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CORPORATE RESEARCH
NEW VENTURES SUMMARY
Fourth Quarter 1978

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BFG-3029-A

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the goal - an efficient way to add high melting blocks to elastomeric polymers. Routes to block polymers by sequential vinyl polymerization are now being explored. The concept of a very stable radical at the end of a polymer chain which would dissociate to allow chain growth has been studied. An extremely stable radical will be required. Many candidates studied rearrange so that the attached group is no longer thermally labile. This approach cannot be ruled out but results are not encouraging.

Polymer chains which cleave to produce radicals seems more promising. Efforts are now being concentrated on the production of polymeric initiators of the general type: benzoyl peroxide linkage - percarbonate linkage alternating. There is adequate literature to show that this route can give block polymers. The alternating initiator types is essential to avoid excessive amounts of homopolymer. A number of synthetic routes have been devised. Key reactions with model systems are now in progress. One of the primary reactions - formation of peroxide from a benzoyl chloride in the presence of a chloroformate, goes quite smoothly. Mixed products do not appear to be a problem. However, the unexpected cleavage of an ester by an acid chloride has required some modification in one synthesis.

Passive Dosimeters: (Feasibility Study 4032A) M. A. Centanni and M. P. Dreyfuss -- The objective of this project is to develop new and novel passive personnel monitoring badges for specific pollutants. We envisage the basis to be chemical fixation of the pollutants in combination with new rapid electronic measurement techniques.

Chemical Fixation: M. P. Dreyfuss -- The nature of the interaction of the platinum ethylene complex with acrylonitrile (AN) and its limitations are becoming much clearer. Field desorption mass spectroscopy (FDMS) (R. P. Lattimer) has proved to be very useful in sorting out the puzzle. Only molecular ions were observed. The platinum complex in liquid AN forms a diANdichloroplatinum complex. The IR spectrum indicates bonding of the AN is via the nitrile nitrogen rather than π bonding of the vinyl double bond. However, the considerable amount of insoluble product which also forms suggest a combination of nitrile bonding and π bonding may lead to a polymeric complex. Thus a very stable product results and this is desirable for a fixant candidate. FDMS was also used to study the effect of styrene and butadiene on the platinum ethylene complex. Butadiene did not react, while styrene displaced the π bonded ethylenes stepwise. The reaction with styrene is slower than with AN, but exposure to a mixture of styrene and AN showed reaction with both materials. Thus interference from styrene could be a problem in any application of this complex as an AN fixant.

We hoped the corresponding platinum propylene complex would be more reactive or more selective at low levels of AN. This complex was more difficult to prepare and it offered no advantages over the

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