

NOVEL POLYMERS BY THE DIELS-ALDER REACTION, CYCLOPOLYMERIZATION,  
AND THE POLYMERIZATION OF OPTICALLY ACTIVE MONOMERS

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The purpose of this work is to find new ways to prepare polymers which are resistant at high temperatures. Three approaches are described here:

- 1) The preparation of asymmetric polymers. Currently we are concentrating our efforts on polycondensation polymers which have asymmetric units in the chain although we are also considering polymers with asymmetric units in the main chain and the side chain as well. Results to date have indicated that new polyamides having high melting points and high crystallinity can be prepared in this way while retaining increased solubility over non-branched structure.
- 2) Synthetic techniques devised to prepare ladder or strand polymers.
- 3) Preparation of cyclo polymers which result in stiffer chains, higher order and higher melting points.

ABSTRACT

D(-)  $\beta$  methyl- $\epsilon$ -caprolactam has been prepared and polymerized to give a high melting, crystalline polymer.

The optical activity and intrinsic viscosity of the polymer have been determined and in mixtures of cresol and chloroform and the results given a tentative explanation.

Dibenzylidene succinic anhydride and diisopropenyl succinic anhydride have been prepared. A material has been prepared from dibenzylidene succinic anhydride and maleic anhydride.

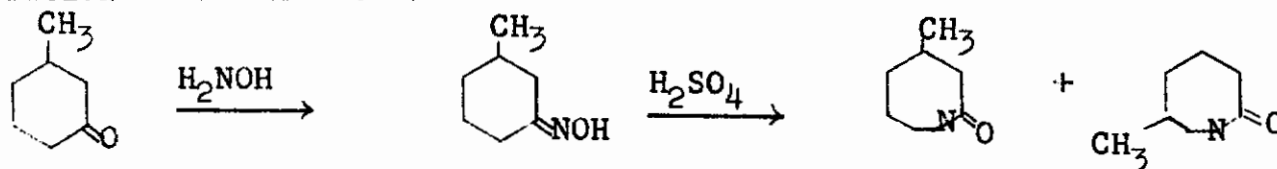
Glutaraldehyde has been polymerized thermally to give a soluble polymer. From its infrared spectrum the polymer is thought to have the structure of cyclopolymers. The polymer is soluble but unstable. Glutaraldehyde also has been polymerized at  $-80^{\circ}\text{C}$ . with aluminum triisobutyl. The polymer is insoluble but stable. The polymer has been shown by X-ray analysis to have some crystallinity.

OPTICALLY ACTIVE POLYAMIDES - Naturally occurring proteins and polypeptides are the best known examples of polymers containing optically active centers in the main chain. Many of the unusual properties of these materials such as the formation of an  $\alpha$  helix in the solid state (1) and in solution (2) are directly or indirectly due to the presence of an optically active asymmetric carbon atom.

# Contrails

The number of synthetic polymers other than poly  $\alpha$  amino acids which possess an optically active carbon atom include, polypropylene oxide (3,4), lactide (5) and propylene imine (6). Volkenstein (7) has prepared polymers from D(+) 3-methyl adipic acid and 1,6-hexanediamine and from the corresponding racemic diacid and 1,6-hexanediamine. In all of these cases, the melting point and crystallinity is higher in the optically active polymer than its racemic analogue. We have undertaken a study of these effects on polymers derived from D(-)  $\beta$ -methyl- $\epsilon$ -caprolactam and D,L  $\beta$ -methyl- $\epsilon$ -caprolactam.

DL- $\beta$ -Methyl- $\epsilon$ -caprolactam and D(-)  $\beta$ -methyl- $\epsilon$ -caprolactam were chosen because of their easy accessibility. The optically active compounds were first prepared by Wallach (8) from naturally occurring pulegone. The optically inactive compounds and their polymers were described by Schaffler and Ziegenbaum (9). The monomer preparation is shown below.



Lactam separation is effected through fractional crystallization, the  $\delta$ -methyl- $\epsilon$ -caprolactam being the more soluble.

Polymerization of the racemic and optically active  $\beta$ -methyl- $\epsilon$ -caprolactam was carried out according to the procedure of Rogovin et al (10). Water (1%) was used as catalyst at 230° for 20 hrs. The racemic DL  $\beta$ -methyl- $\epsilon$ -caprolactam yielded a discolored rubbery solid; the optically active compound yielded a white fibrous solid. Yields and melting points for these compounds and Nylon 6 prepared by the same procedure are shown below.

### Properties of Polyamides

Monomer	D(-) $\beta$ -Methyl- $\epsilon$ -caprolactam	DL $\beta$ -Methyl- $\epsilon$ -caprolactam	$\epsilon$ -Caprolactam
Yield %	52	56	90
M.P. *	220-225	135-145	210-215

\* Hot stage polarizing microscope

In order to raise the yield and molecular weight of poly D(-)  $\beta$ -methyl- $\epsilon$ -caprolactam over that which was obtained at 230° we have also used polymerization at temperatures below the polymer melting point. Wichterle (27) has recently reported the polymerization of  $\epsilon$ -caprolactam at temperatures below the melting point of the polymer. He used anionic initiators in order to obtain reasonable rates at temperatures of from 150-200°. He was able to show that at these temperatures the amount of monomer in equilibrium with the polymer is considerably lower than would be expected from extrapo-

lation of results obtained at temperatures above the polymer melting point. These results are explained in terms of the crystalline polymer phase being excluded from the monomer polymer equilibrium. We found that polymerization using 1/2 percent water as catalyst at 200° was very slow but resulted in substantial increase in the yield (80%) and in the molecular weight ( $\bar{M}_w = 0.96$ ) over results obtained at 230°.

Solution Properties of Poly D(-)  $\beta$ -Methyl- $\epsilon$ -Caprolactam - The relationship between polymer conformation and the optical activity of optically active polyamides has been discussed only in terms of  $\alpha$ -helix formation (11). Poly D(-)  $\beta$ -methyl- $\epsilon$ -caprolactam solutions in cresol-chloroform mixtures have been found to give curves which show a strong dependence of the specific rotation, at the D line of sodium one the solvent composition and exhibit a very sharp maximum. Doty et al (11) for solutions of poly- $\gamma$ -benzyl glutamate in dichloroacetic acid-chloroform obtained curves of  $[\alpha]_D^{25}$  versus solvent composition which are discontinuous and clearly show the formation of an  $\alpha$ -helix by rotatory dispersion measurements. Tanford et al (12) for solutions of  $\beta$  lactoglobulin in mixtures of water and organic solvents obtained curves which are similar to the curves obtained for poly D(-)  $\beta$ -methyl- $\epsilon$ -caprolactam which we have studied.

To determine the conformation of the polymer in the cresol - chloroform mixtures the optical rotatory dispersion of the solutions was measured at four wavelengths. For a simple non-helical conformation one would expect (13) the dispersion to follow the Drude relationship.  $[\alpha]_{\lambda}^{25} = K/\lambda^2 - \lambda_c^2$  where  $\lambda_c$  equals the characteristic or cotton effect wavelength. For helical polyamides the Moffitt equation has been shown to apply (14):  $[\alpha]_{\lambda}^{25} = a_0 \frac{\lambda_c^2}{\lambda^2 - \lambda_0^2} + b_0$

$\frac{\lambda_0^4}{(\lambda^2 - \lambda_0^2)^2}$ , where  $b_0$  is a measure of helix content. The conformation of a polymer may also be followed by measurements of its intrinsic viscosity (14).

The data which we have obtained for poly D(-)  $\beta$ -methyl- $\epsilon$ -caprolactam is summarized in Table I and figures 1,2 and 3. Rotations at wavelengths other than the sodium D line have been omitted.

TABLE 1

Relationship of Polymer Conformation and Optical Activity of Poly D(-)  $\beta$  Methyl- $\epsilon$ -Caprolactam in Cresol-Chloroform Mixtures

Mole % Chloroform	$[\alpha]_D^{25}$	$[\eta]$ dl/g	$\lambda_c$ (Drude equation)
29.14	44.09	0.980	173
77.46	57.19	1.160	-
71.71	56.01	1.447	220
20.34	45.92	0.980	182
52.38	50.30	1.375	200
62.35	54.00	-	-
75.34	58.32	1.316	178

# Contrails

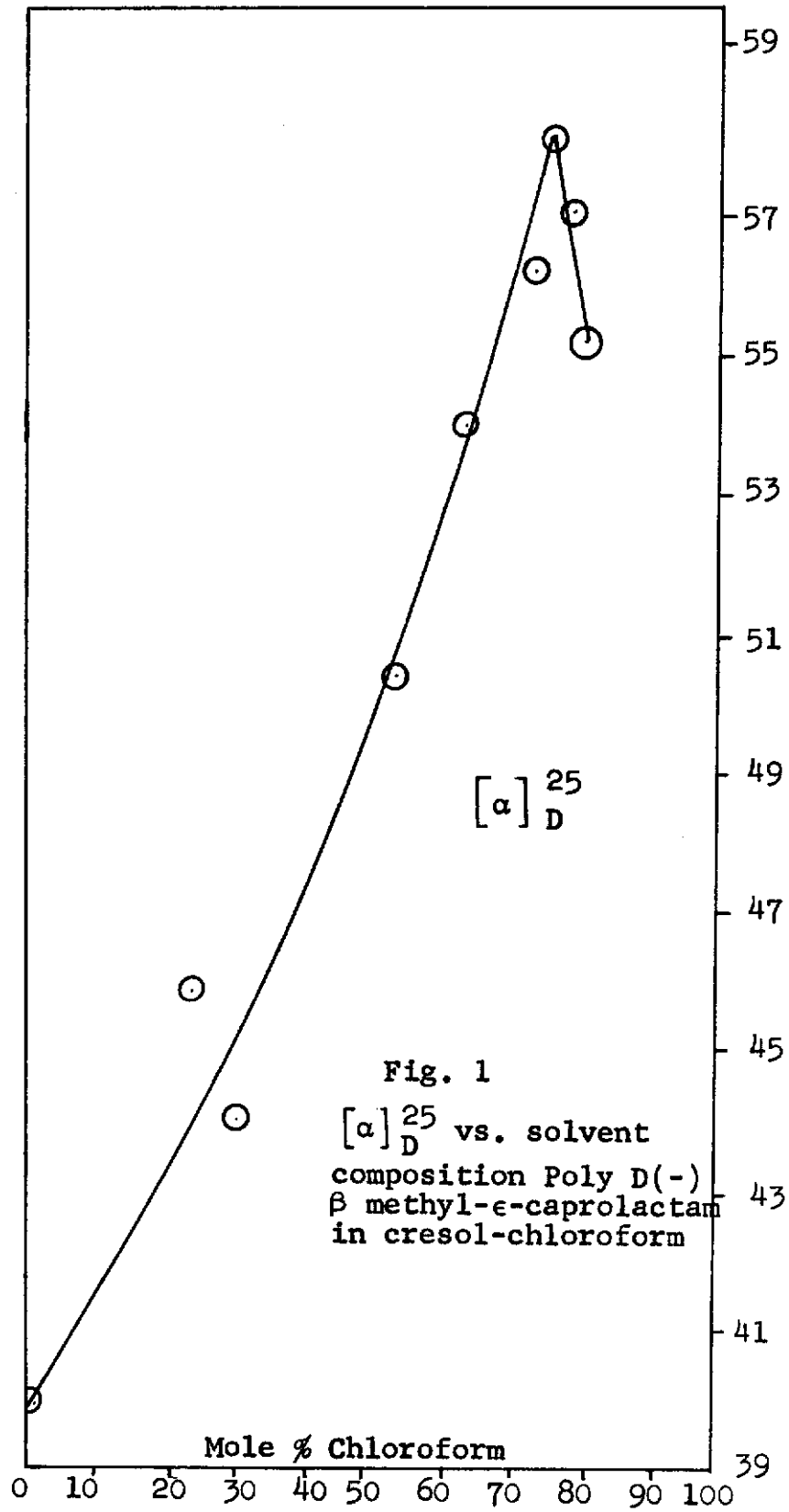


Fig. 2  
 $[\eta]$  vs. Mole % Chloroform  
 in cresol-chloroform

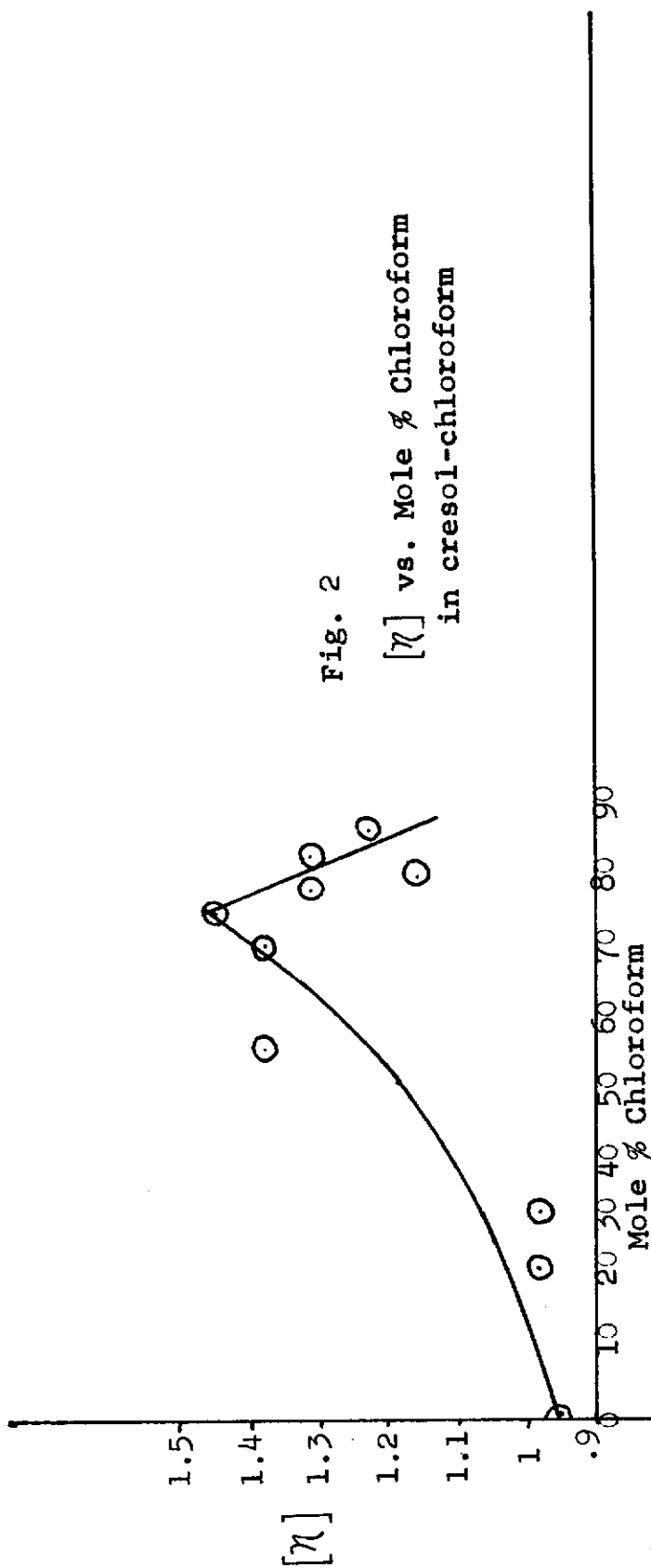


Fig. 3  
 $\lambda_c$  vs. Mole % Chloroform

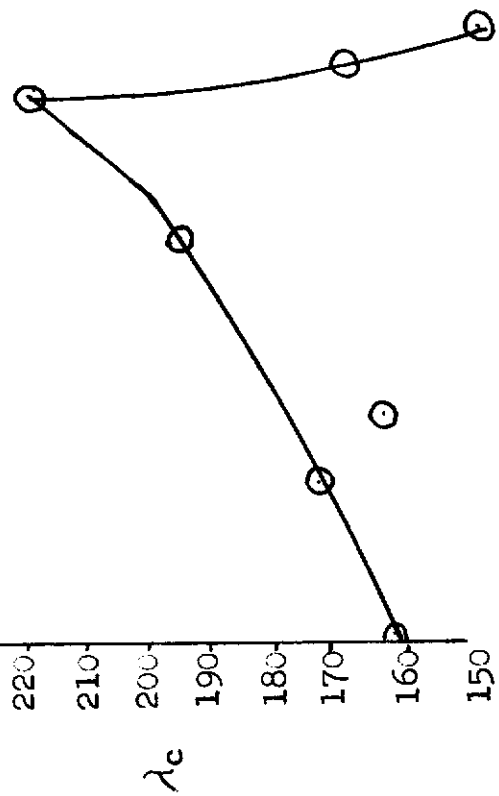
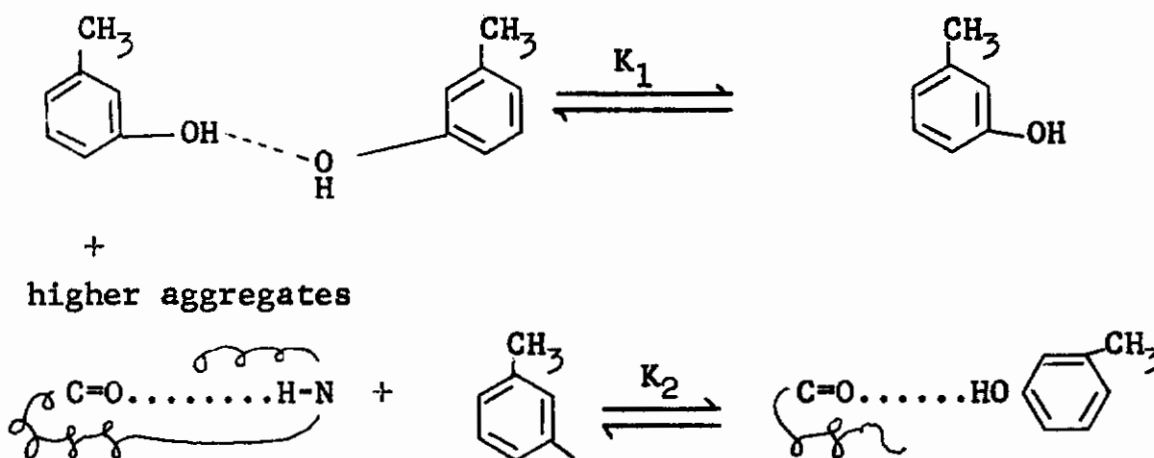


Table I (Continued)

Mole % Chloroform	$[\alpha]_{25}^D$	$[\eta]$ dl/g	$\lambda_c$ m $\mu$ (Drude equation)
0	39.60	0.960	171
83.52	-	1.227	-
66.87	-	1.372	-

The optical rotatory dispersion data follow the Drude equation for all solvent compositions indicating that there is no helix present in these solutions. The data can be interpreted as a gradual solvation of the coil as the cresol is diluted with chloroform. Pakshver, et al (15) have postulated that the solution of polyamides, in mixtures of hydrogen bonding and non-hydrogen solvents, can be interpreted in terms of increasing chain solvation as the hydrogen bonding component is diluted. There are two equilibria which seem to be important



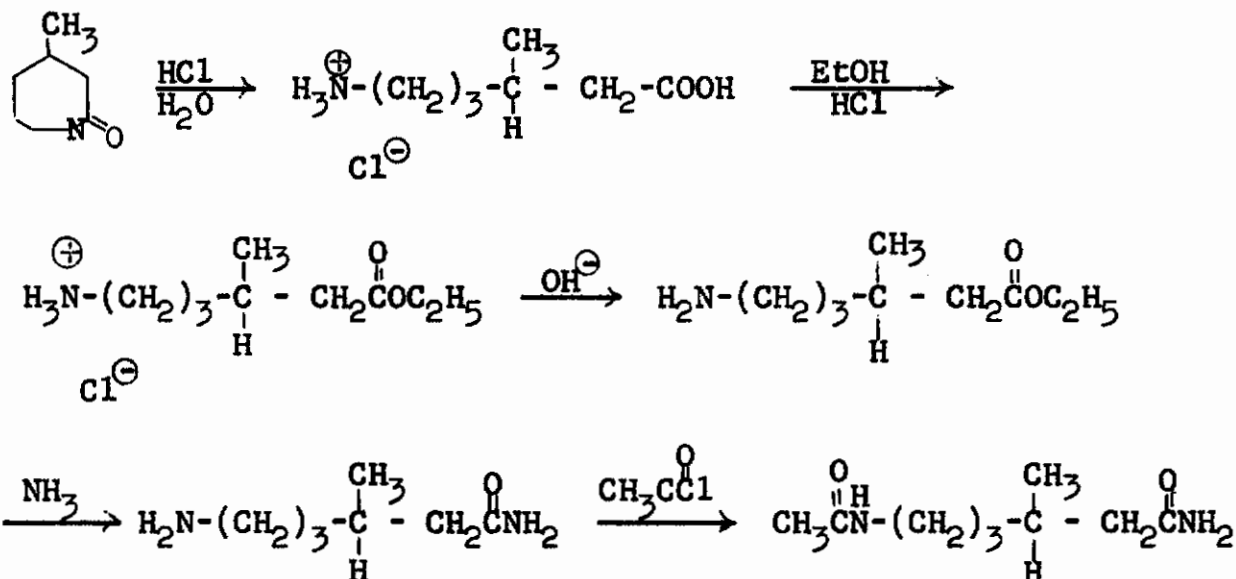
The addition of chloroform would shift both equilibria to the right thus changing the hydrogen bonding of the amide carbonyl from an intramolecular C=O...HN bond to a C=O...HO-C<sub>6</sub>H<sub>4</sub>-CH<sub>3</sub> bond. The values of  $\lambda_c$  shown in Table I demonstrate that the optically active chromophore is indeed the amide carbonyl (13). Thus both the optical activity and the intrinsic viscosity would be reflections of the solvation of the polymer. While the absolute magnitude of the rotation of a carbonyl hydrogen bonded to an amide nitrogen and the absolute magnitude of a carbonyl hydrogen bonded to cresol cannot be estimated, it is reasonable to assume that the measured rotation is simply a linear sum of the individual rotation of free carbonyl plus the two hydrogen bonded species.

$$[\alpha]_{\text{exp}} = [\alpha]_{\text{C=O}} + [\alpha]_{\text{C=O-HN}} + [\alpha]_{\text{C=O}\dots\text{H-solvent}}$$

# Contrails

The intrinsic viscosity of a polymer also represents this hydrogen bonding in a poor solvent most of the hydrogen bonds would be intramolecular ones to amide nitrogen as the carbonyl became more highly solvated the random coil would simultaneously expand.

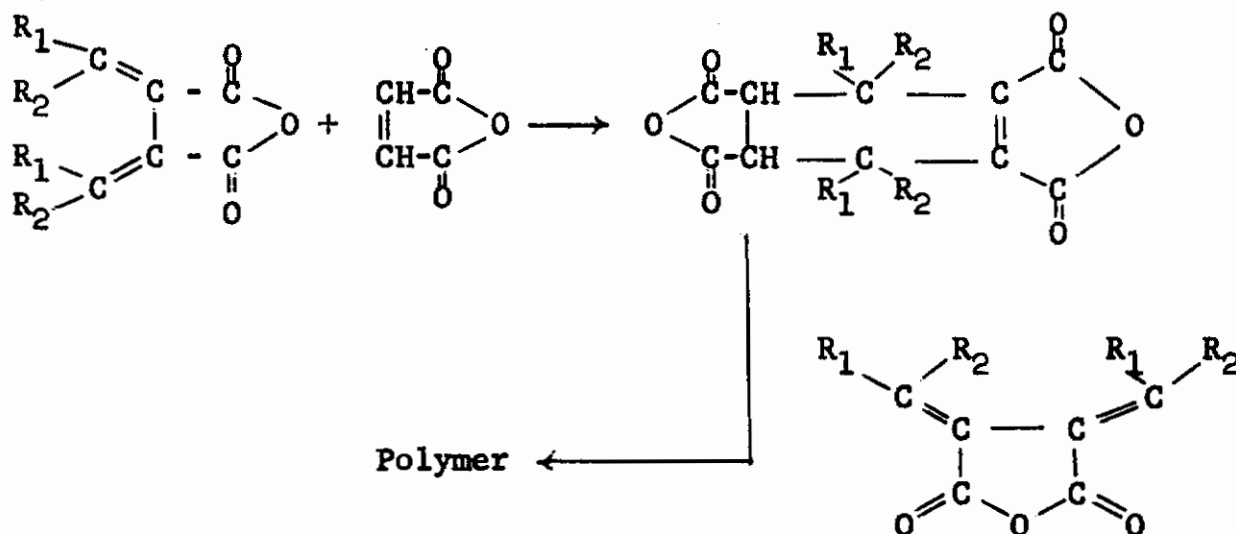
In the previous explanation generalized solvent effects have been neglected. If the argument is to be strengthened further it is necessary to find the optical rotation of the low molecular weight analogue of the polymer. Work has therefore begun on the synthesis of D(-) 6-acetamido-3-methyl-hexanamide. The projected route is similar to Marvel's (16) synthesis of 6-aminohexanamide and is shown below:



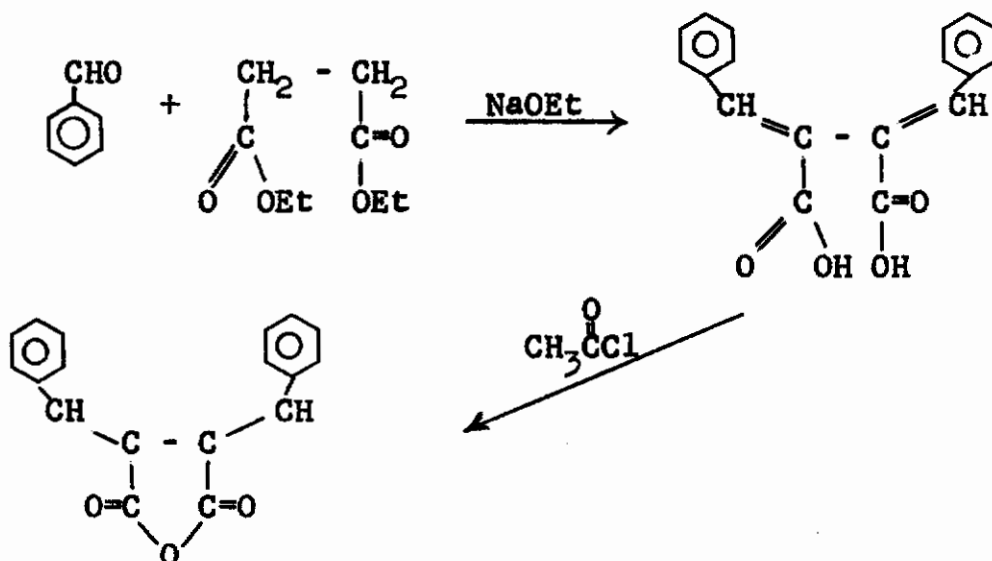
**DIELS-ALDER POLYMERS** - The preparation of ladder polymers via the Diels-Alder reaction is being studied as a means of preparing soluble, high melting, thermally stable polymers. A Diels-Alder polymer can be prepared by condensation of a bifunctional diene with a bifunctional dienophile or by self-condensation of a molecule which can function both as a diene and as a dienophile. Polymers of the first type have been studied by Bailey (17), Stille (18), Whelan (19), and Kraiman (20). Soluble polymers with good thermal stability have been prepared. However, high molecular weight materials were not obtained because monomer impurities prevented exact stoichiometry.

We are investigating Diels-Alder monomers of the second type. Dimethylene succinic anhydride and several substituted analogs are being prepared as monomers. These materials should polymerize as follows:

# Contrails



Dibenzylidene succinic anhydride ( $R_1 = H, R_2 = C_6H_5$ ) and diisopropenyl succinic anhydride ( $R_1 R_2 = CH_3$ ) have been prepared by Stobbe (21) condensation of the corresponding aldehyde or ketone with diethyl succinate.

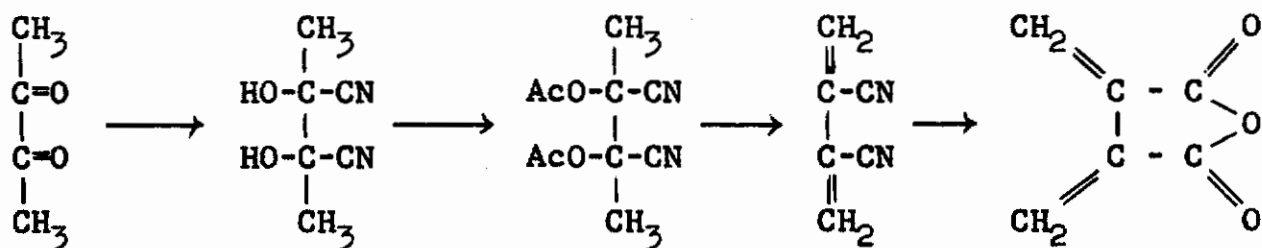


Initial attempts to polymerize these monomers at atmospheric pressure and  $200^\circ C$ . with a small amount of maleic anhydride as an initiator did not yield polymer. However, reaction of dibenzylidene succinic anhydride in a closed system at  $200^\circ$  and 200 psi has yielded a material with a melting point of  $255-256^\circ C$ . This material may be a polymer but preliminary characterization indicates it may be 3,4-diphenyl-1,2-dicarboxy-cyclobutene-1 anhydride. Further



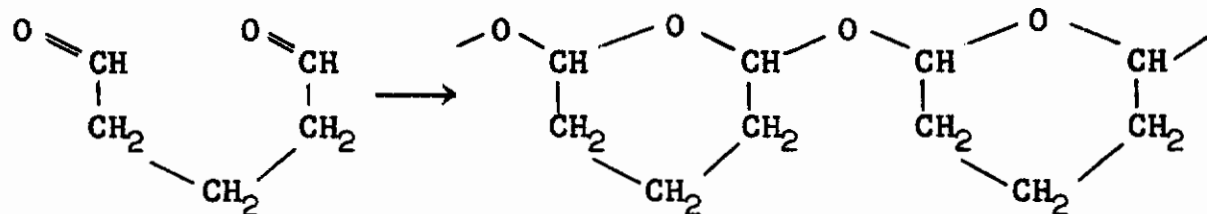
characterization is in progress.

2,3-Dicyanobutadiene has been prepared by pyrolysis of 2,3-butadiene bis cyanohydrin diacetate as described by Prill (22).



This monomer will also be used for the preparation of  $\alpha,\beta$ -dimethylene succinic anhydride.

CYCLOPOLYMERIZATION OF GLUTARALDEHYDE - A number of aliphatic aldehyde polymers have been described (23,24,25). These materials range from solid crystalline polymers to rubbery amorphous ones. The cyclopolymerization of dialdehydes is being undertaken to improve the thermal stability of these polyethers. Glutaraldehyde is the first dialdehyde which has been selected for the preparation of cyclic polyethers. It is expected to polymerize as shown below:



Pure glutaraldehyde itself has a tendency to polymerize at room temperature without any additional catalyst (26). We have found that the polymer is soluble in common organic solvents. It is unstable at room temperature, if freed from the monomer by reprecipitation, a monomer-polymer equilibrium seems to be reestablished. The infrared absorption at  $1730 \text{ cm.}^{-1}$  due to carbonyl group is fairly weak in freshly precipitated polymer. The absorption due to hydroxyl groups can be seen at approximately  $3500 \text{ cm.}^{-1}$ . These facts seem to imply that the polymer is mainly composed of the structure shown above with hydroxyl groups at the ends. The instability of the polymer makes it difficult to elucidate more fully the structure by elementary analysis or some other means.

Glutaraldehyde also polymerizes at low temperatures with aluminum triisobutyl as a catalyst. The polymerization has been carried out in toluene at the temperature of a Dry-Ice acetone bath ( $-80^\circ\text{C.}$ ). The reaction mixture appears to be homogeneous and becomes thick after a certain time. The polymer when precipitated and freed from the solvent is insoluble in solvents so far tried such as toluene, dimethylformamide, chloroform, or tetrahydrofuran.

## *Contrails*

A trace portion of the polymer is extractable with chloroform. After the extraction, the polymer shows the presence of a crystalline part by X-ray analysis. The infrared spectrum of the polymer is essentially the same as that of the thermally polymerized material. The insolubility of the polymer is presumably due to its crystallinity, although the possibility of the presence of crosslinkages cannot be excluded. The insoluble polymer is much more stable.

In an attempt to obtain soluble stable polymer, other catalysts such as boron trifluoride - etherate and other conditions such as thermal polymerization in toluene solution are under investigation.

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