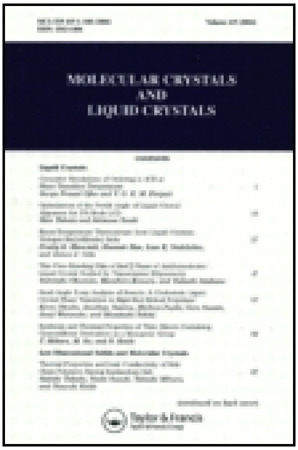

Molecular Crystals and Liquid Crystals

Polymer Architectures Based on Oxazoline Monomers

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Polymer Architectures Based on Oxazoline Monomers

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Nonaqueous dispersion copolymerization of 2-isopropenyl 2-oxazoline (IPRO) with methyl methacrylate (MMA) and chloromethylstyrene (CMS) was studied. The resulting copolymers were analyzed with FT-IR and FT-NMR techniques. The morphologies and average diameter were investigated for the characterization of the resulting particles.

When the comonomer was MMA the particle size was dependent upon the molar ratio MMA/IPRO in copolymer.

MMA content in the resulting copolymers is influenced by the type of stabilizing agent. Narrow size distribution was obtain for copolymer rich in IPRO.

When CMS was the commoner, polymerization occurred via two mechanisms: radicalic and cationic with preference for the last one.

Keywords: chloromethylstyrene; dispersion polymerization; methyl methacrylate; oxazoline

INTRODUCTION

Monodisperse polymer particles in the micron and nano range attracted great interest due to their various potential applications. Dispersion polymerization is often prefered for the preparation of such

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particles, because of the simplicity of the process. The nonaqueous dispersion polymerization is initiated in a homogenous medium where all components are miscible. When the molecular weight of the polymer exceeds a critical limit, polymer phase separates and aggregates. Steric stabilization of polymer particles is achieved when dispersing agents, usually block copolymers, are added. After nucleation, polymerization continues in bulk in the monomer-swollen particles. Provided that no new nucleation occurs, it is possible to obtain fairly narrow particle size distribution.

Functional groups are usually incorporated by copolymerization of functional monomers such as: acrylic acid, hydroxyethylmethacrylate [1], chloromethylstyrene [2] and unconventional monomers like azo [3] or acetal [4] groups containing methacrylates. They can be used for various purposes like post-polymerization reactions [5], crosslinking of particles [6], reaction with binder system [4], or dynamic vulcanization [3].

Oxazoline functional polymers have been prepared by nonaqueous dispersion polymerization [7]. Micro-size monodisperse PMMA particles have been prepared by dispersion copolymerization using hydrophilic poly(2-alkyl-2-oxazoline) macromoner instead of using homopolymer as a stabilizer. The macromonomer acted as both a stabilizer and a commoner [8]. The aim of this article is the preparation of micron-size particles based on IPRO with narrow size distribution using two different steric stabilizers.

EXPERIMENTAL

Materials

2-isopropenyl-2-oxazoline (IPRO), chloromethylstyrene (CMS) were used as supplied, methyl metacrilate (MMA), Aldrich, was distilled prior to use, maleic anhydride-dicyclopentadyene copolymer (AM-DCPD) was obtained in laboratory ($M_n = 2800\,g/mol$). 1,4-dioxane, n-hexane, bis-azo-iso-butyronitrile (AIBN, Fluka) were used as received. Ethoxylated C_{16} alcohol (50 moles ethyleneoxyde) (EA) from “Detergenti” company, Timisoara, Romania was used as supplied.

Dispersion Copolymerization

A typical run was as follows. Under argon, MMA (or CMS) was dissolved in n-hexane (mixture 1) and IPRO, stabilizer agent and AIBN were dissolved in dioxane (mixture 2). The molar concentration of both comonomers in the system was 4 mol/l. Mixture 1 was added

TABLE 1 Substrate Compositions (Molar Percent)

	x_i [% mol]				
Sample name	IPRO	MMA	CMS	AM-DCPD	EA
A_v	4.7	89.2	–	6.1	–
B_v	8.92	4.7	–	6.1	–
C_v	47	47	–	6	–
D_v	5	95	–	–	–
E_v	4.7	89.2	–	–	6.1
V_{CMS}	4.7	–	89.2	6.1	–

while stirring to mixture 2 at room temperature. The reaction mixture was heated at 60°C under stirring for 4 h.

Conversion was followed gravimetrically by precipitation in methanol of samples withdrawn from the dispersion.

The chemical nature of comonomer, the monomer content and type of dispersant agent were varied in the dispersion copolymerization of oxazoline. Experimental details are listed in Table 1.

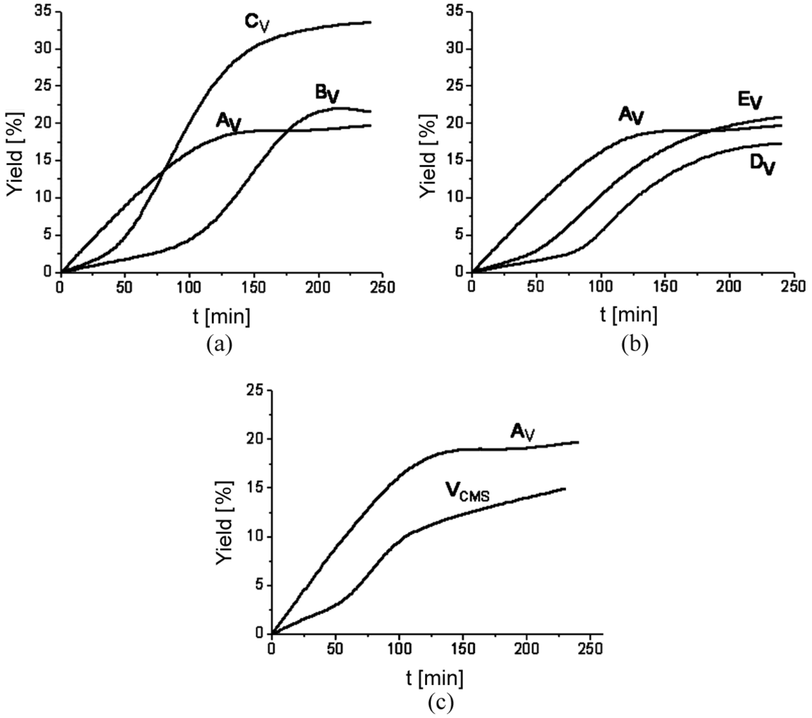
Characterisation

The FT-IR spectra were recorded with a Bruker Vertex 70 spectrometer fitted with a Harrick MVP2 diamond ATR device. ^1H and ^{13}C FT-NMR spectra were recorded on a Varian Unity 400 spectrometer in DMSO-D_6 at room temperature. Scanning electron micrographs (SEM) were performed on a Hitachi S-2600N. The DLS measurements were performed on diluted dispersions in DMSO, using a Malvern Zetasizer Nano Zs.

RESULTS AND DISCUSSION

The particle size produced by nonaqueous free radical dispersion polymerization is dependent upon solubility of the formed polymers in the medium as well as on the type and content of the dispersant. The polymer solubility is again a function of molecular weight, monomer concentration, and the chemical composition of the polymer.

The experimental curves (Figs. 1a–c) tend in an asymptotic maner to 35% conversion. For the poor MMA substrates an increase of the induction period was observed. The probable reason for this behaviour is the hindered access of the MMA in the phase containing the initiator.



(a)

(b)

(c)

FIGURE 1 Kinetic plots for 2-isopropenyl-2-oxazoline copolymerization initiated with AIBN. (a) influence of molar ratio of comonomers in substrate; (b) influence of the dispersing agent nature; (c) influence of the nature of the comonomer; Molar ratios in substrate MMA/IPRO (dispersing agent): $A_v = 19{:}1$ (AM-DCPD); $B_v = 1{:}19$ (AM-DCPD); $C_v = 1{:}1$ (AM-DCPD); $D_v = 19{:}1$ (without); $E_v = 19{:}1$ (EA); CMS/IPRO $V_{CMS} = 19{:}1$ (AM-DCPD).

The kinetic evolutions for the copolymerization of IPRO and MMA emphasizes the major role played by the reaction medium in the process of particle formation and proves that the molar ratio between the two comonomers is decisive for the location of growing step.

When using diferrent stabilizing agents at the same molar ratio between comonomers (Fig. 1b) the kinetic plot reveals:

- no induction period when using AM-DCPD as stabilizing agent;
- reduction of induction period when using EA compared to unstabilized process;
- the three kinetic evolution are identical from the point of view of reaction rate.

The experimental curve for CMS copolymerization (Fig. 1c) does not fit to dispersion polymerization pattern.

For IPRO-MMA copolymers the IR spectra (Figs. 2 and 3) show a strong band centered at 1720 cm^{-1} due to $\nu_{C=O}$ ester and 1652 cm^{-1} due to $\nu_{C=N}$ from oxazoline ring.

For the IPRO-CMS copolymers (Fig. 4) analyses reveal the presence of two oxazolinic species generated by different mechanisms: radicalic and cationic. Besides $\nu_{C=N}$ at 1652 cm^{-1} a new $\nu_{C=O}$ ester stretching band appears at 1729 cm^{-1} accounting for the cationic polymerization of 2-isopropenyl-2-oxazoline.

While IR spectroscopy offers only a qualitative image of the structure of the copolymer, the ^{1}H NMR and ^{13}C NMR (Figs. 5, 6, and 7) spectra allow quantitative calculations of the ratios MMA(CMS)/IPRO.

The IPRO-MMA copolymers ^{13}C NMR spectra exhibit signals at 67 ppm and 55 ppm attributed to the methylene carbon of oxazoline ring. The broad signal at 42–45 ppm is assign to the methylene carbons of the backbone.

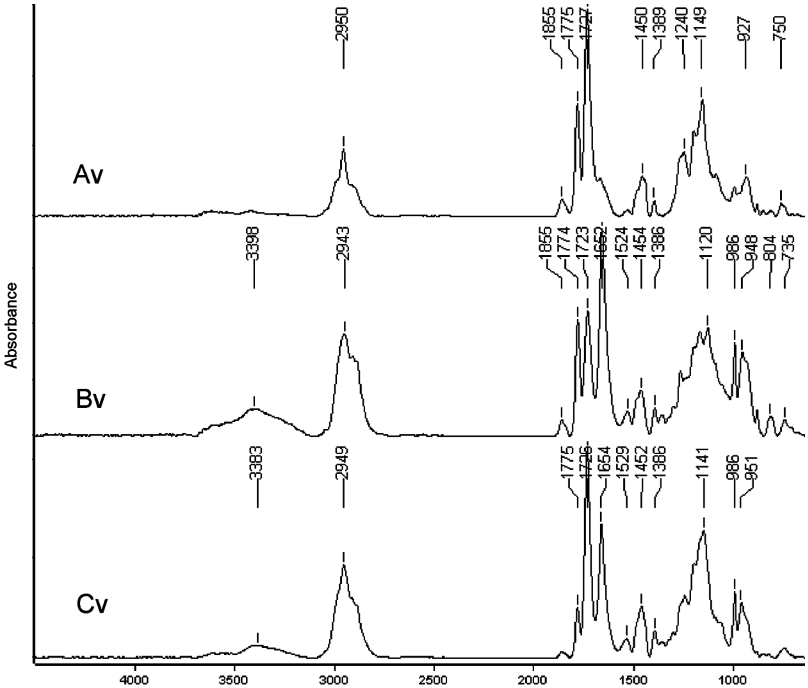


FIGURE 2 IR spectra for MMA-IPRO copolymers stabilized with AM-DCPD; Molar ratios $A_v = 1.5{:}1$; $B_v = 1{:}5$; $C_v = 1{:}2.5$ calculated from NMR spectra.

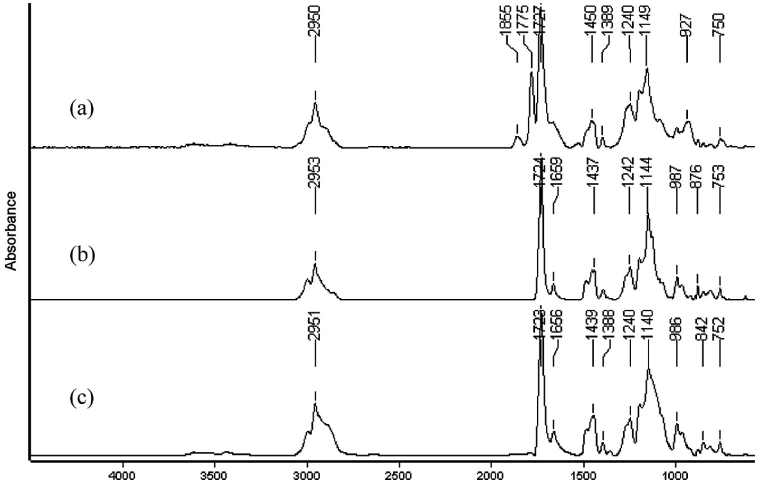


FIGURE 3 IR spectra for MMA-IPRO copolymers with various stabilizing agents: (a) AMDCPD; (b) without; (c) EA.

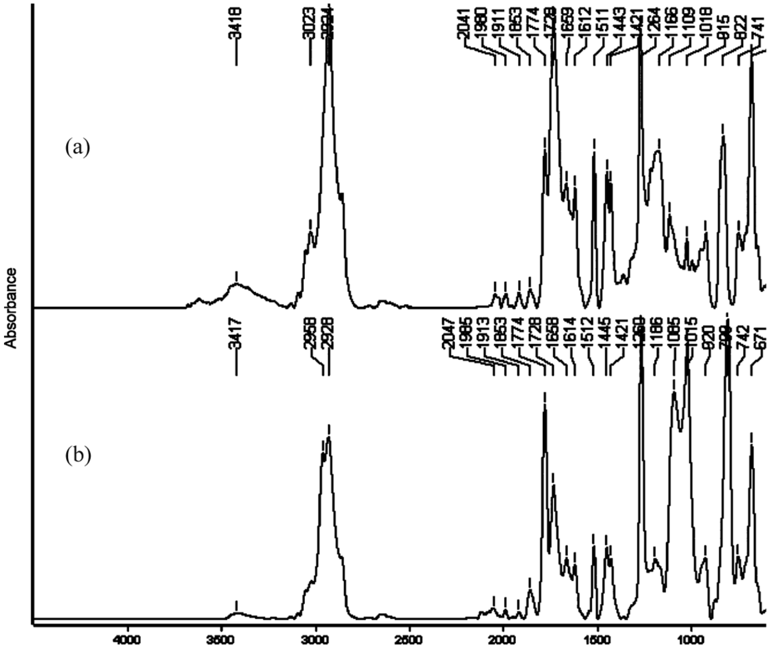


FIGURE 4 IR spectra for CMS-IPRO copolymers stabilized with AM-DCPD; (a) solid phase; (b) liquid phase.

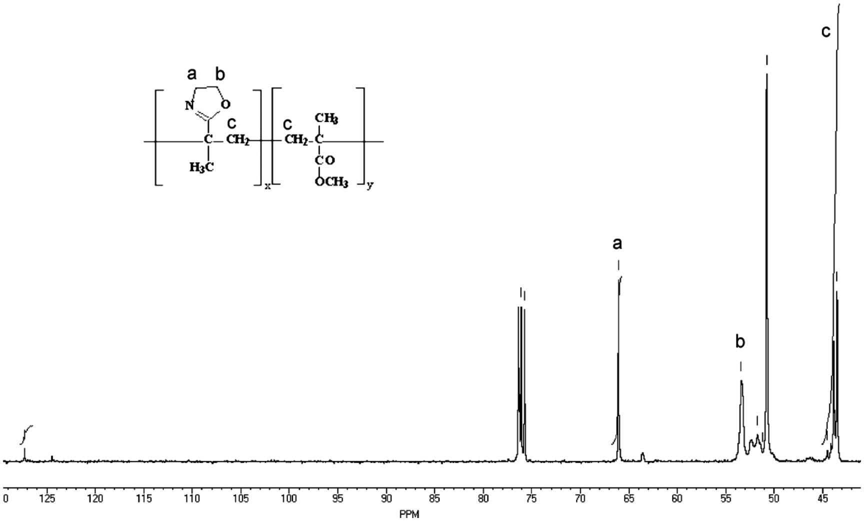


FIGURE 5 ^{13}C NMR spectrum for MMA-IPRO copolymer (without stabilizing agent).

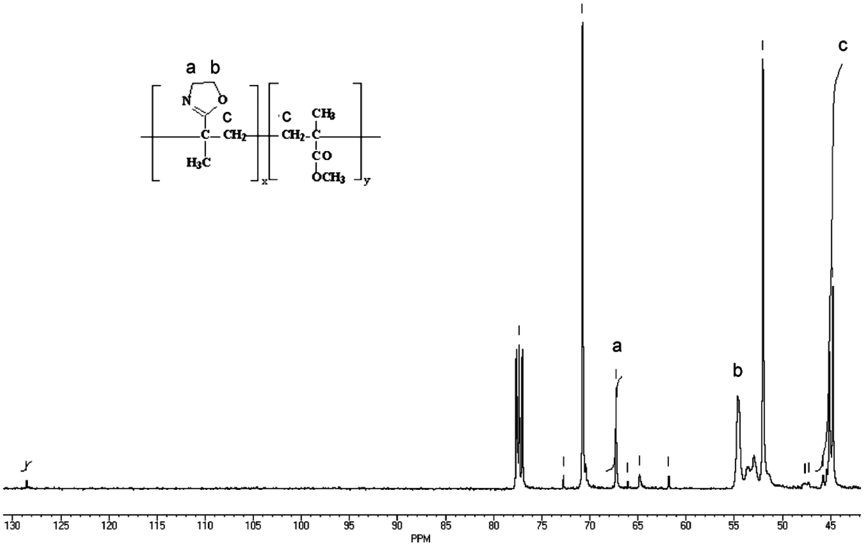


FIGURE 6 ^{13}C NMR spectrum for MMA-IPRO copolymer (EA stabilizing agent).

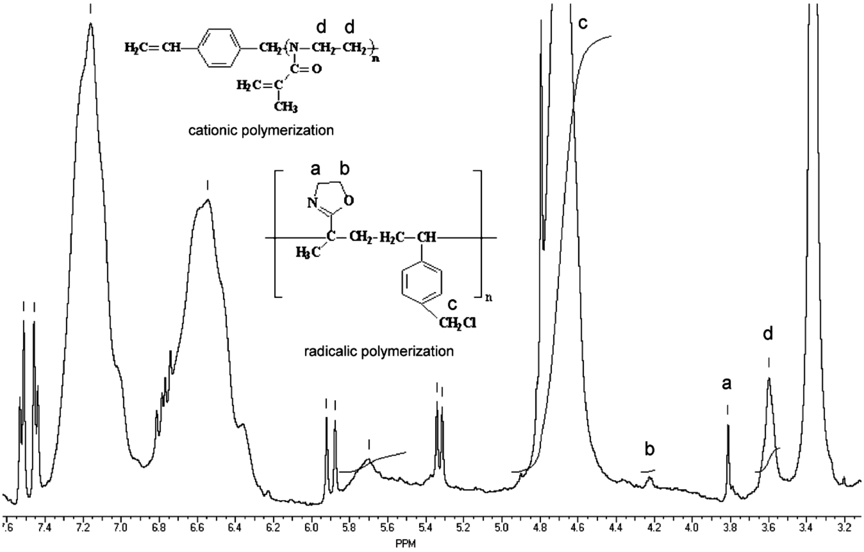


FIGURE 7 ^{1}H NMR spectrum for CMS-IPRO copolymer in solid phase (AM-DCPD stabilizing agent).

Using the integrals of these signals we calculated the compositions presented in Table 2.

The compositions calculated from NMR analysis allow us to sugest that the AM-DCPD stabilizer hampers the comonomer access to the polar (dioxane) phase. The EA, a well known tenside, with micellar properties, favourises the diffusion at the interface allowing higher MMA/IPRO ratios in the copolymer.

When the comonomer was CMS the polymer was found to be in both phases: liquid and solid. The IPRO-CMS copolymer composition for the solid phase was evaluated from the ^{1}H NMR spectrum (Fig. 7). The “a”, “b” protons in the oxazoline ring give signals at 3.8 and 4.3 ppm, while the “c” protons in CMS are placed at 4.5–4.8 ppm. The presence of the signals at 3.6 ppm assigned to “d” type protons of the backbone proves the cationic polymerization of 2-isopropenyl-2-oxazoline.

TABLE 2 MMA-IPRO Molar Ratio in Copolymers Calculated from NMR Spectra

Sample name	A_v	B_v	C_v	D_v	E_v
$n_{MMA}:n_{IPRO}$	1.5:1	1:5	1:2.5	3:1	4:1

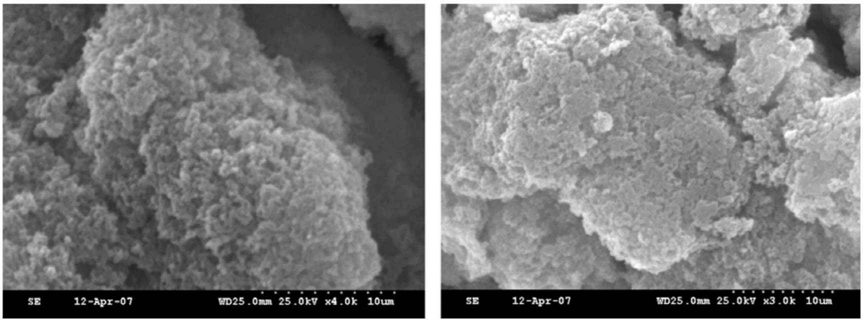


FIGURE 8 SEM micrographs for MMA:IPRO copolymer (1.5:1 molar ratio).

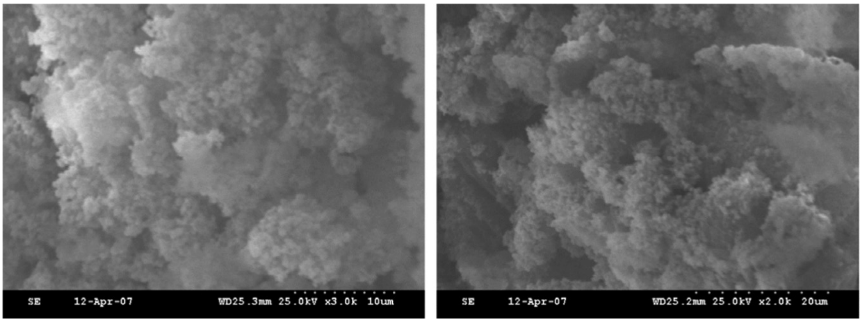


FIGURE 9 SEM micrographs for MMA:IPRO copolymer (1:5 molar ratio).

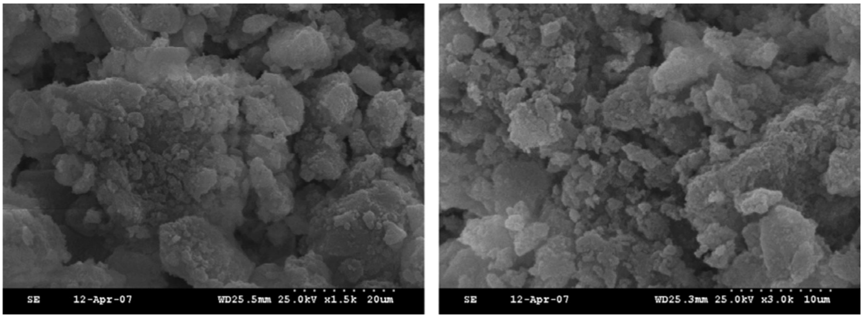
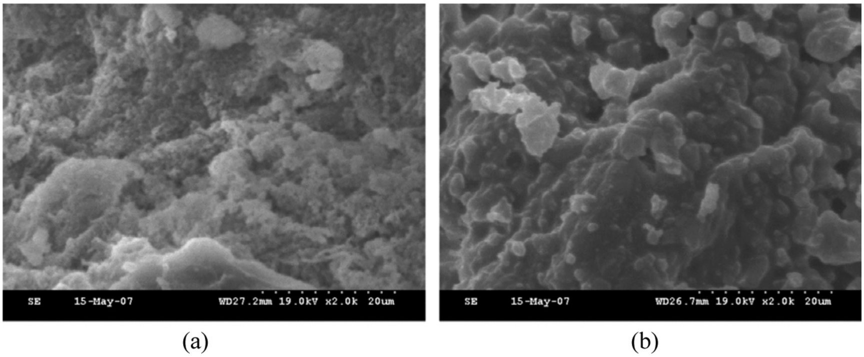


FIGURE 10 SEM micrographs for MMA:IPRO copolymer (1:2.5 molar ratio).



(a) (b)

FIGURE 11 SEM micrographs for CMS:IPRO copolymer: (a) liquid phase; (b) solid phase.

The ^{1}H NMR spectrum emphasizes that the solid phase shows two different tipes of insertion for 2-isopropenyl-2-oxazoline: radicalic and cationic with preference for the last one. The liquid phase exhibited cationic insertion only.

As expected, the comonomer molar ratio has important influence on the process of particle formation, as showed by SEM micrographs.

Images in Figure 8 reveal that nucleation takes place in small particles but it is followed by an intense agglomeration for A_v sample. This may be due to a poor anticoagulating capacity of the stabilizer.

For B_v sample the SEM micrographs (Fig. 9) reveal a regular structure. The particles are very small and very well defined with aggregation tendency.

In C_v case (Fig. 10) small and large particles were formed with broad distribution and various shape.

When CMS is used as comonomer particles which came from liquid fraction (Fig. 11a) have a marked tendency for agglomeration in large fragments probably due to the lack of stabilizing agent. In the solid phase (Fig. 11b) aggregates of two or three particles form sticks.

The DLS analysis sustain the interpretation of the SEM micrographs. The average diameter (by intensity) of the particles is listed in Table 3.

TABLE 3 Average Diameter (by Intensity) of the Particle Resulted from DLS Analysis

Sample name	A_v	B_v	C_v
Particle size [nm]	548	280	4000

At high MMA molar ratio in copolymer the stabilizer becomes ineffective resulting in particle coalescence.

CONCLUSIONS

Nonaques dispersion copolymerization of 2-isopropenyl-2-oxazoline with MMA and CMS was studied. When the comonomer was MMA the particle size was dependent upon the molar ratio MMA/IPRO in copolymer. MMA content in the resulting copolymers is influenced by the type of stabilizing agent. Narrow size distribution was obtained for the copolymer rich in 2-isopropenyl-2-oxazoline. When CMS was the commoner, polymerization occurred via two mechanisms: radicalic and cationic with preference for the last one.

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