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AQUEOUS DEGRADATION OF POLYALKYL-ALPHA-CYANOCRYLATES . PART II. BRANCHED CHAIN ALCOHOL ESTERS

J. Nelson, et al

Walter Reed Army Medical Center
Washington, D.C.

November 1967

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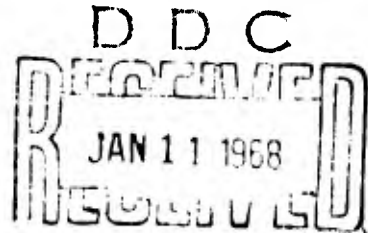
AQUEOUS DEGRADATION OF POLYALKYL- α -CYANOACRYLATES

Part II - Branched Chain Alcohol Esters

Reported by

J. Nelson
R.K. Kulkarni

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ABSTRACT

Heterogeneous hydrolytic treatment of branched chain polymers of alpha cyanoacrylic esters resulted in a somewhat higher rate of degradation than those of the corresponding straight chain alcoholic ester polymers. However, this rate of degradation was still slower than that of the methyl alpha cyanoacrylate polymer.

I. INTRODUCTION

The hydrolytic chain scission of the polymers of the α -cyanoacrylic acid esters of the straight chain alcohols, under heterogeneous aqueous environments was the subject of study in the last technical report (No. 6508, 1965). It was found that the rate of degradation decreases rapidly as the homologous series of alcoholic esters was ascended, with concomitant decrease of histotoxicity. However, the degradation of esters of n-propyl-n-butyl and higher was so extremely low as to be negligible, from the point of view of biological degradation. This was also corroborated by separate in vivo implantation studies.

In the preliminary experimental work it was found that the in vitro aqueous degradation of the polymers of the branched chain alcoholic esters of the cyanoacrylic acid degraded fairly rapidly. A more detailed study therefore, was undertaken to investigate these polymers which, because of their more rapid degradability showed promise of being more suitable as adhesives and hemostatic agents for internal bodily use. The in vitro degradation of some of the branched chain esters under heterogeneous aqueous situations are reported in this paper.

II. EXPERIMENTAL

The following alpha cyanoacrylate polymers were evaluated for heterogeneous in vitro hydrolytic degradation:

1. Isopropyl - methanol water initiated**
2. Isobutyl - " " "
3. Isoamyl - " " "
4. Ethyl hexyl - water with pyridine initiated
5. Cellusolve - water initiated
6. Cyclo Hexyl - " "

The polymers were later washed thoroughly with water and methanol and dried under high vacuum at 40°C. overnight. Heterogeneous degradation of the polymers was accomplished as previously described.*

* Leonard, F. et al, J. Appl Pol Sci 10, 259 (1966)

** MR 2-65 - Preparation of Polymers from α -Cyanoacrylate Monomers
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In addition to the above polymers an attempt was made to hydrolytically degrade the polymers of secondary butyl alpha cyanoacrylate (methanol water initiated), and butyl cellosolve α -cyanoacrylate (water with pyridine initiated). In both cases the polymers clumped and fused readily under reflux conditions resulting in none or very low amounts of formaldehyde produced.

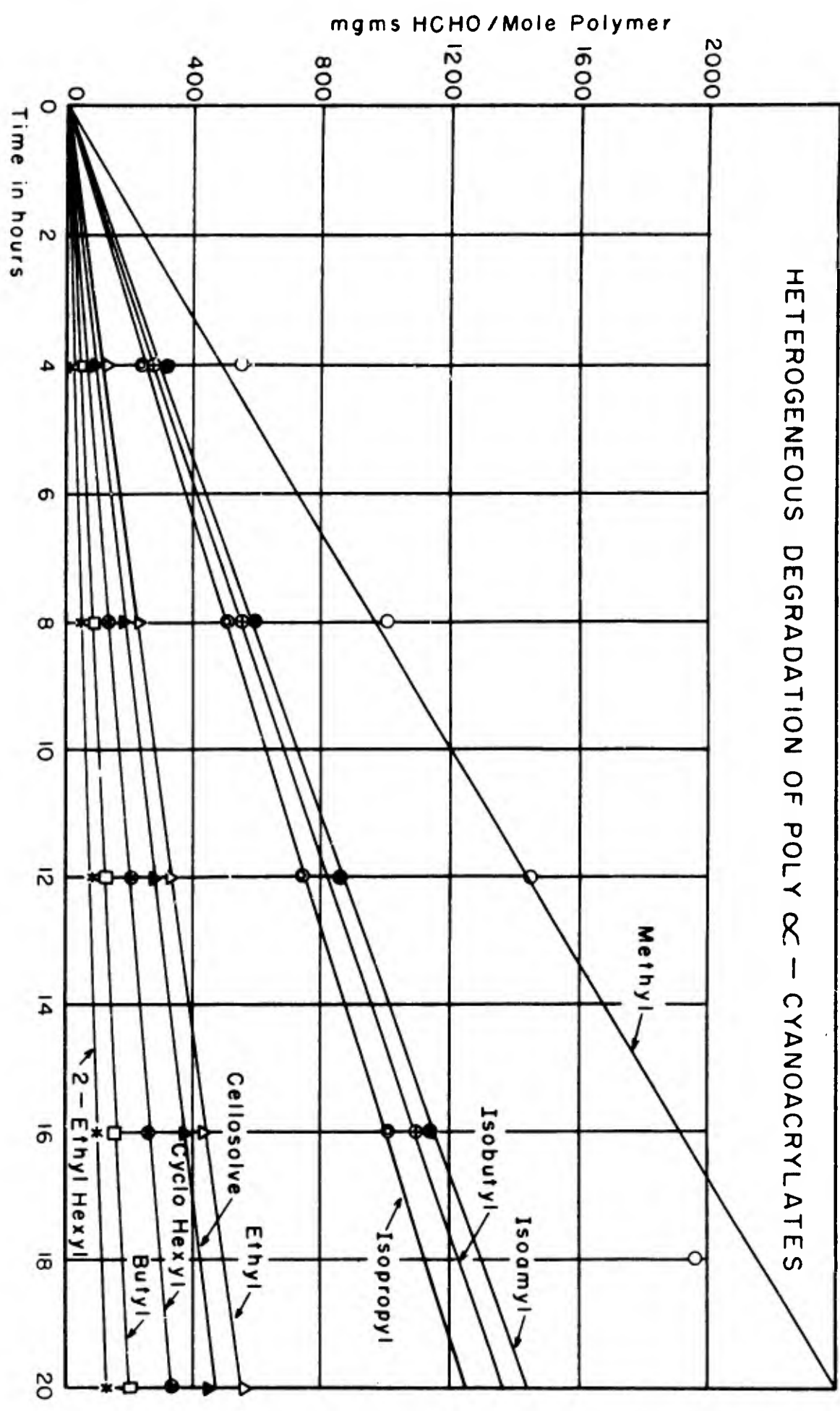
III. RESULTS AND DISCUSSION

Figure I is a graphical illustration of the rate of aqueous degradation for the poly alpha cyanoacrylates previously mentioned as compared to the rate of degradation of the methyl, ethyl, and butyl α -cyanoacrylate polymers. From the graph the group of polymers consisting of isoamyl, isobutyl and isopropyl α -cyanoacrylates degrade at a rate faster than that of the ethyl polymer but still slower than that of the methyl polymer. The results indicate that the branched chain isomers of the poly α -cyanoacrylates are degraded more readily than that of the corresponding straight chain polymers. From the results it would seem that a polymer such as secondary butyl α -acrylate should degrade at still a faster rate than those depicted on the graph. However, as previously noted the secondary butyl polymer fused and clumped when subjected to degradation by hot water. This fusing could be due to the possible low softening temperature of this polymer.

IV. CONCLUSIONS AND RECOMMENDATIONS

In vitro studies of the polymers of alpha cyanoacrylic esters indicate that the branched chain polymers degrade at a faster rate than those of the corresponding straight chain alcoholic ester polymers. In vivo studies should be undertaken for either the isoamyl, isopropyl, or isobutyl polymers in an effort to correlate the in vitro results.

In vitro degradation of secondary butyl, isoamyl and methyl alpha-cyanoacrylate polymers should be run at 50°C. Degradation of the polymers at this temperature should obviate the fusion observed with secondary butyl alpha cyanoacrylate polymer at higher temperatures due to the polymer's apparently low second order transition temperature.



(Figure I)

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