

# ELECTRON SPIN RESONANCE STUDIES IN ACRYLAMIDE POLYMERIZATION USING RHENIUM COMPLEXES AS PHOTSENSITIZERS

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## RESUMEN

La Acrilamida puede ser polimerizada usando nuevos sistemas catalizadores. Estos son basados en complejos de renio como fotosensibilizadores usando trietilamina (TEA). La espectroscopía de Resonancia de Espín Electrónica fue utilizada para la detección de especies radicalarias las cuales fueron formadas en el proceso de polimerización. Además, se emplearon las técnicas de "Spin Trapping" para confirmar la presencia del radical acrilamida. Cálculos AM1 e INDO fueron utilizados para calcular las constantes hiperfinas teóricas de radical acrilamida. Los resultados están de acuerdo con un proceso cíclico en el cual la TEA es un agente donador de electrones que reacciona con el complejo de renio excitado. En este sistema, se postula la presencia de la especie excitada  $[\text{Re(II)(CO)}_3\text{L}^-(\text{CF}_3\text{SO}_3)]^*$  en la polimerización catalítica de acrilamida.

**PALABRAS CLAVES:** ESR, polimerización, acrilamida, complejos de renio, "Spin Trapping".

## SUMMARY

Acrylamide can be polymerized using new catalytic systems. These are based on rhenium complexes as photosensitizers with triethylamine (TEA). Electron Spin Resonance (ESR) was used for the detection of radicals species which were formed in the polymerization process. Also, we used Spin Trapping to confirm the presence of the acrylamide radical. AM1 and INDO calculations were performed to obtain the optimized geometries and theoretical hyperfine constants of the acrylamide radical. Our results agree with a cyclic process where triethylamine is an electron donor agent reacting with an excited rhenium complex. In this system, we postulate the  $[\text{Re(II)(CO)}_3\text{L}^-(\text{CF}_3\text{SO}_3)]^*$  as the activated species in the catalytic polymerization of acrylamide.

**KEYWORD:** ESR, polymerization, acrylamide, Re complexes, Spin Trapping.

## INTRODUCTION

The use of radical species as initiating agents in the polymerization of acrylamide have allowed high conversions and variable molecular sizes to be attained. These species can be generated by thermal decomposition of some compounds or by means of a sequence of reactions. Free radical generation using UV-vis light and an appropriate photosensitizer is an alternative system to obtain faster polymerization.

ESR has been employed in the study and characterization of polymerization reactions providing the identification of the radicals and their corresponding kinetics and mechanism<sup>1-3</sup>.

Kuzaya et al. reported a mechanistic study on the mechanochemical polymerization of acrylamide. The structure of the free radical formed was identified as equivalent to a polymer-chain propagating radical<sup>1</sup>.

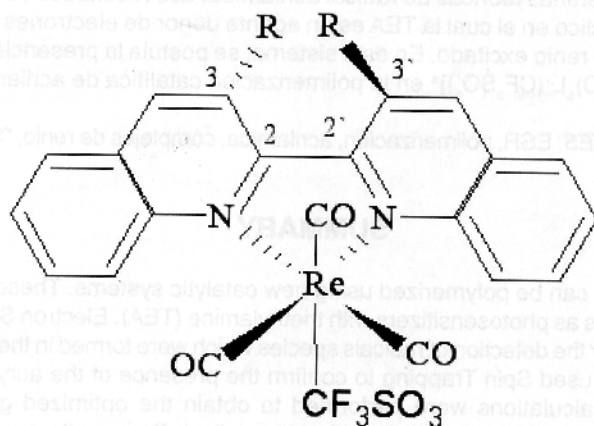
Rhenium complexes have been assessed as promoters of the thermal polymerization of styrene<sup>4,5</sup>. Also, these compounds and their derivatives have been tested in the polymerization of acrylamide by a photolytic process<sup>6</sup>.

The present work shows the application of the ESR and Spin Trapping techniques in the characterization of intermediate radicals involved in acrylamide polymerization, using novel rhenium complex catalysts as photosensitizers. To estimate the theoretical hyperfine constants INDO-SCF calculations were carried out. The geometry of acrylamide in both spin paired and free radical forms was fully optimized using AM1 methodology. Finally, we have postulated a possible mechanism involving free radical species.

## EXPERIMENTAL

### Materials

Photopolymerizations of acrylamide (Aldrich) were developed using systems based on  $\text{Re}(\text{CO})_3\text{L}(\text{CF}_3\text{SO}_3)$  complexes as photosensitizers (Figure 1). The synthesis of these compounds has been reported previously<sup>7-10</sup>.



**Fig. 1.** Rhenium complexes employed as photosensitizing agents: 2,2'-biquinoline, (R = -H); 3,3'-dimethyl-2,2'-biquinoline, (R = -CH<sub>3</sub>); 3,3'-dimethylene-2,2'-biquinoline, (R = -CH<sub>2</sub>-CH<sub>2</sub>- bridged) and 3,3'-trimethylene-2,2'-biquinoline, (R = -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- bridged).

### ESR Spectral Measurements

The monomer and the rhenium complex were dissolved in THF (2.0 mol/L and  $5 \times 10^{-4}$  mol/L respectively). Later, triethylamine was added until a concentration of 0.5 mol/L was reached. The system was purged with N<sub>2</sub> during 10 minutes and then transferred to an ESR cell and irradiated with a 300 VA Ultra-Vilatux UV-vis lamp (230 V, E27) emitting around 400 nm while the ESR spectra were recorded. The ESR spectra were obtained at 19°C-20°C in the X band (9.78 GHz) using a Bruker ECS 106

spectrometer, a rectangular cavity and a 50 KHz modulated field. PBN (Sigma) was dissolved in THF and added to the rhenium complex-acrylamide-TEA system to give a final concentration of 50 mmol/L.

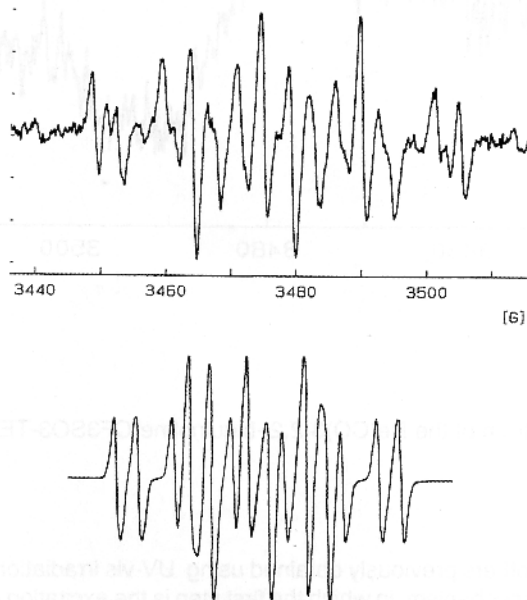
### Theoretical Calculations

Full geometry optimizations of acrylamide in spin-paired and free radical forms were carried out by AM1<sup>11</sup>. INDO calculations were done employing the open shell UHF option.

## RESULTS AND DISCUSSION

Preliminary results have shown that the system  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3$ -acrylamide-TEA dissolved in a water-THF mixture, efficiently promotes acrylamide polymerization when it is irradiated in the metal ligand charge transfer region (around 400 nm)<sup>6</sup>. In order to characterize this process, ESR studies were done under the same experimental condition but in an inert atmosphere.

No ESR spectrum could be recorded for the  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3$ -acrylamide-TEA system in the absence of UV-vis radiation. Well resolved spectra were obtained when the UV-vis radiation was applied. (Figure 2). The interpretation of the ESR spectra by mean of simulations led to the determination of the coupling constants for all the magnetic nuclei, confirmed by theoretical calculations.

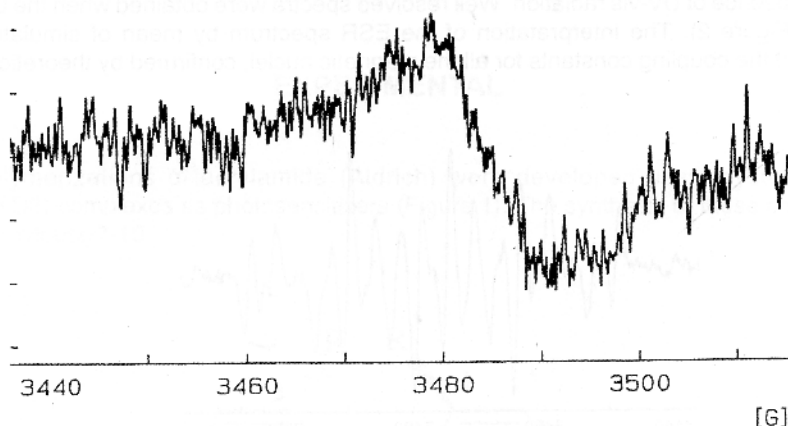


**Fig. 2.** Experimental and simulated ESR spectra of the  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3$ -acrylamide-TEA system.

The ESR spectrum of acrylamide was analyzed and simulated in terms of a triplet from two equivalent hydrogen nuclei ( $a_{\text{H}_2} = 10.00$  G), a triplet due to an amine group nitrogen atom ( $a_{\text{N}} = 7.80$  G) and a doublet from one hydrogen atom ( $a_{\text{H}} = 2.97$  G). INDO calculations were performed in order to obtain the theoretical hyperfine constants, using the geometries from the AM1 calculations. The theoretical hyperfine constants were  $a_{\text{H}_2} = 11.95$  G,  $a_{\text{N}} = 8.3$  G and  $a_{\text{H}} = 3.2$  G. Also, the theoretical calculations indicated a small spin distribution on the amine hydrogens which, however, was not observed in the experimental spectrum. The results are in agreement with the assignment of hyperfine constants.

In order to confirm the type of radical formed, spin trapping studies were conducted. PBN was added to the  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3$ -acrylamide-TEA system. A characteristic ESR spectrum of PBN appeared. The spectrum had six lines with constant values of  $a_N = 14.4 \text{ G}$  and  $a_H = 2.3 \text{ G}$ , a typical of trapping of a carbon centered free radical by PBN.

We also studied different target systems. In the absence or presence of radiation no ESR signals were observed for the  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3/\text{THF}$ , acrylamide/THF or acrylamide-TEA/THF and TEA/THF systems. Also, when the binary system  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3$ -TEA/THF was analyzed without irradiation, free radical species were not observed. However, when this system was irradiated, a broad ESR signal was obtained (Figure 3). Taking this into account, it can be considered as evidence for the involvement of an intermediate rhenium complex species ( $[\text{Re}(\text{I})(\text{CO})_3(2,2'\text{-biquinoline})-(\text{CF}_3\text{SO}_3)]$ ) in the acrylamide polymerization. Similar results were found with all the rhenium complexes used.



**Fig. 3.** Experimental ESR spectrum of the  $\text{Re}(\text{CO})_3(2,2'\text{-biquinoline})\text{CF}_3\text{SO}_3$ -TEA system.

These results, added to others previously obtained using UV-vis irradiation and flash photolysis,<sup>12</sup> allow us to postulate a possible mechanism, in which the first step is the excitation of the rhenium complex ( $[\text{Re}(\text{II})(\text{CO})_3(2,2'\text{-biquinoline})-(\text{CF}_3\text{SO}_3)]^*$ ) followed by its reductive quenching to the  $[\text{Re}(\text{I})(\text{CO})_3(2,2'\text{-biquinoline})-(\text{CF}_3\text{SO}_3)]$  species with the tertiary amine which acts as an electron donor. Finally, this species would be oxidized to the basal state by the monomer generating the acrylamide radical which would initiate the chain propagation process (its structure, observed by ESR, in Figure 2) and the rhenium complexes decay of basal state, closed the cycle of polymerization initiation.

## ACKNOWLEDGMENTS

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