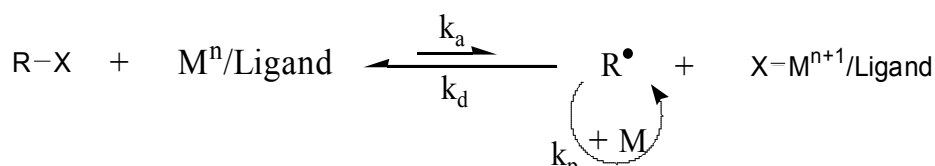


NEW CYCLOMETALATED RU(II) COMPOUND AS A CATALYST FOR ATR POLYMERIZATION OF BUTYLACRYLATE, METHYL METHACRYLATE AND STYRENE: USE AND IMPROVEMENT

Díaz-Camacho F.¹, Le Lagadec. R.², Vera-Graziano. R.¹, Alexandrova. L.¹

¹Instituto de Investigaciones en Materiales, ²Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior s/n, C. U., México, D. F., 04510

Abstract- Metal-catalyzed living radical polymerization (ATRP) has progressed enormously during the last decade to become one of the most efficient methods to prepare polymers with predictable molecular weights and narrow polydispersity. The method has been applied to a wide range of the monomers including styrenes, methacrylates, acrylamides, etc. and the polymerization may be conducted in bulk, solution or emulsion.¹⁻⁶ The key reaction herein is the reversible homolysis of a carbon-halogen bond of an alkyl halide initiator by a metal catalyst (see scheme 1).



Scheme 1.

Introduction

In this process the metal complexes undergo single electron oxidation into a higher state via the abstraction of the halogen from the target species. Thus the metal complexes should be able to receive a halogen and they should be easily oxidized and the oxidized form should be able to be easily reduced to the original state. Until now no general theory exists which can predict the activity of the catalysts, but it is commonly accepted that complexes with lower redox potentials demonstrate higher activity. The catalysts activity in each specific case can be tuned by changing the ligands of the complexes. A number of transition metals have been investigated as catalysts for ATRP, such as Cu, Ru, Fe, Ni, etc. together with a variety of ligands. Among these the Cu and Ru compounds are the most frequently used for this purpose. Cu catalysts are the most extensively studied while for others, the process mechanism is still not so well established.

Recently synthesis and properties of a series of new cyclometalated Ru(II) complexes⁸ have been reported. Some of them have labile ligands and demonstrate relatively low redox potentials. Taking into account all these together with the highly effective and simple synthetic route, we considered that it would be interesting to verify these complexes as catalysts for ATRP. Hereby, we report the application of one of such complexes, [Ru(Phpy)(MeCN)₄]⁺PF₆⁻ (see Fig. 1 for the structure), for the polymerization of butyl acrylate, methyl methacrylate and styrene. It is known that polymerization occurs only in the presence of Lewis acid, such as Al(iOPr)₃.

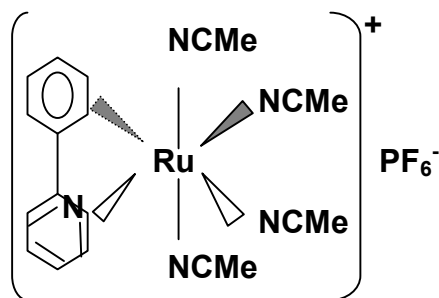


Figure 1

The polymerization rates were very fast in the cases of butyl acrylate and methyl methacrylate, with high conversions (above 60-70%) reached for 40-50 y 80-90 min, respectively at 80°C. The obtained polymers showed poorly controlled molecular weights, especially butyl acrylate, and broad polydispersities (between 2.1 and 2.4). The styrene polymerization was much slower, conversions around 80% were obtained after 6 hours, and were better controlled: a linear dependence of the molecular weights from conversion and polydispersitis less than 1.9 were observed.

However, the control was significantly improved when SnCl_2 was added as a deactivator. A wide range of SnCl_2 concentrations (from 1 to 50% in relation to the Ru(II) complex) were investigated. In general, a better control and longer reaction times were observed at higher SnCl_2 concentrations. A very good linear dependence of the molecular weights from conversion and narrow polydispersities for all polymers were obtained starting from a 20% relative concentration of SnCl_2 . When 50% of SnCl_2 was added, the polymerization was much slower and polymers with polydispersities as narrow as 1.1 were obtained. For example, for butyl acrylate the conversion obtained after 2-3 hours of reaction was about 70-80%, and the molecular weights exhibit a linear behavior with polydispersities between 1.3-1.4. In the case of methyl metacrylate, the conversion reached after 3-4 hours was approximately 50-60% and the polydispersities obtained were under 1.2. Finally, styrene polymerization gave a 60-70% of conversion after 9-10 hours of processing and the polydispersity was as lower as 1.1.

The mechanisms of the polymerization will be discussed.

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