

Polymerization Mechanism of α,α' -bis(Tetrahydrothiopheno)-*p*-xylene Dichloride

Marcela Almassio and Raúl O. Garay

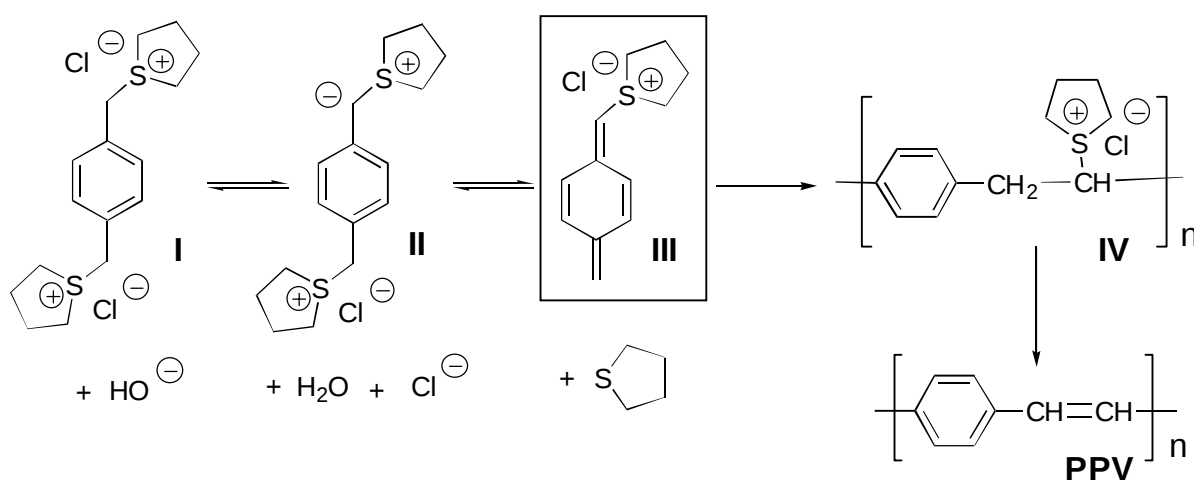
INIQA, Universidad Nacional del Sur, Avenida Alem 1253, 8000 Bahía Blanca, Argentina
Tel/Fax +54 (291)-459-5187, E-mail: rgaray@criba.edu.ar

Abstract: A experimental study was performed regarding the influence of the base nature and solvent on the reactive intermediate concentration in the base-promoted *bissulfonium* salts polymerization. Such polymerization reaction is part of a synthetic procedure used to prepare conjugated polymers. In addition, a theoretical study suggest that a one-electron transfer could be involved in the initiation step.

Keywords: conjugated polymers, poly(phenylene vinylene), precursor route.

Introduction

The interest on poly(*p*-phenylene vinylene)s, PPV, lies on its unique photoconducting, electroactive, and non-linear optical properties. Although there are numerous ways to synthesize PAV's, the route through a precursor polyelectrolyte, **IV**, as show in Scheme 1, yields the highest molecular weight attainable for these systems and allows to cast films of very good optical quality. It is well known that the reactive intermediate **III** is formed *in situ* when the *bissulfonium* salts are treated with a base[1]. However, the polymerization reaction mechanism is still not known in detail, thus radical and anionic mechanisms were proposed; being the first mechanism the most accepted at present [2]. Moreover, the initiator nature and the termination mechanism step are not known.



Scheme 1.

Experimental

The appearance and decay of the intermediate **III** in the reaction mixture was observed through its band in the UV-Vis spectra; $\lambda_{\max}$ 312nm, using water or water:acetonitrile-(1:4) as solvents and a spectrophotometer equipped with temperature controlled sample chambers at 25°C. The molecular modeling was performed with the semiempirical programs PM3 and AM1.

Results and Discussion

The UV-Vis spectroscopy study showed that a decrease in solvent polarity accelerated the formation of the intermediate **III** as well as its decay. We also observed that higher concentrations of the ylid did not affect **III** decay rate. However, **III** decay rate was dependent on base concentration. These results may suggest that the base OH^- could be involved in the polymerization initiation step either as an electron-transfer agent or as polar group that promotes secondary reactions which produce free-radicals [3]. Nevertheless, additional studies are necessary to confirm these assumptions. As a initial step towards this objective, a computational study was carried out in order to determine if the base OH^- can act as an electron-transfer agent. Therefore, the products and reactants heat of formations of the reaction **III** + OH^- was calculated by semiempirical methods. These calculations indicated that the electron-transfer reaction was thermodynamically feasible and that the LUMO(**III**) has a lower energy than the HOMO(OH^-). In addition, the calculations were repeated in the solvent box, water.

Table. Heat of formation (kcal mol^{-1}).

	III	OH	OH	Radical Anion of III	ΔH_R
AM1	187.05	-14.12	0.63	41.08	-131.22
PM3	208.13	-17.52	2.82	63.52	-124.27
AM1*	165.96	-6.89	-12.10	32.13	-139.04

* Heat of formation in water.

Acknowledgments: Financial support for this research was provided by ANPCyT and SGCyT-UNS. M. A. thanks SGCyT-UNS for a fellowship.

References and Notes

1. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. Electroluminescent conjugated polymers-Seeing polymers in a new light. *Angew. Chem. Intern. Ed.* **1998**, *37*, 402.
2. Denton, F. R. III; Lahti, P. M.; Karasz, F. E. *J. Polym. Sci. A.* **1992**, *30*, 2223.
3. Sawyer, D. T.; Roberts, J. L. Hydroxide ion: an effective one-electron reducing agent? *Acc. Chem. Res.* **1988**, *21*, 31.