

# PHOTO-INDUCED CURING OF THYMINE-BASED BIOINSPIRED POLYMERS. A CHEMOMETRIC ANALYSIS

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**Abstract**— The curing process of new materials based on styrene monomers functionalized with thymine and charged ionic groups was studied using UV-vis spectroscopy in combination with chemometric models. The effect of the copolymer molecular weight on the immobilization point was analyzed. The evolution of the curing process of the copolymer (4-vinylbenzyl) thymine (VBT) - vinylbenzyl triethyl ammonium chloride (VBA) involved three species, which absorb in the spectral region analyzed. The contributions of each species to the total signal at each irradiation time were determined, and the kinetic constant of the crosslinking reaction was estimated. The study allowed evaluating the consistency of the chemometric decomposition, obtaining a reasonable correlation between the frequency spectra and the time evolution calculated with the algorithm. The chemometric analysis showed to be a powerful tool to provide complementary information on photo-induced immobilization of VBT-VBA films, which is crucial for developing new environmentally benign materials and new energy-saving methods.

**Keywords**— biopolymers, thymine, curing kinetics, UV-vis spectroscopy, chemometrics.

## I. INTRODUCTION

During the last decades, extensive research has been done to design environmentally benign synthetic polymers containing nucleic acid bases (Takemoto, 1976 and references therein; Inaki, 1992; Blackburn and Davies, 1966; Lamola and Mittal, 1966). In light of bioinspiration, polymers based on a new synthetic monomer, (4-vinylbenzyl) thymine (VBT), were designed to have the ability to photo-crosslink upon irradiation with the short-wavelength ultraviolet (UV) component of sunlight (Cheng *et al.*, 1995; Grasshoff *et al.*, 1995a; Grasshoff *et al.*, 1995b). This process is bioinspired on the photo-dimerization of adjacent thymine pendant groups in DNA under UV irradiation (such as direct sunlight exposure), which disrupts the helical structure of DNA.

The VBT-based photo-polymers have potential applications in a variety of fields ranging from hair care products (Warner *et al.*, 2004) to printed circuit boards and photo-imaging systems, (Grasshoff *et al.*, 1997; Grasshoff *et al.*, 1998; Lloyd-Kinstrand and Warner, 2003; Trakhtenberg *et al.*, 2005) as well as controlled

release systems for pharmaceutical and agricultural use (Saito *et al.*, 2007; Saito and Warner, 2009; Kaur *et al.*, 2011). Several studies related to the synthesis, the curing process, the properties and the applications of thymine-based VBT-vinylbenzyl triethyl ammonium chloride (VBA) polymers had been published (Lamola and Mittal, 1966; Cheng *et al.*, 1995; Grasshoff *et al.*, 1995a; Grasshoff *et al.*, 1995b; Warner *et al.*, 2004; Grasshoff *et al.*, 1997; Grasshoff *et al.*, 1998; Lloyd-Kinstrand and Warner, 2003; Trakhtenberg *et al.*, 2005; Saito *et al.*, 2007; Saito and Warner, 2009; Kaur *et al.*, 2011; El-Hayek, 2004; Kiarie *et al.*, 2005; Barbarini *et al.*, 2010a; Trakhtenberg *et al.*, 2007; Casis *et al.*, 2007; Martino *et al.*, 2008; Barbarini *et al.*, 2010b; Warner *et al.*, 2003; Whitfield *et al.*, 2005). Saito *et al.* (2007, 2009) synthesized a series of micelle-forming block copolymer systems in aqueous solution and showed that guest materials could be encapsulated by hydrogen bonding with the attached thymine in the core. It was found that the enzyme DNA photolyase can “unzip” the crosslinking by catalyzing the reverse photocrosslinking in thymine-containing styrene derivatives (Warner *et al.*, 2003; Whitfield *et al.*, 2005). Martino *et al.* (2008) reported a sensitization study on a family of water-soluble photo-polymers based on thymine, which clearly demonstrated that the presence of sensitizer molecules could promote the photo-dimerization of thymine-containing polymers in the visible range. In Casis *et al.* (2007) the synthesis of VBT-VBA polymers in solution at low temperatures (65°C) was theoretically and experimentally studied. A mathematical model for the free radical copolymerization of VBT and VBA was developed. The model allows predicting the global variables (conversion, composition) and the molecular structure (molecular weight distribution –MWD, chemical composition) of the copolymers along the reaction. Barbarini *et al.* (2010b) investigated the photo-induced UV curing kinetics of VBT-VBA copolymers from the UV absorption spectra measured along the process. The immobilization point, related to the gel point, was determined following the evolution of the absorbance peaks of the copolymer solution after UV irradiation. The kinetics of the crosslinking reaction was estimated from the evolution of thymine concentration before the immobilization point considering additive contributions of VBT and VBA repetitive unit absorbances. A second order kinetics was observed and a significant effect of the film preparation on the degree of crosslinking was