

Modifying the kinetics of nanoscale diacetylene polymerization for time-temperature indicator applications

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ABSTRACT

The crystal structure of ethyl and propyl urea substituted diacetylenes are governed by the presence of hydrogen bonding between the urea subunits of adjacent diacetylenes. They present, however, different crystal packing and this results in different reactivity. Alternatively, the use of different solvents for recrystallization provides an important means for modifying polymerizability for time-temperature indicator applications.

Keywords: diacetylene, time-temperature indicator, kinetics

1 INTRODUCTION

Diacetylenes are an important class of molecules that can react in the solid state, by nanoscale processes, to transform a colorless monomer to a highly colored conjugated 1,4-addition polymer (Figure 1). In rare instances, this polymerization reaction is able to convert a large monomer single crystal to a large polymer single crystal having similar structural perfection [1]. Depending upon the monomer molecular structure, the monomer crystal structure obtained by crystallization, and the degree of polymerization, the thermally polymerized monomer is typically blue, black, red, or even metallic.

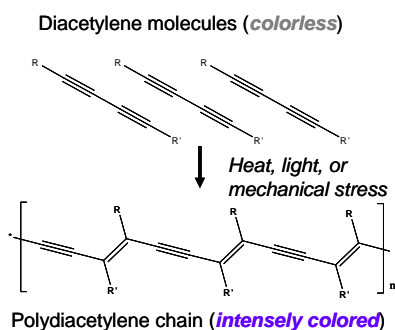


Figure 1. Schematic of the solid-state 1,4-addition polymerization.

The kinetics of polymerization depends upon the associated atomic displacements required for polymerization, which is a function of crystal packing [2]. Such kinetics of color change, for crystalline powders printed as an ink on a label, are matched to the degradation kinetics of important perishable products, like vaccines, to provide time-temperature indications whose color changes integrate the effect of times and temperatures during thermal exposure in the same way that this thermal exposure effects product quality.

According to a non-profit world health organization [3], Temptime time-temperature indicators for vaccines (already sold in several billion quantities), are expected to save 140 thousand lives in a decade – since they indicate when measured thermal abuse is expected to produce an inactive vaccine. The present study describes the crystal structures of selected diacetylene molecules that can be useful for time-temperature indicator applications, and important methods for modifying polymerization kinetics for these applications. Different powder x-ray diffraction patterns, corresponding to different crystal structures, provide clear signatures of higher and lower reactivity phases. The kinetics of polymerization is studied by optical density measurements in the solid state.

2 MATERIALS AND METHODS

The crystal structure of the diacetylenes was studied by single crystal x-ray diffraction collected in a Bruker D8 GADDS general purpose three-circle X-ray diffractometer at 110K. The kinetics of polymerization was studied by several methods. Reflectance measurements as a function of time at three temperatures were used for activation energy calculations. Relative reactivity parameters of all samples were measured at 60°C by determining the evolution of color.

3 RESULTS AND DISCUSSION.

Diacetylenes incorporating the urea functionality, such as 1,6-bis(*n*-alkylurea)-2,4-hexadiyne are interesting candidates for this approach because hydrogen bonding in the direction of the urea moiety provides a predictable lattice parameter of about $\sim 4.6 \text{ \AA}$ —close to the $\sim 4.9 \text{ \AA}$ distance between repeat units along an ideal polydiacetylene chain. [4] The crystal structures of the ethyl and propyl derivatives have been obtained from single crystal x-ray diffraction. A slow evaporation process in 80% ethanol produces needle like crystals of good quality for X-ray diffraction.

The crystal structures of both ethylurea and propylurea di-substituted diacetylenes are characterized by hydrogen bonding between the two urea subunits in adjacent molecules along the *b* crystal axis. This hydrogen bonding constrains the diacetylene units in adjacent molecules into a reactive orientation with a d_1 and γ_1 values of 4.620 \AA and 49.5° for the ethyl, and 4.594 \AA and 47.9° for the propyl substituted diacetylene. These values agree with those for which a reactive orientation for solid-state polymerizations of diacetylenes has been predicted. [5]

There are two main differences between the structures of the ethyl and propyl urea substituted diacetylenes. First, the ethyl substituted structure is triclinic whereas propyl substituted structure is monoclinic, with a screw axis between adjacent layers formed by hydrogen bonding sheets. This causes the hydrogen-bonding network to alternate in direction along the *c* axis with each layer. The second difference is a change in the orientation of the alkyl bonds toward the plane formed by the *b* and *c* axes. This is a result of the odd-even effect of the alkyl substituent of an ethyl *versus* propyl group. The terminal carbon-carbon bond is oriented more parallel to the plane in the propyl substituted diacetylene. This affects the placement of the carbon atoms, being the $\omega-1$ carbon atom closer to the interface in the ethyl substituted diacetylene.

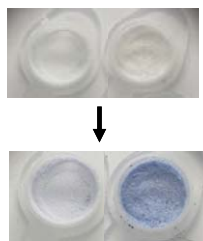


Figure 2. Two different diacetylenic compositions before and after treatment for several hours at 60°C .

As a consequence of these differences in crystal packing the ethyl substituted crystal has a greater calculated density. As a result of the differences in crystal structure, both

compounds present a different solid state reactivity, with measurable differences in the rate of color change. (Figure 2)

Besides the different substituent, for each alkylurea the rate of color change also depends on the crystallization solvent, probably through minor changes in crystal structure. Figure 3 shows the optical density values obtained from reflectance measurements at 37°C and 45°C for the ethyl substituted diacetylene crystallized in different solvents.

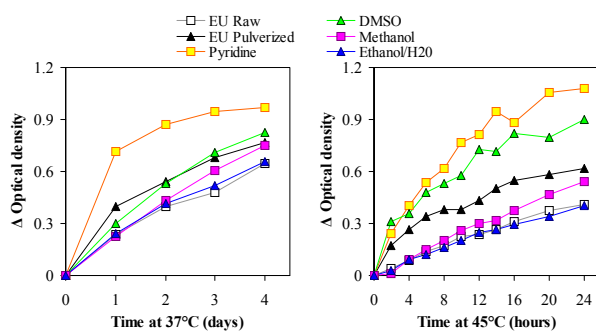


Figure 3. Color change kinetic tests at 37 and 45°C for diacetylene monomer powders.

The reflectance provides the optical density values through equation 1. The activation energy of the process can be derived from the slope of the curves at different temperatures.

$$OD = -\log_{10}(R/100\%) \quad (1)$$

The results suggest that by controlling the crystallization conditions of a reactive diacetylene, the reactivity of the resulting material can be tuned so that it can be used as time-temperature indicator and it matches the reactivity of the product of interest. An enhancement of the reactivity is observed for very fast cooled samples, probably due to the small particle size. A precise establishment of the achieved specific reactivity for each condition is crucial for its use as time-temperature indicator.

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