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The photoinitiation of MMA polymerization in the presence of iron complexes

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Abstract

The photoinitiated polymerization of methyl methacrylate (MMA) by Fe(III) complexes was studied in aqueous and organic solvents. Although $[Fe(bpy)_3]^{3+}$ and $[Fe(DMSO)_6]^{3+}$ initiate the polymerization in the presence and absence of co-initiators, polymerization was also observed just dissolving $FeCl_3$ in the solvents. The complexes $[Fe(CH_3OH)_6]^{3+}$ and $[Fe(MMA)_6]^{3+}$ initiated the polymerization when irradiated in the visible LMCT band. The photoinitiation by both complexes proceeds by different mechanisms due to the different binding of MMA and methanol to the central atom in the complex. It was found that the methanol complex is more effective in producing initiating radicals than the MMA complex. A good agreement is observed between the experimental reaction rates and those calculated assuming different effectiveness for both complexes.

Keywords: Photoinitiation; MMA; Iron complexes

1. Introduction

In the last years, many attempts have been made to initiate the polymerization of vinyl monomers using inorganic photoinitiators [1–9]. Many of these studies involved the use of complexes of Ru [1,2], Cu [10], Co [11,12] etc. Some authors also reported the photoinitiation of vinyl polymerization using Fe(III) like oxalate [13] and bipy-complexes [14,15]. In most of these cases the use of co-initiators like amines was also involved. Only for systems containing Ru complexes a more thorough insight in the initiation mechanism was done. Here, the excited central metal accepts an electron from the co-initiator, generating a free radical. In the case of Co complexes containing the azide ligand there seems to be a direct reduction of the ligand which is expelled form the complex as the $N_3^{\bullet}$ radical [12]. The main interest for these studies resides in the possibility of irradiating the LMCT or MLCT bands of the complexes, which generally present a very appropriate large absorption band in the visible region [16].

Iron complexes (like $[Fe(bpy)_3]^{3+}$) have been reported to be effective in photoinitiating the polymerization of methyl methacrylate (MMA) in the presence of amines [14,15], due to its LMCT band which extends from the near UV to the visible region. The Fe(III) ion in the excited complex is reduced by the bipyridine, which in turn reacts with the amine generating the initiating radical. On the other hand, previous studies indicate that the mechanism of the photopolymerization in aqueous solution proceeded by a radical mechanism in which the Fe(III), present as the hexaaquo complex, oxidizes water to form $OH^{\bullet}$. This radical then initiates the polymerization which occurred by the well-known addition mechanism [17].

In this paper, we revisited the photopolymerization of MMA by Fe(III), analyzing different systems involving Fe(III) complexes. Specifically, we want to present new results on the Fe(III) photoinitiated polymerization of MMA in organic solvents.

2. Experimental

2.1. Chemicals

Hexaaquo iron(III) chloride, $FeCl_3{\cdot}6H_2O$ (Across Organics, 99%) and bipyridine (bipy, Aldrich, 99+%) were used as received. MMA (Fluka, 99%) was distilled to an ice bath under reduced pressure in the presence of hydroquinone, washed twice with 5% NaOH in water and dried over $CaCl_2$. Triethylamine (TEA, Fluka, 99.5%) was vacuum-distilled before use.

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2.2. *Iron complexes*

The iron(III) complexes $[\mathrm{Fe(DMSO)_6}](\mathrm{ClO_4})_3$ and $[\mathrm{Fe(bpy)_3}](\mathrm{ClO_4})_3$ were synthesized using freshly prepared $\mathrm{Fe(ClO_4)_3 \cdot 10H_2O}$. In the first case, DMSO was added dropwise until the precipitation of green-yellowish crystals, which were filtered and vacuum-dried [18]. To obtain the bipyridine complex, $[\mathrm{Fe(DMSO)_6}](\mathrm{ClO_4})_3$ was mixed with bipyridine in a 1:3 proportion [19].

2.3. *Photopolymerization procedure*

The light-induced polymerization of MMA in the presence of the Fe(III) containing photoinitiator systems was conducted in a dilatometer [20–23]. The solution was thoroughly deoxygenated by bubbling oxygen-free nitrogen. The dilatometer consisted of two capillaries (internal diameter 0.18 cm) attached to a cylindrical reaction vessel (internal diameter 2.2 cm, volume 8 ml), which was placed in a constant temperature bath (30.00 ± 0.01 °C) in front of the irradiation source. Irradiation light was obtained from a 200 W Hg(Xe) lamp in an Oriel Universal Arc Lamp source. Depending on the system studied, a 430 nm cut-off filter or a 370 ± 10 nm bandpass filter were placed between the lamp and the reaction cell.

The polymerization rates (R_p) were calculated using

$$R_p = \frac{\Delta v}{Ftf}[\mathrm{MMA}]\ (\mathrm{mol\,l^{-1}\,s^{-1}}) \qquad (1)$$

where Δv is the contraction in volume in the capillary (calculated from the variation in a cathetometer) at time t; f the volume fraction of MMA monomer in the solution; F the volume contraction related to the densities of polymer and monomer in solution $[F = (d_p - d_m)/d_p]$, and [MMA] corresponds to the monomer molar concentration. Conversion percentages were calculated by multiplying the polymerization rates by the irradiation time and dividing by the concentration of pure monomer (9.1 M).

After irradiation, the polymers (poly-MMA) were precipitated by addition of cold methanol, washed, filtered, dried in a desiccator and characterized by gel permeation chromatography on Shimadzu LC-10 AD HPLC chromatograph with a refraction index detector. A combination of two Styragel HR4 and one Styragel HR5 columns were used and the results MW were calculated comparing with a poly-MMA kit of the American Polymer Standards Corp.

Actinometry was performed using ferrioxalate/phenanthroline salt. The quantum efficiency of this actinometer is ∼1.0 at wavelengths below 405 nm [24]. Milli-Q purified water, methanol (Mallinckrodt), and dimethylsulfoxide (DMSO, Fluka, 99.5%) were used as solvents. UV-Vis spectra were recorded with a Hitachi U-2000 spectrophotometer.

3. Results and discussion

3.1. *$[\mathrm{Fe(bpy)_3}]^{3+}$ and $[\mathrm{Fe(DMSO)_6}]^{3+}$ complexes*

In order to investigate the detailed mechanism of the photoinitiation of MMA by $[\mathrm{Fe(bpy)_3}]^{3+}$ in the presence of TEA, the polymerization of this system was undertaken trying, initially, to use irradiation light limited to the visible or near UV region. As can be seen from the spectrum in Fig. 1, there is a LMCT band which extends over that region. Previous authors [14,15] used the entire light emitted by a Xe-arc lamp, which would also excite the UV bands at ∼230 nm. The use of a 430 nm filter should avoid the excitation of the higher energy metal-centered LF transitions, as well as the

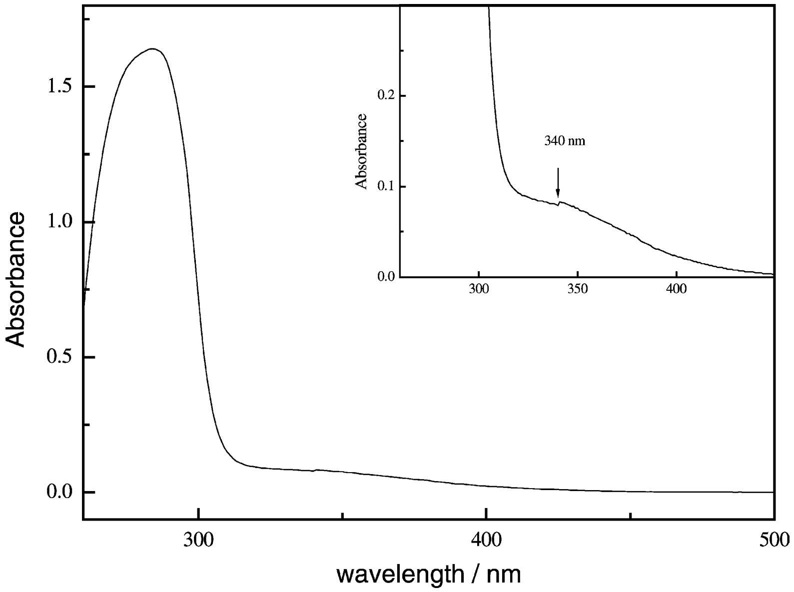

Fig. 1. Spectrum of $[\mathrm{Fe(bpy)_3}]^{3+}$ in DMSO. Inset shows the blow-up of the region corresponding to the LMCT band.

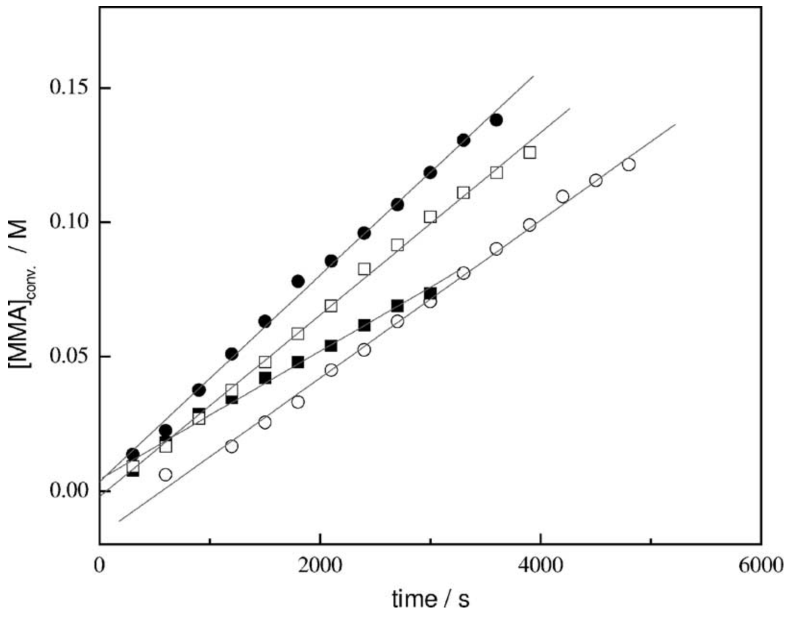

Fig. 2. Conversion percentages of MMA in methanol in the presence of $FeCl_3$ (2.5×10^{-4} M). MMA concentrations are 4.0 M (■), 6.0 M (□), 8.0 M (●), and pure MMA (○).

ππ* ligand transition (at ~285 nm and lower). Under these conditions, and in the presence of the co-initiator TEA, a polymerization rate constant of 5.6×10^{-6} M s^{-1} was obtained.

The use of a bipy 0.01 M solution as a filter for the ligand absorption, placed between the irradiation source and the polymerizing system had no noticeable effect, the constant now being 6.3×10^{-6} M s^{-1}. These results were practically identical with those obtained using a 298 nm cut-off filter. The results obtained, summarized in Table 1, show that there is no point in trying to initiate the polymerization of MMA using a $[Fe(bpy)_3]^{3+}$ system, as similar results can be obtained just using a Fe(III) ion salt by itself.

Furthermore, qualitative experiments showed that the complex $[Fe(DMSO)_6]^{3+}$ also was effective in photoinitiating the polymerization of MMA in the presence or absence of TEA. Therefore, there is no reason for using Fe(III) complexes with organic ligands to initiate the polymerization of MMA. It seems to be sufficient to just dissolve the $FeCl_3$ in an appropriate solvent to obtain an effective polymerization photoinitiator without the need of any co-initiator.

Table 1
Photoinitiated polymerization of MMA by $[Fe(bpy)_3]^{3+}$ systems

Initiation system	Filters	R_p (M s^{-1})
$[Fe(bpy)_3]^{3+}$/TEA[a]	No filter	++
$[Fe(bpy)_3]^{3+}$/TEA	<298 nm	7.7×10^{-6}
$[Fe(bpy)_3]^{3+}$/TEA	<430 nm	5.6×10^{-6}
$[Fe(bpy)_3]^{3+}$/TEA	<430 nm + bipy 0.01 M	6.3×10^{-6}
$[Fe(bpy)_3]^{3+}$	No filter	++
$[Fe(DMSO)_6]^{3+}$	No filter	++

++ Observed polymerization.

[a] Refs. [14,15].

3.2. $[Fe(MeOH)_6]^{3+}$ and $[Fe(MMA)_6]^{3+}$ complexes

3.2.1. Photopolymerization of MMA

Fig. 2 shows some of the results corresponding to the photopolymerization of MMA initiated in the presence of $FeCl_3$ in methanolic solution using a 370 (±10) nm bandpass filter. As can be seen, there is the expected increase in the rate and in the quantum yield when the MMA concentration is increased, except for the reaction performed in pure MMA. The obtained rate constants, as well as the polymerization quantum yields are shown in Table 2.

The quantum yields follow the same trend than the polymerization rates. Their values (~200) are consistent with the values of the molecular masses of the MMA polymers, implying that there is no substantial chain transfer during the process and that almost all excited iron complexes generate an initiating radical.

Table 2
Polymerization rates, conversion percentages, molecular weights and quantum yields for the photopolymerization of MMA in methanol in the presence of $FeCl_3 = 2.5 \times 10^{-4}$ M, using a 370 nm filter

[MMA] (M)	R_p (M s^{-1})	Conversion (%)	M_w (g/mol)	ϕ_p (mol einstein^{-1})
4.0	2.38×10^{-5}	7.4	262000	172
5.0	2.67×10^{-5}	9.0	385000	192
6.0	3.39×10^{-5}	12.3	421000	244
7.0	3.68×10^{-5}	12.6	494000	265
8.0	3.84×10^{-5}	13.8	497000	276
8.5	3.95×10^{-5}	14.2		284
8.9	3.99×10^{-5}	14.4		288
9.1[a]	2.93×10^{-5}	12.0		211

[a] Pure MMA.

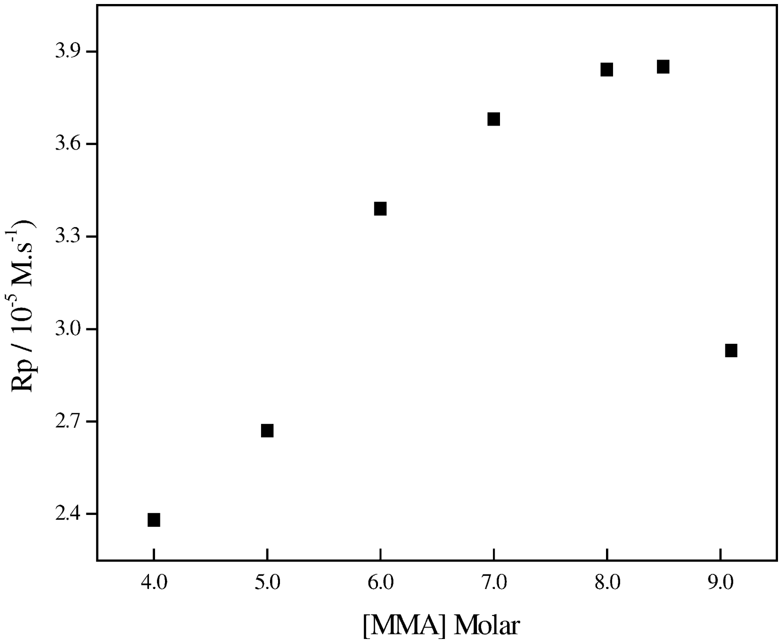

Fig. 3. Photopolymerization rates for different MMA concentrations in methanol.

Changes in the amount of $FeCl_3$ did not change significantly the quantum yields, which varied from 210 to 240 (15%) for initiator concentrations changing form 1.5×10^{-4} to 5.0×10^{-4} M (230%). On the other hand, using a 348 nm cut-off filter the polymerization rates were about twice as fast, possibly due to the larger amount of absorbed light as compared to the experiments using the 370 nm band filter.

The difference between the polymerization rate (and the other parameters shown in Table 1) is better visualized in Fig. 3. This effect can be attributed to the formation of iron complexes with different ligands, which might initiate the polymerization through different mechanisms.

3.2.2. Properties of the iron complexes

The photopolymerization of MMA in the presence of Fe(III) ion was possible because most of the ferric complexes with hexacoordinated organic compounds have typical LMCT absorption bands which extend into the visible region [25–29]. The spectrum of the iron complex in methanol (shown in Fig. 4) shows two well-defined bands

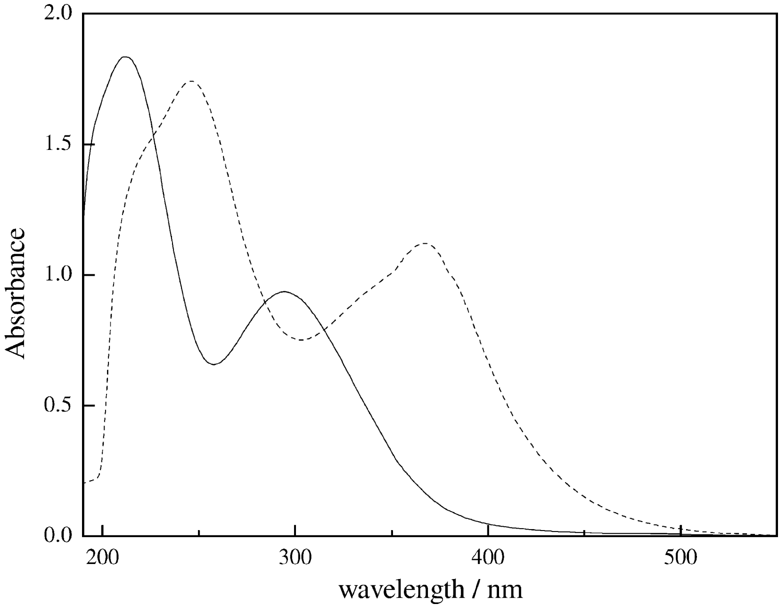

Fig. 4. Spectra of iron(III) chloride in water and in methanol. $[FeCl_3] = 2.5 \times 10^{-4}$ M.

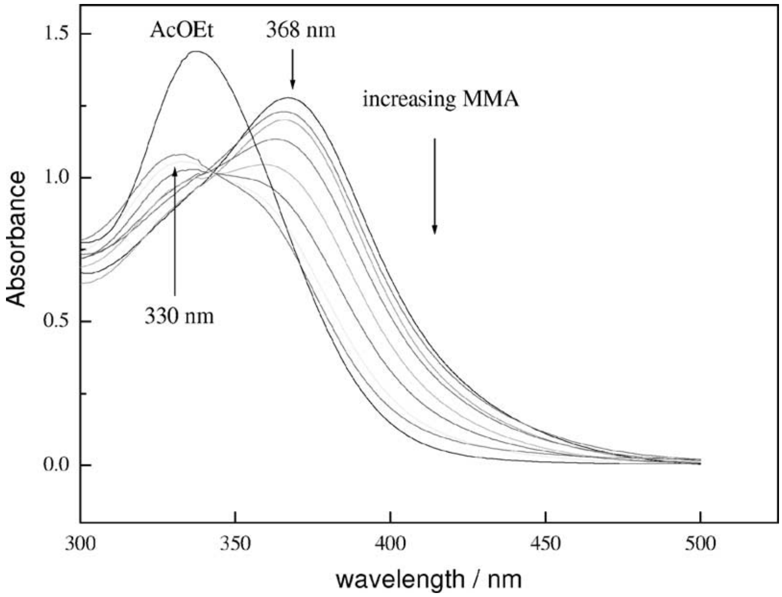

Fig. 5. Spectra of iron(III) chloride in methanol/MMA mixtures and ethyl acetate (AcOEt). $[FeCl_3] = 2.5 \times 10^{-4}$ M.

around 250 and 360 nm. These bands are displaced towards the red by about 30 and 60 nm, respectively, from those corresponding to the iron salt in water. Therefore, it can be assumed that the species present in the methanol solution is no longer the $[Fe(H_2O)_6]^{3+}$ complex, but the complex were the water-ligand molecules were replaced by methanol, i.e., $[Fe(CH_3OH)_6]^{3+}$. On the other hand, when increasing the amounts of MMA are added to a methanolic solution of $FeCl_3$ a new peak develops at approximately 330 nm (see Fig. 5), which can be assigned to the LMCT band of the iron complexed to MMA. The LMCT peak of the iron complex with ethyl acetate is observed at a similar same wavelength (∼337 nm), confirming that the bond between the central metal ion and the MMA and AcOEt ligands are of the same type.

This might be the reason for the fall in the polymerization rate, which could be initiated with different efficiencies by the excitation of iron complexes with different ligands. In the case of iron complexed with methanol, the mechanism will follow a mechanism similar to that reported for the photopolymerization in water. The central iron ion in the excited complex will accept an electron from one of the methanol ligands, which will then be ejected as a free radical that can initiate the polymerization process [30]

$$[Fe^{III}(CH_3OH)_6]^{3+} + h\nu \rightarrow {}^*[Fe^{III}(CH_3OH)_6]^{3+} \quad (2)$$

$$^*[Fe^{III}(CH_3OH)_6]^{3+} \rightarrow [Fe^{II}(CH_3O^{+\bullet}H)(CH_3OH)_5]^{3+} \quad (3)$$

$$[Fe^{II}(CH_3O^{\bullet}H)(CH_3OH)_5]^{3+} \rightarrow [Fe^{II}(CH_3OH)_5]^{2+} + CH_3O^{+\bullet}H \quad (4)$$

$$CH_3O^{+\bullet}H + CH_3OH \rightarrow CH_2OH^{\bullet} + CH_3OH_2{}^{+} \quad (5)$$

On the other hand, when the ligands are MMA molecules, the reaction will proceed via the direct oxidation of the monomer to yield an initiating cation radical

$$[Fe^{III}(MMA)]^{3+} + h\nu \rightarrow {}^*[Fe^{III}(MMA)_6]^{3+} \quad (6)$$

$$^*[Fe^{III}(CH_2{=}C(CH_3)COOCH_3)(MMA)_6]^{3+} \rightarrow [Fe^{II}(CH_2{}^{+}{-}C^{\bullet}(CH_3)COOCH_3)(MMA)_5]^{3+} \quad (7)$$

$$[Fe^{II}(CH_2{}^{+}{-}C^{\bullet}(CH_3)COOCH_3)(MMA)_5]^{3+} \rightarrow [Fe^{II}(MMA)_5]^{2+} + CH_2{}^{+}{-}C^{\bullet}(CH_3)COOCH_3 \quad (8)$$

Assuming two initiation pathways with different efficiencies and using molar fractions for the solvent, the overall rate constant can be written as

$$\mathbf{k}_p = {}^A\mathbf{k}_p x_A + {}^B\mathbf{k}_p x_B \quad (9)$$

where $\mathbf{k}_p$ stands for the experimental overall polymerization rate constant obtained by dividing the polymerization rates by monomer concentration. ${}^A\mathbf{k}_p$ and ${}^B\mathbf{k}_p$ are the overall rate constants for the initiation by methanol and MMA complexes and include the true propagation rate constant k_p, the termination rate constant k_t; the amount of absorbed light I_a; and the efficiency of initiating radical production η. The superscripts A and B refer to methanol and MMA, respectively.

$$\mathbf{k}_p = k_p \left(\frac{I_a \eta}{k_t}\right)^{1/2} \quad (10)$$

Fig. 6 shows the representation of the experimental overall rate constant together with the calculated values using the equation above. The parameters used for ${}^A\mathbf{k}_p$ and ${}^B\mathbf{k}_p$ were 0.66×10^{-5} and 0.37×10^{-5}, respectively. A reasonable agreement between both sets of points can be observed,

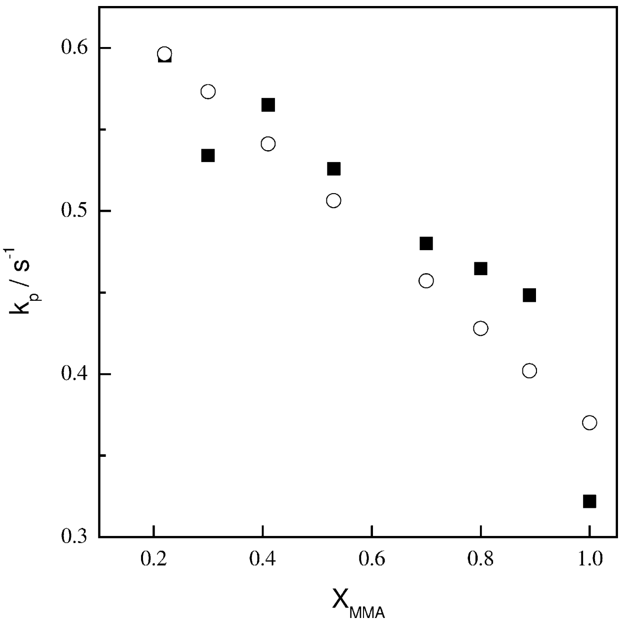

Fig. 6. Comparison between the calculated (○) and experimental (■) overall rate constants for the photoinitiated polymerization of MMA in methanol in the presence of $FeCl_3$.

confirming the same trend. Therefore, it seems reasonable to assume that the decrease in the polymerization rate when the amount of MMA in the reaction mixture is increased is due basically to the lower radical production efficiency of the $[Fe(III)(MMA)]^{3+}$ complex. The difference should not be ascribed to the lower absorption of the MMA-complex as the quantum yields also follow the same trend.

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