Analysis

Particle sizes were determined by transmission electron microscopy (TEM) with a Tesla BS 513 A apparatus. The samples were prepared by spraying diluted dispersions containing approximately 0.01 wt % solids onto carbon-coated copper grids. Image processing gave the number average ($\bar{D}_n$) and weight average ($\bar{D}_w$) of the particle diameters, calculated as follows:

$$\bar{D}_n = \sum N_i D_i / \sum N_i \qquad (1)$$

$$\bar{D}_w = \sum N_i D_i^4 / \sum N_i D_i^3 \qquad (2)$$

where N_i is the number of the counted particles that have the diameter D_i. The polydispersity index (PI) is defined as:

$$C_6H_5\text{-}CH_2Br + MOZO \quad \Rightarrow \quad C_6H_5\text{-}CH_2\text{-}(N\text{-}CH_2\text{-}CH_2)_{m\text{-}1}\text{-}N \cdot \quad + \cdot \, O\,Br^-$$

(with the cyclic structure):

```
                                         CH₂-CH₂
                                         /      \
C₆H₅-CH₂ -(N-CH₂-CH₂ )ₘ₋₁-N .   + . O Br⁻
          |                      \ . . /
         C=O                        C
          |                         |
         CH₃                       CH₃
```

⇓ **C₆H₅-CH=CH-COOH**

C₆H₅-CH₂ -PMOZO------OCO - CH=CH - C₆H₅

Scheme 1

$$PI = \bar{D}_w/\bar{D}_n. \tag{3}$$

RESULTS AND DISCUSSION

Macromonomer Synthesis

A series of PMOZO macromonomers bearing one or two cinnamoyl end groups with various degrees of polymerization were prepared by termination with cinnamic acid of the living oxazolinium-propagating species, according to the reaction in Scheme 1.

Three halogenated initiating systems—methyl iodide, benzyl bromide and 1,4-dibromo-2-butene—were used to verify the effect of its counterion nature and growing chain functionality on functionalization efficiency. As in the literature, the degree of polymerization values for the products, presented in Table I, were in good agreement with the feed ratios of monomer to initiator (fast initiation, slow propagation).[14] The end-capping reaction was carried out in the presence of two different proton scavengers, TEA and a copolymer of vinylpyridine with divinylbenzene (Py-DVB beads). For comparison, a second approach—synthesis of α,ω-dihydroxy-PMOZO followed by its coupling with cinnamoyl chloride—was also developed.

The coupling products were characterized by spectral techniques. In the IR spectra, in addition to the signals characteristic of PMOZO, at 1650 cm^{-1} (ν —CO—N—) and 2950 cm^{-1} (ν —CH$_3$, —CH$_2$—), another one, attributed to the newly formed ester groups, appeared at 1730 cm^{-1} (ν —CO—O—).

The ^{1}H-NMR spectra also presented new signals, ascribed to the inclusion in the macromer structure of unsaturated groups from the cinnamic acid moieties. They are at δ = 6.2–6.4 ppm (d, —CH=CH—CO—) and 7–7.7 ppm (m, —C$_6$H$_5$), as can be seen in Figure 1.

End-group functionalities (F), expressed as the number of cinnamoyl groups per molecule, were determined from ^{1}H-NMR spectra, from the integral ratio of the peaks of the methine protons of the cinnamoyl end-groups ($\delta_{—CH=CH—CO—}$ = 6.2-6.4 ppm), and from those corresponding to the initiator fragment (at $\delta_{CH3—N—}$ = 3 ppm for MI, at δ_{C6H5} = 7.3 ppm for BB, and at $\delta_{CH=CH}$ = 5.5 ppm for DBB). The functionalization efficiency ($f\%$) could be calculated as a ratio of this value and the theoretical end-group functionalities according eq. (4).

$$f(\%) = F/F_t \cdot 100 \tag{4}$$

As shown in Table II, functionalization generally proceeded quantitatively and was easier for the sample obtained with alkyl iodide (sample Cin 1).
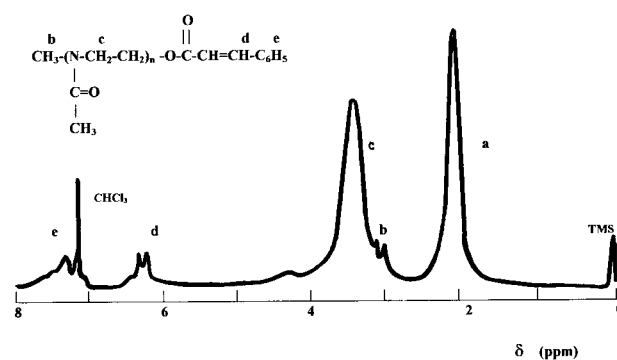
Figure 1 Typical ^{1}H-NMR spectrum of the macromer (sample Cin 1).

Table II   Functionalization Data

Sample Code	Functionalization f^a (%)
Cin 1	95
Cin 2	98
Cin 3	91
Cin 4	88
Cin 5	95
Cin 6	~ 100
Cin 7	98
Cin 8	~ 100

[a] From ^{1}H-NMR spectra.

This is normal if taken into account is the known dependence of the equilibrium between the ionic and covalent propagating species in the polymerization of oxazoline on the nature of the initiating system. The coexistence of ionic and covalent active centers in the polymerization of oxazoline was well documented by Saegusa et al.[1,2] Data in the literature provides evidence of the increased contribution of ionic species to chain growth in the presence of an iodine counteranion (almost exclusively ionized centers) as compared to the presence of a bromine counteranion. Thus, better results are expected in the first case, of an end-capping reaction with appropriate nucleophilic compounds. The experimental data included in Table II sustain this assumption. There are not observable differences for the bifunctional growing chains between the two active centers in the coupling reaction (Table I, samples Cin 4 and Cin 5].

In conclusion the use of the macromolecular scavenger and the end-capping method are in that order the most convenient alternatives because the yield is greater and fewer preparation steps are involved (Table I, samples Cin 3–Cin 6 as compared to samples Cin 2, Cin 7, and Cin 8).

Dispersion Copolymerization

Polymeric particles of controlled size and surface properties have received much attention in recent years because they have a large number of commercial applications in the biomedical, information, and microelectronics fields. Among the methods for their preparation, one-step dispersion polymerization in polar media is a more attractive, convenient alternative to large-scale preparation, as compared with the other multistage procedures (successive seeded polymerization and swollen emulsion polymerization), which are often tedious and difficult to carry out. In dispersion polymerization the colloidal stability of the growing particles is maintained by a steric stabilizer, which can be structurally classified in homopolymers and random copolymers, macromonomers, amphiphilic block and graft copolymers, and unsaturated polymers. Recently, hydrophilic poly(2-oxazoline) macromers have been reported to be very effective as a stabilizer for the preparation of monodisperse poly(methyl methacrylate)[10] or polystyrene particles.[1,15] Therefore, we used hydrophilic PMOZO-synthesized macromers as a macromonomer-type stabilizer. Dispersion polymerization is very sensitive to many variables, such as solvency of the polymerization medium, concentration and ratio of the monomers, temperature, concentration and type of initiator and steric stabilizer. The final particle size and size distribution are determined by the inherent polymer aggregation behavior under a given set of these parameters. Thus, we performed an extensive experimental study to obtain a clear picture of how the individual components of the polymerization mixture affect the characteristics of the micron-size particles and the stability of the polymerization system. Styrene was chosen as a monomer and an ethanol–water mixture as the reaction medium.

Investigated first was the effect of macromer dimension and concentration. The results are presented in Table III and Figures 2 and 3. As can be seen, the stability of the polymerization system was enhanced by the increase in dimension of the PMOZO chain, the macromer acting not only as a comonomer but also as a stabilizer. No stable system could be obtained for macromers with less than 15 structural units. A similar behavior was also reported for other dispersion polymerization systems using poly(2-alkyl-2-oxazoline) macromers.[1,16] The content of macromer was varied from 0 to 11 wt % of the total amount of monomer. The best results—that is, the highest final monomer conversion (68%)—and a narrow particle-size distribution were obtained for a concentration of 3 wt % of total monomer (Fig. 2). Except for this experiment, the particle yield was in the range of 40–50%. These low values and the decrease of yield with increased macromer content above a certain concentration level were related mainly to the low reactivity of this macromer in comparison to the vinyl comonomer, a specific feature of such functional polymers. Formation of an increased amount of soluble oligomers is also possible. Av-

Table III   Dispersion Copolymerization of PMOZO Macromers with Styrene

|	Macromer							Dispersion Characteristics			
Code	Type	DP_{PNAI}	Weight[a] (%)	Yield (%)	Solvent (v/v)	Initiator Type	Temperature (°C)	D_n (nm)	D_w (nm)	PI	Stability
D_0	—	—	—	33	70/30	ACV	70	—	—	—	—
D_1	Cin 1	8	11	20	70/30	ACV	70	—	—	—	—
D_2	Cin 3	15	11	31	70/30	ACV	70	679	751	1.10	−+
D_3	Cin 2	30	11	61	70/30	ACV	70	615	731	1.19	++
D_4	Cin 2	30	3	68	70/30	ACV	70	951	1050	1.12	+

[a] Macromonomer concentration with respect to total monomer.

erage particle size decreased slightly with an increasing macromer stabilizer concentration because of the increased number of forming nuclei resulting from increasing stabilizer concentration, leading to more particles but of a smaller size (Fig. 3). It must be mentioned that in the dispersion polymerization of MMA using a poly(2-ethyl-2-oxazoline) homopolymer ($M_w \geq 40,000$) as

a steric stabilizer, more than 10 wt % was always necessary to obtain micron-size particles with a narrow size distribution.[17] By comparison, and similar to the results presented here, a much lower content of polar poly(2-alkyl-2-oxazoline) macromer ($\leq$ 1 wt % of the total monomer) was sufficient to produce such monodisperse particles in the dispersion copolymerization of methyl methacrylate, showing that high hydrophilic mac-
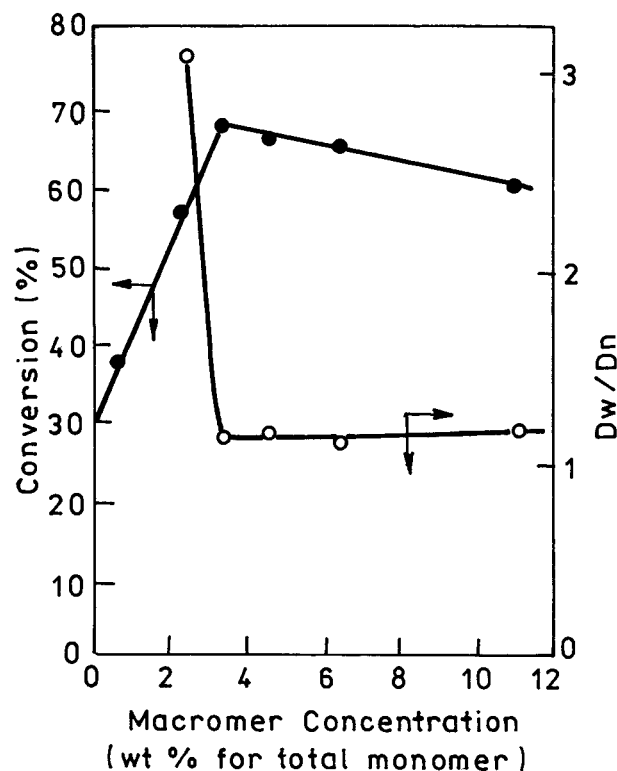
Figure 2   Effect of macromer concentration on yield and particle-size distribution (reaction conditions: alcohol/water 70/30 v/v; 10 vol % monomers; 3 wt % ACV relative to monomers; 70°C).
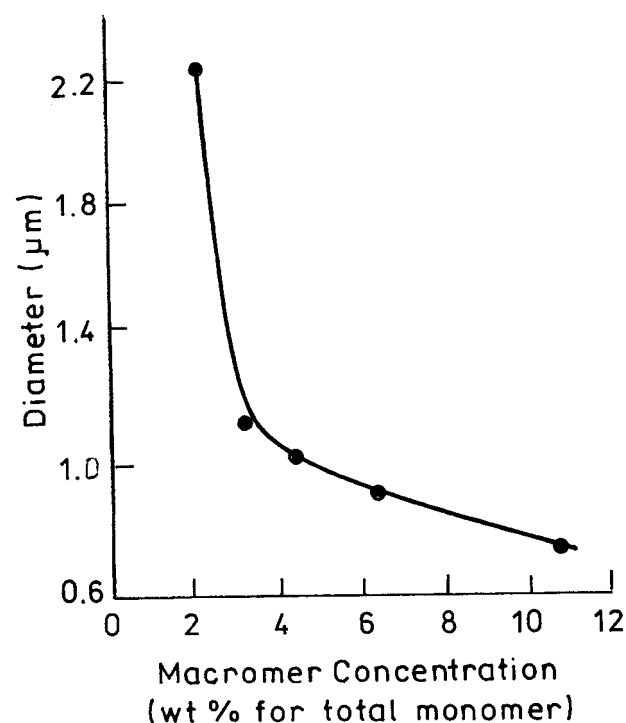
Figure 3   Dependence of the average particle size on the macromer amounts (reaction conditions: alcohol/water 70/30 v/v; 10 vol % monomers; 3 wt % ACV relative to monomers; 70°C).

Table IV   Photocopolymerization Data

| Sample Code | Macromer | | | Yield (%) | Solvent | | Initiator Type | Temper- ature (°C) | Dispersion Characteristics | | |
	Type	DP_{PNAI}	%		Ethanol Water (v/v)	δ $(\mathrm{cal/cm}^3)^{1/2}$			D_n (nm)	D_w (nm)	PI
D_5	Cin 2	30	2	51	70/30	16.1	ACV	35	952	1047	1.05
	Cin 8	15	1								
D_6	Cin 2	30	3	45	70/30	16.1	ACV	35	2067	3164	1.50
D_7	Cin 2	30	3	33	70/30	16.1	AIBN	35	1488	1942	1.30
D_8	Cin 2	30	3	35	70/30	16.1	POB	35	886	1132	1.28
D_9	Cin 6	40	3	53	80/20	14.9	POB	35	410	492	1.20
D_{10}	Cin 6	40	3	78	90/10	13.7	POB	35	560	572	1.02
D_{11}	Cin 6	40	2	80	90/10	13.7	POB	35	683	752	1.10
	Cin 8	15	1								

romonomers stabilize polymer particles more effectively.[10,16]

In consideration of cinnamoyl group peculiarities, we also performed some photochemical polymerization experiments. Data from the literature recommends the use of benzoyl peroxide or specific photoinitiators in the case of cinnamic acid derivatives.[11] As can be observed from ACV, AIBN and POB (Table IV), using the last one seems the best alternative. Considering the earlier-mentioned results, a macromonomer with a polymerization degree of 40 for the hydrophilic PMOZO chain was selected in order to assure efficient stabilization of the polymerization system. A concentration of 3 wt % of total monomer was used.

Solvent composition was varied to obtain adequate conditions for a narrow particle-size distribution. The solubility parameter of the initial reaction mixture was calculated as the root-mean-square volume-weighted average of the solubility parameters of the solvents and monomers.[18] Parameters for the macromer (steric stabilizer) and the initiator were not taken into account, as their concentrations are negligible. The solvency of the reaction medium, expressed by the solubility parameter (Table IV), is known to play an important role in dispersion polymerization because it controls the critical molecular weight above which the polymer will precipitate during the nucleation stage and thus controls the size of the particles. Because water is a poorer solvent for the resulting graft copolymer than ethanol, the critical chain length of the precipitated oligomers decreases

with water content. Thus a slight increase in the amount of water used increases the polarity of the dispersion medium and decreases the average bead size (Table IV and Fig. 4), a general trend for dispersion polymerization of vinyl monomer in an alcohol–water medium.[10,15,19–21]

The final monomer conversion value increases with an increase in the polarity of the dispersion
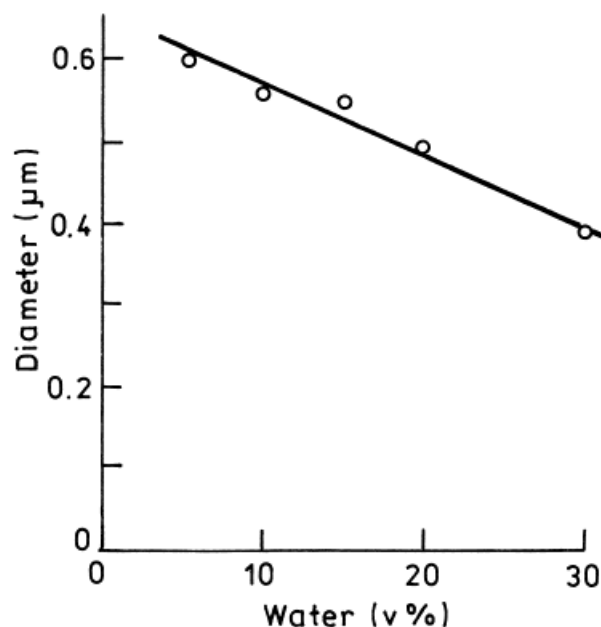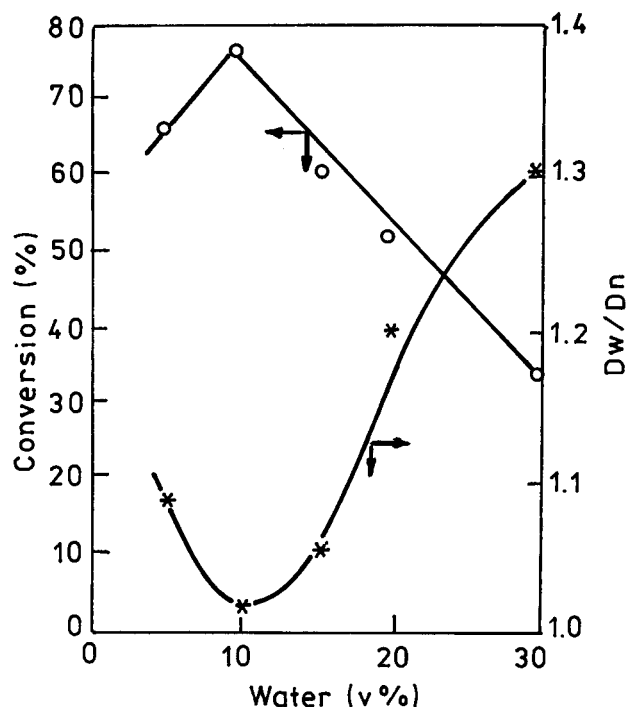

Figure 4   Variation of particle size with alcohol/water ratio (reaction conditions: 10 vol % monomers; 3 wt % Cin 6 relative to total monomer; 3 wt % POB relative to monomers; 35°C; 6 h UV irradiation)
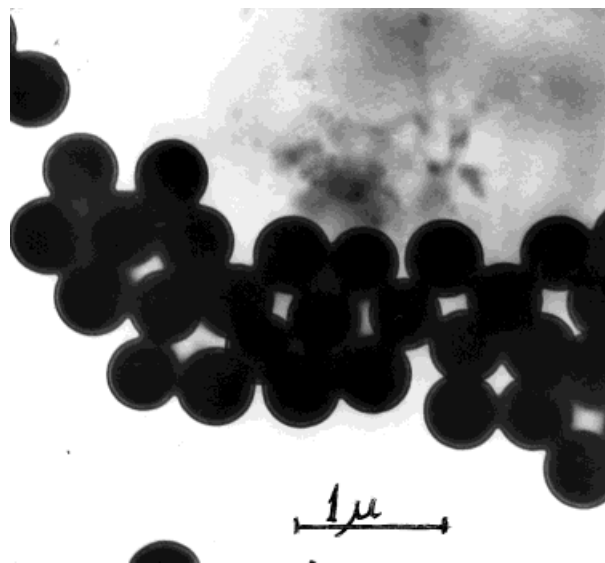
medium because more monomer and initiator are transferred to the forming particles when the water content increases. Particles with a narrow size distribution were obtained in high yield for a water content between 7–13 vol %, with a minimum point in the polydispersity index at about 10–12 vol % water (Fig. 5).

As shown in Table IV (samples D_5 and D_{11}) and Figure 6, relatively uniform polymeric beads, in the micron range, also were obtained using a mixture of mono- and bifunctional PMOZO macromers with adequate chain lengths.

The size, monodispersity, and surface properties of the polymeric microspheres are important in biomedical applications. In the dispersion copolymerization of hydrophilic macromers the mechanism for microsphere formation suggests that hydrophilic chains cover a hydrophobic core to produce core–shell type particles. This characteristic is a supplementary argument for using the presented polymeric materials in this domain.[10] Further studies on this research theme are in the course of being done.

Figure 6 TEM micrograph of the final micron-size polymer particles (sample D_{11}).

CONCLUSION

The study of the dispersion copolymerization of mono- or bifunctional hydrophilic poly(2-methyl-2-oxazoline) macromonomers containing cinnamoyl polymerizable groups with styrene demonstrated that in appropriate conditions they are able to produce monodisperse polymer particles in the micron range in size.

The paper is dedicated to Professor Cristofor I. Simionescu, on the occasion of his 80th birthday anniversary, in recognition of his outstanding contribution to the progress of polymer science.

Figure 5 Dependence of particle size distribution and yield on percentage of water in polymerization mixture (reaction conditions: 10 vol % monomers; 3 wt % Cin 6 relative to total monomer; 3 wt % POB relative to monomers; 35°C, 6 h UV irradiation).

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