MALDI-TOF-MS Characterization of Polycyanoacrylate Generated under Acidic Conditions using "Super Glue" or the Cyanoacrylate Fingerprint Fuming Method*

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The cyanoacrylate fuming method is the single most successful technique for developing latent fingerprints on non-porous surfaces. The print to be examined is placed in the vapors of ethyl cyanoacrylate and the monomer reacts with water and other possible fingerprint components deposited in the fingerprint. The primary component of latent fingerprints is sweat, which dries rather quickly leaving a residue of organic compounds comprising the print on the surface. A way to regenerate clean prints that have been aged up to five months has been developed by first exposing the print to acetic acid, and then using the fuming method[1]. Understanding the chemistry of the ethyl cyanoacrylate reaction is a prerequisite for developing an improved process for fingerprint analysis. For this reason, these studies have focused on polymer initiation and propagation mechanisms.

Before we studied the chemistry of fingerprints, we needed a reliable means of assaying their molecular masses, especially because relatively rapid degradation has been shown to occur for polycyanoacrylates in solution ((i.e., during gel permeation chromatography (GPC))[2]. The range of the GPC verifies that the molecular mass seen in the MALDI (matrix assisted laser desorption) samples supports our assumption that in MALDI we are observing the actual spectra and were are not just seeing degradation products (i.e. during laser desorption). To assist in molecular mass characterization, a reference polymer was prepared by mixing ethyl cyanoacrylate with acetic acid and lactic acid in a weighing dish. Lactic acid was included in the reference sample preparation because it is prevalent in sweat. This reference sample was run in GPC. Three fractions were collected for a little over four minutes.

We analyzed fingerprints which were made on a glass surface and processed using the cyanoacrylate fuming method. These prints were of varying age and only some were exposed to acetic acid. A Bruker Reflex II[3] was used to elucidate the mechanism of the cyanoacrylate fuming process from developed latent fingerprint samples. Furthermore, the presence of the acid reduces the molecular mass of the polymer so that the end groups can be identified in the mass spectrometer. The samples were mixed in a ratio of 2:10:2 of polymer, matrix ((indole-3-acrylic acid (IAA)) and salt ((potassium iodide (KI)) in acetone. The mixture was then deposited by electrospray onto the MALDI target. Using Polymerix as the analysis software we identified seven series.

Series Label	Alpha End Group	Repeat	Omega End Group	Adduct	Series Formula
S1	CH_3CO_2	$C_6O_2N_1H_7$	H	K+	CH_3CO_2 $[C_6O_2N_1H_7]$n H + K+
S2	OH	$C_6O_2N_1H_7$	$C_4H_2O_2N$	K+	OH $[C_6O_2N_1H_7]$n C4H2O2N + K+
S3	OH	$C_6O_2N_1H_7$	H	K+	OH $[C_6O_2N_1H_7]$n H + K+
S4	OH	$C_6O_2N_1H_7$	CH_3	K+	OH $[C_6O_2N_1H_7]$n CH3 + K+
S5	$C_3H_5O_3$	$C_6O_2N_1H_7$	H	K+	$C_3H_5O_3$ $[C_6O_2N_1H_7]$n H + K
S6	$C_3H_5O_3$	$C_6O_2N_1H_7$	H	Na+	$C_3H_5O_3$ $[C_6O_2N_1H_7]$n H + Na +
S7	$C_3H_5O_3$	$C_6O_2N_1H_7$	$C_4H_4O_3N$	Na+	$C_3H_5O_3$ $[C_6O_2N_1H_7]$n $C_4H_4O_3N$ + Na+

S1, which is a major peak in our reference sample, is a minor peak in the fingerprints. Figures 1-

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4, show the mass spectra of the fingerprint samples. In all fingerprint samples the main peak series is **S2**, which is formed by OH initiation with the loss of CH_2CH_3. **S3** is an OH initiated cyanoacrylate. **S2** and **S3** are K cationized peaks. There are several other minor peaks, of which possible structures are identified above, but at this time we do not feel confident of our interpretation. **S3, S4** and **S5** appear to increase in relative intensity as the fingerprint ages.

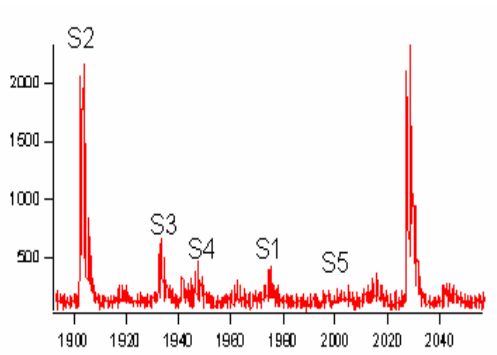

Figure 1. Fresh fingerprint exposed to acetic acid.

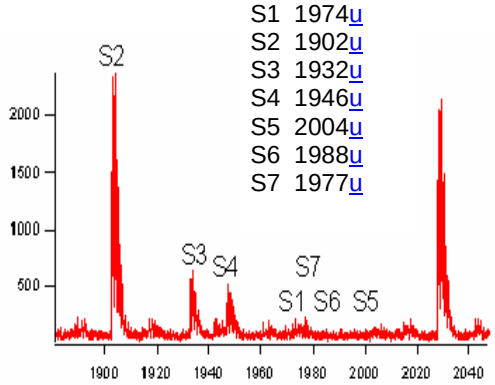

Figure 2. Fresh fingerprint exposed to acetic acid, aged one day.

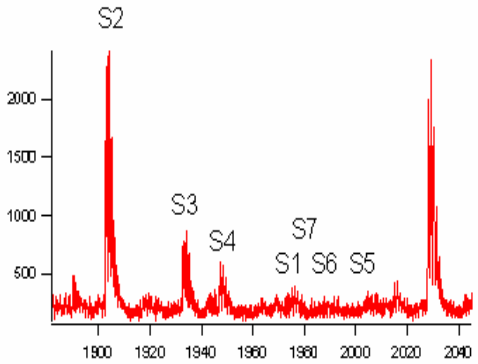

Figure 3. Fresh fingerprint exposed to acetic acid, aged two days.

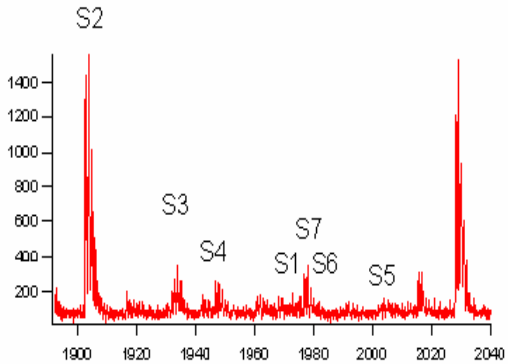

Figure 4. Comparison fresh fingerprint, not exposed to acetic acid.

The polyethylcyanoacrylate is not degrading due to the MALDI sample preparation, because the GPC and MALDI-TOF-MS gave comparable Mw values. We feel we have identified actual polymerization initiators but we now need to understand the process of degradation. Future work will need to be done with both clean and oily prints as this initial work was done using clean prints.

Deleted: Our reference sample was also run in Gel Permeation Chromatography (GPC). Three fractions were collected over a little over four minutes. The Mw given by the GPC verifies that the Mw seen in the MALDI samples is in the correct range and were are not just seeing degradation. ¶

[1] Lewis,L.;Smithwick, R., DeVault, G. Oak Ridge National Laboratory Project Report January, 2004
[2] Robello, D.R., Eldridge, T.D., Swanson, M.T., *Journal of Polymer Science Part A*, 37, 4570-4581, 1999.
[3] Certain commercial equipment is identified in this article in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the items identified are necessarily the best available for the purpose.