

Synthesis of Latex Particles by Ring-Opening Metathesis Polymerization in Dispersed Medium

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SUMMARY : Colloïdal particles of polyalkenamers were obtained by ring-opening metathesis polymerization of norbornene (NB) or cyclooctadiene (COD) in dichloromethane/methanol medium, using α -norbornenyl poly(ethylene oxide) macromonomer as steric stabilizer. The dispersions obtained were characterized by electron microscopy and dynamic light scattering.

Depending upon the experimental conditions used, the size of these particles was found to range from 150 nm to 15 μ m. In particular, the particle size was shown to decrease upon increasing the concentration and molar mass of the macromonomer. Beside these factors, it appears that the main parameter that governs the size of the particles formed is the ability of these macromonomers to randomly copolymerize with either NB or COD.

Introduction

While there are numerous papers on dispersion polymerization via more common chain addition processes, very little can be found in the literature on ring-opening-metathesis polymerization (ROMP) carried out in dispersed media. Lu et al.¹⁾ were the only authors to report true dispersion ROMP. For their polymerizations they utilized RuCl_3 , an initiator that is active in water and a steric surfactant. They showed that the size of their latex particles decreases when the surfactant concentration was increased. The latex particle diameters were in the range 20 nm to 200 nm.

The present work deals with the synthesis of particles based on polynorbornene and polybutadiene. Such particles were respectively obtained by ROMP of norbornene and cyclooctadiene in dichloromethane/ethanol medium, using α -norbornenyl poly(ethylene oxide) macromonomer as stabilizer and well-defined ruthenium metalla-alkylidenic complex $\text{Ru}(\text{PCy}_3)_2\text{Cl}_2\text{CH}=\text{CHPh}$ as initiator. To our knowledge it is the first time that a polymerizable surfactant is used to obtain latex particles by dispersion ROMP process of cycloolefins. These

PEO-based macromonomers function both as co-monomer of the cycloolefin in the ROMP process and stabilizer of the polyalkenamer formed.

The presence of the norbornenyl group at one end helped these novel surfmers to be chemically anchored onto the particles, whereas the hydrophilic part served as steric barrier.

The molar mass and concentration of macromonomer are two very important parameters that govern the size particle.

Other factors such as the initiator concentration, the medium composition also influence the size of the particles formed, but above all it is the reactivity of the cycloolefin considered towards the macromonomer, that controls the overall process of particle formation.

Experimental Part

Materials : All reagents were dried, and degazed then stored and used under inert atmosphere. ROMP were carried out under inert atmosphere. The ruthenium complex used was prepared following literature methods²⁾. α -norbornenyl poly(ethylene oxyde) macromonomer was synthesized as previously reported³⁾. After deactivation the reaction medium by adding ethylvinylether, conversions were determined by gas chromatography with undecane as internal standard. Conversion of macromonomer was evaluated using a standard method⁴⁾.

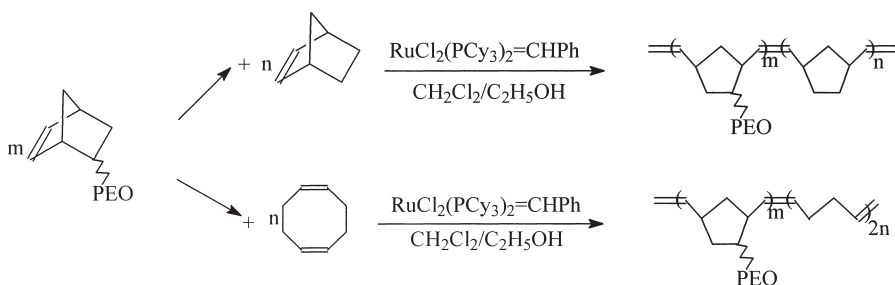
The particle sizes were determined by electron microscopy using a Laborlux K apparatus and by quasi-elastic light scattering using a Malvern zetasizer 3000 equipped with a He-Ne laser. Before measurements, latexes were diluted 100 times to minimize particle-particle interactions.

Dispersion Polymerization The dispersion polymerizations were carried out at room temperature in a 100 ml glass reactor under inert atmosphere and stirring. In a typical synthesis 20mg ($2.4 \cdot 10^{-5}$ mol.) of catalyst was dissolved in 10 ml of $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ mixture (50/50% vs volume) in presence of 1 ml of undecane. The mixture of monomer ($8 \cdot 10^{-3}$ mol.) and macromonomer ($1.4 \cdot 10^{-5}$ mol.) was dissolved in 14 ml of $\text{CH}_2\text{Cl}_2/\text{C}_2\text{H}_5\text{OH}$ solution (35/65%) containing the catalyst.

The deactivation of the reaction medium was performed by addition of 0.1 ml of ethyl vinyl ether.

Results and discussion

Two monomers, norbornene (NB) and cyclooctadiene (COD), were polymerized in the presence of α -norbornenyl poly(ethylene oxide) macromonomer as stabilizer (Scheme 1).



Scheme 1 : ROMP of NB and COD in the presence of PEO macromonomers

The initiator used was the well-defined ruthenium based metalla-alkylidenic complex $\text{Ru}(\text{PCy}_3)_2\text{Cl}_2\text{CH}=\text{CHPh}$ which is known to be stable and retain its reactivity in protic solvents. Starting from a clear homogeneous solution, the reaction medium became turbid at the early stage of polymerization in the case of norbornene and later when cyclooctadiene was used. The results obtained under different experimental conditions are given in tables 1 and 2.

Table 1 : Results of dispersion ROMP of norbornene at 25°C

[NB] mol.	$\overline{M}_{n,\text{macrom.}}$ g/mol.	[macrom.] mol.	[A] mol.	EtOH ml	CH_2Cl_2 ml	NB cvs. %	Macrom. cvs %	D^a nm
$8.1 \cdot 10^{-3}$	2800	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	14	10	100	➤ 95	123
$8.1 \cdot 10^{-3}$	4800	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	14	10	100	➤ 95	70
$8.1 \cdot 10^{-3}$	7500	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	14	10	100	➤ 95	63
$8.1 \cdot 10^{-3}$	4800	$8.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$	14	10	100	➤ 95	144
$8.1 \cdot 10^{-3}$	4800	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	0	24	100	➤ 95	No dispersion
$8.1 \cdot 10^{-3}$	4800	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	19	5	100	➤ 95	122
$8.1 \cdot 10^{-3}$	4800	$1.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	14	10	100	➤ 95	aggregation

a) : diameters of particles measured using quasi elastic light scattering

Table 2 : Results of dispersion ROMP of cyclooctadiene at 25°C

[COD] mol.	$\overline{M}_{n,\text{macrom.}}$ g/mol.	[macrom.] mol.	[A] mol.	EtOH ml	CH_2Cl_2 ml	COD cvs. %	Macrom. cvs. %	D^a μm
$8.1 \cdot 10^{-3}$	3200	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	14	10	65	70	3-9
$8.1 \cdot 10^{-3}$	4800	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	14	10	55	60	3-7
$8.1 \cdot 10^{-3}$	7500	$1.4 \cdot 10^{-4}$	$2.4 \cdot 10^{-5}$	14	10	60	65	2-5
$8.1 \cdot 10^{-3}$	4800	$8.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$	14	10	60	100	2-8
$8.1 \cdot 10^{-3}$	4800	$8.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$	5	19	65	70	No dispersion
$8.1 \cdot 10^{-3}$	4800	$8.5 \cdot 10^{-5}$	$2.4 \cdot 10^{-5}$	19	5	50	-	2-3
$8.1 \cdot 10^{-3}$	4800	$1.4 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	14	10	65	70	8-15

a) : diameters of particles measured using electron microscopy

Dispersion ROMP of NB and COD in the presence of PEO macromonomers

Under identical experimental conditions ([I], [Macromonomer], [Monomer], solvent composition, etc...), it appears that the outcome of the dispersion ROMP is totally different for the two cycloolefins, with quite contrasted results from one monomer to another. Obviously, PEO macromonomers fitted with norbornenyl unsaturation are remarkably well-suited to stabilize the particles formed by dispersion ROMP of norbornene, affording narrowly distributed colloidal materials in the hundred nm size. Both macromonomer and norbornene were totally consumed by random copolymerization, forming one unique population of graft copolymers as shown by size exclusion chromatography (SEC). In contrast, particles of much larger size and broader distribution were obtained in the μm scale with cyclooctadiene as cycloolefin. Not all macromonomer could be consumed in the latter case and only 60% of COD was polymerized after 24h. A better solubility of polynorbornene in the reaction medium can be ruled out to account for the formation of nanosized particles in the latter case, since the ethanol/dichloromethane mixture is a precipitating medium for both polynorbornene and polybutadiene. As a matter of fact, the differences exhibited by the two systems stem from the quite contrasted reactivity of α -norbornene-ended macromonomers towards NB or COD, respectively. As they likely exhibit similar reactivity, both NB and the norbornenylmethylether unsaturation of macromonomers tend to undergo a random copolymerization that eventually go to completion. The PEO grafts that are formed after insertion of the macromonomer along the copolymer backbone are certainly randomly distributed. In such a case, a PEO graft should be dangling from the copolymer backbone every 60 repeating units which is particularly propitious to an efficient stabilization of the precipitating copolymer into a nanosized particle.

Totally different is the situation prevailing in the case of the copolymerization of COD with norbornene-ended macromonomers. In contrast to NB and its derivative, COD is a lowly strained cycloolefin which is sluggish to polymerize and the resulting polybutadiene is prone to transfer reactions. As a result of the rather low reactivity of COD, the overall rate of polymerization is slowed down, favoring the irreversible deactivation of active species before all monomer and macromonomer are consumed. As to the bicyclic norbornenyl unsaturations of PEO macromonomers, they certainly polymerize first because of their highly strained nature : the copolymers that are formed under these conditions are therefore characterized by a strong tendency to blockiness. In brief, COD and macromonomers of PEO do not randomly copolymerize because of their very contrasted reactivity ; the presence of two populations of macromolecules in the SEC eluogram seems to confirm this inference, but it could also be due

to the occurrence of intermolecular cross-metathesis. As PEO grafts are unevenly distributed along the copolymer backbone, they are unable to effectively play their role of steric stabilizer as in the previous case. This results in the formation of particles of much larger size, that may contain pure polybutadiene and are stabilized by PEO-g-PB copolymers exhibiting a strong tendency to blockiness. Macromonomers carrying an end-standing unsaturation that could actually copolymerize with COD should give better results and afford particles of small size. Attempts to use PEO-b-PB diblock copolymers as steric stabilizer will also be made.

Effect of molar mass of the stabilizer :

Among the factors that govern the size of the particles formed, the molar mass of the stabilizer is certainly one of the most crucial. The effect of the latter parameter was investigated by using three macromonomers of PEO whose molar masses ranged from 2800 to 7500 g/mol.. It clearly appears that the particle size decreases as the molar mass of the PEO macromonomer increases. Even though the effect of the stabilizer molar mass has not only been marginally studied, it can be easily understood that stabilizer of larger size enhance the colloidal stability by mere steric effect. With macromonomers of bigger dimensions the particle gets stabilized at an early stage of the polymerization and therefore remains small.

Effect of stabilizer concentration :

The initiator and monomer concentrations being maintained constant the stabilizer concentration was varied from $8.5 \cdot 10^{-5}$ mol. to $1.4 \cdot 10^{-3}$ mol.. The results obtained in the case of norbornene polymerization show that the particle size tends to decrease with an increase in the concentration stabilizer. This feature arises from the fact that a higher stabilizer concentration enables the stabilization of a larger surface area which in turn results in a larger number of particles of smaller size.

In contrast no significative trend on the particle size could be observed in the case of COD because of the reasons previously discussed. PEO grafts being unevenly distributed, the blocky structure formed could not as efficiently stabilize the particles as would have done a random distribution of stabilizers. As a result, it was not possible to generate small particles in spite of the use of higher concentrations of stabilizer.

Effect of the reaction medium :

Earlier studies⁵⁾ showed that in dispersion polymerization the size distribution as well as the average particle size strongly depend on the quality of the solvent mixture.

In order to study the effect of the latter parameter on the colloidal dispersion of polynorbornene and polybutadiene, polymerizations were carried out with varying composition of ethanol/CH₂Cl₂. In the absence of EtOH or with a very low concentration of

the latter solvent, the polymerization medium is entirely homogeneous and the polymer formed is soluble. When increasing the EtOH concentration a dispersion tends to form. Higher alcohol concentrations afford particles with narrower size distribution. This feature can be accounted for upon considering that the medium becomes a better solvent for the stabilizing chains as the concentration of EtOH increases.

Effect of initiator concentration :

A series of experiments was carried out with a same concentration of macromonomer and monomer, the only varying parameter being the initiator concentration which ranged from $2.4 \cdot 10^{-5}$ to $1.2 \cdot 10^{-4}$ mol. As clearly stated in the literature⁶⁾ the particle size increases with the initiator concentration. Higher initiator concentrations indeed lead to shorter polymer chains which are more soluble in the medium. Accordingly, the effect due to the stabilizer is less pronounced which results in the formation of particles of larger size. In the case of norbornene, the latex particles even tend to aggregate with increasing concentration of initiator in ethanol/ether.

Conclusions

Polynorbornene and polybutadiene particles have been obtained by polymerization of norbornene and cyclooctadiene in the presence of α -norbornenyl poly(ethylene oxide) as polymerizable surfactant. For these experiments that were conducted in ethanol/CH₂Cl₂ mixture, a well-defined ruthenium complexe was used. Particles of small size and narrow distribution were obtained in the case of polynorbornene because the macromonomer was able to randomly copolymerize with norbornene.

Parameters like the size and the concentration of the polymerizable surfactant, the initiator concentration and the composition of the medium have been investigated.

To our knowledge, this work represents the first example of synthesis of latex particles obtained by ROMP in the presence of polymerizable surfactant.

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