



# Synthesis and radical polymerization of methacrylic monomers with crown ethers in the ester residue: 1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate

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## Abstract

The synthesis and radical polymerization of 1,4,7,10-tetraoxacyclododecan-2-ylmethylmethacrylate (CR4MA) is described. The polymerization reactions of CR4MA were carried out at different temperatures and the kinetic curves of monomer depletion against time were obtained by direct measurements of the instantaneous monomer concentrations by using nuclear magnetic resonance (NMR) spectroscopy. At the same time electron paramagnetic resonance (EPR) spectroscopy was used to determine the actual polymer radical concentration during all the reaction time. The conjunction of both techniques (NMR and EPR) allowed the determination of the polymerization rate parameter ( $2fk_p/(k_t)^{1/2}$ ) and separately of  $k_p$  and  $\langle k_t \rangle / f$ , where  $f$ ,  $k_p$  and  $\langle k_t \rangle$  are, respectively, the initiator efficiency factor and the overall averages of propagation ( $k_p$  is considered to be practically independent of the chain length) and termination rate constants. The values found for this ratio and for  $k_p$  were comparatively higher than those recently reported in the literature for its lateral open chain counterpart, the methacrylic monomer with equal number of oxyethylene units in the residue ester (TTEMA). However, the  $\langle k_t \rangle$  values were similar for the polymerization of both monomers CR4MA and TTEMA. The polymer, PCR4MA, is soluble in water as its open chain homologous, and exhibits a glass transition temperature in the vicinity of the ambient temperature (about 35 °C), much higher than the value found for the homologous polymethacrylate derived from the TTEMA.

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## 1. Introduction

In recent works, the polymerization reactions of alkyl methacrylates, open chain oxyethylene methacrylates with a number of oxyethylene units [1,2] between 2 and 6, cyclohexyl methacrylate [3] and trimethylsilyloxysilyl methacrylate [4] have been studied by UV, NMR and EPR spectroscopy. It was observed that, while the gel effect starts at relatively low conversions in methyl and cyclohexyl methacrylate, higher conversions are required in the case of ethyl and dodecyl methacrylate. No gel effect was observed even at conversions higher than 90%, in the bulk polymerization of trimethylsilyloxysilyl methacrylate as well as in the polymerization of the oxyethylene methacry-

late monomers in which the number of oxyethylene units was higher than four [1,2].

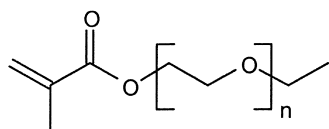
Nevertheless, very few researches have been performed on the synthesis and polymerization of meth(acrylic) monomers with crown ethers in the ester residue [5–9] and their influence on the kinetic parameters. Particularly in the researches carried out with monomers bearing crown ethers in the chain, the main target was to obtain polymers able to form complexes with polyanions [7], polymers terminated with end groups capable to extract potassium or sodium cations [8] or liquid crystals polymers containing macroheterocyclic ligands [9]. No attention was devoted to study the radical polymerization kinetics.

The aim of this work is to study by NMR and EPR spectroscopies the bulk and solution polymerization of 1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate in order to determine the values of the propagation and termination rate parameters and to analyse comparatively

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the results with those obtained for the open chain oxyethylene methacrylate monomers of general structure named hereafter EEMA, DEMA, TEMA and TTEMA for  $n = 1, 2, 3$  and  $4$ , respectively.



## 2. Experimental

### 2.1. Materials

All materials and solvents used for the synthesis of the monomers were commercially available, and they were used as received unless otherwise indicated. Tri (ethylene glycol) monomethyl ether (Aldrich, 95%) was purified by vacuum distillation. Dioxane (Aldrich, 99%) was distilled twice: the first time over sodium hydroxide and the second time over sodium. Benzene (Merck) was freshly distilled prior to use. Dichloromethane (Merck, 99.5%) was purified by distillation over  $\text{CaCl}_2$ . Triethylamine (Fluka, 98%) was distilled over sodium hydroxide. 4-Hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPOL) (Aldrich, 98%) was used as received. 2,2'-Azobisisobutyronitrile, AIBN, (Fluka, 98%) was recrystallized from methanol, and dried under high vacuum at room temperature.

### 2.2. Synthesis of the monomer

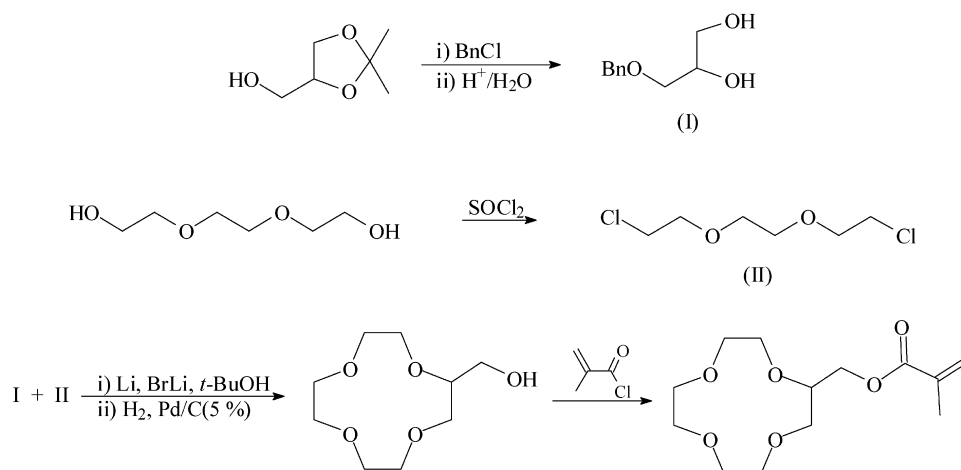
The synthetic route followed to prepare the 1,4,7,10-tetraoxacyclododecan-2-ylmethyl methacrylate is depicted in Scheme 1. To obtain the monomer, it was necessary to prepare different intermediates, which were synthesized according to the following procedures:

### 2.3. Intermediates

**2,2-Dimethyl-4-benzyloxymethyl-1,3-dioxolan.** 100 g (0.76 mol) of 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolan (Aldrich, 98%), 98 g (0.77 mol) of benzyl chloride, 9.1 g (0.04 mol) of benzyltriethylammonium chloride and 400 mL of dichloromethane were cooled to  $0^\circ\text{C}$  in a 500 mL round bottom flask fitted with a mechanical stirrer and a condenser. Then, a freshly prepared solution of 120 g (3.0 mol) of NaOH in 120 mL of distilled water were added drop wise to the reaction vessel under vigorous stirring. After that, the cooling was discontinued and the reaction proceeded further for 12 h. Subsequently, 200 mL of dichloromethane was added to the reaction mixture, and the organic layer was washed thoroughly with water, dried with anhydrous sodium sulfate, filtered off, and the solvent removed by rotary vacuum distillation. The crude yellowish liquid was purified by vacuum distillation ( $90^\circ\text{C}$ , 0.1 mm Hg) rendering 138 g (83%) of pure colorless 2,2-dimethyl-4-benzyloxymethyl-1,3-dioxolan.

**3-Benzoyloxymethyl-1,2-propanediol.** 100 g (0.45 mol) of 2,2-dimethyl-4-benzyloxymethyl-1,3-dioxolan, 100 mL of distilled water and 30 mL of conc. HCl were mechanically stirred in a 500 mL round-bottomed reaction vessel overnight. After that, anhydrous sodium carbonate was added portion wise until a neutral solution was obtained. Subsequently, 200 mL of dichloromethane were added to the reaction mixture, and the organic layer was dried with anhydrous sodium sulfate, filtered off, and the solvent removed by rotary vacuum distillation. The crude colorless liquid was purified by vacuum distillation ( $145^\circ\text{C}$ , 0.1 mm Hg). Yield 75 g (90%).

**1,8-Dichloro,3-6-dioxaoctane.** 63.0 g (0.42 mol) of tri (ethylene glycol), 77 mL (1.06 mol) of thionyl chloride, 0.1 mL of DMF and 240 mL of dry heptane was heated to reflux for 2 h in a 500 mL round bottom flask fitted with a stirrer and a condenser. Heptane and excess thionyl chloride were removed by distillation, to yield a viscous yellowish



Scheme 1.

oil. The product was vacuum distilled (76 °C, 0.1 mm Hg) to render a pure colorless liquid. Yield: 70.6 g (90%).

**Benzyloxymethyl-12-crown-4.** A 3 L three-necked flask equipped with a reflux condenser, an addition funnel, and a mechanical stirrer was charged with 1500 mL of *t*-butyl alcohol and 4.1 g (0.59 mol) of lithium, while a blanket of dry N<sub>2</sub> was maintained over the mixture. The system was heated to reflux and the temperature was maintained for one hour. After that, at reflux temperature, 50 g (0.27 mol) of 3-benzoyloxy-1,2-propanediol were added drop wise, and the solution became heterogeneous and cloudy. Then, a mixture of 23.4 g (0.27 mol) of anhydrous LiBr and 51.4 g (0.27 mol) of 1,8-dichloro,3-6-dioxaoctane was added all at once to the heterogeneous solution. The mixture was refluxed and stirred for a further 16 days, until dichloride disappearance upon gas chromatography analysis. Then, the heating was discontinued and the solvent was removed by distillation. After that, 100 mL of water were added to the crude residue, and the product was extracted with diethyl ether. The organic layer was washed with water, dried with anhydrous sodium sulfate, filtered off, and the diethylether removed by rotary vacuum distillation. The resulting liquid was purified by flash column chromatography using ethyl acetate/hexane (1:1) as mobile phase and silicagel as stationary phase, rendering a colorless liquid product. Yield: 72 g (90%).

**Hydroxymethyl-12-crown-4.** Benzyloxymethyl-12-crown-4 (44 g, 0.15 mol) was dissolved in absolute ethanol (200 mL) in a hydrogenation vessel, and palladium (5%) over activated carbon (0.7 g) was added. The reactor was purged with hydrogen several times, heated to 50 °C and charged with hydrogen at 5 atm and stirred. Several charges of hydrogen were consumed until pressure remained constant for 1 h. The catalyst was filtered off and the solvent was removed by rotary evaporation under reduced pressure, resulting a colorless liquid that was vacuum distilled (115 °C,  $1 \times 10^{-4}$  mm Hg). Yield of hydroxymethyl-12-crown-4 was quantitative.

**1,4,7,10-Tetraoxacyclododecan-2-ylmethyl methacrylate.** This monomer was prepared by conventional reaction of the hydroxymethyl-12-crown-4 with methacrylic chloride in ether solution and triethylamine as absorbent of the hydrogen chloride evolved. To achieve high purity, the product was purified twice by flash column chromatography using ethyl acetate/hexane (1:1) as mobile phase and silicagel as stationary phase, rendering a colorless liquid product. Yield: 28 g (75%).

For analyses of intermediates and monomer see Table 1.

#### 2.4. Techniques

The NMR spectra of polymers were recorded on a Varian INOVA 400 spectrometer operating at 399.92 MHz (<sup>1</sup>H) and 100.57 MHz (<sup>13</sup>C), using deuterated chloroform as solvent and tetramethylsilane (TMS) as internal standard.

The purity of monomers was analyzed by gas chroma-

Table 1  
Microanalysis of intermediates and monomer

Compound	Analysis	
	C (%)	H (%)
2,2-Dimethyl-4-benzyloxymethyl-1,3-dioxolan	Calc.	70.24 8.16
	Found	70.02 7.98
3-Benzyloxymethyl-1,2-propanediol	Calc.	65.91 7.74
	Found	65.81 7.71
1,8-Dichloro,3-6-dioxaoctane	Calc.	38.52 6.47
	Found	38.30 6.59
Benzyloxymethyl-12-crown-4	Calc.	64.84 8.16
	Found	65.01 7.97
Hydroxymethyl-12-crown-4	Calc.	52.41 8.80
	Found	52.22 8.53
1,4,7,10-Tetraoxacyclododecan-2-ylmethyl Methacrylate	Calc.	56.92 8.08
	Found	57.09 7.88

tography with mass spectrometric detection (GC/MS 5890 Series II Hewlett–Packard apparatus equipped with a Hewlett–Packard HP1 capillary column) and by high performance liquid chromatography (HPLC WATERS PUMP Model 510 fitted with a Waters Nova-Pak C18 3.9 × 150 mm column operating at 1 mL/min with a UV Waters 486 tunable absorbance detector).

The thermal properties of the polymer were determined calorimetrically with a Perkin–Elmer Pyris I calorimeter at a heating rate of 10 °C min<sup>-1</sup>.

The Analysis Service of the SCAI of the Universidad de Burgos carried out microanalyses.

A Varian GEMINI 200 NMR spectrometer with temperature controlled at ±0.05 °C was used to control the changes in monomer concentration during the polymerization reactions. In NMR experiments, both deuterated benzene and dioxane were used as solvents and TMS as internal standard.

The concentrations of the radical species in the polymerization reactions were determined by EPR spectroscopy. The spectra were recorded on bulk, benzene and dioxane solutions of the monomers at 0.1 M initiator concentrations in 3 mm diameter quartz tubes at temperatures in the range 50–75 °C by using a Bruker ESP 300 spectrometer. The conditions to register the spectra were: microwave frequency, 9.5 GHz; modulation frequency, 100 kHz; modulation amplitude, 3 G; conversion time, 40 ms; time constant, 655 ms; sweep time, 42 s; power, 6.32 mW; receiver gain  $3 \times 10^5$ ; scan number, 5.

#### 2.5. Polymerizations

Bulk, dioxane and benzene solutions radical polymerizations of the monomer were carried out at temperatures between 50 and 75 °C, using AIBN as initiator. The monomer concentration in all the solution polymerizations was 1 mol L<sup>-1</sup>, whereas the AIBN concentration was 0.1 mol L<sup>-1</sup>. In the bulk NMR and EPR experiments the AIBN concentration was 0.1 mol L<sup>-1</sup>. An example of one

of these reactions is the following: 0.082 g of AIBN and 1.37 g of CR4MA were solved in deuterated dioxane in a flask of 5 mL, 0.75 mL of this solution were introduced in a 5 mm NMR tube, previous elimination of oxygen by bubbling nitrogen into the solution. The reaction was carried out at 60 °C up to 75% of conversion after 58 min. The kinetics of polymerization were followed by measuring changes in the monomer concentrations by NMR spectroscopy. The area changes in the resonance signals corresponding to the methylene protons of the double bond of the methacrylic residue that appear at 5.6 and 6.1 ppm from TMS were used to determine the variation of monomer concentration.

Some examples of the changes with time in monomer concentration, measured by NMR spectroscopy, are shown in Fig. 1 for the polymerization of CR4MA at different temperatures.

## 2.6. Characterization of the polymer

The tacticity of the polymers was determined by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, using an Inova 400 spectrometer, deuterated chloroform as solvent and TMS as internal standard. The  $^{13}\text{C}$  spectrum of the polymer PCR4MA with the corresponding assignment of the resonance signals is shown in Fig. 2. The splitting into well resolved peaks in the resonance of quaternary carbons of the main chain, the  $\alpha$   $\text{CH}_3$  and the  $\text{C}=\text{O}$  carbon of the polymer was observed. Three resonance signals appear for each carbon, except for the  $\text{C}=\text{O}$  that presents greater sensitivity to the stereochemical configuration. Following classical assignment in other methacrylic polymers [10–12], the resonance signals were attributed to different tactic triads and pentads (in the

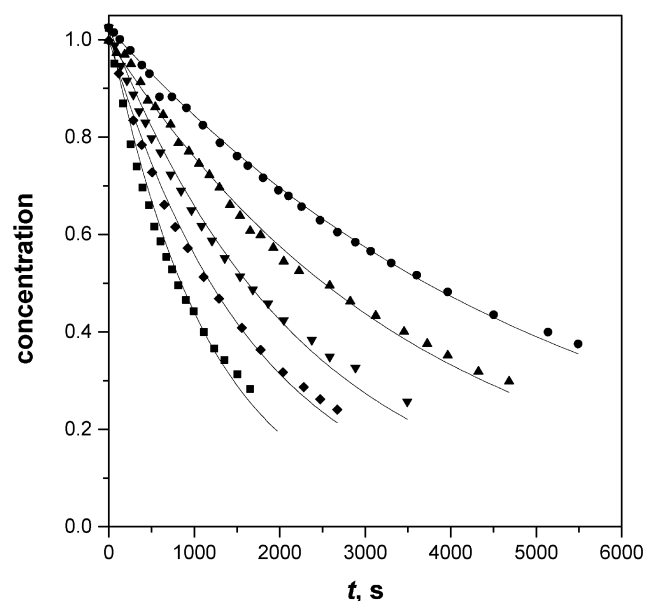


Fig. 1. Variation of the monomer concentration vs. time for the radical polymerization of CR4MA in dioxane solution at 70 (■), 65 (◆), 60 (▼), 55 (▲) and 50 °C (●). ( $[M_0] = 1 \text{ mol L}^{-1}$ ,  $[I_0] = 0.1 \text{ mol L}^{-1}$ ).

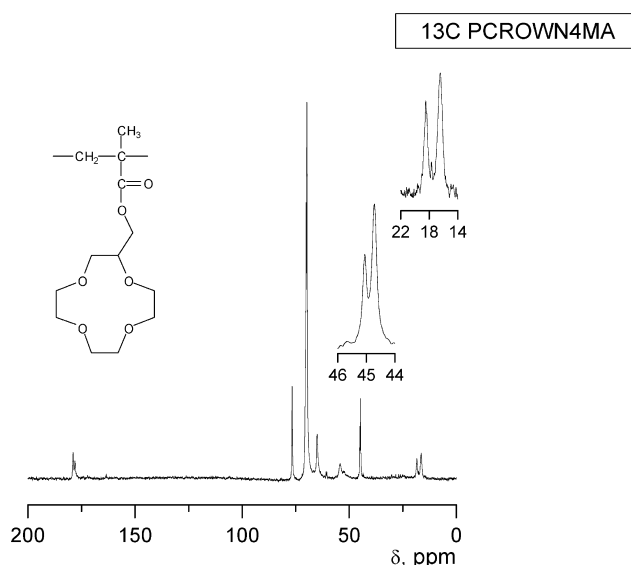


Fig. 2.  $^{13}\text{C}$  NMR spectrum of PCR4MA.

case of the carbonylic carbon), from which the molar fractions of different configurations were calculated. An average molar fraction of syndiotactic dyads of  $0.83 \pm 0.05$  was obtained, and its comparison with the values of the triad and pentad units indicates Bernoullian stereochemical control [13]. The predominance of syndiotactic sequences over isotactic is similar to that found for other methacrylic polymers prepared by radical polymerization.

The value of the calorimetric glass transition temperatures ( $T_g$ ) of the polymer was determined at a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . The value of  $T_g$ , taken at the onset of the separation of the endotherm from the baseline, was  $35 \text{ }^\circ\text{C}$ , whereas the  $T_g$  of the corresponding open chain poly(methacrylate) [poly(tetraethyleneglycol monoethyl ether) methacrylate] [2] was significantly lower,  $-48 \text{ }^\circ\text{C}$ , what remarks the influence of the linear or circular pendant chain on intra molecular interactions.

## 3. Results and discussion

### 3.1. Kinetics of polymerization

The data of radical polymerization kinetics are currently analyzed by using Eq. (1), which is straightforwardly derived from the classical radical polymerization scheme by assuming equal initiation and termination rates,

$$\frac{-d[M]}{dt} = k_p \left( \frac{2fk_d[I]}{\langle k_t \rangle} \right)^{1/2} [M] \quad (1)$$

Here  $k_d$  is the rate constant for initiator decomposition,  $k_p$  and  $\langle k_t \rangle$  are the overall averages of propagation ( $k_p$  is considered to be practically independent of the chain length) and termination rate constants, respectively.  $[M_0]$  and  $[M]$  are the initial and instantaneous concentrations of monomer, respectively,  $[I_0]$  is the initial concentration of initiator, and

$f$  is the efficiency of the initiator. Eq. (1) is valid provided that the parameters involved  $f$ ,  $k_p$  and  $\langle k_t \rangle$  remain constant during all the reaction.

From the slopes at zero time of the experimental variation of  $[M]$  with time and by using the averaged values of  $k_d$  for AIBN reported in the literature [14–17], the values of the rate parameter  $(2f)^{1/2}k_p/\langle k_t \rangle^{1/2}$  at different temperatures were determined and the results appear in Table 2.

The values of  $(2f)^{1/2}k_p/\langle k_t \rangle^{1/2}$  for the crown monomer are very high, exceeding almost two fold those corresponding to their open chain methacrylates homologues [1,2]. Thus the polymerization rate for this monomer resembles the values observed in the polymerization of functional hydrophilic monomers such as 2-hydroxyethylmethacrylate (HEMA) [18] and 2,3-dihydroxypropylmethacrylate [19], although for these last monomers this behavior may be attributed to other causes.

### 3.2. Kinetic parameters $k_p$ and $\langle k_t \rangle f$

The polymerization rate in radical polymerizations is dependent on  $k_p$  and  $\langle k_t \rangle$ . At first glance it seems that, at least in methacrylic monomers, the effect of the termination rate coefficients must be much more important than the propagation rate itself, as it was observed in the polymerization of methacrylic monomers that incorporate different groups in the ester residue [1,2,4,19–21]. Therefore, to know the real influence of the monomer chemical structure on the kinetics of polymerization, it is necessary to determine the absolute values of  $k_p$  and  $\langle k_t \rangle$ , at least at the beginning of the polymerization reactions.

The EPR spectra of the polymer radicals, registered at different monomer conversions in the bulk and solution polymerizations, show a similar spectral pattern that may be assigned to a 13-lines spectrum, as can be seen in the examples shown in Figs. 3 and 4. These spectra can be adequately simulated by using two hyperfine coupling for the methylene protons of the radical and one for the corresponding methyl proton as indicated elsewhere for other methacrylic radicals [1,2,4,22–27]. The best hyperfine couplings necessary for the simulation of the 13 lines spectra were 22.4 for the methyl protons and 14.7 and 8.1 G

Table 2

Kinetic constants (averaged values of three experiments) for the polymerization of CR4MA in 1 M dioxane and benzene solution. The last column lists the values of  $k_d$  used for the calculations and the values in parentheses correspond to the polymerization in benzene solution

$T$ (°C)	$(2f)^{1/2}k_p/\langle k_t \rangle^{1/2}$ (L <sup>1/2</sup> mol <sup>-1/2</sup> s <sup>-1/2</sup> )	$k_p$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$\langle k_t \rangle f \times 10^{-6}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$k_d \times 10^6$ (s <sup>-1</sup> )
70	0.48 <sub>0</sub> (0.48 <sub>1</sub> )	821 (910)	5.9 (7.2)	36.5
65	0.464 (0.46 <sub>6</sub> )	770 (661)	5.5 (4.0)	18.6
60	0.45 <sub>6</sub> (0.45 <sub>6</sub> )	586 (587)	3.3 (3.3)	9.1
55	0.44 <sub>4</sub> (0.42 <sub>7</sub> )	501 (344)	2.5 (1.3)	4.5
50	0.42 <sub>7</sub> (0.41 <sub>6</sub> )	262 (265)	0.7 (0.8)	2.2

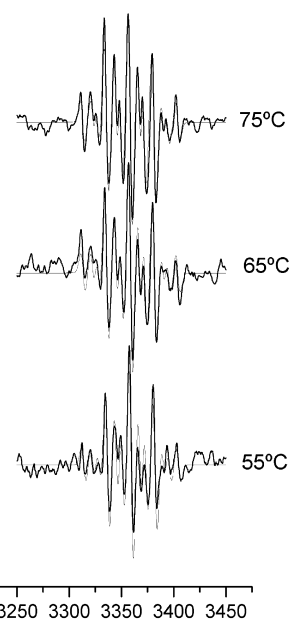


Fig. 3. Simulated and experimental EPR spectra of the radicals corresponding to the solution polymerizations of CR4MA at 55, 65 y 75 °C. The more intense lines correspond to the registered spectra.

for each proton of the methylene group. For the simulations, the program Winsim [28] was utilized.

A qualitative idea of what occurs in these polymerization reactions can be obtained by simple observation of the spectra. In solution polymerization of the monomer, the shape and intensities of the spectral signals remain almost invariable with monomer conversion and appreciable changes were not observed even at very high conversions (>90%). The intensities of the spectral signals do not change or even decrease, presumably as a consequence of the decrease in the value of the efficiency factor [1], due to the monomer concentration decrease. This effect must be

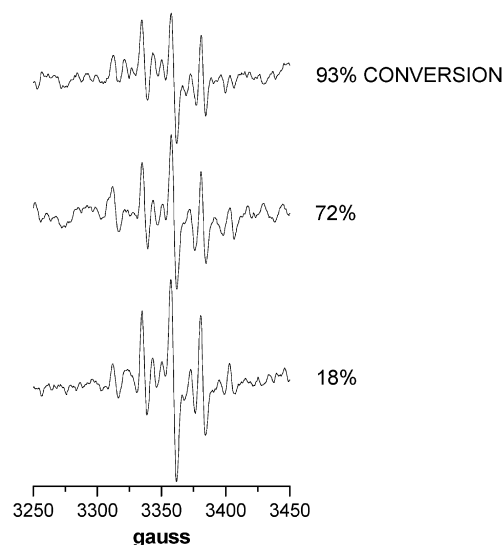


Fig. 4. Changes with conversion of the EPR spectral intensity for the bulk polymerization of CR4MA at 70 °C.

more important than the expected decrease in  $\langle k_t \rangle$  with conversion that tends to increase the radical concentration. On the other hand, the 13 lines spectrum does not evolve to the 9 lines spectrum, characteristic of the polymer radicals observed in other polymerizations of methacrylic monomers at relatively high conversions.

In bulk polymerizations, similar results were obtained, although, a slight increase in radical concentration, as it is shown below, was observed up to relatively low conversions after which the radical concentration decreases. Fig. 5 shows a comparative example of the changes with conversion in the EPR spectral pattern of different macroradicals belonging to the polymerization of the homologous open chain methacrylic monomers TEMA and TTEMA, and CR4MA. At increasing conversions, a very marked increase in the intensities of the signals belonging to the monomer with lower number of oxyethylene units can be seen, whereas in the others the intensity of all the signals diminishes.

To quantify the radical concentration, the double integration of the current spectra of the polymer CR4MA radicals, was carried out in the usual manner as indicated elsewhere [1,20,22] and compared with that corresponding to the EPR spectrum of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as a standard. Up to very high conversions, the radical concentrations slightly decrease with conversion or remain almost unchanged in solution polymerization. In bulk polymerizations, confirming the qualitative results indicated above, the radical concentration slightly increases during the first steps of the reaction and then diminishes as it is shown in Fig. 6.

The behavior shown in Fig. 7 for the bulk polymerization of CR4MA is similar to that observed in the polymerization of some of its open chain homologous methacrylates [1,2] whereas different to that found in the polymerization of monomers where a marked gel effect takes place, such as methyl methacrylate (MMA), where the radical concentration increases until a maximum radical concentration is attained and after that remains

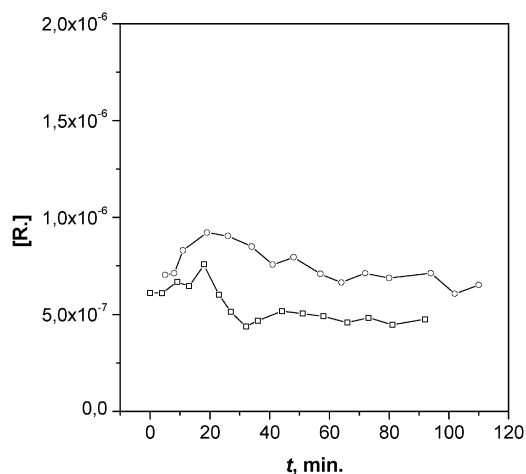


Fig. 6. Variation of the radical concentration with the reaction time in the bulk (○) and solution (□) ( $[M_0] = 1 \text{ mol L}^{-1}$ ) polymerizations of CR4MA at 50 °C.  $[I_0] = 0.1 \text{ mol L}^{-1}$ .

practically invariable due to the trapping of the radicals. The results indicated above on the time dependence of the radical concentration suggest that in the bulk polymerization of CR4MA, the gel effect is inappreciable, as occurs in the monomers of the oxyethylene series in which  $n$  is  $> 3$ , where it was observed that the higher the flexibility of the macroradicals in the reaction medium, the lower the possibility that the autoacceleration phenomena takes place [1,2].

In order to calculate the absolute values of the termination rate coefficients, it would be necessary to determine the real value of the efficiency factor at different conversions. As it was shown elsewhere [1], the values of  $f$  are changing during all the reaction and we consider more appropriate to give the values of the ratio  $\langle k_t \rangle / f$  in place of  $\langle k_t \rangle$ , given the difficulties involved in its determination.

Values of  $\langle k_t \rangle / f$  and  $k_p$  were obtained by measuring the stationary concentration of free radicals and from the polymerization rates by using the approximate Eqs. (2)

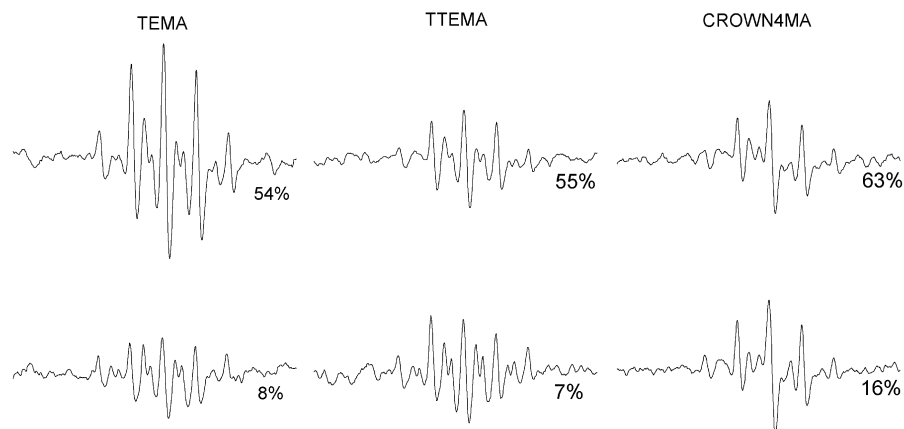


Fig. 5. Comparative changes with conversion of the EPR spectral intensity for the bulk polymerizations of CR4MA, TEMA and TTEMA at 70 °C.

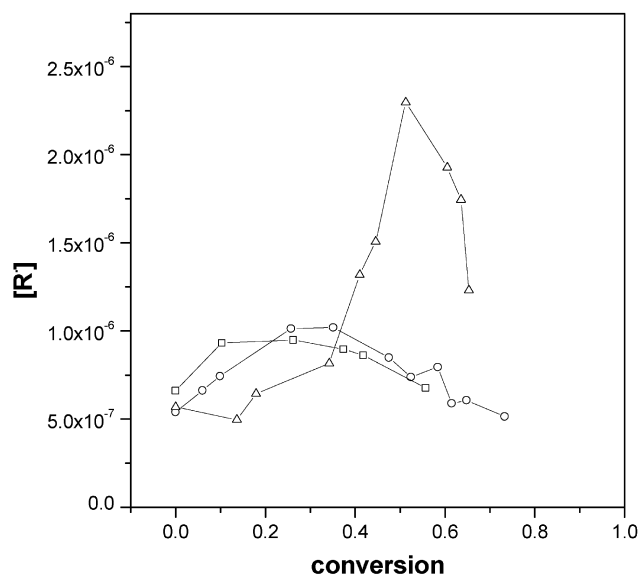


Fig. 7. Variation of the radical concentration with the monomer conversion in the bulk polymerizations of CR4MA (○), TEMA (◇) and TTEMA (□) at 50 °C.  $[I_0] = 0.1 \text{ mol L}^{-1}$ .

and (3), as it was indicated elsewhere [1,2]

$$\frac{\langle k_t \rangle}{f} = \frac{2k_d[I]}{\left( \sum_{i=1}^{\infty} [R_i] \right)^2} \quad (2)$$

and

$$k_p = - \frac{1}{\sum_{i=1}^{\infty} [R_i]} \frac{d \ln[M]}{dt} \quad (3)$$

where  $[R_i]$  is the concentration of growing radicals of chain length  $i$ .

The results obtained for  $k_p$  and  $\langle k_t \rangle/f$  at the beginning of the polymerization reactions at the different temperatures for the CR4MA monomer are shown in Table 2. These results indicate that the increase in the polymerization rate of the studied monomer may be attributed to higher values of  $k_p$  in comparison with those reported for the polymerization of MMA [29] and of the open chain monomers [1,2], all them measured by using EPR techniques. On the other hand, the values of  $\langle k_t \rangle$  are lower in comparison to those reported for the polymerization of MMA [29] and of EEMA and DEMA [1], but relatively similar to those corresponding to the higher members of the series TEMA, TTEMA [2] and so on. In this last series, it is indicated that the longer the lateral oxyethylene chain, the lower the  $\langle k_t \rangle$  values, as occurs in the polymerization of alkyl methacrylates [30] where a similar behaviour was observed longtime ago by Burnett et al. [30], as well as North and Reed [30] and Plate and Ponomarenko [30] which reported changes of two orders of magnitude in  $\langle k_t \rangle$  on going from methyl to cetyl methacrylate.

Due to the high changes in  $\langle k_t \rangle$  observed in acrylic and

methacrylic monomers of different ester length, these results can not be attributed to the viscosity of the reaction medium, and it was concluded that the observed differences were due to lower segmental diffusion in macroradicals with higher number of methylene groups and, therefore, translational diffusion is not the rate determining step.

Along the time many different models [30] have tried to explain the mechanisms involved in bimolecular termination reactions that take into account different variables such as chain flexibility, polymer coil size, influence of solvent, chain-length dependence, etc. Most of them consider the segmental diffusion as the rate determining step, although models in favor of translational diffusion have been given by others [30].

In any case, the results of  $\langle k_t \rangle/f$  for the open chain oxyethylene methacrylates may be adequately explained at low conversions by analogy with those obtained for alkyl methacrylates, applying the same arguments indicated above. In the case of the CR4MA, the comparison with other monomers, even with those belonging to the family of oxyethylene methacrylates is complex. However, one possible explanation may equally come from its intrinsic segmental and/or translational diffusion in such a way that its values might be approximately equivalent to those corresponding to the TTEMA macroradicals. Obviously, two macroradicals from two different monomers would be considered as equivalent in the sense of bimolecular termination reactions if the conditions of equal translational and segmental mobility were accomplished. Then it is not risky to affirm that only the dimensions of the random coils and the segmental mobility control the termination reaction. It therefore seems that, at least at the beginning of the polymerization reaction the degree of freedom for the motion of the polymer chain ends must be of extraordinary importance, probably much more than the translational diffusion itself. Our results as well as those obtained for alkyl methacrylates confirm this idea given by Mahabadi [31]. If we assume that two macroradical polymer coils must first come into contact by center of mass diffusion and that after a segmental reorientation must occur to bring the two radicals in close proximity, then the accessibility of both radicals is of capital importance. The conformational possibilities of the chain ends, considering only the substituents linked to the tertiary radicals, increase greatly with the number of bonds in the lateral chains and, thus, the higher this number is, the lower the probability of radical-radical encounters what must originate a decrease in the value of  $\langle k_t \rangle$ . As in a qualitative manner the flexibility of polymeric chains may be expressed by their glass transition temperatures, and taking into account the experimental results obtained for the polymerization of alkyl and oxyethylene methacrylates, it is not surprising that the values of  $\langle k_t \rangle$  decrease the lower the  $T_g$  of the corresponding polymers. The  $T_g$  value of the PCR4MA polymer is intermediate between that corresponding to its homologous open chain polymers PTTEMA and the PMMA polymer. By

using a similar reasoning we can argue that an intermediate value of  $\langle k_t \rangle$  should be obtained, what is not the case, indicating that only in homologous series it seems possible to establish a correlation between flexibility and  $\langle k_t \rangle$  because other factors influence the termination reaction. However, preliminary results corresponding to the polymerization of the crown5 methacrylate, which forms a polymer less flexible than the PCR4MA, have shown that its  $\langle k_t \rangle$  values are higher than those corresponding to CR4MA, in agreement with the statements postulated above. Work is in progress trying to establish a correlation between partition function or conformational entropy of the lateral chain and  $\langle k_t \rangle$  for homologous series of methacrylates.

On the other hand, when the values of  $\langle k_t \rangle/f$  are graphically represented (Fig. 8) as a function of the monomer conversion for the bulk polymerization of CR4MA and of the monomers of the oxyethylene methacrylates series, apparently two behaviors are observed. For the three first members of the series, the values of  $\langle k_t \rangle/f$  greatly diminish with conversion from the beginning of the reaction up to a given conversion, after which it increases. The minimum value of  $\langle k_t \rangle/f$  that is attained is at least one order of magnitude lower than the initial one and the most important changes in the value of this ratio occurs for the monomer of  $n = 1$ . In the case of the polymerization of CR4MA and of the monomers in which  $n$  is  $>3$ , the decrease of  $\langle k_t \rangle/f$  is very low or negligible, although it also increases over given conversions, which are lower than those observed for the other monomers.

By considering that even during the first steps of the polymerization reaction, the termination reaction is controlled by diffusion [30] and that, therefore, the viscosity of

the reaction medium plays a very important role, it is difficult to understand the different behaviour of  $\langle k_t \rangle/f$  with conversion for the indicated monomers. A possible explanation to these findings may be that in the latter polymerizations (monomers with low number of bonds in the lateral chain) segmental diffusion controls the termination reaction at the beginning of the reaction, but over very low conversions it is the translational diffusion the controlling factor. On the contrary in the former polymerizations,  $\langle k_t \rangle/f$  is little affected by conversion because the control is by segmental diffusion. The increase in  $\langle k_t \rangle/f$  observed in both kinds of polymerizations at medium/high conversions may be attributed to the decrease of  $f$  with conversion.

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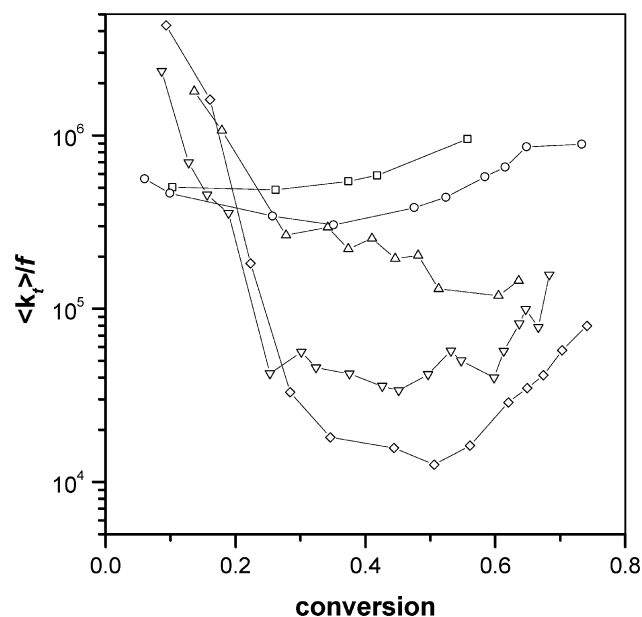


Fig. 8. Experimental variation of  $\langle k_t \rangle/f$  vs. conversion in the bulk polymerizations of CR4MA (○) and of the methacrylic monomers EEMA (◇), DEMA (▽), TEMA (△) and TTEMA (□) at 50 °C.  $[I_0] = 0.1 \text{ mol L}^{-1}$ .



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