Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: B. M. Ramirez , G. Diaz De Delgado & J. M. Delgado (1992): Synthesis, Characterization and Solid State Reactivity Studies of Mn and Zn Derivatives of 4-Ethenyl Benzoic Acid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 219:1, 163-167

To link to this article: http://dx.doi.org/10.1080/10587259208032130

Mol. Cryst. Liq. Cryst. 1992, Vol. 219, pp. 163–167
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Printed in the United States of America

SYNTHESIS, CHARACTERIZATION AND SOLID STATE REACTIVITY STUDIES OF Mn AND Zn DERIVATIVES OF 4-ETHENYL BENZOIC ACID.

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(Received March 26, 1992)

Abstract Mn and Zn derivatives of 4-ethenyl benzoic acid (eba) were prepared as part of our investigations on the crystal chemistry and solid state reactivity of metal complexes of unsaturated mono and dicarboxylic acids. The complexes were synthetized by reaction in water of the appropriate stoichiometric amounts of the metal carbonate and eba. After filtration, the clear solutions were allowed to evaporate slowly at room temperature to yield crystalline materials. The compounds, before and after exposure to heat or gamma radiation, were characterized by FT-IR and by x-ray diffraction methods. The results are presented in this paper.

Keywords: Thermal polymerization, Solid state Polymerization, 4-Ethenyl benzoic acid, Powder X-ray Diffraction, Gamma Irradiation

INTRODUCTION

The study of the solid state reactivity of α,β-unsaturated carboxylic acids and ketones was initiated with the systematic investigations carried out by Schmidt and collaborators in the early 1960s[1,2,3].

As part of our investigations on the crystal chemistry and solid state reactivity of metal complexes of unsaturated mono and dicarboxylic acids, we have carried out studies on the metal derivatives of 4-ethenyl benzoic acid (eba). Based on the report[4] that eba polymerizes in the solid state upon heating, at 100°C for 15 days, producing a crystalline polymer and that, at 120° C, the product is an amorphous polymer, we decided to follow closely the course of the thermal polymerization of eba by FT-IR, ^{1}H-NMR and ^{13}C-NMR[5]. We extended the study to the metal salts and complexes of eba, even though its potassium salt does not appear to polymerize under the same conditions[4].

EXPERIMENTAL

Synthesis

Metal derivatives of 4-ethenyl benzoic acid [1075-49-6] (eba) were prepared by reaction in water of stoichiometric amounts of the acid (Aldrich, 6.70×10^{-3} mol) and the apropriate metal carbonate. The mixtures were stirred at room temperature for periods of up to two days and were subsequently filtered. The clear solutions were

allowed to evaporate slowly at room temperature to produce crystalline materials. The filtered residues were washed with water and allowed to dry for further analysis.

Characterization

The Mn and Zn ethenyl benzoates were characterized by IR spectra in KBr pellets using a Perkin-Elmer PE-1725X FT-IR spectrophotometer. The extremely low solubility of the Zn complex in common deuterated solvents and the magnetic behavior of the Mn complex did not allow detailed ^{1}H-NMR and ^{13}C-NMR studies.

X-ray powder diffraction patterns, obtained using a Guinier camera (Enraf-Nonius) equiped with a curved Johansson monochromator (λ $CuK_{\alpha 1}$ = 1.54056 Å), were used to identify the presence of unreacted metal carbonate and/or eba in the residues and to follow the course of the reaction. The powder patterns obtained were compared with the patterns reported in the JCPDS Database[6] and with the pattern obtained in the same conditions for the commercially available eba.

Reactivity

A preliminary examination of the thermal behavior of the materials was carried out in a Fisher-Johns Melting Point Apparatus. Small amounts of each material were then placed in Pyrex ampoules sealed under vaccum. Both samples were heated at 240°C.

For the radiation induced experiments, the samples were enclosed in glass vials and exposed to a dose of 5000 Rads from a ^{60}Co source at *Hospital Universitario de Los Andes.*

RESULTS AND DISCUSSION

The reactions of eba and the Zn and Mn carbonates are characterized by high yields of insoluble material mainly composed of the desired ethenyl benzoates with small amounts of unreacted eba, as shown by FT-IR spectra and Guinier powder patterns.

Zn(eba) before and after heating, is insoluble in water and in most common organic solvents. On the other hand, Mn(eba) is soluble in methanol and partially soluble in water and acetone. After heating it is insoluble in methanol.

The IR spectra of the synthesized metal derivatives of eba, Figures 1(a) and 2(a), show very small differences between them. The strong, sharp absorption of the aromatic C=C stretch, observed at 1579 cm^{-1} for Mn(eba) and at 1587 cm^{-1} for Zn(eba), obscures the absorption of the vinyl C=C stretch. The **asymmetric and symmetric stretches** of the carboxylate group appear at 1541 and 1412 cm^{-1} for Mn(eba) and at 1543 and 1419 cm^{-1} for Zn(eba). Other important absorptions appear at 990 and 905 cm^{-1} for Mn(eba) and at 990 and 906 cm^{-1} for Zn(eba). Based on the assignment made by Nyquist[7] of the spectrum of pure eba taken in Nujol mull, these bands may correspond to the $CH{=}CH_2$ twist (991 cm^{-1}) and the ${=}CH_2$ wag (912 cm^{-1}) modes.

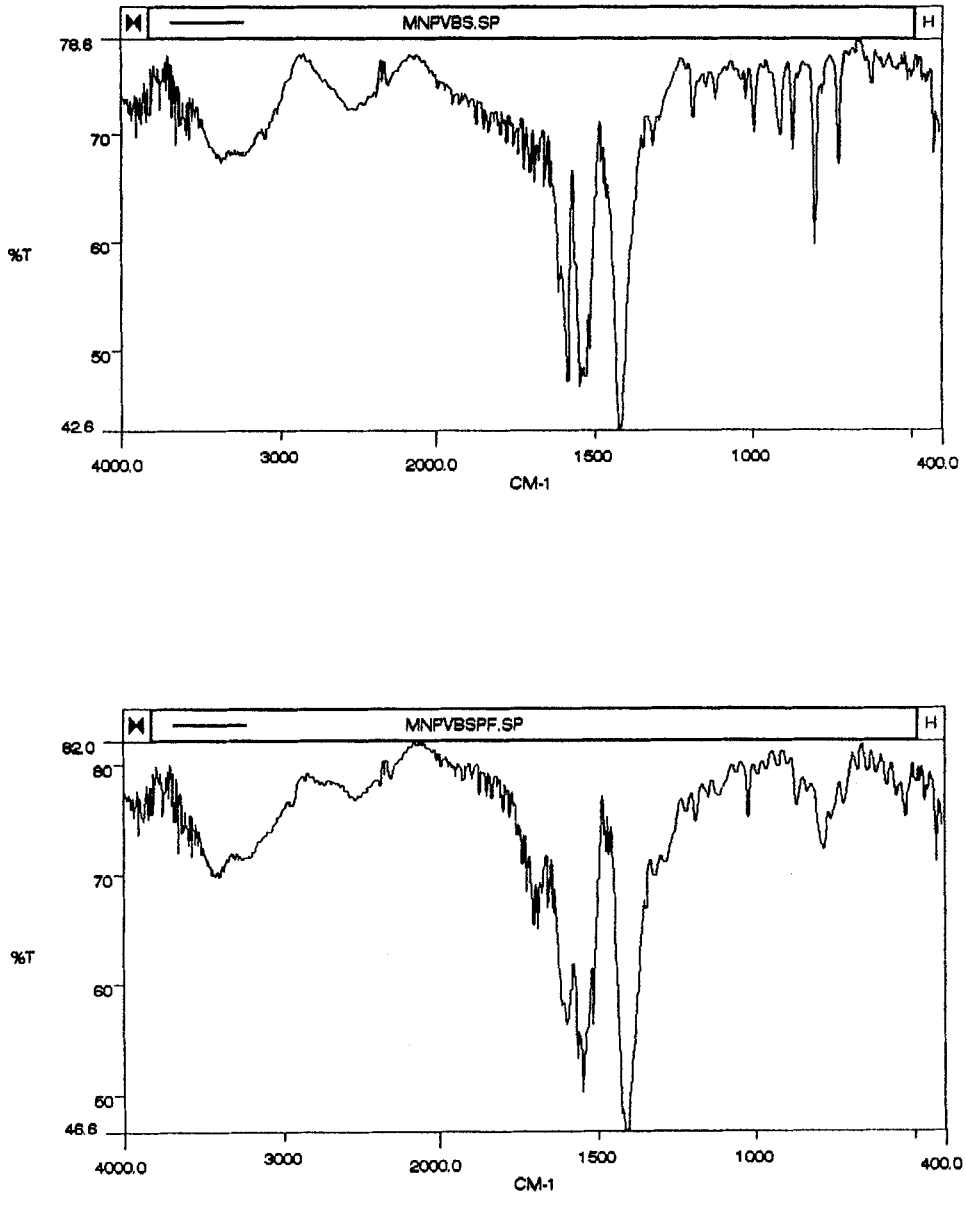

FIGURE 1 FT-IR spectra of Mn(eba) : (a) before treatment, (b) after heating at 240°C.

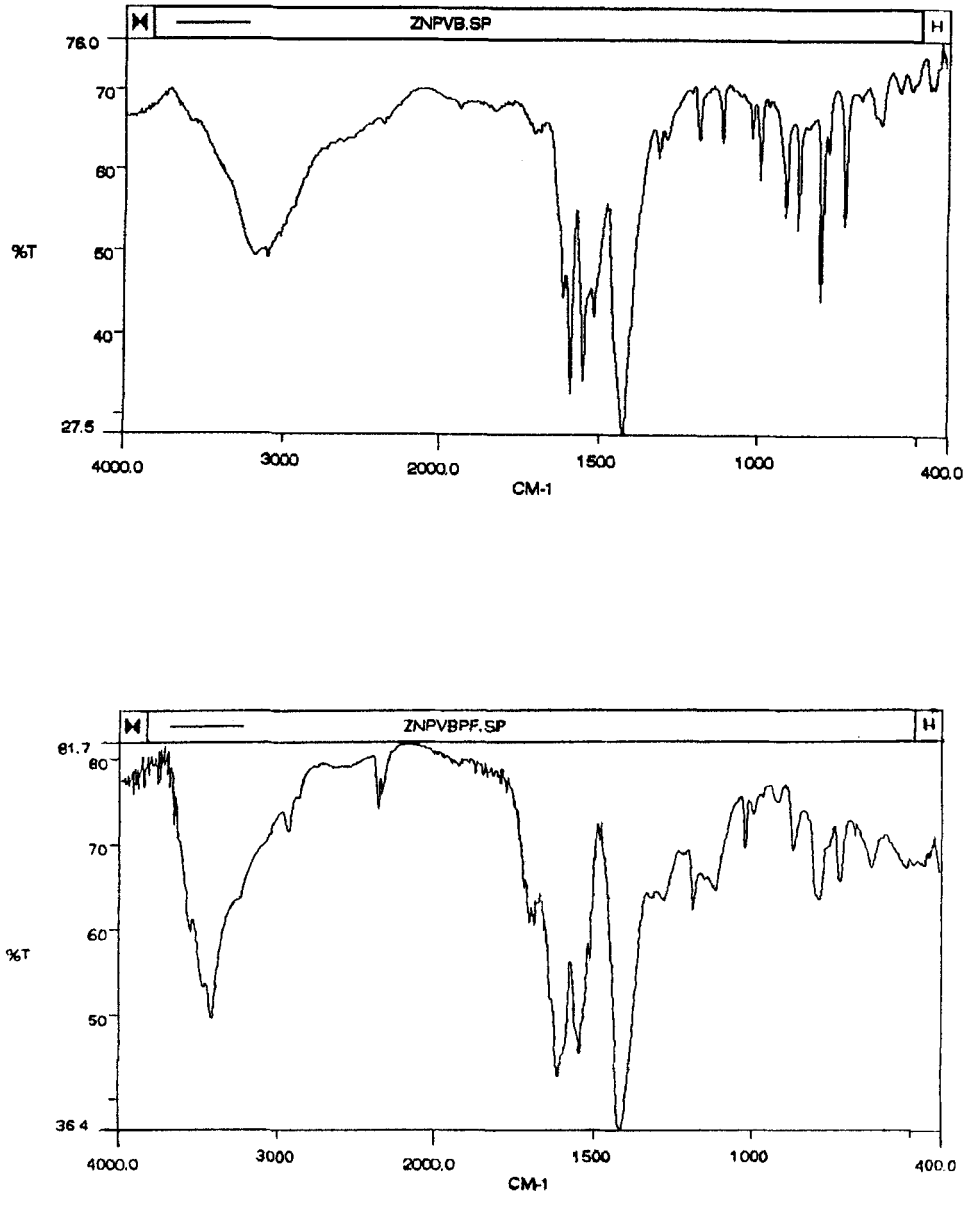

FIGURE 2 FT-IR spectra of Zn(eba) : (a) before treatment, (b) after heating at 240°C.

Upon heating in the melting point apparatus, the soft, colorless crystals of Mn(eba) turned golden-brown at 150°C. Zn(eba), also colorless, turned light yellow at 90°, dark-yellow at 190°C, and brown-yellow at 240°C. Both compounds harden when heated.

According to the IR spectra, Figs. 1(b) and 2(b), the two compounds behave in a similar manner upon heating. A loss of spectral resolution is observed. Since the presence of the C=C stretch is not obvious in the IR spectra, the disappearance of the vinyl absorptions at 990 and 905-906 cm^{-1} is the best indication that reaction has taken place. The x-ray powder patterns show total loss of crystallinity.

After exposure to a low dose of gamma rays (5000 Rads) there are no appreciable changes in the IR spectra and x-ray powder patterns of Mn(eba) and Zn(eba). Heating for 5 days at 60°C of the previously irradiated samples produced a small change in the relative intensities of some absorptions, in particular those of the ring C=C and the asymmetric carboxylate stretches, and the vinyl twist and wag modes for both Mn and Zn ethenylbenzoates. However, neither the x-ray powder patterns nor the solubility changes after exposure to gamma radiation.

Detailed studies of the percent conversion with time and the nature of the products obtained from the thermal reaction of the Mn and Zn complexes are underway. The solid state behavior of other metal derivatives of eba are also being investigated.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support from CDCHT-ULA for research grant C-435-90. Purchase of the Perkin-Elmer PE-1725X FT-IR spectrophotometer was possible through grant F-15 from CONICIT. We thank Mr. L. Ceballos and Mr. O. Trejo for their technical assistance and to Dr. G. D'Lacoste and Mr. A. Cabrera from *Hospital Universitario de los Andes* for their help with the ^{60}Co-irradiation of the samples.

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